Fritz-Haber-Institut der Max-Planck-Gesellschaft Berlin

18th Meeting of the Fachbeirat

Berlin, 2nd - 4th November 2015

Reports

Fritz-Haber-Institut der
Max-Planck-Gesellschaft
Berlin

18th Meeting of the Fachbeirat

Berlin, 2nd – 4th November 2015

Reports

Members of the Fachbeirat 2015

Prof. Dr. Friedhelm Bechstedt
Friedrich-Schiller-Universität Jena
Institut für Festkörpertheorie und -optik
Max-Wien-Platz 1
07743 Jena, Germany
Tel. +49-(0)3641-947150
Fax. +49-(0)3641-947152
bech@ifto.physik.uni-jena.de

Prof. Dr. Charles T. Campbell
Department of Chemistry
University of Washington
Box 35 1700
Seattle, WA 98195-1700, USA
Tel. +1-206-616-6085
Fax +1-206-616-6250
campbell@chem.washington.edu

Prof. Dr. Roberto Car
Department of Chemistry
213B Frick Lab.
Princeton University
Princeton, NJ 08544-1009, USA
Tel. +1-609-258-2534
Fax +1-609-258-6746
rcar@princeton.edu

Prof. Dr. Tony F. Heinz
Departments of Physics and Electrical Engineering
Columbia University
500 West 120th St.
New York, NY 10027, USA
Tel. +1- 212-854-6564
Fax +1- 212-854-1909
tony.heinz@columbia.edu

Prof. Dr. Manfred Kappes
Institut für Physikalische Chemie
Karlsruhe Institut für Technologie (KIT)
Fritz-Haber-Weg 2
76131 Karlsruhe, Germany
Tel. +49-(0)721 608-42094
Fax +44-(0)721 608-47232
manfred.kappes@kit.edu

Prof. Dr. Maki Kawai
RIKEN Institute of Physical and Chemical Research
University of Tokyo
2-1 Hirosawa, Wako
351-1098 Saitama, Japan
Tel. +81-48-462 1446
Fax +81-48-462 4604
maki@riken.jp

Prof. Dr. Frédéric Merkt
Department of Physics
Laboratory of Physical Chemistry
Wolfgang-Pauli-Str. 10
8093 Zürich, Switzerland
Tel. +41-44-632-4367
Fax +41-44-632-1021
merkt@xuv.phys.chem.ethz.ch

Prof. Dr. Elisa Molinari
CNR-NANO, S3 Center
University of Modena and Reggio Emilia
Via Campi 213 a
41125 Modena, Italy
Tel. +39 059 2055628
Fax +39 059 2055651
elisa.molinari@unimore.it

Prof. Dr. Daniel M. Neumark
Department of Chemistry
University of California at Berkeley
420 Latimer Hall
Berkeley, CA 94720-1460, USA
Tel. +1-510-642-3502
Fax +1-510-642-3635
dneumark@berkeley.edu

Prof. Dr. Susannah Scott
Department of Chemical Engineering
University of California
10 Mesa Road
Santa Barbara, CA 93106-5080, USA
Tel. +1-805-893-5606
Fax +1-805-893-4731
sscott@engineering.ucsb.edu

Prof. Dr. Hans-Peter Steinrück
Lehrstuhl für Physikalische Chemie II
Department of Chemistry und Pharmazie
Universität Erlangen-Nürnberg
Egerlandstr. 3
91058 Erlangen, Germany
Tel. +49-(0)9131 85-27343
Fax +49-(0)9131 85-28867
Hans-Peter.Steinrueck@chemie.uni-erlangen.de

Prof. Dr. Wataru Ueda
Department of Material and Life Chemistry
Kanagawa University
3-27-1, Rokkakubashi, Kanagawa-ku
Yokohama, 221-8686, Japan
Tel. +81-45-481-5661
Fax +81-45-413-9770
uedaw@kanagawa-u.ac

Prof. Dr. Evan R. Williams
Department of Chemistry
University of California
B84 Hildebrand hall
Berkeley, CA 94720-1460, USA
Tel. +1-510-643-7161
Fax +1-510-642-8669
erw@berkeley.edu

Contents

Department of Inorganic Chemistry (AC)
Director: R. Schlögl

Department of Chemical Physics (CP)
Director: H.-J. Freund

Department of Molecular Physics (MP)

Former Director: G. Meijer
Interim Director: M. Wolf

Department of Physical Chemistry (PC)

Director: M. Wolf

MPRG for Structural and Electronic Surface Dynamics

Head: R. Ernstorfer

Theory Department (TH)

Director: M. Scheffler

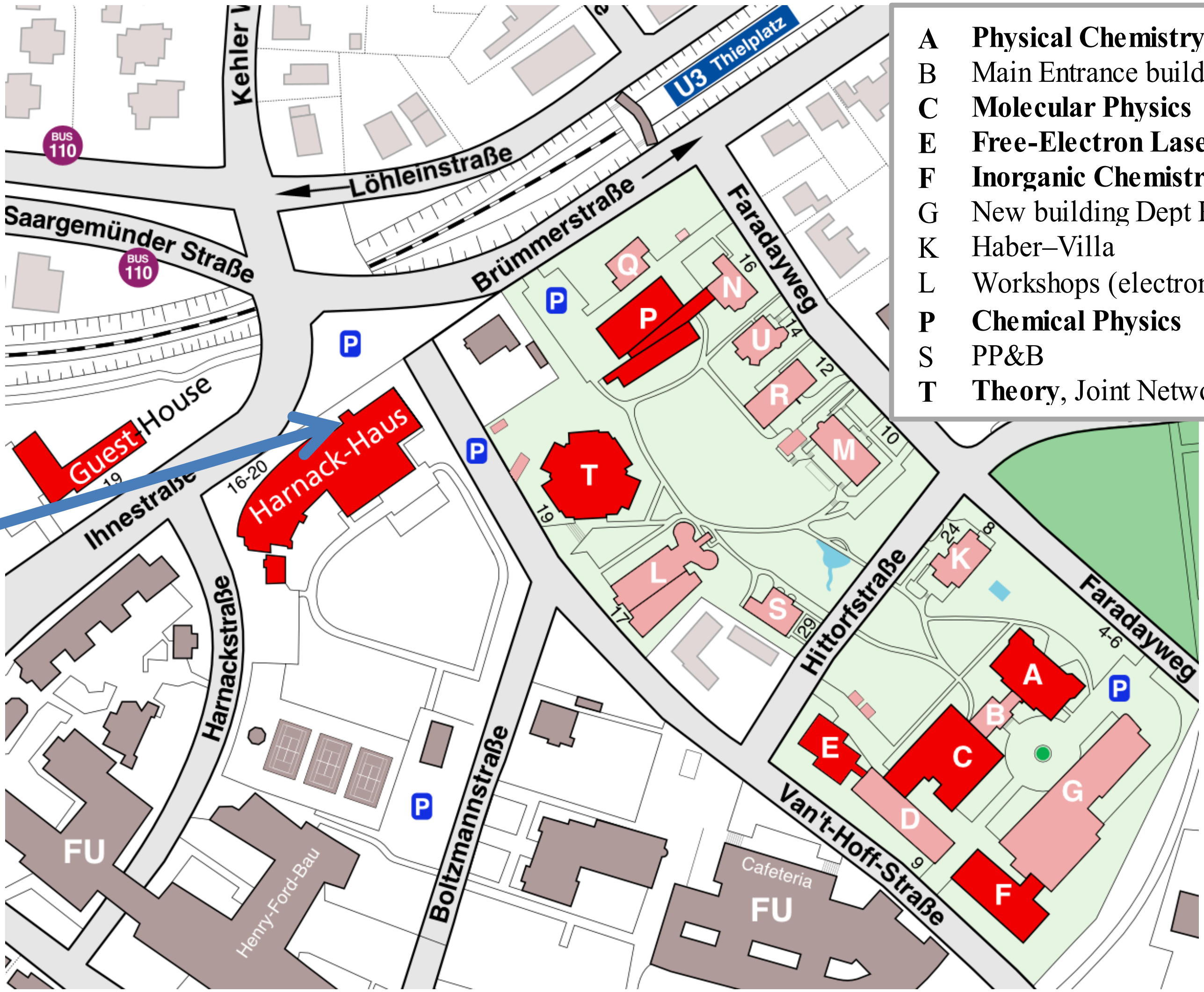
ERC Group on Organic Functional Materials and Intermolecular Interactions

Head: Alexandre Tkatchenko

Local Map

Lectures, meetings of the Fachbeirat
(Harnack-Haus)

Tuesday from 2.30 - 5.30 p.m.:
Poster Sessions at the Departments
(see legend)



A	**Physical Chemistry, Library**
B	Main Entrance building A, Reception
C	**Molecular Physics**
E	**Free-Electron Laser (FEL)**
F	**Inorganic Chemistry**
G	New building Dept PC *(under construction)*
K	Haber–Villa
L	Workshops (electronics and mechanical)
P	**Chemical Physics**
S	PP&B
T	**Theory**, Joint Network Center (GNZ)

Monday at 5 p.m.:
Optional visit of the FEL
(see legend)

Research Departments of the Fritz Haber Institute

Inorganic Chemistry	**Chemical Physics**	**Molecular Physics**	**Physical Chemistry**	**Theory**
Robert Schlögl	Hajo Freund	Martin Wolf Interim director	Martin Wolf	Matthias Scheffler

Group leaders

Malte Behrens[1]	Markus Heyde	Bretislav Friedrich	Kramer Campen	Carsten Baldauf
Sebastian Cap	Helmut Kuhlenbeck	Gert von Helden	Markus Eiswirth	Luca Ghiringhelli
Maik Eichelbaum[2]	Thomas Schmidt		Karsten Horn	Sergey Levchenko
Axel Knop-Gericke	Shamil Shaikhutdinov		Tobias Kampfrath	Patrick Rinke[6]
Julian Tornow[3]			Takashi Kumagai	Matthias Rupp
Annette Trunschke			Alexej Melnikov	Igor Ying Zhang
Marc Willinger			Alexander Mikhailov	
			Alexander Paarmann	
			Julia Stähler	
Sylvia Becker (née Reiche)[a]	ERC Group Martin Sterrer[3]	Knut Asmis[b]	Max Planck Research Group Ralph Ernstorfer	Angel Rubio[d]
Kevin Kähler[a]	ERC Group Swetlana Schauermann[4]	Gabriele Santambrogio[c,5]		ERC Group Alexandre Tkatchenko

Main affiliation

a MPI for Chemical Energy Conversion, Muelheim a.d. Ruhr
b Leipzig University, part time at FHI
c Institute for Optics of the CNR, Florence, part time at FHI
d MPI for the Structure and Dynamics of Matter, Hamburg, part time at FHI

Active until

1 May 2014
2 February 2015
3 September 2014
4 April 2015
5 January 2015
6 August 2014

Administration, Facilities, and Service Groups

Administration
G. v. Helden/
R. Nädele

Free-Electron Laser
W. Schöllkopf

Joint Network Center (GNZ)
G. Schnapka

IT Services (PP&B)
H. Junkes

Library
U. Siebeky

Electronics Workshop
G. Heyne

Mechanical Workshop
P. Bischoff

Electron Microscopy
M. Willinger

Crystal Lab

As per September 9, 2015

Recent Developments in the Fritz Haber Institute

Managing Director: Martin Wolf

1. General Remarks

This report by the managing director concentrates on general and organizational aspects of the institute, while the five departments present recent research results and departmental issues in their reports, beginning on p. 63. Since the last meeting of the Fachbeirat the board of directors has undertaken several measures concerning the future development of the institute.

- We have worked out a scientific concept for the evolution of the FHI into the next decade, entitled "*Processes at Interfaces: From Atomistic Understanding to Intricacy*", which will be outlined in more detail below.
- After an extensive search process for a new director, the board of directors proposed a candidate to the MPG section for chemistry, physics and technology (CPTS) in February 2015. At the time of the completion of this report the appointment process is ongoing, and we will report on the most recent development at the meeting of the Fachbeirat in November 2015.
- The FHI infrared free-electron laser (FHI FEL), a project originally initiated by Gerard Meijer, started regular operation in November 2013 and is now run as a facility of the institute. In its present mode the FEL covers the mid-infrared wavelength range (3.6 to 50 µm) and is successfully employed for vibrational spectroscopy of (bio)molecules and clusters as well as for the investigation of non-linear optical properties of solids. We have developed a concept for a future upgrade of the FHI FEL to enable two-color experiments, synchronization of a femtosecond tabletop laser with the FEL, and to extend the wavelength range to the far-infrared. This would open the door for unique scientific applications. More details will be given below and in a special section of this booklet (p. 31 ff).
- To enhance scientific exchange across the institute two institute retreats with FHI group leaders and postdocs were organized in 2014 and 2015. One synergetic activity arising from these workshops is the "*CO_2 Project at FHI*" aiming at the understanding of the chemical options to activate CO_2 with the focus on heterogeneous reaction pathways.

Before addressing these topics in more detail, some general aspects, special events and developments at the institute are presented.

Since the last meeting of the Fachbeirat the institute has strengthened its collaborations by the nomination of new Max Planck partner groups and a Max Planck Fellow:

- Three Max Planck partner groups have been established in 2015, aiming to promote the career of excellent junior scientists following their postdoc period at the institute: (i) Dr. *Fernando Stavale*, Brazilian Center for Physics Research and (ii) Prof. *Junling Lu*, University of Science and Technology of China collaborate with the Department of Chemical Physics and (iii) Prof. *Xinguo Ren*, Hefei University of Technology, China with the Theory Department, respectively.
- Prof. *Claudia Draxl*, Humboldt Universität zu Berlin was appointed Max Planck Fellow of the institute in July 2014. The work program includes studies on hybrid inorganic/organic systems, electron-phonon coupling, thermoelectric materials, and in particular the NoMaD (Novel Materials Discovery) project. The latter maintains a repository (see next paragraph), and it concerns a recently established European Center of Excellence (CoE) to develop a *Materials Encyclopedia* and *Big-Data Analytics* tools for materials science and engineering. Eight European complementary research groups of highest scientific standing in computational materials science along with four high-performance computer centers form the synergetic core of this NoMaD CoE.

In the context of the annual project 2015 funded by donations of the Fördernde Mitglieder (Supporting Members of the MPS) the Theory Department established a world-wide operating repository for input and output files of *ab initio* electronic structure calculations. The purpose of this „NoMaD repository“ is to host, organize, and share materials data. This enables the confirmatory analysis of computational materials data, their re-use, and repurposing for applications which may not correspond to the intention of the original calculations and publications.

The FHI continues to be involved in many activities within the Berlin-Brandenburg region, across Germany, and throughout the world, of which only a few can be mentioned here. The Cluster of Excellence UniCat and three Collaborative Research Centers (CRCs, Sonderforschungsbereiche) are funded by the German Research Foundation (Deutsche Forschungsgemeinschaft) and connect the institute with Berlin universities:

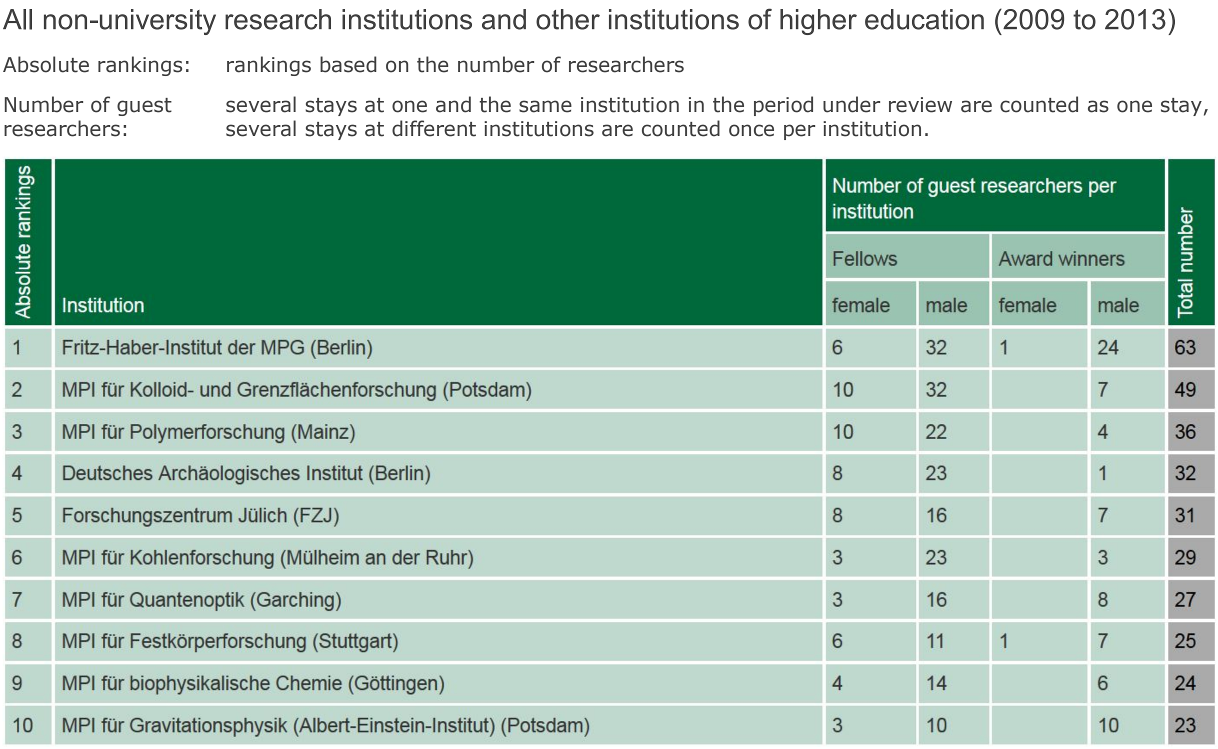
- The UniCat cluster plays a leading role in the Berlin area for interdisciplinary research in the fields of catalysis and chemical energy research, with a strong contribution from the FHI. Furthermore, the joint laboratory BasCat founded by UniCat, the Technische

Universität Berlin, and the chemical company BASF SE in 2011 runs its research program on oxidation catalysis with substantial input from the FHI.

- CRC 658: Elementary Processes in Molecular Switches at Surfaces
- CRC 951: Hybrid Inorganic/Organic Systems for Optoelectronics
- CRC 1109: Understanding of Metal Oxide/Water Systems at the Molecular Scale: Structural Evolution, Interfaces, Dissolution

Robert Schlögl acts as the founding director of the Max Planck Institute for Chemical Energy Conversion in Mülheim (see his report p. 63 ff). Furthermore, the FHI is a partner in the Max Planck-EPFL Center for Molecular Nanoscience and Technology in Lausanne/Switzerland and the Max Planck-UBC Center for Quantum Materials in Vancouver/Canada.

The FHI is international renowned for its research at the boundary between physics and chemistry and attracts a remarkably high number of guest scientists. One of the best known institutions in Germany for funding scientific excellence, the Alexander von Humboldt (AvH) Foundation, regularly publishes an analysis of those institutions where foreign scientists choose to go with their AvH fellowships or research awards (also called "voting with their feet"). Table 1 shows the top 10 entries for non-university research institutions of the last



All non-university research institutions and other institutions of higher education (2009 to 2013)

Absolute rankings: rankings based on the number of researchers

Number of guest researchers: several stays at one and the same institution in the period under review are counted as one stay, several stays at different institutions are counted once per institution.

Absolute rankings	Institution	Number of guest researchers per institution				Total number
		Fellows		Award winners		
		female	male	female	male	
1	Fritz-Haber-Institut der MPG (Berlin)	6	32	1	24	63
2	MPI für Kolloid- und Grenzflächenforschung (Potsdam)	10	32		7	49
3	MPI für Polymerforschung (Mainz)	10	22		4	36
4	Deutsches Archäologisches Institut (Berlin)	8	23		1	32
5	Forschungszentrum Jülich (FZJ)	8	16		7	31
6	MPI für Kohlenforschung (Mülheim an der Ruhr)	3	23		3	29
7	MPI für Quantenoptik (Garching)	3	16		8	27
8	MPI für Festkörperforschung (Stuttgart)	6	11	1	7	25
9	MPI für biophysikalische Chemie (Göttingen)	4	14		6	24
10	MPI für Gravitationsphysik (Albert-Einstein-Institut) (Potsdam)	3	10		10	23

Table 1: *The top 10 non-university institutes in Germany chosen by AvH fellows and AvH award winners. The full list can be found at https://www.humboldt-foundation.de/web/humboldt-rankings-2014.html*

survey in 2014 which covers the period from 2009 to 2013. As in the previous surveys the FHI ranks first.

On another note, the institute is also well connected to other institutions through its younger scientists who receive their education and training at the FHI and later find positions at various institutions worldwide. As an example we show in Table 2 the names of junior researchers of the institute who received an academic "call" and were appointed to positions at a professorship-level within the last five years. The FHI has produced a remarkably large number of high level academics in its field (among those are 13 calls in 2014 and 2015). This demonstrates the quality of our young scientists and also underlines the high level of education and training provided by the FHI.

Person	University	since	Person	University	since
Knut R. Asmis	Universität Leipzig, DE	2014	Niklas Nilius	Universität Oldenburg, DE	2012
Malte Behrens	Universität Duisburg-Essen	2014	Xinguo Ren	University of Science and Technology of China, CN	2013
Saswata Bhattacharya	Indian Institute of Technology, Dehli, IN	2015	Zefeng Ren	Peking University, CN	2012
Volker Blum	Duke University, US	2013	Patrick Rinke	Aalto University, FI	2014
Florencia Calaza	National University of the Littoral, AR	2015	Swetlana Schauermann	Universität Kiel, DE	2015
Yi Cui	Chinese Academy of Science, CN	2015	Martin Sterrer	Universität Graz, AT	2014
Ignacio Franco	University of Rochester, US	2013	Dangsheng Su	Chinese Academy of Sciences, CN	2011
Leonhard Grill	Universität Graz, AT	2013	Alexandre Tkatchenko	University of Luxemburg, LU	2015
Bothina Hamad	University of Jordan, Amman, JO	2012	Julian Tornow	Institut Energiesysteme und Energiewirtschaft	2014
Ville Havu	Aalto University, School of Science, FI	2013	Simon Wall	Institute for Photonic .Science, ES	2012
Raimund Horn	Technische Universität Hamburg-Harburg, DE	2013	Hua Wu	Fudan University, CN	2011
William Kaden	University of Central Florida, US	2014	Guo-Xu Zhang	Harbin Institute of Technology, CN	2015
Wei Liu	Nanjing University of Science and Technology, CN	2015	Qiang Zhang	Tsinghua University, CN	2011
Sebastiaan Y.T. v. d. Meerakker	Radboud University Nijmegen, NL	2011	Bum Suk Zhao	ULSAN National Institute of Science and Technology, KR	2011

Table 2: *List of 28 former members of the FHI who were appointed to academic positions (comparable to W-level positions in the German system) within the last five years (2011-2015)*

This page was corrected on 06. November 2015

We highlight here just a few of the awards, important grants and other distinctions earned by members of the institute:
Robert Schlögl received the Alwin Mittasch Award 2015 from the German Society for Catalysis und DECHEMA; *Hajo Freund* received the 2015 Michel Boudart Award for the Advancement of Catalysis, and was awarded an ERC Advanced Grant 2014/15 by the European Research Council (ERC); *Swetlana Schauermann* was awarded an ERC Starting Grant and a W2 Minerva Group; *Julia Stähler* obtained a W2 Max Planck Research Group and *Tobias Kampfrath* received the Karl Scheel Prize 2014 of the German Physical Society in Berlin.

While it is questionable to judge scientific quality by metrics, some indicators may give an impression of scientific output and productivity. The number of invited talks may serve as such a measure, since people are invited because of their novel results and the insight they offer. The total number of invited talks of members of the FHI was 343 in 2012, 356 in 2013, 324 in 2014 and 257 during the first nine months of 2015. Thus, almost every day of the year, there is one invited talk given by a member of the FHI worldwide.

Considering a longer time span a comparison of the annual number of publications with an FHI affiliation with their citations may be interesting. If we look over a period of 20 years the annual number of FHI papers is rather constant, however the number citations has steadily increased. For papers published between 1995 and 2014 it has now reached more than 17,000 per year compared to 5,300 citations in 1995 for the period 1976-1995 (see Fig. 1).

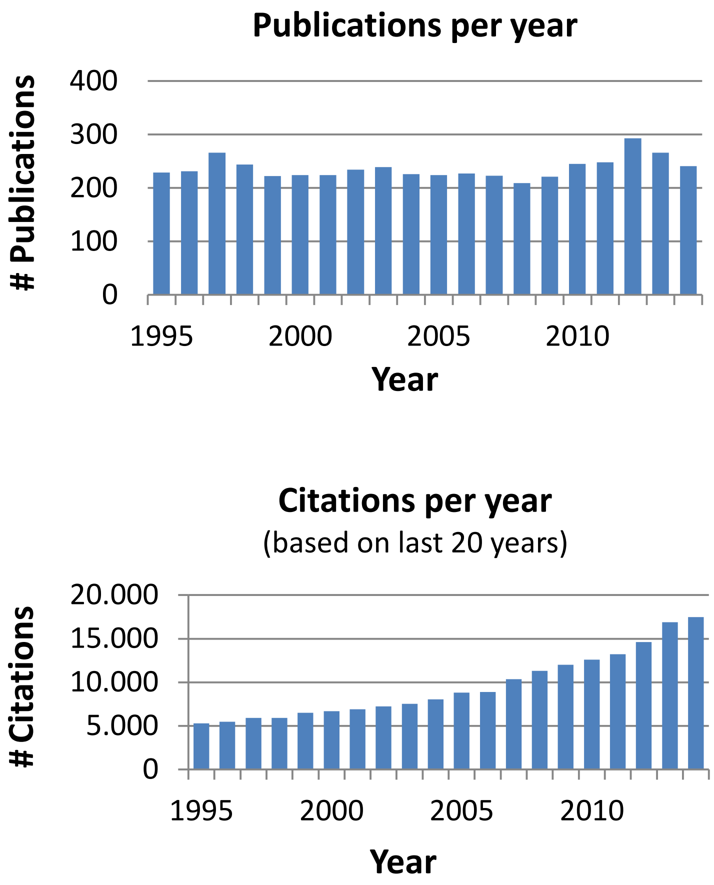


Figure 1: *Number of publications per year and number of citations of papers emerging from the FHI over a time span of 20 years according to ISI Web of Science, August 17, 2015*

A particular highlight of scientific events at the institute are the *Gerhard Ertl Lectures*, which since 2008 have been awarded by the three Berlin Universities, the Cluster of Excellence *UniCat*, BASF, and the FHI to outstanding colleagues from the fields of surface science and heterogeneous catalysis. The 2014 award recipient was Prof. *Richard Catlow*, following the previous winners: Gabor Somorjai (2008), Jens Nørskov (2009), Sir John Meurig Thomas (2010), Roald Hoffmann (2011), Charles T. Campbell (2012) and John T. Yates Jr. (2013). The *Gerhard Ertl Lecture 2015* will be given by Prof. Maki Kawai.

In April 2015 the Fritz Haber Institute organized, together with the Max Planck Institute for the History of Science, an international symposium to commemorate the centenary of the chemical attack with chlorine gas on 22nd April 1915 at Ypres, Belgium, in which Fritz Haber played a leading role. The symposium examined key aspects of chemical warfare – including ethical, legal, and dual use issues – from research on and deployment of chemical weapons in World War I to the development and use of chemical warfare during to the present day as well as ongoing international efforts to control the possession and elimination of chemical weapons. All contributions to the symposium will be published in a proceedings book. (see http://www.100-jahre-giftgaskrieg.de/).

Sprecher:
Wolfgang Eckart
Walter Grunden
Jeanne Guillemin
Jeremiah James
Jeffrey Johnson
Doris Kaufmann
Olivier Lepick
Roy MacLeod
Matthew Meselson
Karin Mlodoch
Götz Neuneck
Johannes Preuß
Florian Schmaltz
Ulf Schmidt
Edward Spiers
Hans Christof Graf von Sponeck
Margit Szöllösi-Janze
Ralf Trapp
Milos Vec

100 JAHRE
GIFT
GAS
KRIEG

Forschung, Einsatz, Folgen
chemischer
Massenvernichtungswaffen

SYMPOSIUM

21. und 22. April 2015
Harnack-Haus

Tagungsstätte der Max-Planck-Gesellschaft
Ihnestraße 16–20 · 14195 Berlin

Veranstalter:
Fritz-Haber-Institut der MPG
MPI für Wissenschaftsgeschichte

MAX-PLANCK-GESELLSCHAFT

Registrierung über
www.100-Jahre-Giftgaskrieg.de

Figure 2: *Announcement of the International Symposium on 100 Years of Chemical Warfare: Research, Deployment, Consequences, 21st and 22nd April 2015*

2. Concept for the Evolution of the Institute

In the context of the search process for a new director we have worked out a concept for the evolution of the FHI into the next decade, entitled “*Processes at Interfaces: From Atomistic Understanding to Intricacy*“. Within the portfolio of the Max Planck Society the FHI is the institute for Physical Chemistry and stands for the investigation of *processes* (e.g. reactions, their mechanisms and dynamics) at the boundary between physics, chemistry and materials science in contrast to other institutes aiming more at synthesis or material properties or even applied aspects.

The research area of the FHI is illustrated below spanning a triangle of controlled preparation of various interfaces, the study of elementary and molecular processes at such interfaces as well as fundamental aspects of chemical reactions and heterogeneous catalysis. This includes the growth and characterization of atomically well-defined interfaces, the study of reactivity and performance of stoichiometric and catalytic reactions, and the investigation of the underlying elementary processes and their dynamics on the relevant length and time scales. These range from the quantum level up to mesoscopic dimensions of e.g. supra-molecular arrays of nanostructures at solid-solid interfaces.

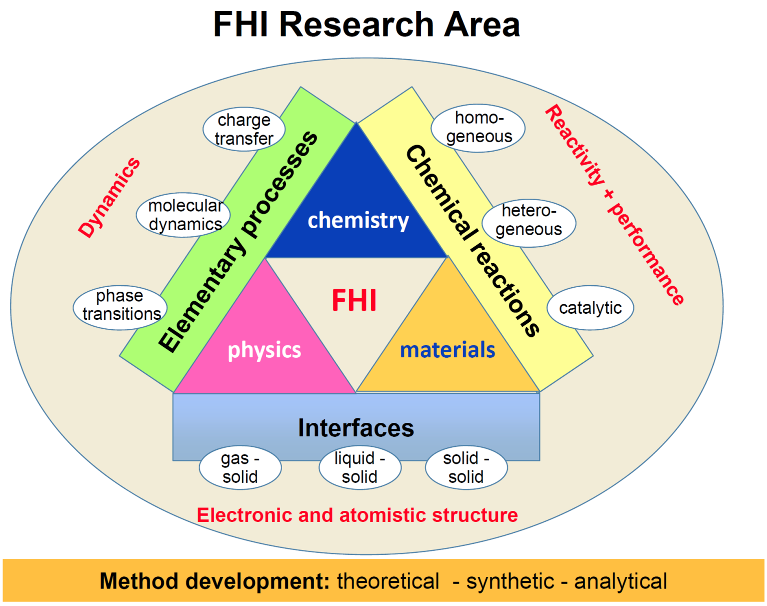


Figure 3: *FHI research field at the boundary between physics, chemistry, and material science*

The investigation of processes requires the analysis of temporal phenomena from ultrafast electron dynamics to chemical dynamics and microkinetics. A particular strength of the institute lies in its expertise to develop new experimental and theoretical methods and instrumentation, which range from analytical, spectroscopic and microscopy techniques (using synchrotron radiation, lasers, electrons or chemical probes) to the development of electronic structure theory and software packages used worldwide. Such method development provides a strong basis to address the intricacy of elementary processes and chemical reactions at interfaces with different degrees of complexity.

The FHI focuses its research on processes at interfaces between homogeneous and heterogeneous phases. The understanding of the structure and properties of such interfaces is quite differently developed in their maturity. It appears that our understanding of interface processes is far from being complete; in some areas being even in its infancy. In particular, solid-liquid and liquid-gas interfaces are probably by far the least understood. There exists a large "terra incognita" waiting to be explored by new approaches and methods. The FHI follows the strategy to investigate processes at gas-solid interfaces of increasing degree of intricacy at the atomistic level and will proceed towards the highly relevant, but less understood areas of (molecular) processes at liquid-gas and solid-liquid interfaces. Meeting this challenge will require massive method development to provide the tools to unravel the structure and dynamics of those interfaces at the atomistic level.

3. Search Process for a New Director

The FHI started the search process as soon as Gerard Meijer announced in 2012 that he would leave the institute. Following discussions with the Outlook Committee (Perspektiven-kommission) of the CPT Section, it was concluded that the search should be broad and independent of the existing research fields of the Molecular Physics department. In particular, research on ultracold molecules was considered to have little overlap with the general theme of the FHI, and the search did explicitly not include this topic. The board of directors of the FHI extensively discussed possible names and their respective research directions. The key criterion was scientific excellence, along with the goal to identify a candidate, who would provide scientific leadership for the FHI for the next decades.

Shortly before the visit of the Fachbeirat in February 2014 it turned out that the appointment process for our first candidate (proposed in 2013) would be not successful. The search process was thus restarted, considering quite a broad range of topics such as nanostructures, electrochemistry, solid state chemistry, functional materials and molecular processes in liquids and now including also possible candidates working in the field of theory. To aid the process, advertisements were placed in national and international research journals and further candidates were identified after discussions with members of the Fachbeirat and colleagues outside the FHI and evaluating other information like, *e.g.,* lists of recipients of ERC Starting Grants. Eight candidates were finally invited to visit the FHI to give a seminar and engage in intense discussions with the board. The search process was evaluated in the context of the scientific concept for the FHI outlined above. As pointed out in our concept, the institute aims at proceeding into new areas of interface science, which are much less understood and which require dedicated development of new methods. Based on this plan for the institute and the criterion of scientific excellence the board of directors proposed a candidate to CPT Section who is currently being evaluated by an appointment committee of the Max Planck Society. We will report on the most recent developments at the meeting of the Fachbeirat in November 2015.

4. FHI Institute Retreats

In May 2014 and 2015 we have organized two institute retreats where the directors, group leaders and senior postdocs discussed current research topics of the institute. These workshops were very beneficial to foster exchange between the scientists of all departments. One spinoff resulting from these retreats is the "*CO_2 Project at FHI*", a joint activity of all departments aiming at understanding of the chemical options for CO_2 activation. Furthermore, the current status and the concept for the future development of the FHI FEL were discussed. More details are given below.

4.1 The FHI Free-electron Laser Facility

The FHI FEL started regular operation in November 2013 and is now successfully employed for vibrational spectroscopy of molecules and clusters in the gas phase and for non-linear optics of solids (for details see report p. 31 ff). The current setup opens new possibilities for IR spectroscopy of a broad range of systems ranging from (bio)molecules in He droplets to metal clusters on oxide surfaces. In the present mode of operation electrons from a linear accelerator with energies up to 50 MeV generate a train of intense light pulses in the mid-infrared (MIR) wavelength range (from 3.6 to 50 μm) in an IR laser cavity with an undulator. A further mode of low-repetition rate operation combined with sub-picosecond synchronization with a femtosecond laser oscillator is currently under development.

We propose a future machine upgrade of the FHI FEL for two-color experiments and an extended wavelength range into the far-infrared (FIR), which would enable a new class of experiments and make the FHI FEL a unique instrument worldwide. This will open the door for new applications, such as two-dimensional IR-spectroscopy in the MIR regime, two-color action spectroscopy pumping several vibrational modes or double resonant sum-frequency generation. Such novel techniques will provide fundamental insights into the coupling between different vibrational modes which are not accessible by table-top experiments, and may significantly enhance the microscopic understanding of molecular processes.

For such two-color operation, a technical design concept has been developed to modify the electron accelerator and beamline system as illustrated schematically in Fig. 4. It is based on the generation of two trains of micro-bunches of alternating energies by an 500 MHz "after-burner" cavity, which are separated in dispersive magnet structures and synchronously seed two IR cavities with undulators in the mid- and far-infrared regime. In this manner two trains of synchronized laser pulses are generated, which are independently tunable over a large wavelength range.

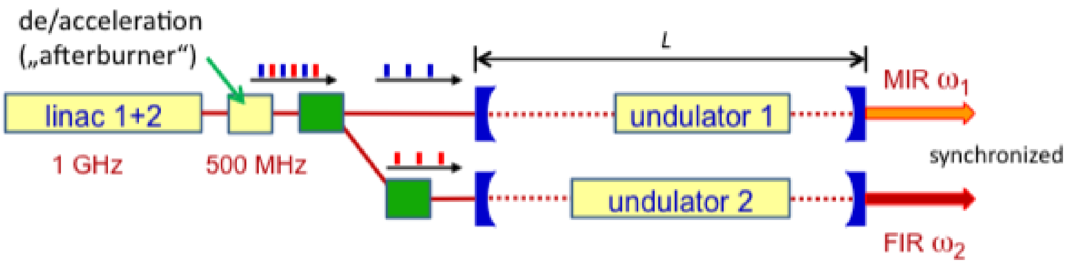


Figure 4: *Schematic diagram of the proposed two-color upgrade of the FHI FEL*

Furthermore, it will also be highly interesting to extend the wavelength range accessible by the FEL to longer wavelengths. By appropriate design of a second FEL branch the wavelength range can be extended into the far-infrared region (beyond 100 µm) to study low-frequency modes at THz frequencies, such as vibrations involving heavier atoms, e.g. in clusters, collective motions in bio-molecules and correlated atomic motions in solids.

4.2 The CO_2 Project at FHI

During the FHI institute retreats within the last two years it was found that all departments have an interest in and can contribute to a generalized understanding of the chemical options to activate CO_2. This is a "hot topic" at present and has also long-standing roots in FHI activities. The research concept consists of a commonly developed hypothesis on how the family of reactions comprising "CO_2 activation" may work, plus a set of experiments conducted individually or jointly in each of the departments. A "CO_2 team" of group leaders and interested co-workers from all departments of the FHI meets regularly to discuss progress and to eventually refine the working hypothesis. Selected results of individual experiments are described in the departmental sections of this report.

In Fig. 5 the cumulative options for activating CO_2 without complete rupture of the molecule are shown. Pathway (A) represents the direct reduction of CO_2 with an energetic electron. The resulting bent CO_2 carboxyl is quite reactive and can either react with a base to form thermodynamically stable –ate anions (carbonate, carbamate) or react with a proton and form a formate species that can further react to methanol and hydrocarbon fragments. This is the path of heterogeneous surface activation reactions. Pathway (B) involves reaction of CO_2 with molecular nucleophiles or electrophiles in the form of metal coordination compounds leading to molecular activated forms. Pathway (C) describes the interaction with a Lewis-acid-base pair leading to a bent uncharged form of activated CO_2.

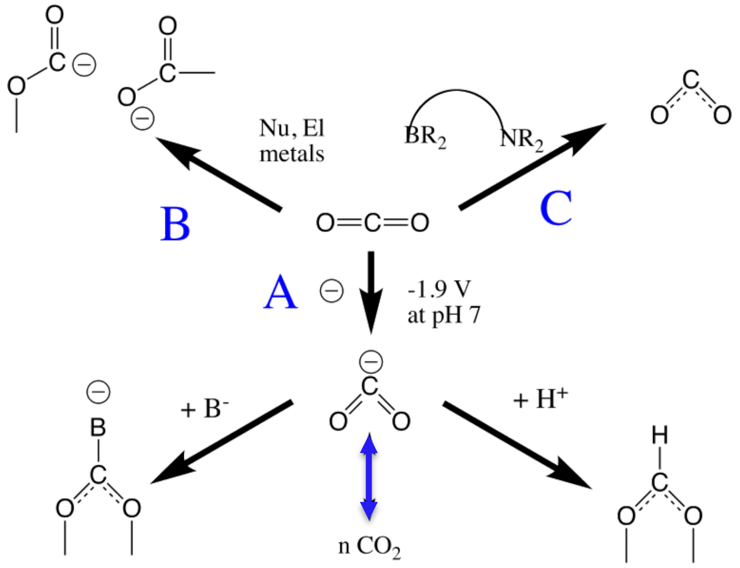


Figure 5: *Different possibilities (A, B, C) for reactions of CO_2. indicate principal pathways. The double arrow (blue) highlights the importance of solvation of the intermediate with either additional molecules or (not shown) with solvents*

We have decided to study the reductive activation with catalysts providing electrons with sufficient reducing potential. One group of systems stems from doped metal oxides carrying a gold nanostructure as „antenna“ for a negative charge. Such systems were prepared and functionally studied extensively in the CP department and can be synthesized in polycrystalline form for reaction studies in the AC department. Doped metal oxides with local charges but without gold can also serve for CO_2 activation. They are studied theoretically in the TH department and will be synthesized for performance studies in the AC department. The target reaction is here activation of CO_2 in the Sabatier reaction to methane. A particular relevant oxide in this context is Cr_2O_3, a system that was studied for CO_2 activation upon doping with Pd earlier on in the FHI. These studies will be resumed again jointly between the CP and AC departments.

Another focus system for CO_2 activation is ZnO. It can be reduced such that it provides electrons from its semiconducting band structure in addition to the co-existence of Lewis acid and Lewis base sites at the surface. This interplay with and without hydrogen stimulating the charge carrier dynamics is studied in the PC department. In a collaboration between the departments PC and AC, the methods of time-resolved photoemission and THz spectroscopy will be used in an in-situ mode to track the possible relation of catalytic activity and charge carrier dynamics. A mechanism of how ZnO interacts with Cu in the famous „synergy“ of high pressure methanol synthesis may be a spill-over driven partial reduction of ZnO (for which the systems in the PC department are then the functional models) occurring at a perimeter interface between Cu and ZnO. Such systems are prepared as planar model systems in the CP department and are now studied for their reactivity. Again the AC department synthesizes polycrystalline ZnO/Cu systems to investigate the relation of such geometries to the technical nanostructured Cu/ZnO/X promoted performance catalyst. The role of solvating CO_2 in activated form by molecular species in homoleptic and heteroleptic environments is the target of a study started using gas-phase clusters of enzymatically activated CO_2 and vibrational spectroscopy at the FHI-FEL. In the MP department there is expertise in studying Zn-containing bio-molecules and, of course, in analyzing solvation clusters of ionic species.

In summary, the wide range of experimental and theoretical expertise of the departments in the FHI is focussed on the analysis of reaction pathways of the CO_2 molecule. At present we deliberately omit the electrochemical activation of CO_2 as this seems a still too complex undertaking given the methodical deficits in analyzing liquid-solid and liquid-gas interfaces. We concentrate on the heterogeneous reaction pathway and are ready to share our observations with studies conducted in the UniCat COE focussing on molecular pathways of CO_2 activation.

5. Staff, financial and organisational aspects

In January 2015, 400 people - 92 Ph.D. students, 62 postdocs, 38 senior scientists, scientific guests as well as 150 technicians and other supporting (i.e. non-scientific) staff members - worked at the FHI. Among the 192 scientists, 23% are female, however it can be also noted that this percentage drops from 32% for Ph.D. students to 19% for postdocs and to only 8% for senior scientists. We believe that these numbers are typical for the field of physical chemistry and cannot be easily improved. In order to support young parents, for example, the

FHI provides places in a Max-Planck- day care center, a family room at the FHI, and also offers enhanced travel support for young parents for visiting scientific conferences.

Recently, the Max Planck Society implemented new regulations for the support of junior scientists, which went into effect on 1. July 2015. According to these regulations, new graduate students can only be hired on regular employment contracts including social benefits, while the support in form of a stipend is no longer permitted (with the exception of short term stays in the framework of a guest program). For postdoctoral researchers, a regular employment contract will be standard, and stipends can only be given to a limited number of researchers, also within the framework of a guest program. Contracts or stipends currently in place are not affected. The goal of the Max Planck Society is to reduce the number of postdoctoral researchers with stipends to a maximum of 1/3 of the entire number of postdocs; it is expected that these goals are reached in 2019 at the latest.

Even before those regulations were announced, the majority of graduate students and postdoctoral researchers at the FHI were already employed via contracts, and stipends were awarded when the type or duration of research or other circumstances deem a stipend to be the better choice of support. For example, in January 2015, 60% of the graduate students at the FHI were supported by means of an employment contract. At the postdoc level, employment contracts accounted for 55%. Due to the new regulations, no new stipends will be awarded for PhD student, so that the goal of the MPG that all graduate students will be supported by means of a contract will be reached automatically within the next few years. Stipends for researchers at the postdoc level will be awarded within the framework of a FHI guest program and the board of directors will pay attention to satisfy the regulations.

Three years ago, the Max-Planck-Society experienced financial difficulties which were also felt by the FHI. In the meantime, the situation has stabilized, and presently, the core budget allocated by the institute is stable with a slight compensation towards price and wage increases. Additional flexibility in research comes from contracts via external funding sources as well as from peer-reviewed, internal MPS project schemes. Among the external funding sources, the DFG, the EU (including several ERC grants), activities funded by the Federal Ministry of Research (BMBF), and the Alexander von Humboldt Foundation are the largest contributors.

When walking across the FHI campus, one will notice a flurry of construction activities. The two most important ones are the new laboratory and office building for the Physical

Chemistry department, which has made substantial progress, as well as the general infrastructure project consisting of a range of concerted activities to replace and modernize aging electrical, water and sewage as well as communication infrastructure. So far, all of activities progress well and are within schedule.

A vital part of the FHI is the International Max Planck Research School (IMPRS) “Functional Interfaces in Physics and Chemistry”, which creates an interdisciplinary platform for PhD education that combines cutting edge research with a thorough training of the students and has been prolonged until September 2020. I am acting as the spokesperson and Tobias Kampfrath as the coordinator. A detailed description is given in a separate report (p. 17 ff).

Furthermore, our service groups form a crucial part of the institute’s infrastructure, since they provide important support for the construction of complex equipment or IT solutions which are not easily available on the market. Their activities are described in this booklet on p. 53 ff.

In conclusion, we are very pleased to report that the whole institute, including the non-academic staff, creates an extremely pleasant, friendly and productive atmosphere that helps our scientists to work hard and to be creative. Many thanks go to all our coworkers for their invaluable efforts. We hope that the Fachbeirat will also sense some of this spirit during its visit.

As the managing director and in the name of the Kollegium as well as the whole Fritz-Haber-Institute, I wish to thank the members of the Fachbeirat for their continuing support and guidance. We are all looking forward to fruitful and stimulating scientific discussions and would like to warmly welcome you to Berlin in November 2015.

Berlin-Dahlem, September 15, 2015

Martin Wolf

Martin Wolf

International Max Planck Research School
'Functional Interfaces in Physics and Chemistry'

Spokesperson

Martin Wolf, FHI[1]

Coordinator

Tobias Kampfrath, FHI

Faculty Members

Mario Dähne, TU
Claudia Draxl, HU
André Fielicke, TU
Katharina Franke, FU
Hans-Joachim Freund, FHI
Norbert Koch, HU
Beate Paulus, FU
Klaus Rademann, HU
Thomas Risse, FU
Peter Saalfrank, UP
Joachim Sauer, HU
Matthias Scheffler, FHI
Robert Schlögl, FHI
Reinhard Schomäcker, TU
Martin Weinelt, FU
Martin Wolf, FHI

PhD-Student Members

Alexandr Alekhin, *Russia*
Matthias Baldofski, *Germany*
Kevin Bethke, *Germany (since 10/14)*
Kamil Bobowski, *Germany (since 09/14)*
Stefan Böttcher, *Germany (until 11/14)*
Bo-Gaun Chen, *Taiwan (until 04/15)*
Earl Davis, *Great Britain (since 10/14)*
Jan-Christoph Deinert, *Germany*
Petr Dementyev, *Russia*
Emre Emmez, *Turkey*
Felix Feiten, *Germany*
Edoardo Fertitta, *Italy (since 03/14)*
Vinzenz Fleischer, *Germany*
Alexander Fuhrich*, Germany (since 10/14)*
Francesca Genuzio, *Italy*
Vivekanand Gobre, *India*
Lukas Hammerschmidt, *Germany*
Maria Heenemann, *Germany*
Mallikarjun Karra*, India (since 09/14)*
J. Frieder Kettemann, *Germany (since 04/14)*
Sophia Ketterl*, Germany (since 09/14)*
Arpan Kundu, *India*
Adrián Lewandowski, *Argentina (since 07/15)*
Xiaoke Li, *China*
Bo-Hong Liu, *Taiwan*
Lukas Marsoner, *Italy*
Francesca Mirabella*, Italy (since 03/14)*
Christopher Nicholson*, Scottland*
Andrzej Niedziela, *Poland*
Leandro Pascua, *Spain (until 06/15)*
GiovanniMaria Piccini, *Italy (until 04/15)*
Nina Richter, *Germany*
Daniela Rolf, *Germany (since 10/14)*
Nora Salas Illanes, *Chile*
Robert Scholz*, Germany (since 05/15)*
Thorsten Schulz*, Germany (since 01/15)*
Jianchao Si*, China (since 12/14)*
Xin Song, *China*
Christian Stemmle, *Germany (since11/14)*
Christian Stiehler*, Germany (until 07/15)*
Stefanie Stuckenholz, *Germany*
David Yubero Valdivielso*, Spain (since 03/14)*
Elisabeth Wolf, *Germany (since 09/14)*
Jonas Wirth, *Germany (until 02/15)*

---

[1] Abbreviations: FU: Freie Universität Berlin; HU: Humboldt-Universität zu Berlin;
TU: Technische Universität Berlin; FHI: Fritz-Haber-Institut; UP: Universität Potsdam

General Remarks

The International Max Planck Research School (IMPRS) 'Functional Interfaces in Physics and Chemistry' (http://www.imprs-cs.mpg.de), launched in 2002 under the former name 'Complex Surfaces in Materials Sciences', is a structured PhD program that aims at attracting outstanding students from all over the world to the Fritz Haber Institute (FHI). It creates an interdisciplinary platform for PhD education that combines cutting-edge research with a thorough training of the students in the broad field of surface and interface science. The school is settled not only at the five departments of the FHI, but also involves various groups at the Freie Universität, the Humboldt-Universität, the Technische Universität (all Berlin-based), and (since 2012) at the Universität Potsdam (see Figure 1). Owing to its interdisciplinary character, the IMPRS is able to offer PhD projects in such fields as heterogeneous catalysis, surface science, thin-film magnetism, physics of ultrafast processes, and computational chemistry. This variety in the scientific program in conjunction with close and regular interactions between the school members is the main strength of the IMPRS and an important prerequisite for its success.

In September 2014, the IMPRS has completed its second funding period which started with the first positive evaluation of the school in 2006. In October 2014, the school has entered its third funding period (10/2014-09/2020), following a second, again successful evaluation of the previous funding period and of the prolongation proposal by a committee of international, high-ranking reviewers in May 2013. The start of the new funding period was accompanied by several gentle readjustments of the school structure.

After unexpected budget cuts on the order of 20% in 2012 and 2013 (announced by the General Administration of the MPG in 2012), the school is now back at the requested funding level of 348 T€ per year. An additional ~200 T€ per year enter the IMPRS budget in the form of salaries paid directly by the FHI and the partner universities. Currently, two stipends are funded for one year by the Friede Springer Foundation. The sum of these contributions provides a stable and generous financial frame for our activities and allowed us to simultaneously award more than ten fellowships to our school members. The remaining budget is used to pay our secretary and to finance all school activities including guest speakers, seminars and workshops for the students.

We currently look at a total of 98 IMPRS students, counting the present (38) students as well as those (60) who graduated from 2004 to 2015. About 55 % of the students came from sixteen different foreign countries, for example Italy, Scotland, Russia, China, Taiwan, South

America and India. The total published output amounts to an average of 4-6 papers per student. On a statistical average, 3.7 years were required to obtain a doctoral degree, close to the target value of 3.5 years. Most of the students finished their PhD either with mark ‘very good’ (‘magna cum laude’: 76%) or ‘with distinction’ (‘summa cum laude’: 18%), and no student failed to graduate at the end of the membership in the school. Particularly positive events were the awards of distinguished prizes to six of our students, who either received the ‘Otto Hahn Medal’ of the Max Planck Society for an outstanding thesis, the ‘Klaus Tschira Award’ or the ‘Wilhelm-Ostwald-Nachwuchspreis’.

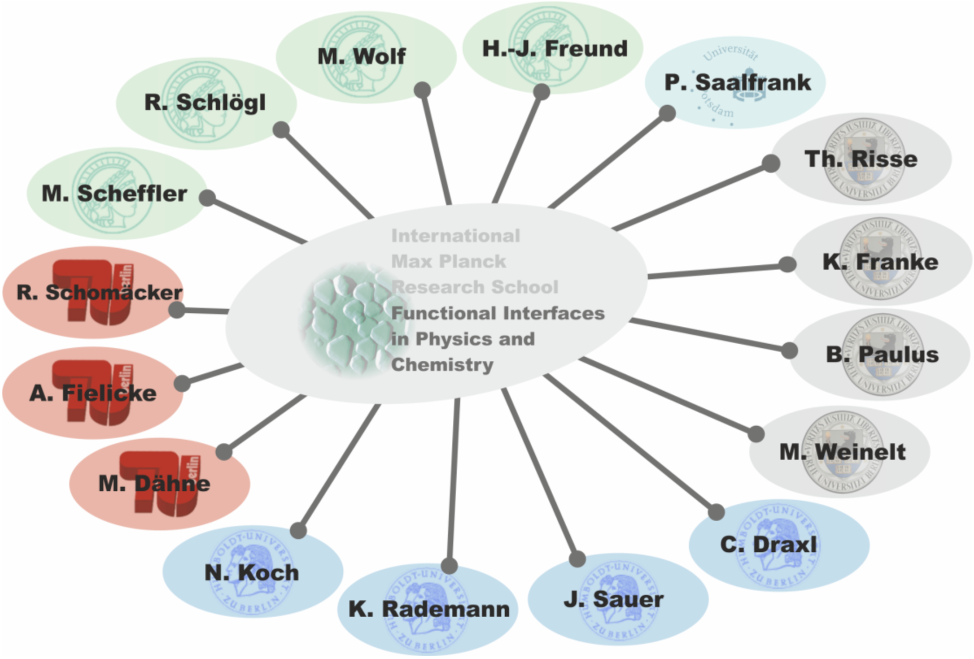


***Figure 1:** Scientific members of the IMPRS ‘Complex Surfaces in Materials Science’ as of October 2013 (green: FHI, grey: Freie Universität Berlin, blue: Humboldt-Universität Berlin, red: Technische Universität Berlin, light-blue: Universität Potsdam). The figure already shows the new name of the School (‘Functional Interfaces in Physics and Chemistry’) after renewal in a third period (2014-2020).*

Two general trends may be identified when analyzing the career perspectives of our students after obtaining a PhD. The first group almost instantaneously found positions in the R&D or management units of big German enterprises, in particular in technologically oriented companies (Siemens, Bosch, Volkswagen, SAP), in the chemical industry (BASF and Bayer) and in the financial and administration sector (Deutsche Bank, McKinsey, Allianz Group). This first route was often chosen by students who were fluent in the German language. The other portion of our members continued a scientific career, typically with a postdoctoral position in a recognized research institute or a university outside Germany.

Research

The research conducted in the framework of the IMPRS mirrors the development in surface and interface science over the last decades. The activities progressed from studies of highly idealized single crystals towards complex surfaces and interfaces, comprising nanocrystalline and amorphous materials, layered systems, materials with a well-defined dopant level or magnetic order. In the new funding period, new member groups augment the scientific profile of the school with such topics as interface-specific and ultrafast spectroscopies and charge-transfer processes across interfaces of organic photovoltaic materials. In addition to experimental work, a broad range of theoretical activities is accomplished within the school, and the close connection between theory and experiment is one particular aim of the IMPRS.

All material systems are analyzed with respect to their structural, electronic, magnetic and optical properties. For example, adsorption and reactivity studies are performed in order to provide insight into chemical processes taking place at complex surfaces and interfaces. Ultrafast spectroscopy provides insights into elementary processes that evolve on femtosecond time scales. In particular in terms of catalysis, experiments performed in a laboratory environment are relevant to industrial applications. All studies aim at gaining a better understanding of the equilibrium and dynamic properties of heterogeneous systems and their microscopic origin, potentially resulting in synthesis of complex materials with yet unrivalled catalytic, electronic or photonic properties.

Student training

A comprehensive education of our students, both in scientific aspects and secondary skills is one of the central goals of the IMPRS ‘Functional Interfaces in Physics and Chemistry’. In the second funding period, we have dedicated major efforts to achieve this goal, as detailed in the following. On the basis of a structured curriculum that is mandatory for our students, all academic school members and many external experts were engaged in this training program. The curriculum is based on three fundaments, (i) two week-long block-courses per year, (ii) every 2 months discussion meetings with the coordinator, and (iii) a number of soft-skill seminars organized by external experts.

The *block courses* try to impart the necessary background knowledge in the methodology, concepts, and theoretical foundations of surface science and chemistry. They are divided into two parts. The fundamental courses (held in spring) provide an introduction into the basics of physics and chemistry of surfaces. Typical topics are ‘Structures of crystalline solids’, ‘Electronic properties of surfaces’, and ‘Experimental methods of surface science’. To give an example of a fundamental course, we have added the schedule of the 2014 spring course as Table 1 to this report. The advanced courses (held in fall) address more specialized topics associated with surfaces and interfaces, such as ‘Group theory’ and ‘Ultrafast chemistry’. Each block course contains an average of 16 lectures of 90 minutes duration and is given by senior scientists of the FHI, professors from the Berlin universities and external specialists in the field.

Courses address the basics and latest developments in surface/interface science, including spin physics, ultrafast processes, and organic/inorganic interfaces which are, for example, of central importance in organic light-emitting diodes. It is very important to mention that these scientifically diverse phenomena are based on very similar fundamental principles (such as the theory of electronic structure and interface states, perturbation theory, or the concept of charge transfer). In this manner, the block courses bridge language barriers between the different fields and provide a common experimental and theoretical background for all IMPRS students with their different background (chemistry, physics, material science). The practical component of the specialized courses is enhanced by enabling more hands-on experience of various experimental and theoretical methods.

	Mon, 7 Apr	**Tue, 8 Apr**	**Wed, 9 Apr**	**Thu, 10 Apr**
9:00-10:30h	**H.-J. Freund (FHI):** *Introduction to surfaces and their characterization*	**R. Schomäcker (TU):** *Fundamental aspects of applied heterogeneous catalysis (part 1)*	**T. Kampfrath (FHI):** *Signal theory: Fourier analysis, signal sampling and reconstruction*	**H. Junkes (FHI):** *Interfaces (serial, USB, ethernet) and their characteristics, IP network*
11:00-12:30h	**M. Wolf (FHI):** *Electronic structure of solids and their surfaces*	**R. Schomäcker (TU):** *Fundamental aspects of applied heterogeneous catalysis (part 2)*	**H. Junkes (FHI):** *Basics of data acquisition: analog-to-digital conversion, sampling resolution, noise, cables, bandwidth*	**H. Junkes (FHI):** *Data acquisition with realtime-systems. Usage of Matlab, LabVIEW, EPICS*
14:00-15:30h	**H. Appel (FHI):** *Introduction to static and time-dependent density functional theory*	**N. Koch (HU):** *Introduction to organic semiconductors*	**H. Junkes (FHI):** Exercise: *Setting up a Raspberry Pi with I/O interfaces as a Linux-based acquisition system*	**H. Junkes (FHI):** Exercise: *Setting up EPICS on the Raspberry Pi* http://www.aps.anl.gov/epics
16:00-17:30h	**T. Risse (FU):** *Thermodynamics and kinetics of surface processes*	**N. Koch (HU):** *Organic (opto-) electronic devices and their interfaces*	**H. Junkes (FHI):** Exercise (continued): *Setting up a Raspberry Pi* http://www.raspberrypi.org	**H. Junkes (FHI):** Exercise (continued): *Building a demonstration of DAQ, FFT, aliasing etc.*

Table 1: *Program of the lecture series held in April 2014*

The *discussion meetings* (held every two months) include all students and the coordinator and provide an informal platform to review recent research developments in the school, welcome new members and organize coming activities. In addition, three students per meeting present their scientific results in a 20-minutes talk followed by 15 minutes of discussion. These regular talks in front of the school stimulate the students to improve their presentation skills, but also provide critical feedback on their scientific work. For example, each speaker receives written feedback in the form of templates that two students fill out and that address various aspects of the quality of the presentations. In general, the discussion meetings are important to establish and maintain the scientific coherence of the school, as all ongoing research activities are introduced and analyzed. As the main advantage of these meetings, we want to emphasize their open, casual, and informal atmosphere that fosters an active participation (especially of young students) and provides room for scientific exchange.

Finally, the *soft-skill seminars* aim at improving the soft and secondary skills of the school members, such as their presentation and writing abilities. For this purpose, we have organized a variety of courses and workshops in order to prepare the young scientists for a possible academic or non-academic career. In the period from 2013 to 2015, the following soft-skill seminars have been organized by the School (Table 2).

Date	Topic	Lecturer
19. - 22. Feb.2013	Introduction to LabView programming	Marcel Krenz
25. - 26. Feb. 2014	Effective Presentations	F. Steven Weir
10. - 11. Jul. 2014	Academic Writing: “How to create good texts”	Prof. B. Warren-Kretzschmar
25.-26. Nov. 2014	Application Standards - Personal Strategies	Dr. Simon Golin
04.-05. June 2015	Academic Writing	Prof. B. Warren-Kretzschmar

Table 2: *Examples of soft-skill seminars in the IMPRS*

Special highlights of our activities are the external workshops, the last of which was carried out in the beautiful venue of Ringberg Castle in Bavaria in February 2015 (see http://www.imprs-cs.mpg.de/workshop2015). The school members had the unique possibility to organize a conference themselves, and they selected and invited 16 outstanding researchers from all over the world. A special conference concept that was developed in particular for this occasion provided a maximum of communication and interaction between the invited speakers and the school members. Due to this open atmosphere, the meeting was an unrivalled experience for our students, giving them insight into the international scientific landscape and the chance to make contacts for their future professional career.

List of lecture courses organized by the IMPRS (2013 – 2015)

Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,
Fritz-Haber-Institut der MPG, October 2012 - Febr. 2013.
IMPRS-Block Course: ‘Aspects of Physics and Chemistry of Surfaces’,
Fritz-Haber-Institut der MPG, March 21- 26, 2013.
IMPRS-Block Course: ‘Dynamic processes at interfaces and surfaces’,
Technische Universität Berlin, Sept. 27- Oct.02, 2013.
Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,
Fritz-Haber-Institut der MPG, October 2013 - Febr. 2014.
IMPRS-Block Course: ‘Interface/surface science and data acquisition/analysis’,
Fritz-Haber-Institut der MPG, April 07 – 10, 2014.
IMPRS-Block Course: ‘Hands-on course’ on different projects of the IMPRS
Fritz-Haber-Institut der MPG, October 06 -10, 2014.
Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,
Fritz-Haber-Institut der MPG, October 2014 - Febr. 2015
IMPRS Workshop: ‘Micro to Macro’,
Schloß Ringberg, Tegernsee, Febr. 09 – 13, 2015
IMPRS-Block Course: 'Excited States: Properties, Dynamics and Spectroscopy',
Freie Universität Berlin, October 05 – 08, 2015.

PhD-Projects within the IMPRS (2013-2015)

Alekhin, Alexandr, Russia, Supervisors: Prof. Wolf/Prof. Weinelt (FHI/FU),
“Ultrafast hot carrier driven magnetization dynamics”.
Baldofski, Matthias, Germany, Supervisors: Prof. Sauer/Prof. Freund (HU/FHI),
“Micro-kinetic modeling of the oxidative coupling of methane”.
Bethke,Kevin, Germany, Supervisors: Prof. Rademann/Prof. Freund (HU/FHI)
“Thin Film Thermoelectrics”.
Bobowski, Kamil, Germany, Supervisors: Prof. Weinelt/Dr. Ernstorfer (FU/FHI),
“Study of ultrafast dynamics in magnetic thin film systems”.
Böttcher, Stefan, Germany, Supervisors: Prof. Risse/Prof. Horn (FU/FHI)
“Functionalization of Graphene”.
Chen, Bo-Gaun, Taiwan, Supervisors: Prof. Rademann/Dr. Christen (HU),
“Interactions of clusters with modified silicon surfaces”.

Davis, Earl, Great Britain, Supervisors: Prof. Freund (FHI),
“Growth and Characterisation of Fe3O4 and Fe3S surfaces”.

Deinert, Jan-Christoph, Germany, Supervisors: Prof. Wolf/Prof. Dähne (FHI/TU),
“Zinc Oxide Surfaces and Interfaces: Electronic Structure and Charge Carrier Dynamics”.

Dementyev, Petr, Russia, Supervisors: Prof. Freund/Prof. Schomäcker (FHI/TU),
“Energetics of Gas-Surface Interactions by Single Crystal Adsorption Calorimetry”.

Emmez, Emre, Turkey, Supervisors: Prof. Rademann/Prof. Freund (HU/FHI),
“The Reactivity Studies of Aluminosilicate (Zeolite) Thin Films grown on Ru (0001) Substrate”.

Feiten, Felix E., Germany, Supervisors: Prof. Freund/Prof. Risse (FHI/FU),
“The Surface Structure of V2O3(0001) determined by I/V-LEED and STM”

Fertitta, Edoardo, Italy, Supervisors: Prof. Paulus (FU),
“Ab initio calculations of metal chains and rings”.

Fleischer, Vinzenz, Germany, Supervisors: Prof. Schomäcker/Prof. Schlögl (TU/FHI),
“Resolution of the surface and gas phase contributions to the mechanism of the oxidative coupling of methane (OCM) at Na2WO4-Mn-SiO2-catalyst”.

Fuhrich, Alexander, Germany, Supervisors: Prof. Freund/Prof. Fumagalli) (FHI/FU),
“Spectromicroscopic investigations of Nanoparticles on ultra-thin oxide films”.

Genuzio, Francesca, Italy, Supervisors: Prof. Freund/Prof. Winter (FHI/HU),
“Spectroscopic characterization of metal nano-particles on thin hematite films”.

Gobre, Vivekanand, India, Supervisors: Prof. Scheffler/Dr. Tkatchenko (FHI),
“Van der Waals interactions for adsorption on ionic solids”.

Hammerschmidt, Lukas, Germany, Supervisors: Prof. Paulus/Prof. Risse (FU)
“Theoretical investigation of nano-structured thermoelectric materials”.

Heenemann, Maria, Germany, Supervisors: Prof. Schlögl/Dr. Eichelbaum (FHI),
“The influence of charge transport in high performance oxidation catalysts on activity and selectivity: Contactless measurements of Hall mobilities and charge carrier concentrations under reaction conditions “.

Karra, Mallikarjun, India, Supervisors: Prof. Friedrich (FHI/FU),
“Study of configurations of van der Waals complexes controlled via London dispersion forces as revealed by the means of Stark spectroscopy in He-nanodroplest”.

Kettemann, J. Frieder, Germany, Supervisors: Prof. Rademann/Prof. Freund (HU/FHI),
“Growth Mechanisms of Bimetallic Nanoparticles”.

Ketterl, Sophia, Germany, Supervisors: Prof. Weinelt/Prof. Rader (FU/HZB),
“Two-Photon Photoemission on Topological Insulators”
Kundu, Arpan, India, Supervisors: Prof. Sauer/Dr. Christen (HU),
“Accurate energy and free energy calculation of small molecule and surface”.
Lewandowski, Adrián, Argentina, Supervisors: Prof. Freund (FHI),
“Scanning probe microscopy on doped silica thin films”.
Li, Xiaoke, China, Supervisors: Prof. Sauer/Prof. Freund (HU/FHI),
“Density functional calculations of interactions between molecules and oxide surfaces”.
Liu, Bo-Hong, Taiwan, Supervisors: Prof. Freund/Prof. Risse (FHI/FU),
“Preparation and Structure of Ultra-Thin Zinc Oxide Films on Pt(111), Ag(111) and Cu(111)”.
Marsoner Steinkasserer, Lukas E., Italy, Supervisors: Prof. Paulus (FU)
“Theoretical first-principles investigation of graphene nano-structures on metallic surfaces”.
Mirabella, Francesca, Italy, Supervisors: Prof. Freund/Prof. Rademann (FHI/HU),
“Reaction kinetics on supported nanoparticles studied by molecular beam techniques/Time resolved IR spectroscopy”.
Nicholson, Christopher, Scottland, Supervisors: Prof. Wolf/Prof. Weinelt (FHI/FU)
“Ultrafast Dynamics in Solids probed by time-resolved ARPES”.
Niedziela, Andrzej, Poland, Supervisors: Prof. Sauer/Dr. Sierka (HU) ,
“Efficient optimization methods for large scale systems as used in heterogenous catalysis“.
Pascua Arcusin, Leandro, Argentina, Supervisors: Prof. Freund/Prof. Pascual (FHI/FU),
“Exploring the Luminescence Characteristics of Zinc Oxide Thin Films: The Role of Defects, Impurities and Metal Ad-Particles “.
Piccini, GiovanniMaria, Italy, Supervisor: Prof. Sauer (HU) ,
“Ab Initio Free Energies of Adsorption from Anharmonic Vibrations “.
Richter, Nina, Germany, Supervisors: Prof. Risse/Prof. Freund (FU/FHI),
“Defect chemistry of thin metal oxide films”.
Rolf, Daniela, Germany, Supervisors: Prof. .Franke/Prof. Wolf (FU/FHI),
“Electron transport through magnetic molecules on surfaces”.
Salas Illanes, Nora, Chile, Supervisors: Prof. Draxl/Prof. Scheffler (HU/FHI)
“Electronic Structure by Means of Many-body Perturbation Theory “.
Scholz, Robert, Germany, Supervisors: Prof. Saalfrank (Uni Potsdam),
“Laser- and electron driven adsorbate dynamics at metal surfaces: Electronic friction approaches and beyond”.

Schultz, Thorsten, Germany, Supervisors: Prof. Koch (HU) ,
“Manipulation of energy levels at inorganic/organic semiconductor interfaces".

Si, Jianchao, China, Supervisors: Prof. Rademann/Dr. Christen (HU),
“Laser interaction with Unary and binary nanoparticles”.

Song, Xin, China, Supervisors: Prof. Weinelt/Prof. Freund (FU/FHI)
“Surface phases of (Ti, V) mixed oxide on TiO2 (110) “.

Stemmle, Christian, Germany, Supervisors: Prof. Paulus (FU),
“Development of Local Correlation Methods for strongly correlated Systems”.

Stiehler, Christian, Germany, Supervisors: Prof. Freund/Prof. Weinelt (FHI/FU),
“The Impact of Molecular Adsorption on the Quantized Electronic Structure of Oxide-Supported Nanoparticles: A Model System for Heterogeneous Catalysis “.

Stuckenholz, Stefanie, Germany, Supervisors: Prof. Freund/Prof. Dähne (FHI/TU),
“Combining High-Resolution Scanning Probe Microscopy Studies with Thermal Desorption Spectroscopy of Metal Supported MgO Thin Films “.

Yubero Valdivielso, David, Spain, Supervisors: Prof. Fielicke/Prof. Dopfer (TU),
“Struktur und Reaktivität von Metallclustern der Platingruppe“.

Wirth, Jonas, Germany, Supervisors: Prof. Saalfrank (Uni Potsdam),
“Chemical Reactions in Substrate-Adsorbate Systems: A Kinetic Perspective”.

Wolf, Elisabeth, Germany, Supervisors:Prof. Schlögl/Prof. Risse (FHI/FU),
“Charge transport in metal/metal oxide composite catalysts under reaction conditions”.

Recent Developments of the FHI Free-Electron Laser Facility

Head: Wieland Schöllkopf

Summary

The free-electron laser facility at the Fritz Haber Institute (FHI FEL) started regular operation in November 2013 and first results from user experiments were reported already at the last Fachbeirat in spring 2014. Meanwhile, as of August 1st, 2015, a total of 172 user shifts have been provided to 6 user groups and additional machine shifts have been used to characterize and continuously improve the performance of the FHI FEL. Currently, the FEL provides continuously tunable, powerful pulsed laser radiation at any wavelength between 3.6 and 50 µm covering the mid-infrared (MIR) wavelength range. The first 1½ years of operation have opened up new possibilities for research in gas phase spectroscopy of molecules and clusters, non-linear optics, and surface chemistry at the FHI. In this report we give a brief overview of results from our user groups and show some of the highlights.

Furthermore, new modes of operation, like low-repetition rate operation combined with laser synchronization, are currently under development. In addition, a concept for a future machine upgrade for two-color experiments has been developed, which would open the door for unique experiments, like two-dimensional IR-spectroscopy in the MIR regime, two-color action spectroscopy pumping several modes or double resonant sum-frequency generation. Such novel techniques would provide fundamental insights into the coupling between different vibrational modes, which are not accessible by table-top experiments. By setting up a second FEL branch the wavelength range can be extended into the far-infrared (FIR) and Terahertz (THz) region beyond 100 micron wavelength. For two-color operation, we lay out a proposal to modify the electron accelerator and beamline system to allow for simultaneous operation of both FEL branches, thereby generating FEL radiation at two independently tunable wavelengths.

1. Introduction

The majority of molecular vibrations but also many elementary excitations in solids and nanostructures, *e.g.* lattice phonons, excitons or low-energy electronic transitions lie in the mid- to far-infrared wavelength region. The fundamental vibrational modes of molecules in the fingerprint region (~5 to 100 μm) can serve as a direct probe of molecular structure, which is why IR spectroscopy is one of the basic methods for molecular structure determination. Prominent examples are various excitations of the amidic molecular backbone in peptides or proteins. As such samples are typically optically thin there is a clear need for intense and continuously tunable, narrowband radiation in the MIR, which can only be generated with an infrared free-electron laser. There are a number of applications which require specific aspects of the FEL pulse parameters and go beyond FTIR spectroscopy:

- Spectroscopy of optical thin samples exploiting the high average photon flux
- Resonant (vibrational) pumping using narrow bandwidth excitation
- Nonlinear optical IR spectroscopy exploiting the high field strength

The radiation from the FHI FEL comes in 5 to 10 μs long bursts (macro-pulses at 5-10 Hz repetition rate) containing thousands of micro-pulses. The length of the micro-pulses is on the order of 1 ps with a pulse-to-pulse separation of 1 ns. The micro-pulse energy is typically 5 to 10 μJ, corresponding to a macro-pulse energy of 50 to 100 mJ. This peculiar time structure of the FEL pulses is advantageous when lots of photons are needed on a time scale of tens of microseconds. For instance, multiple-photon excitation of dilute samples of molecules or clusters in the gas phase, in many cases, can only be realized by applying this kind of intense bursts from an FEL. For other studies, such as time-resolved pump-probe experiments in the condensed phase, a pulse structure with a reduced micro-pulse repetition rate might be better suited to minimize heating and accumulation effects. As described below, this additional mode of operation is also available at the FHI FEL.

The IR radiation from the FHI FEL has, so far, been applied for a variety of investigations including: (i) vibrational spectroscopy of clusters in the gas phase (including metal, metal-oxide, and water clusters); (ii) vibrational spectroscopy of bio-molecules (including macro-molecules such as peptides and small proteins) in the gas phase as well as embedded in helium nano-droplets at a temperature of 0.4 K; and (iii) nonlinear spectroscopy based on second-harmonic generation in the Reststrahlen bands of solids such as cadmium telluride or silicon carbide.

2. Design of the FHI FEL

The FHI FEL includes two oscillator FELs; a MIR branch for wavelengths up to about 50 µm and a FIR branch for wavelengths from, possibly, about 40 to 400 µm. The MIR FEL has been commissioned and is fully operational whereas the FIR FEL has been projected as a future upgrade. A normal-conducting linear accelerator provides electrons of up to 50 MeV energy with a beam transport system feeding either of the two FEL branches or the electron diagnostics beamline as illustrated in Fig. 1. Detailed descriptions of the FHI FEL can be found in recent publications [1,2].

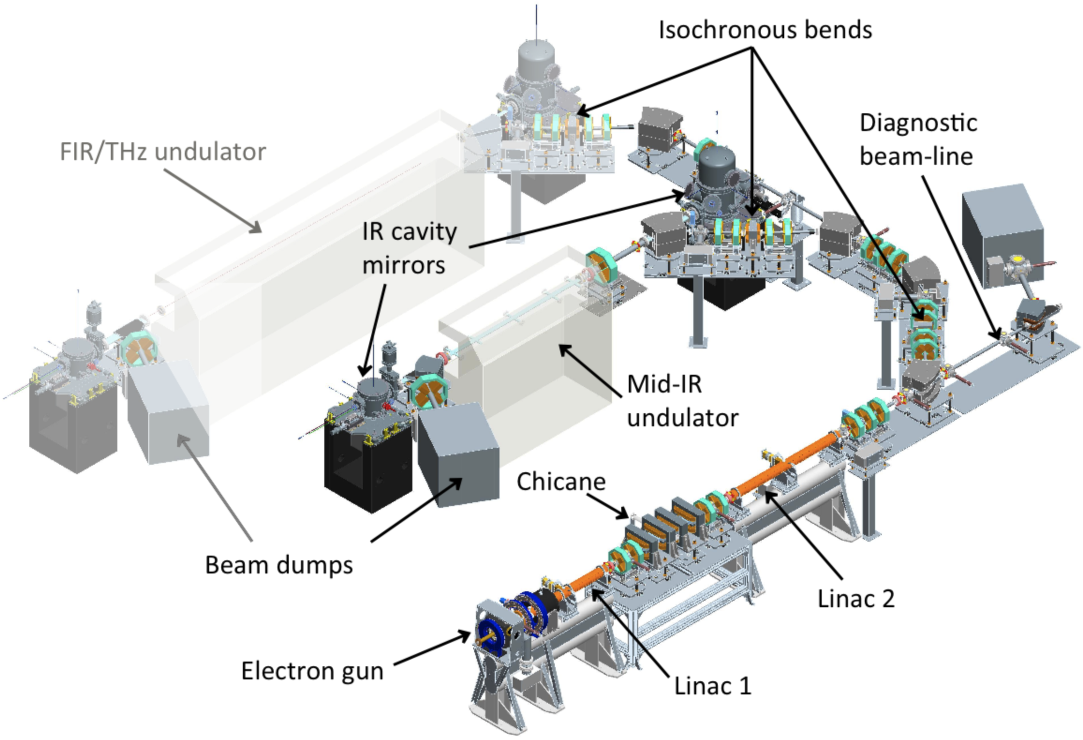


Figure 1: *Overview of the FHI FEL installation showing the electron accelerator system, the MIR FEL (operational), as well as the (not yet existing) FIR FEL as it was envisaged previously. A slightly modified FIR FEL design, which allows for two-color IR/IR pump-probe experiments is outlined at the end of this report.*

2.1 Electron Accelerator

The accelerator system was designed and built by Advanced Energy Systems, Inc. It combines a thermionic electron gun, a sub-harmonic buncher cavity, and two S-band (2.99 GHz) standing-wave copper linacs. The first of the two linacs accelerates the electron bunches to a constant energy of 20 MeV. The second linac accelerates or decelerates the electrons to any final energy between 15 and 50 MeV. The accelerated electron bunches form bunch trains (macro-bunches) containing thousands of micro-bunches at a repetition rate of 1 GHz. The micro-bunch length can be compressed down to a minimum of 1 ps rms by a chicane between the linacs. The macro-bunches are repeated at 5 or 10 Hz. The IR radiation pulses essentially inherit the time structure from the electron bunches leading to the above mentioned micro/macro-pulse structure. Tab. 1 summarizes the specifications of the accelerator system.

Parameter	Unit	Typical
Electron energy	MeV	18, 23, 26, 31, 36, or 41
Energy spread	keV	< 50
Energy drift per hour	%	< 0.1
Bunch charge	pC	220
Micro-bunch rep. rate	GHz	1
Micro-bunch length	ps	1 – 5
Macro-bunch length	μs	10, 12
Macro-bunch rep. rate	Hz	5, 10

Table 1: *Summary of typical electron beam parameters of the linear accelerator system of the FHI FEL. Different electron energies are used to cover different IR wavelength ranges as can be seen in Fig. 2.*

2.2 MIR FEL: Undulator and Cavity

In the MIR FEL a planar hybrid-magnet undulator is located within the IR cavity. The undulator is 2 m long containing 50 periods of 40 mm. It employs permanent magnets made out of NdFeB. At a minimum gap of nominally 16.5 mm, a maximum root-mean-square undulator parameter K_{rms} of more than 1.6 is reached. This, in combination with the minimum electron energy of 15 MeV, corresponds to a theoretical maximum wavelength of more than 50 μm for the MIR system.

The 5.4 m long MIR FEL cavity is formed by an end mirror and an out-coupling mirror. These are gold-plated copper mirrors of concave spherical shape. The waist of the cavity mode is located at the undulator center. A motorized in-vacuum mirror changer permits to select one out of 5 out-coupling mirrors with different outcoupling-hole diameters of 0.75, 1.0, 1.5, 2.5, and 3.5 mm for optimized performance at different wavelengths regions. In addition, the cavity end mirror is mounted on a precision translation stage allowing for fine adjustment of the cavity length with 1 μm repeatability.

Synchronizing the cavity length to the IR wavelength has turned out to be highly useful. When the synchronization is activated, it keeps the cavity at a length of L_0 - q λ, where L_0 is the nominal cavity length of 5.4 m, λ is the IR wavelength, q is a user defined factor (usually

$0 < q < 5$), and $\Delta L = q\,\lambda$ is the cavity detuning. Keeping the cavity detuning at a constant multiple of λ during a wavelength scan significantly increases the wavelength range accessible by an undulator gap scan for a given electron energy. In addition, it helps to keep the relative bandwidth of the FEL line spectrum constant over the scan range.

2.3 Reduced Repetition Rate Mode

In addition to the standard 1 GHz micro-bunch repetition rate a reduced repetition-rate mode has been implemented. A repetition rate of 1 GHz corresponds to an electron bunch separation of 1 ns in time and, hence, 30 cm in space. As the MIR FEL cavity is 5.4 m long, this results in 36 equally spaced IR pulses circulating the cavity simultaneously. A single-pulse mode with just one IR pulse circulating the cavity can be achieved by reducing the electron-bunch repetition rate by a factor of 36 to 27.6 MHz. The other possible few-pulse modes together with the corresponding repetition rates are listed in Tab. 2. As of summer 2015 we have demonstrated operation of the FEL in the single-pulse mode. Operating the FEL in a reduced repetition rate mode will allow for implementation of pump-probe experiments where the FEL pulses are synchronized to sub-picosecond accuracy with short or ultrashort pulses from table-top lasers.

Rep. rate (MHz)	1000	500	333.3	250	166.7	110.1	83.3	55.6	27.7
Number of pulses	36	18	12	9	6	4	3	2	1

Table 2: *Reduced repetition rates of the electron micro-bunches needed to get different numbers of IR pulses simultaneously circulating the 5.4 m long MIR FEL cavity.*

[1] W. Schöllkopf *et al.,* In: Proc. of SPIE **9512**, 95121L (2015)

[2] W. Schöllkopf *et al.,* In: Proc. of the 36th Free Electron Laser Conference, Basel, Switzerland, 2014, 629 – 634, WEB04, http://accelconf.web.cern.ch/AccelConf/FEL2014)

3. Characterization of the MIR FEL Radiation

The IR pulses coupled-out from the FEL cavity pass through the evacuated IR beamline and propagate a distance of 18 m from the FEL vault to the diagnostic station located in Building D. There, the spectrum of the IR radiation is measured by an in-vacuum Czerny-Turner grating spectrometer allowing for online monitoring of the FEL spectrum for each individual macro-pulse. In addition, various commercial IR detectors are in use to determine the intensity of the FEL-pulses at different levels of sensitivity and temporal resolution.

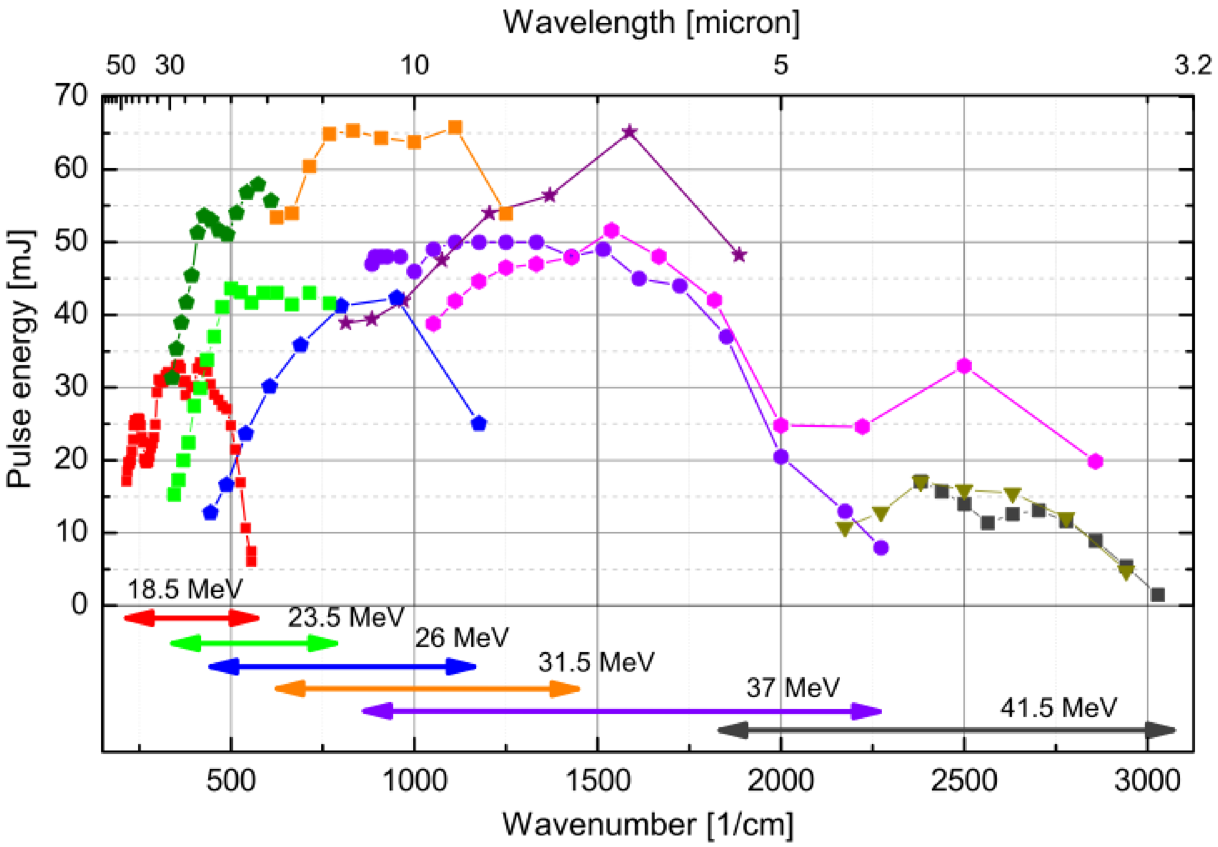


Figure 2: *Macro-pulse energies measured at narrow bandwidth conditions for the six usually used electron energies from 18.5 to 41.5 MeV. Different traces correspond to different electron energies and/or different tunings of the accelerator and/or different settings of the FEL cavity. The arrows at the bottom indicate the wavelength ranges covered by the various electron energies.*

Measurements of the FEL macro-pulse energy as a function of wavelength are shown in Fig. 2. Lasing over the entire MIR wavelength range from 3.5 to 48 µm has been achieved. Each trace in Fig. 2 corresponds to an individual machine tune-up, which can slightly vary depending on the FEL spectral line width requested by the user. All data shown in Fig. 2, however, correspond to narrow line width conditions with a relative FWHM (full widths at half maximum) of 0.3 to 0.7%. So far, a maximum IR pulse energy of more than 200 mJ was observed with a correspondingly broader spectrum.

3.1 Temporal Characterization of the FEL Micro-pulses by Autocorrelation Measurements

To gain information about length and shape of the ps-long micro-pulses, Alexander Paarmann and his group (Dept. PC) have installed an autocorrelation setup shown schematically in Fig. 3(a) (see also Poster PC01). At temporal overlap of the pulses from both paths, nonlinear effects in the CdTe crystal lead to the generation of second harmonic (SHG) radiation. In Fig. 3(b) to (d) we show autocorrelation measurements for three FEL cavity-length detunings.

For the smallest detuning, ΔL = -3 µm corresponding to 0.25 λ, we find a narrow, single-peaked structure with an average delay-time spread of about 600 fs (FWHM). This corresponds to a micro-pulse length of just 420 fs (FWHM), thereby indicating the potential of the FEL to generate ultrashort IR pulses. For the largest detuning, ΔL = -50 µm, a much larger delay-time spread of 8 ps is found. At intermediate detuning such as ΔL = -16 µm additional side peaks appear separated from the central peak by about ±2 ps.

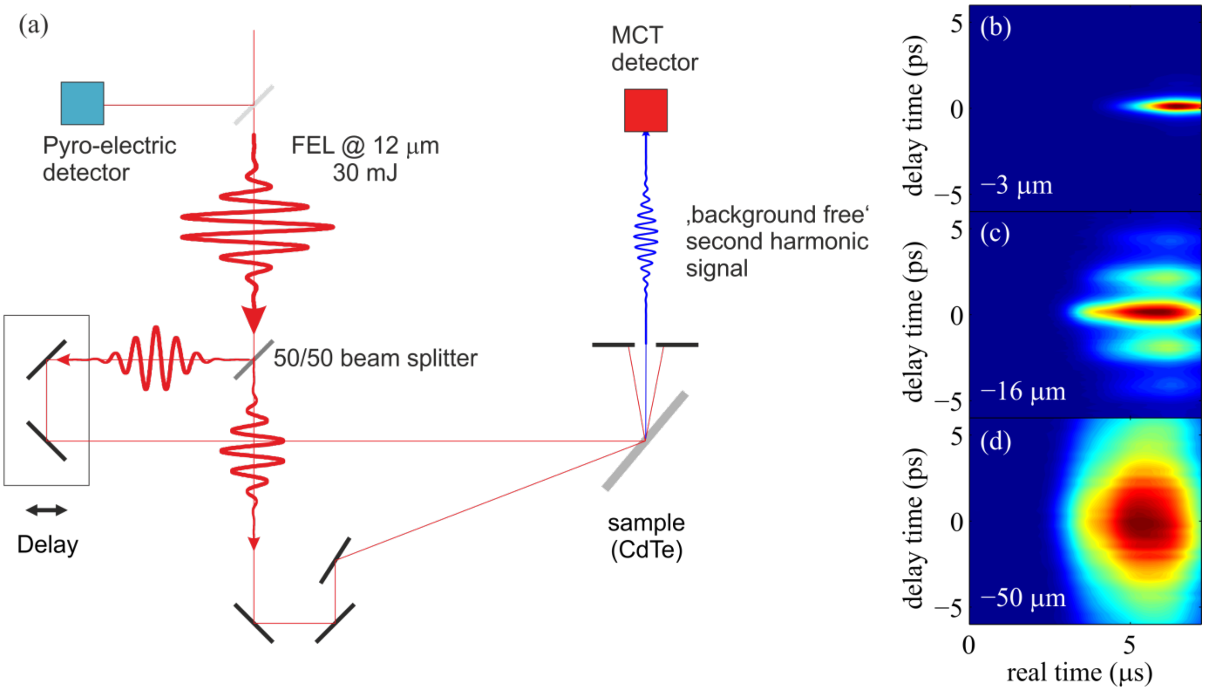


Figure 3: *SHG autocorrelation measurements of the FEL pulses. A schematic of the autocorrelation setup is shown in (a). The second harmonic signal is plotted as a function of the path length difference (delay time) and time from the macro-pulse trigger (real time) for FEL cavity detunings of 0.25 λ (b), 1.3 λ (c), and 4 λ (d). In these measurements at a wavelength of 12 µm the electron macro-bunch length was set to 6 µs leading to 1-4 µs long optical macro-pulses depending on the actual gain for a given detuning.*

The observed features are in good agreement with the expected behavior of an oscillator FEL which can operate in different regimes depending on the cavity detuning. At ΔL = 0 the gain drops to zero and no lasing is achieved. Shortening the optical cavity leads to an increase in gain and a simultaneous decrease in saturation intensity. For small detuning, -0.5 λ > ΔL > -3 λ, the micro-pulses are composed of multiple equally-spaced sub-pulses, just as the ones seen in Fig. 3(c). This is the regime of limit-cycle oscillations, where the FEL power exhibits oscillations over the duration of the macro-pulse. For larger detuning, the laser operates in the so-called stable focus limit, in which single and relatively long pulses are emitted. It is in this regime where one gets narrow bandwidth of about 0.5% (relative FWHM), as it is needed for molecular and cluster spectroscopy.

4. FEL Facility and User Projects

FEL and FEL facility are operated by just two facility staff members; Wieland Schöllkopf (scientist in charge) and Sandy Gewinner (laser engineer). They get support from Gert von Helden (scientist, MP), Wolfgang Erlebach (engineer, MP), Andreas Liedke (electrician, MP) as well as Alexander Paarmann (scientist, PC). In addition, important contributions regarding the machine and facility control system are provided by *Heinz Junkes* from the FHI computer support group *PP&B* (see Poster CP18). Furthermore, starting at September 2015 Yuanfang Xu, a PhD student from the University of Science and Technology China, Hefei, PR China, will be joining the FHI FEL team for 18 months.

Recently, in March 2015, the Berlin state authorities have issued the radiation safety permit to run the FHI FEL facility ("Betriebsgenehmigung") based on our comprehensive report on radiation safety, thereby replacing the preliminary permit issued earlier.

4.1 User Projects at the FHI FEL Facility

A total of 7 beamline stations are now operational in the basement and ground floor of Building D adjacent to the FEL-Building (Bldg. E) as can be seen in Fig. 4. A new experimental setup from the Kuhlenbeck group (Dept. CP) is scheduled to start data acquisition in fall 2015. All other FEL user experiments have been fully operational with the Paarmann lab (Dept. PC) in the 1st floor being the most recent to get operational at the end of 2014. In the following we give an overview of the user projects and point out some of the scientific highlights from each one.

1. Alexander Paarmann I (Dept. PC):
   Nonlinear Solid State Spectroscopy
2. Alexander Paarmann II (Dept. PC):
   FEL short pulse characterization and laser synchronization
3. Helmut Kuhlenbeck (Dept. CP):
   Vibrational spectroscopy of surfaces and deposited clusters
4. Gert von Helden I (Dept. MP):
   IR spectroscopy of bio-molecules combined with ion mobility mass spectrometry
5. Gert von Helden II (Dept. MP):
   IR spectroscopy of bio-molecules embedded in helium nano droplets

6. André Fielicke (Dept. MP & FU Berlin):
   Chemistry of transition metal clusters

7. Knut Asmis I (Dept. MP & U Leipzig):
   Vibrational spectroscopy of gas phase clusters: catalysis, astrochemistry, atmospheric chemistry, and ion solvation

Common to almost all spectroscopic experiments at the FHI FEL is the fact that, unlike in classical absorption spectroscopy, a spectrum is not recorded by measuring the reduction of the transmitted IR intensity as a function of wavelength. Especially for gas phase samples the absorption signal would be too small to yield a decent signal-to-noise ratio. To circumvent this problem *action spectroscopy* is used: Some action of the molecules, clusters, or the solid sample, which is triggered by absorption of one or many FEL photons, is detected and recorded. The action can be, for instance, molecular fragmentation or detachment of a weakly attached tag molecule (detected by mass spectrometry); it can be ejection of a molecule from a helium nano-droplet; or it can be a change of optical or magnetic properties of a solid sample following excitation by the FEL radiation.

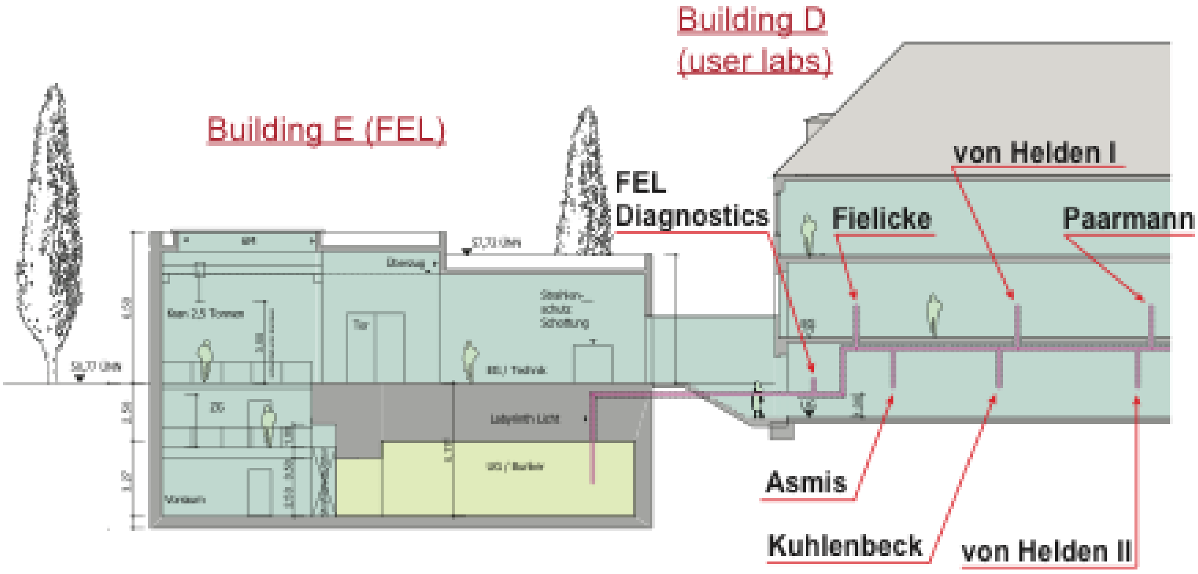


Figure 4: *Cross sectional view of the FHI FEL facility comprising the FEL building (left) and Building D (right), where the currently 7 user experiments are located in the basement and ground floor as indicated.*

4.2 Solid State Spectroscopy and Surface Science

4.2.1 Nonlinear IR Spectroscopy of Solid State Systems (Alexander Paarmann)

The group develops new experimental techniques to study phonon-driven nonlinear phenomena in solids using the FHI FEL. The main focus of the group is the development of novel nonlinear MIR spectroscopy approaches, making use of the high peak intensity of the FEL micro-pulses. They also develop various techniques to characterize and optimize the FEL output specifically for nonlinear solid state spectroscopy, and are installing a FEL-synchronized near-infrared femtosecond laser (see poster PC2).

The large tuning range, narrow bandwidth, and high average power, combined with the picosecond duration of micro-pulses makes the FEL a unique tool for MIR nonlinear optics. Several pilot experiments have been performed in the group, studying for instance phonon driven demagnetization and nonlinear phonon absorption (see posters PC13 and PC02 for details). Also, the group has developed FEL-based second harmonic generation (SHG) spectroscopy, and demonstrated it to be a sensitive tool to investigate the phonon spectrum within the Reststrahl band of a dielectric such as, for instance, SiC [1].

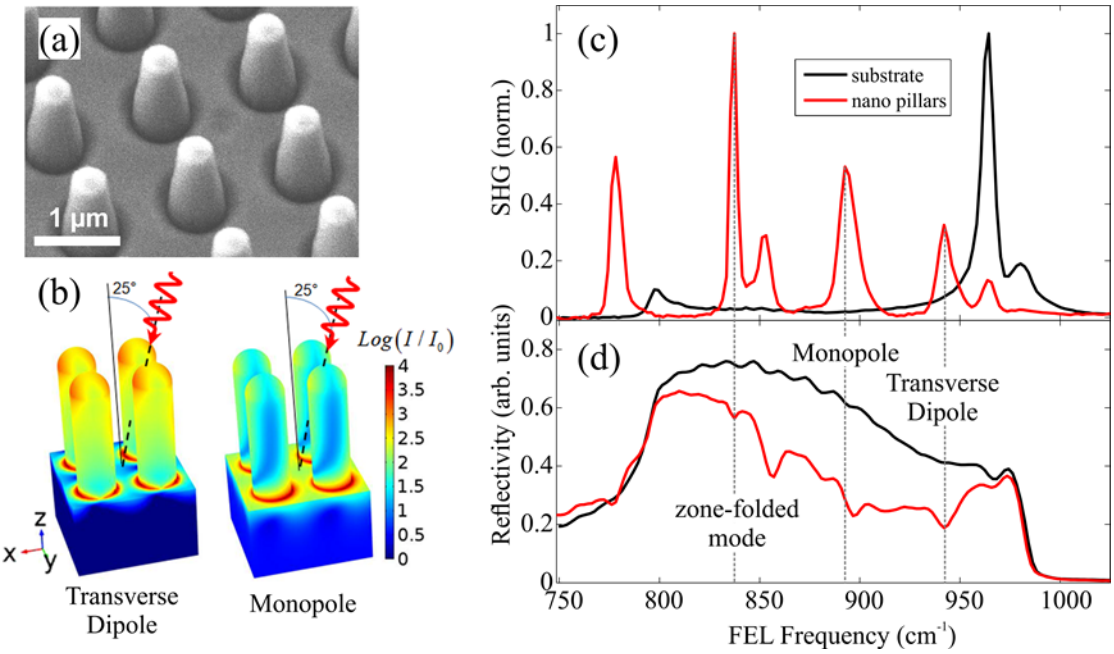


Figure 5: *SHG spectroscopy of sub-wavelength confined surface phonon polaritons. (a) Electron microscope image of a silicon carbide nano pillar sample. (b) Simulations of the field enhancements for different resonant modes, taken from Caldwell et al., Nano Letters* ***13****, 3690, (2013). (c) SHG and (d) reflectivity spectra of the nano-pillar sample. Resonant modes appear as shallow dips in the reflectivity and intense peaks in the SHG spectra.*

As an example shown in Fig. 5, they have applied the SHG spectroscopy to study sub-wavelength-confined surface phonon polaritons, in collaboration with J.D. Caldwell from NRL, Washington D.C., and coworkers. Such nanostructures can support several resonant localized surface phonon polariton modes within the Reststrahl band (see Fig. 5(b)), with prediction of extraordinarily high local field enhancements due to the long lifetime of the optical phonons. So far, the studies of such structures have been limited to linear optics, where resonances appear as shallow dips in the Reststrahl band, see Fig. 5(d). Owing to the nonlinear nature of the SHG, the group's experiments shown in Fig. 5(c) instead produce pronounced resonant peaks that could allow the first direct measurements of these field enhancements.

[1] A. Paarmann *et al.,* Appl. Phys. Lett., **107**, 081101 (2015)

4.2.2 Vibrational Spectroscopy of Surfaces and Deposited Clusters (Helmut Kuhlenbeck)

The goal of the project by the Kuhlenbeck group (FHI Dept. CP) is to measure vibrational spectra of metal clusters deposited on metal and metal oxide surfaces. To get additional (and complementary) information the apparatus includes a low temperature STM/AFM system. The lab space of a former apparatus of the Asmis Group ("Asmis II") was taken over for the newly designed surface science apparatus. As of August 2015 installation is nearing completion and first test measurements with the FEL beam sent to the new apparatus are expected for fall 2015. Details of the setup and the planned experiments are given in this booklet in the report of the Dept. CP and at Poster CP2.

4.3 Spectroscopy of Bio-molecules

4.3.1 IR Spectroscopy Combined with Ion Mobility Spectrometry (Gert von Helden)

In this experiment the FEL radiation is used to reveal information about the structure of bio-molecules in the gas phase. To this end the group combines the method of ion mobility mass spectrometry with IR spectroscopy. In an ion mobility setup the molecules in the gas phase are not only mass-to-charge selected but also isomer and conformer selected by exploiting different drift times through a drift cell filled with several mbar of helium or nitrogen gas.

As an example in Fig. 6 we show IR spectra of two forms of the protonated benzocaine molecule, which were separated according to their different drift arrival times in the ion mobility spectrometer. For each of the forms an IR photo-fragmentation spectrum is obtained separately by recording the depletion of the mass spectrometer signal as a function of FEL wavelength. As can be seen in Fig. 6B significantly different spectra are found for the two forms. By comparison with calculated spectra the molecular forms can be identified with two protomers of distinct localization of the added proton. Benzocaine is a commonly used local anesthetics. An improved understanding of the molecular structure and its dependence on ambient conditions can, potentially, contribute to understand the details of how the anesthetics works.

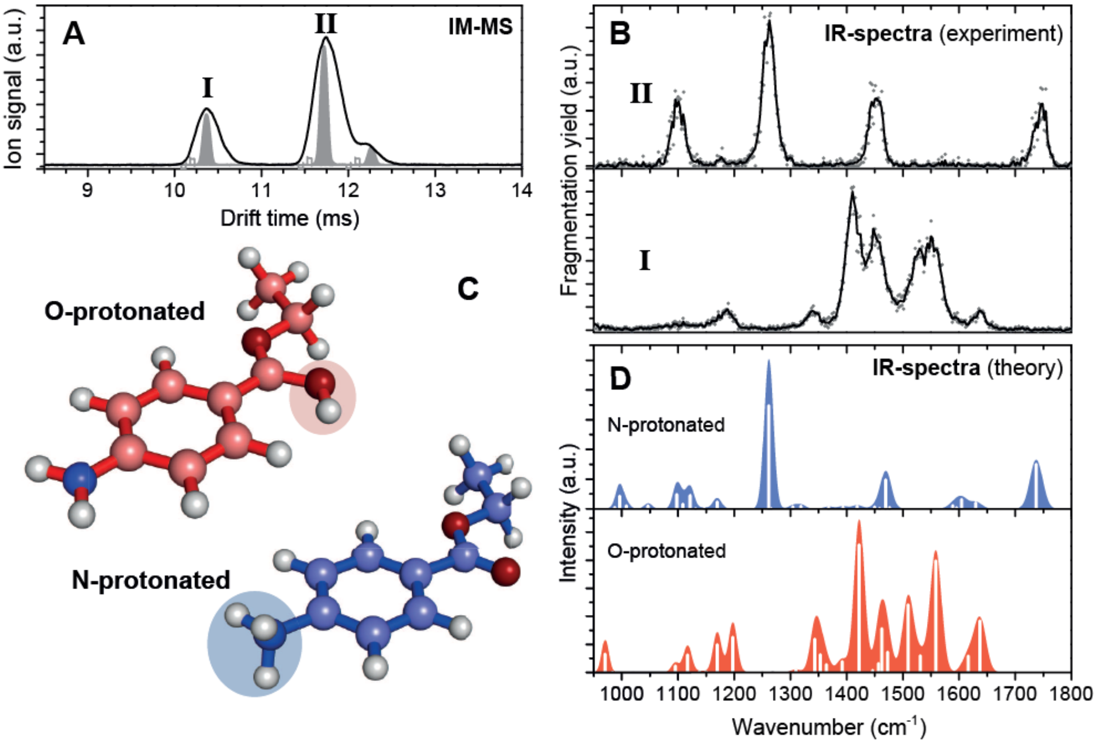


Figure 6: *IR spectra of protonated benzocaine in the gas phase obtained by combining ion-mobility mass spectrometry (IM MS) with IR spectroscopy. Two different forms (labeled I and II) of the molecule are found and separated by their different drift times (A). For each form an IR photo-fragmentation spectrum is recorded (B). By comparison with calculated spectra (D) they can be assigned to the two protomers shown in (C) which differ by the location of the attached proton. This figure is a modified copy from Ref. [1].*

More results from combining ion mobility mass spectrometry with IR spectroscopy are presented by the von Helden group on Poster MP5.

[1] S. Warnke *et al.,* J. Am. Chem. Soc**.**, **137**, 4236 (2015)

4.3.2 Spectroscopy of Charged Peptides and Small Proteins Embedded in Superfluid Helium Nano-droplets (Gert von Helden)

For the last decade helium nano-droplet isolation spectroscopy has been used in many labs to record optical spectra of molecules at ultracold conditions. Molecules embedded to superfluid helium nano-droplets are cooled to the droplet temperature of 0.4 K. Due to the weak interaction between the superfluid helium and the dopant molecule, the droplet causes only little perturbation to the molecular spectra. In addition, helium is optically transparent over the entire optical and IR range.

The group has set up an apparatus where bio-molecules are brought into the gas phase by electrospray ionization, mass-to-charge selected in a mass spectrometer and, subsequently, stored in an ion trap. The helium droplets traverse the trap and pick up the ions. IR spectra of the mass-to-charge selected ions embedded in helium droplets can then be recorded.

One of the first systems studied this way is the penta-peptide leucine-enkephalin (LEK) [1]. The spectral lines observed are much narrower than those measured when using conventional gas-phase methods. The spectrum of the protonated dimer (2LEK+1H) is found to contain fewer peaks than the spectrum of the monomer (LEK+1H). This indicates a uniform structure of the protonated LEK dimers embedded in He droplets A detailed quantitative analysis of the spectra is expected to reveal insight into the structural properties of the small peptides and the bonds they form. More results from the helium nano-droplet project are presented by the von Helden group (Posters MP3 and MP4).

[1] A.I. González Flórez *et al.,* Phys. Chem. Chem. Phys. **17**, 21902 - 21911 (2015)

4.4 Neutral and Charged Clusters in the Gas Phase

4.4.1 Strongly Bound Clusters (André Fielicke)

The group of André Fielicke (FHI and TU Berlin) uses the FHI FEL radiation to investigate structure and chemistry of strongly bound clusters in the gas phase. In their molecular-beam apparatus the group has the capabilities to study neutral as well as charged species. The clusters are produced using either a single-target or a dual-target laser ablation source allowing the generation of pure or alloy clusters of controlled compositions, respectively. Complexes of the clusters with ad-molecules such as CO, O_2, H_2O can be formed and IR spectroscopy is used to characterize the bonding of these species to the clusters.

Systems studied with the FHI FEL, so far, include carbon monoxide bound to transition metal clusters and co-adsorbates of oxygen and water on small gold clusters. Further studies focused on neutral silicon clusters doped by boron or nitrogen atoms. For CO bound to cobalt-manganese clusters, for instance, it was found that the CO vibrational frequency is shifted to lower frequency with increasing manganese content. These studies allow probing the effects of alloying on the d-band center that controls the strength of the π-backbonding to the CO.

4.4.2 Ionic Metal Oxide and Water Clusters in the Gas Phase (Knut Asmis)

The group of Knut Asmis (FHI and University of Leipzig) investigates clusters in the gas phase. They discovered a bidentate binding motif in the structure of the anionic magnesium-CO_2 complex $[ClMgCO_2]^-$, see Fig. 7. These results, gained in collaboration with the group of Einar Uggerud from the University of Oslo, Norway, happened to be the first publication from the FHI FEL facility [1]. In addition, charged aluminum oxide and iron oxide clusters, which are either pure or complexed with one or two H_2O or D_2O molecules, were prepared in an ion trap where they are cooled down to temperatures on the order of 20 K and tagged with one or a few He or D_2. Vibrational excitation of the metal-oxide cluster (or of the attached

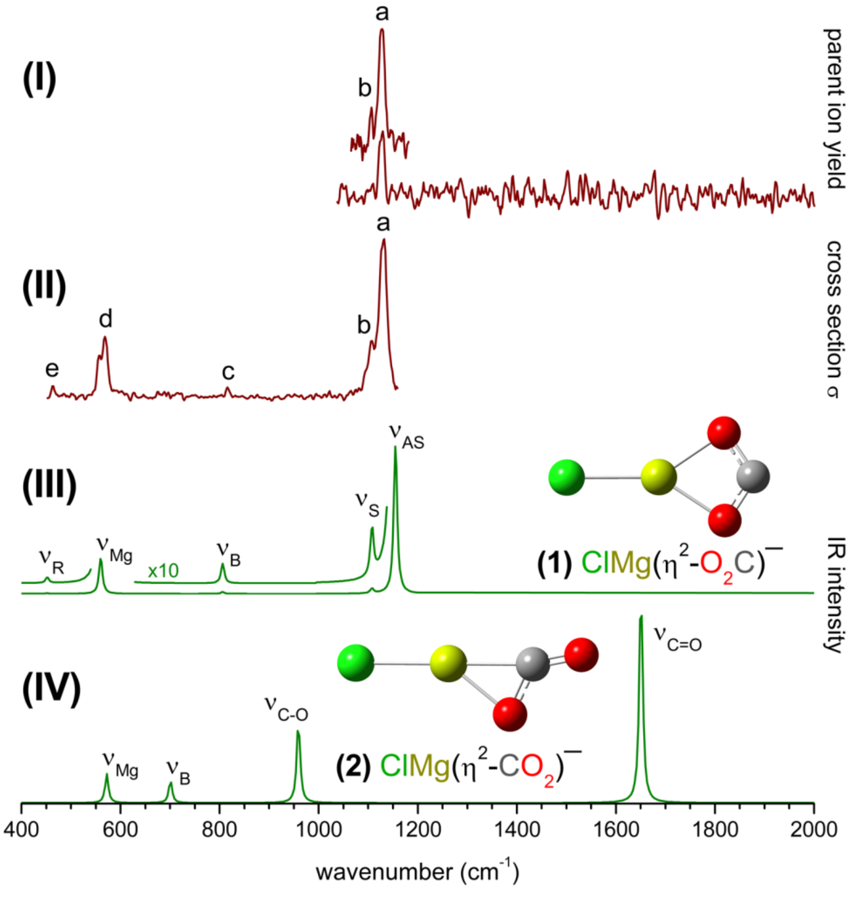


Figure 7: *Structure determination of the anionic magnesium-CO_2 complex $[ClMgCO_2]^-$. Comparison between observed (I, II) and calculated (III, IV) spectra reveal a bidentate binding motif of the CO_2 magnesium bond. Taken from Ref. [1].*

water molecules) by the FEL radiation leads to detachment of the relatively weakly bound tag. Thus, vibrational spectra of the clusters can be acquired by observing the cluster-tag dissociation rate with a mass spectrometer as a function of IR wavelength. Comparison of the observed IR spectra with theoretical ones calculated for various cluster geometries permits uncovering of the cluster structures.

Furthermore, the Asmis group, in collaboration with the group of Mark Johnson from Yale University, also applied the MIR radiation from the FHI FEL to investigate the structural properties of water clusters $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ which are referred to as *magic* clusters because of their enhanced stability [2].

[1] G.B.S Miller *et al.,* Angew. Chem. Int. Ed. **126**, 14635 (2014)
[2] J.A. Fournier *et al.,* PNAS **111** (51), 18132 (2014)

5. Future Directions and Upgrade Plans of the FHI FEL

Over the last century, linear optical spectroscopy, especially when being performed in the IR, contributed substantially to our understanding of molecular structures. In addition, the usage of ultrashort laser sources has allowed to go further by studying not only structure, but also the dynamics of energy flow between different modes in molecular and condensed phase systems, providing a wealth of additional information. Traditionally, these dynamical processes are studied using pump-probe techniques where two time-delayed optical pulses are applied to the sample, and the dynamics and interactions are derived from the sample response as a function of time delay between the two pulses and their frequency or fluence, respectively. Typical single-color experiments allow monitoring the population relaxation of vibrational modes; however, two-color approaches give access to mode-couplings and thus may significantly enhance the attainable microscopic understanding. In particular, both MIR-near-infrared (NIR) and MIR-MIR two-color experiments are interesting, addressing couplings between vibrations and electrons and between different vibrational modes, respectively. Ultimately, it would be intriguing to make use of the high pulse energy delivered by the FEL to also “pump” (drive) molecular processes, reactions or to create new transient states by controlling multiple vibrational motions in a concerted fashion.

Furthermore, it would also be highly interesting to extend the wavelength range accessible by the FEL to longer wavelengths to study lower-frequency vibrations at THz frequencies. The modes of interest here are vibrations involving heavier atoms, for example in clusters, collective motions in bio-molecules and correlated atomic motions in complex solid materials.

As these experiments address optical thin samples or require a high field strength they can be only made possible using an FEL.

We here propose an extension of the FHI FEL which would enable these new classes of experiments and make the FHI FEL a worldwide unique instrument. We hereby follow two independent directions, to allow for MIR-NIR and MIR-MIR two-color operation, respectively, with the IR pulse wavelength tunable beyond the current limit of 50 µm. MIR-NIR spectroscopy will be enabled by installation of a femtosecond tabletop laser producing pulses at 1 µm synchronized with the FEL. MIR-MIR two-color operation could be achieved by installation of a second, longer wavelength undulator. Specifically, we envision this new undulator to be operational simultaneously with the existing one. This would be possible by implementing a unique design, in which an additional RF cavity is used to feed alternating electron bunches into both undulators, respectively. Such an approach is novel and has not been implemented yet at any other FEL facility. Both approaches are described in detail below.

5.1 Synchronization of Pulses from a Table-top Laser to the FEL Micro-pulses

The ability to control the temporal separation between the FEL pulses and pulses from an external laser to better than ~1 ps is key for time resolved pump probe spectroscopy. In addition, the time between subsequent FEL pulses limits the maximum delay time between pump and probe pulse. The reduced repetition rate mode described above allows to increase this time from 1 ns to a maximum of 36 ns in the single-pulse mode. The reduced repetition rate also reduces the heating rate of the sample in cases where solid or liquid samples are used.

The group of *Alexander Paarmann* is currently installing a femtosecond fiber laser that will be synchronized to the FEL micro-pulses (see the group's report in the PC section of this booklet). This is an Yb-doped fiber laser generating 70 fs long pulses of 45 nJ energy at a central wavelength of 1055 nm with 55.6 MHz repetition rate. The latter equals the rate of the FEL's two-pulse mode (see Table 2 above). To synchronize the fs-laser to the FEL micro-pulses a commercial clock transfer system (Libera Sync 3) has been purchased. It transfers the 3 GHz low level RF signal of the FEL's electron accelerator system by an optical fiber link over a distance of about 80 m to the Paarmann group lab (see Fig. 4), where it is used to generate a feed-back signal acting on the fs-laser. We expect the remaining jitter to the FEL pulses, originating from the electron accelerator, as well as from the FEL beamline system to add up to a final jitter of less than 1 ps. A concept for timing jitter measurement for single macro-pulses will be implemented, and could result in an effective time resolution for pump-probe experiments of ~100 fs.

5.2 Future Upgrade of the FHI FEL: Second Undulator and Two-color Mode

The basic layout of the FEL includes the option for a second undulator branch, as shown already in Fig. 1, to cover longer IR wavelengths not accessible with the existing MIR FEL. In the most basic approach the electron beam is steered to either the first or second undulator with no parallel operation of the two branches. However, simultaneous operation of both branches can provide the proposed two-color mode. In such a mode of operation, switching between the two branches has to occur on the nanosecond timescale between individual micro-pulses, which provides a technical challenge. Solving this challenge would, however, be worthwhile, as it would allow synchronous generation of powerful, ps-long, tunable FEL pulses at two infrared wavelengths, which can be overlapped in time and space in an experiment.

Note, that a standard kicker-magnet setup is intrinsically not fast enough. However, we have developed an alternative approach as shown in Fig. 8. It is based on generating micro-bunches of alternating energies by an 500 MHz after-burner cavity which accelerates every second and decelerates every other second micro-pulse coming from the existing accelerator system. Downstream of the 500 MHz cavity a relatively simple dispersive dipole magnet can be used to separate the low-energy from the high-energy bunches and send them to the undulators.

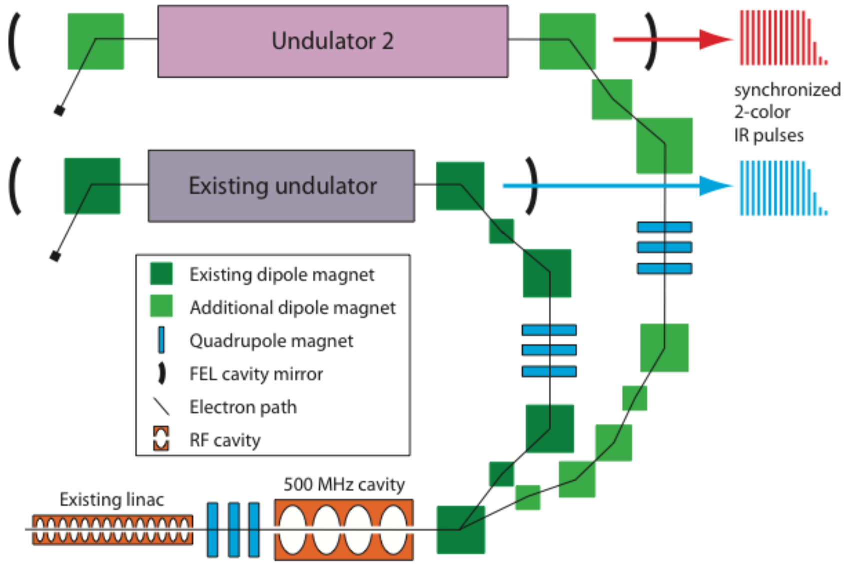


Figure 8: Schematic block diagram of the envisioned two-color upgrade of the FHI FEL.

A technical design and feasibility study of this scheme is under preparation by Lloyd Young (formerly Los Alamos National Lab), who already designed the existing accelerator and beamline system of the FHI FEL. His preliminary results indicate that it is possible to design a 3 or 4 cell 500 MHz cavity of about 1 m length which could add or subtract 5 MeV of energy to subsequent pulses in the electron bunch train. For 45 MeV electrons generated by the existing accelerator this corresponds to 50 MeV and 40 MeV alternating bunches. The energy difference of 10 MeV or 25% is sufficient to allow for angular separation of the two energies and transfer into two adjacent isochronous electron beamlines. In Fig. 8 illustrated the schematic layout of the preliminary design.

The IR wavelength range that can be covered with the second undulator, for a given range of accessible electron energies, is mainly determined by the undulator period. In the two-color scheme the preferable choice would be such that, for any average electron energy (i.e. the energy produced by the linacs), one can still operate both FEL's at identical wavelengths. At the same time, the design of the second undulator should also enable the generation of MIR wavelengths beyond 100 µm. By the usual undulator gap scan one can then vary the wavelengths independently over a large wavelength range.

6. Publications of the FHI FEL Group

2014

Miller, G.B.S, T. Esser, H. Knorke, S. Gewinner, W. Schöllkopf, N. Heine, K.R. Asmis and E. Uggerud: Spectroscopic Identification of a Bidentate Binding Motif in the Anionic Magnesium-CO_2 Complex ($[ClMgCO_2]^-$). Angew. Chem. Int. Ed. **126**, 14635 (2014).

Fournier, J.A., C.T. Wolke, C.J. Johnson, M.A. Johnson, N. Heine, S. Gewinner, W. Schöllkopf, T.K. Esser, M.R. Fagiani, H. Knorke and K.R. Asmis: Site-specific vibrational spectral signatures of water molecules in the magic $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ clusters. PNAS **111**, 51, 18132 (2014).

2015

Warnke, S., J. Seo, J. Boschmans, F. Sobott, J.H. Scrivens, Ch. Bleiholder, M.T. Bowers, S. Gewinner, W. Schöllkopf, K. Pagel and G. von Helden. Protomers of Benzocaine: Solvent and Permittivity Dependence. J. Am. Chem. Soc., **137**, 4236 (2015).

Schöllkopf, W., S. Gewinner, W. Erlebach, H. Junkes, A. Liedke, G. Meijer, A. Paarmann, G. von Helden, H. Bluem, D. Dowell, R. Lange, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch, S.C. Gottschalk: The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. In: Proceedings of FEL 2014, Basel, Switzerland, 2014, 629 – 634, WEB04, http://accelconf.web.cern.ch/AccelConf/FEL2014/, ISBN 978-3-95450-133-5.

Schöllkopf, W., S. Gewinner, H. Junkes, A. Paarmann, G. von Helden, H. Bluem, A.M.M. Todd: The new IR and THz FEL Facility at the Fritz Haber Institute in Berlin. In: Advances in X-ray Free-Electron Lasers Instrumentation III, Sandra G. Biedron, Editor, Proceedings of SPIE Vol. 9512, 95121L (2015), .

Gonzalez Florez, A.I., D.-S. Ahn, S. Gewinner, W. Schöllkopf, and G. von Helden. IR Spectroscopy of Protonated Leu-Enkephalin and its 18-crown-6 Complex Embedded in Helium Droplets. Phys. Chem. Chem. Phys. **17**, 21902 (2015).

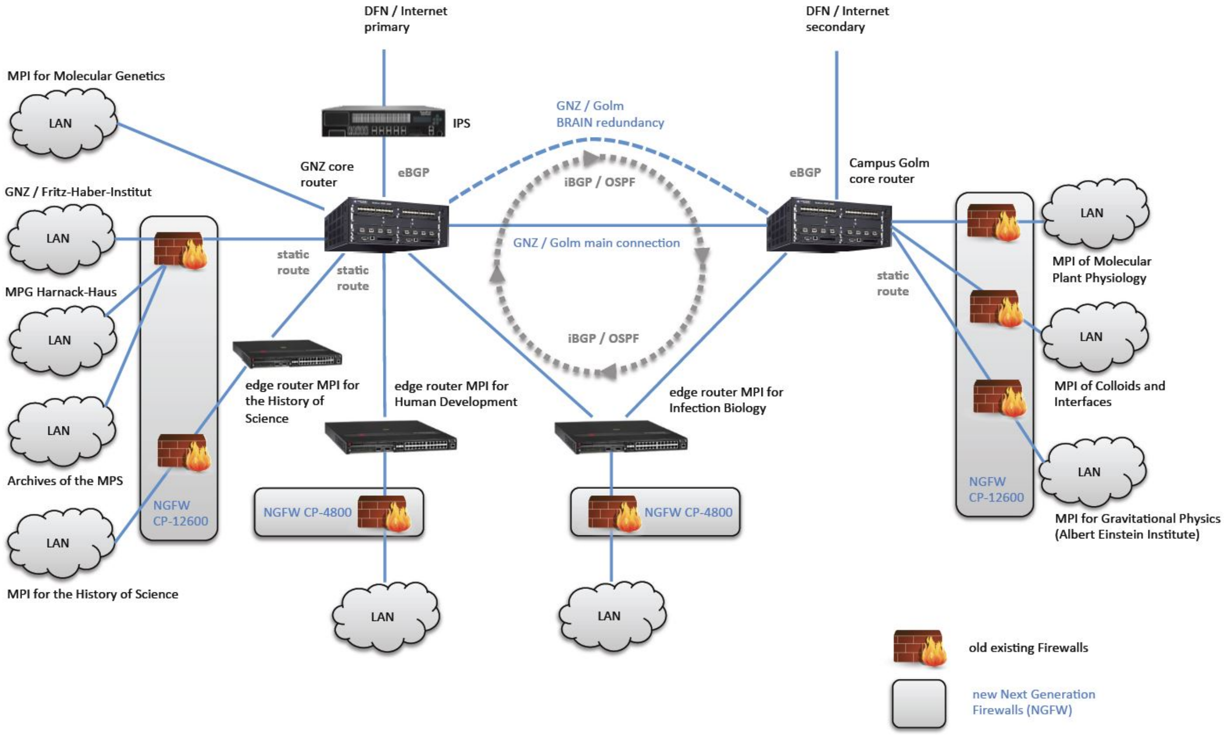
Paarmann, A., I. Razdolski, A. Melnikov, S. Gewinner, W. Schöllkopf, and M. Wolf. Second harmonic generation spectroscopy in the Reststrahl Band of SiC using an infrared free-electron laser. Appl. Phys. Lett. **107**, 081101 (2015). http://dx.doi.org/10.1063/1.4929358

Joint Network Center (GNZ) (Head: Gerd Schnapka)

The *Joint Network Center* (Gemeinsames Netzwerkzentrum, GNZ) of the Berlin/Brandenburg Max Planck institutions is a regional IT competence center. This group focuses on networking, backup, virtualization, cloud and security services. In addition, the GNZ provides consulting services and coordinates IT projects from planning to purchase. At present, the center supports 13 Max Planck institutions in the Berlin/Brandenburg area including all 8 Max Planck Institutes (MPI).

The GNZ deals with wide area (DFN X-WiN), metropolitan area (BRAIN and to Potsdam) and local area (LAN and WLAN) networks. Special emphasis is placed on central manageability and network security (Firewalling, Intrusion Prevention, VPN etc.).

Stateful firewalls were in use for many Berlin/Brandenburg MPIs until 2014. These firewalls were partially operated by the GNZ. Due to the special position of the GNZ as a central data provider it was necessary to obtain a new powerful and fail-safe (next generation) firewall system.



New NGFW structure

In a joint project, the GNZ has taken care of a new next generation firewall system (NGFW). All leading manufacturers have been compared together in several test scenarios. One manufacturer could fulfill all the demands of the different requirements (administration, availability and performance) of each affiliated institution very well. As a result the GNZ carried out the tendering and the order of the new NGFW systems. Four firewalls have been designed where several institutions are supplied via one physical firewall (see picture New NGFW structure). Each installation and configuration was supported by the GNZ. The rollout in the Berlin/Brandenburg MPIs will be completed in 2015.

The group had a leading role in the Max Planck Society (MPS) IPv6 project. All MPIs in Berlin/Brandenburg are now basically enabled to communicate via IPv6. Between the two core routers (GNZ and MPI Campus Golm) the necessary protocols and configurations for IPv6 connections are in operation. The same was applied to the two redundant Internet access gateways of the research network (X-WiN) of the DFN. In addition to the IPv4 network there is now a new IPv6 network available. The IT staff in the MPIs (nationwide) has been trained and the very first IPv6 networks are in productive use.

In order to simplify the procurement of IT equipment (servers, network etc.) for all institutions of the MPS there are framework agreements with IT manufacturers and suppliers, which allow a purchase without tendering. For this purpose the Administrative Headquarters of the MPS is reliant on IT competence, which carries out the technical content of the framework agreements. The GNZ was responsible for the technical content in recent framework agreements for LAN and WLAN. Due to this cooperation all framework agreements with technical leading companies could be successfully completed.

The Advisory Committee for IT Equipment (BAR, Beratender Ausschuss für IT Systeme) advise the President, the Institutes and the Administrative Headquarters of the MPS in fundamental issues of IT use in the MPS and concrete IT procurement projects. The BAR keeps three meetings a year and in addition performs consultations by way of circulation. Currently the committee consists of 20 members and 5 permanent guests. Gerd Schnapka is an appointed member of the BAR since 2014.

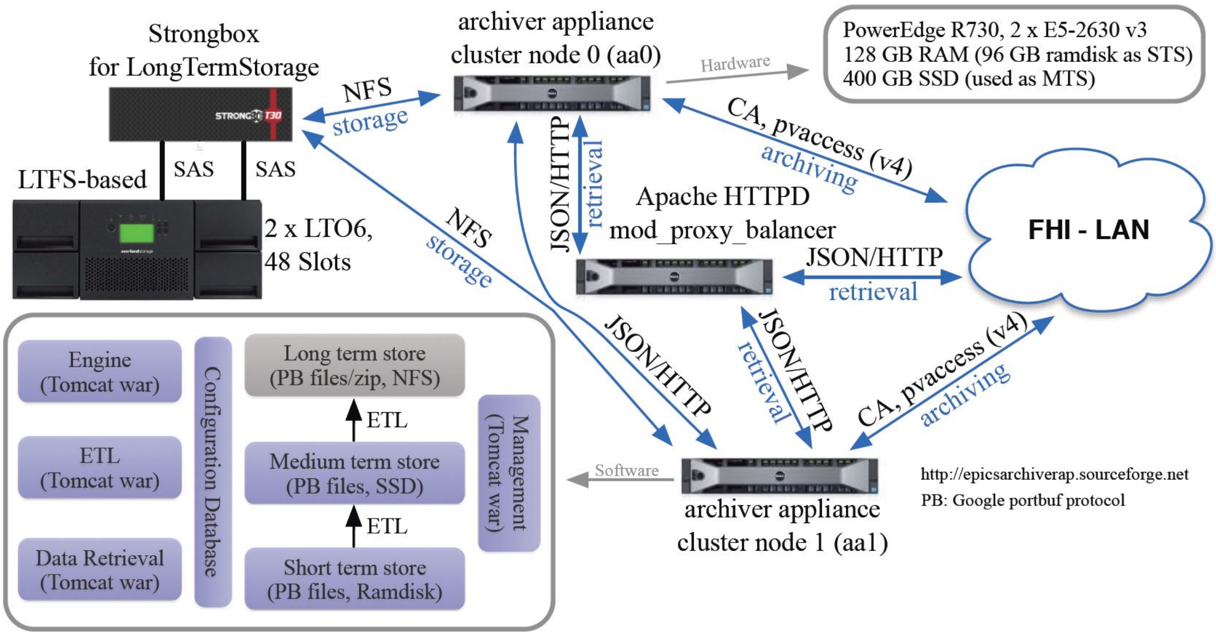
Within the framework of the BAR the GNZ is working at fundamental issue of firewalls. For this purpose common procedures are developed both for the BAR as well as the MPIs. It aims to ensure a cost-friendly and at the same time secure firewall structure within the MPS.

PP&B (Personal Computers, Realtime & Image Processing) (Head: Heinz Junkes)

Based on the data network infrastructure, provided by the Joint Network Center (GNZ), the PP&B group is responsible for the installation and maintenance of the desktop computer systems (including laptops), server systems, telephone system and the electronic building control system. Several server systems perform services for mail, web, printing, number crunching and databases for different archives (elogbook, channel archiver, document archives). The core of it is a high available storage system (Netapp metro cluster, 70 TB), interconnected with redundant 10 Gbit switches. Most server systems are running as so called virtual systems on well equipped hardware devices that are also connected via redundant paths to this 10Gbit Network.

In 2014 an application for a new compute cluster consisting of commodity hardware connected to a 10 Gbit switching factory and centralized storage was submitted to the BAR (Beratender Ausschuss für Rechnersysteme) and was accepted. The new system was put into operation end of 2014 and is well used. In summer 2015 we have built up a clustered channel-archiver appliance which is able to record selected process data (including waveforms and images) from any experiment at the institute and hold it on a long-term read-only archive (LTFS NAS) for retrieval.

The technical consulting service supports scientists of the institute in configuration, modification, acquisition, and adaption of computer equipment to the experiments (in close



Schematic diagram of the EPICS Archiver Appliance Cluster cooperation with the service group of electronics). The group has been deeply involved in a control and archiving system based on EPICS (Experimental Physics and Industrial Control System) which is used to operate the Free Electron Laser [1].

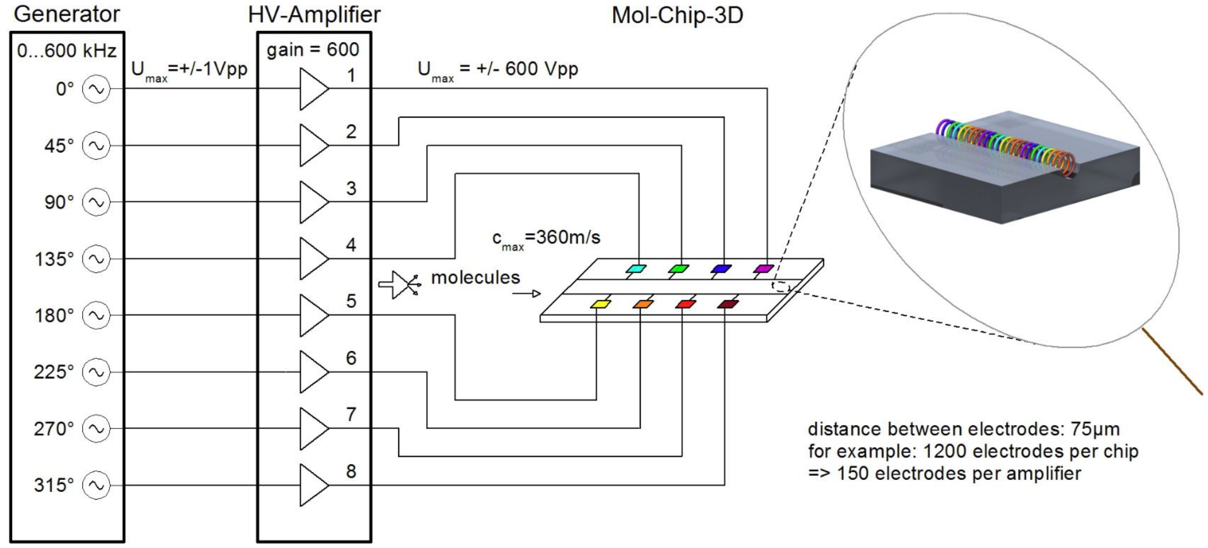
Meanwhile we put the EPICS framework into operation for other experiments. It could be seamlessly integrated into the existing research environment. Each semester a weekly lecture with a practice part is given to promote the EPICS framework in the institute.

[1] Adding site-specific laser-shot-numbers to timestamp, Heinz Junkes, Spring 2015 EPICS Collaboration Meeting, FRIB/NSCL at Michigan State University (MSU)

Electronics Workshop (Head: Georg Heyne)

The service group for electronics is a central facility to support the scientific groups at different levels. Its primary task is the development and construction of complex measuring and control equipment for critical experiments, which are not available on the commercial market. In the last 2 years the E-Lab developed about 225 different devices.

These include for example a very complex electronic controller and surveillance system with regulators for serveral profile reactors, a high speed - high voltage amplifier (DC---600kHz, +/- 600V) for the MolChip-3D ERC-project (Fig. 1), a development and setup for an ESR spectrometer and various controllers for the FEL.



Linear amplifier for the traveling wave, 3D molecule chip

Furthermore, components for computer-controlled data acquisition, for example user-optimized compact microprocessor units for steppermotor (UHV manipulator) and AD- and DA converters with (W-)LAN interfaces were developed.

The technical consultation service supports the scientists in the configuration and modification, the acquisition and adaptation of electronic-equipment and hardware for their experiments.The scientists are basically supported in the development and implementation of LabView software for controlling and measuring in experimental settings.

A large stock of components and rental equipment allows fast and inexpensive pilot tests.The rapid-repair service for damaged devices (more than 150) is often very importend for the scientist to continue their experiments.

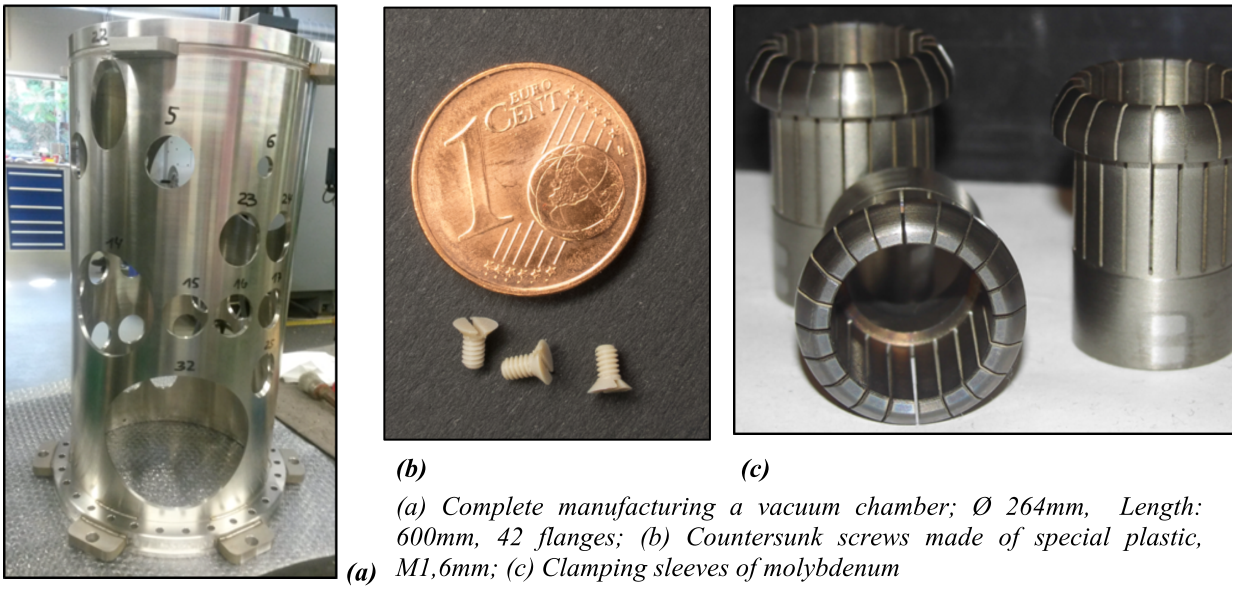
New developments and workflow meshing, layouting, programming of logic array (FPGA), microcontroller with LabView interfaces and construction of printing circuit boards, bring more effectiveness and transparency in the electronic workshop.

Cooperation with the electronics development engineers of the MPG has been enhanced by regular annual meetings. E-Lab staff members take part in trainings for new jobs.

Mechanical Workshop (Head: Petrik Bischoff)

The mechanical workshop deals with the (1) construction and development of scientific instruments, (2) creation of CAD drawings, (3) manufacturing of fine equipment as well as repair of instruments, and (4) processing of different types of materials through conventional manufacturing processes as well as machining by CNC (computerized numerical control) milling / turning, electrical discharge machining, soldering, welding, grinding and polishing.

The workshop is headed by *Petrik Bischoff* since 2013 and is in the process to adapt to new demands set by experimental requirements while building on the established experience and high quality of the workshop. The requirements of increased accuracy and new materials require modernizing the workshop infrastructure as well as the organization and working practice. As first steps in improving the infrastructure a 5-axis CNC milling machine (DMU 60evo) has been purchased, followed by the acquisition of a new electrical discharge machining (EDM) for manufacturing of small holes and structures as well as a new CNC turning center (lathe). The production of complex, intricate parts and assemblies is now easier to implement.


(a) (b) (c)

(a) Complete manufacturing a vacuum chamber; Ø 264mm, Length: 600mm, 42 flanges; (b) Countersunk screws made of special plastic, M1,6mm; (c) Clamping sleeves of molybdenum

An important specialization is wire and die-sinking EDM. Thanks to the highly skilled technicians, precision parts can be produced whilst minimizing material waste.

Through regular meetings of the precision engineering technicians with the designers in the experimental departments, cooperation and communication is intensified. This facilitates the exchange of new and beneficial ideas and suggestions for manufacturing.

Crystal laboratory (Members: D. Jüterbock, M. Schönberg)

In the last years the Crystal-lab continued providing highest-quality single crystal samples for research studies in the entire Institute. The laboratory is equipped with all necessary tools for cutting crystal rods, shaping, polishing, and final orienting crystal surfaces using a Laue type diffractometer with an image editing software tool. Another duty of the lab includes machining fragile, ceramic, and glass-like materials. Since the last report, the laboratory prepared about 130 crystal samples. The high quality of samples delivered by Crystal-lab is acknowledged by many other groups worldwide (Germany, China, USA, etc.) who take advantage of the Crystal laboratory via several collaborative projects.

Library (Head: Uta Siebeky)

The library supports the FHI researchers in all their information needs, providing printed and electronic contents and collects special literature covering the research fields of the institute. The print collection currently includes about 16,000 monographs in a reading room, which is designed as a common room for the whole institute. The room is split in three areas: there is a quiet study area available as well as a conference room for small events, the largest part includes the journal and magazine reading space and the information desk. In this library space the researchers feel free to meet and talk about their research projects in a comfortable and pleasant environment. The physical collection of periodicals contains important journals (about 10,000 volumes) for the major research areas of the institute. Additionally there are 25,000 issues located in the departments of the institute, each collection with their own notation system.

The range of electronic services of the FHI library includes various databases, access terms and conditions for e-journals as well as catalogues. The Library Blog (http://library.fhi-berlin.mpg.de/) offers information with regard to the special interests of the FHI researchers featuring a mixture of news, training resources and collection information. The several eBook collections (i.e. Springer eBook collection 2005-2015) and the offer of about 30,000 currently subscribed electronic journals are licensed locally and by Max Planck wide agreements. An overview of the information resources like library catalogs, databases and e-print-servers available for the staff of the Max Planck Society are provided via the MPG Resource Navigator (rena.mpdl.mpg.de/rena).

The library provides traditional services as interlibrary loan service, acquisition of books and other information material, literature searches and reader service. In addition the library is in close contact with internal and external collaborators. The internal library and PuRe committee and the library group are working together on innovations in the field of information supply. Numerous collaborations exist with various institutions, for example with other Max Planck Institutes, institutes of the Helmholtz Association and libraries of the Fraunhofer institutes, local book shops and international publishers. The library works closely together with local educational institutions (Humboldt-Universität zu Berlin and University of Applied Sciences Potsdam). There are regularly offered internships for students.

The FHI researchers can obtain active support on all matters relating to publication management from the library. Therefore, the library of the FHI, together with the scientists, has developed an elaborated and well established publication workflow for authors. The workflow allows the monitoring of the publication output of the institute, which will be displayed and managed via the electronic repository of the Max Planck Society MPG.PuRe (www.pubman.mpdl.mpg.de). Thereby the institute aims at the deposition of full texts according to the principles of the Berlin Declaration on Open Access. The library supports the authors in the implementation of the Zweitveröffentlichungsrecht (right to secondary publication (§38 Abs. 4 UrhG)) and the Open Access publication for projects funded by ERC and HORIZON 2020.

Department of Inorganic Chemistry

Director: Robert Schlögl

Staff scientists:

Sylvia Becker *(née Reiche)**
Raoul Blume*
Saskia Buller*
Sébastien Cap
Malte Behrens *until 5/2014*
Michael Hävecker*
Frank Girgsdies
Kevin Kähler
Axel Knop-Gericke
Detre Teschner
Olaf Timpe *(FHI Safety Officer*)
Julian Tornow *until 6/2014*
Annette Trunschke
Marc G. Willinger
Sabine Wrabetz

Elmar Zeitler (Emeritus), Manfred Baerns and Klaus-Peter Dinse (Guest Emeriti)

Guest scientists, staying for at least six months:

Marina V. Bukhtiyarova*
Ranjan Chinmoy*
Maik Eichelbaum *until 2/2015*
Elias Frei
Klaus E. Hermann
Pierre Kube
Thomas Lunkenbein
Nickson Perini*
Marina Prenzel*
Julia Schumann
Christoph Sprung
Dangsheng Su *(part-time)*
Andrey Tarasov
Elena Willinger
Gregor Wowsnick *until 11/2014*
Shuchang Wu
Youngmi Yi*

Scientists (temporary) paid from external funds:

Gerardo Algara-Siller
Emilia A. Carbonio
Maria Dimitrakopoulou
Ramzi Farra
Qian Gao
Mark T. Greiner
Xing Huang
Benjamin E. Johnson
Katarzyna Skorupska
Travis E. Jones
David Klein
Sebastian Neugebauer
Johannes Noack
Tania Rodenas-Torralba
Andreu Ruiz de la Oliva
Jorge Salazar Gomez
Joannis Spanos
Juan-Jesus Velasco-Velez

Graduate students:	31	(including 13 from external funds)
	1	IMPRS
	1	joint graduate student TU Berlin / FHI
Technicians:	14	(including 3 from external funds)
	4	for Service Group Electron Microscopy
Trainees:	5	(including 2 master students)
Library Service Group:		Uta Siebeky, Katrin Quetting, Evelyn Prohn

* Based at Max Planck Institute for Chemical Energy Conversion (MPI CEC)

Recent Developments in the Department of Inorganic Chemistry

Director: Robert Schlögl

1. Implementation of Items from Last Report

The department AC consolidated the modifications induced by the foundation of the MPI CEC. We concentrate on our core projects being selective oxidation and metal-oxygen interactions in coin group metals. The focus on energy–related reactions is maintained by electrochemistry, synthesis of functional carbon materials and chemical energy conversion[1] through reaction of hydrogen in the synthesis of methanol and ammonia. Common to all projects is the guidance through the general concept[2] of dynamical interfacial processes. We were busy in continuing our methodical development projects. In the electron spectroscopy activities a core focus was on the creation of the EMIL infrastructure with our endstation CAT at BESSY. We completed successfully the testing of the novel modular experimental environment and are constructing the hardware for CAT during the days of the visit of the Fachbeirat. The inauguration ceremony of EMIL is planned directly after the visit of the Fachbeirat giving interested members the opportunity to inspect the status of the project.

The evolution of the electron microscopy followed the lines indicated in the last report. We took delivery of our high-resolution double aberration corrected (S)TEM instrument and make use of its stable high performance. Our efforts towards chemical electron microscopy were experimentally brought into operation with attaching MEMS device holders to the TITAN instrument, with operating the high-pressure in-situ transfer specimen holder and with casting the necessary instrumental developments with FEI as industrial partner into an application awaiting granting. The collaborative activities concentrated on joining the activities at MPI CEC with those at FHI and on the fruitful operation of the BASCAT joint laboratory with BASF and TU Berlin/UniCat. In this activity we realized seamless and trustful exchange between academia and industry and were able to reach in short time multiple milestones presented by the industrial partner.

Novel collaborative actions are MANGAN, a project founded by BMBF in which 21 groups in Germany under the leadership of MPI CEC collaborate to evaluate the potential of Mn compounds in water splitting reactions. Also at MPI CEC the preparative phase of the large-scale project “CARBONTOCHEM” being the flagship project of the founded technology transfer platform PLANCK (with the company TREK jointly operated through Max-Planck-Society, State of NRW and Fraunhofer Society) started operation with the project HÜGAPROP in which we generate conceptual information and novel analytical technology to evaluate the chemical dynamics of gas streams from steel mills. The inter-MPI collaborative project MAXNET Energy also began its operation focussing on material science for electrochemical reactions and on selective oxidation. The network was extended by an international component comprising the Cardiff Catalysis Centre and the University of Virginia as partners.

2. Organization of the Department

After the last meeting of the Fachbeirat *Raimund Horn* moved to Hamburg taking with him all activities and the equipment on kinetic and spectroscopic experimentation with profile reactors. This allowed for an extension of the experiments on microwave perturbation techniques and EPR. The combination of these activities with NAP XPS and valence band spectroscopy proved useful in elucidating the relevance of the often-neglected semiconductor properties as relevant contribution to the control of chemical reactivity[3]. Soon after the construction of new equipment began and a modern instrument could replace our out-dated EPR spectrometer, the responsible group leader *Maik Eichelbaum* left the institute for a position in the strategy department of the Federal Ministry of Research. We decided to continue the activities and reorganized the groups by joining the electrochemical activities with those of the charge carrier mobility activities under the guidance of Sébastien Cap who still has to adapt to the now diverse research activities. He is supported in this task by a well-working informal collaboration with *Thomas Risse* from the FU Berlin for which we are most grateful. A collaborative project in the framework of UniCat provides a scientific frame for the activities.

Almost simultaneously with this development *Malte Behrens* left the institute immediately after his habilitation for a W2 position at the University Duisburg-Essen. As we are in close collaboration with this university through the MPI CEC, it was decided to transfer the core activity of methanol synthesis and of dry reforming of CO_2 with methane[4] with him to the new place and to resume collaboration with Malte Behrens after he started his own operations. To anchor this activity that is topically compatible with the mission of the MPI CEC and that was already actively pursued there by *Marina V. Bukhtiyarova*, the new group of *Kevin Kähler* was implemented there. The transfer of the methanol project took part in early 2015 and is now largely completed. Some activities will however remain at the FHI as dedicated equipment and in-situ analytics will be needed. *Malte Behrens* left several unfinished doctoral students at the FHI who were not charged with the problems of moving the practical operation of their project to a new university without any dedicated infrastructure. These students all successfully completed their work at the FHI under the joint supervision of the group leaders at the department.

The department AC takes now the following form with six groups organized along competencies required for pursuing our integrated projects on heterogeneous catalysis. The projects are performed in collaboration between all groups. Each group is further responsible for one major collaborative project reaching outside of the FHI. No distinction is made between location of the groups in either FHI or MPI CEC. This integration was made possible by the evolution of the activities at MPI CEC reaching scientific operability during 2014.

Organisational structure of the department AC. The department is located both at the FHI Berlin and at the MPI CEC in Mülheim.

2015	**Group 1**	**Group 2**	**Group 3**	**Group 4**	**Group 5**	**Group 6**
Competence fields	Synthesis, Testing	Electron spectroscopy, Adsorption	Electron microscopy, Geometric structure	Carbon chemistry	Electrochemistry, Charge carrier dynamics	Catalytic technology
Lead	*Trunschke* *Frei*	*Knop* *Teschner*	*Willinger* *Lunkenbein*	*Reiche* *Buller*	*Cap* *Ranjan*	*Kähler* *Bukhtiyarova*
Collaboration	BASCAT	EMIL	CHEMMIC	MANGAN	MAXNET	Carbon2Chem

3. Scientific Highlights

The department AC wishes to highlight for the Fachbeirat one topical and one methodical development from the last 18 month in order to exemplify the scientific approach and the type of activities pursued in the Department. The selection does not imply any superiority of the results against the other activities described in the following section in more detail. The reader is kindly referred to the homepage of the department for a more complete account of the work illustrated in this and the following sections.

3.1 A Novel Family of Selective Oxidation Catalysts

It is firm belief that selective oxidation catalysts must contain either Mo or V or combinations of both elements (“the Bermuda triangle of oxidation”) in order to attain significant performance and useful selectivity. As true as this statement is phenomenologically, as difficult is its conceptual justification. This deficit highlights the level of understanding of selective oxidation catalysis. We try thus to find systems with useful reactivity which do not contain any of the two named elements. The search led earlier to $MnWO_4$, a well-studied oxide system. Its catalytic performance is however, very poor when synthesized by conventional high-temperature methods in full accordance with the general conjecture.

After extensive synthesis efforts it was, however, possible to obtain a family of MnWO$_4$ systems of identical chemical composition and crystallographic structure exhibiting a distribution of aspect ratios of their needle morphology. These systems exhibit unexpectedly high performance oxidative dehydrogenation of propane (Figure 1).[5] We present an example of a vanadium-free oxide that accomplishes efficient activation of propane by establishing a two dimensional Mn oxide layer in form of MnO$_x$ chains at the surface of phase-pure, rod-shaped, nanostructured MnWO$_4$. Oxygen defects can be reversibly replenished and depleted at reaction temperature as shown quantitatively by temperature-programmed oxidation/reduction and confirmed by NEXAFS. X-ray diffraction, RAMAN spectroscopy, and electron microscopy indicate phase purity and high crystallinity of the bulk. Synchrotron-based in-situ XPS evidences Mn-enrichment at the surface that is confirmed by HAADF-STEM. Terminating MnO$_x$ zigzag chains on (010) crystal planes are suspected to bear structurally site-isolated oxygen defects that account for the unexpected good performance of the catalyst in propane activation (Figure 1).

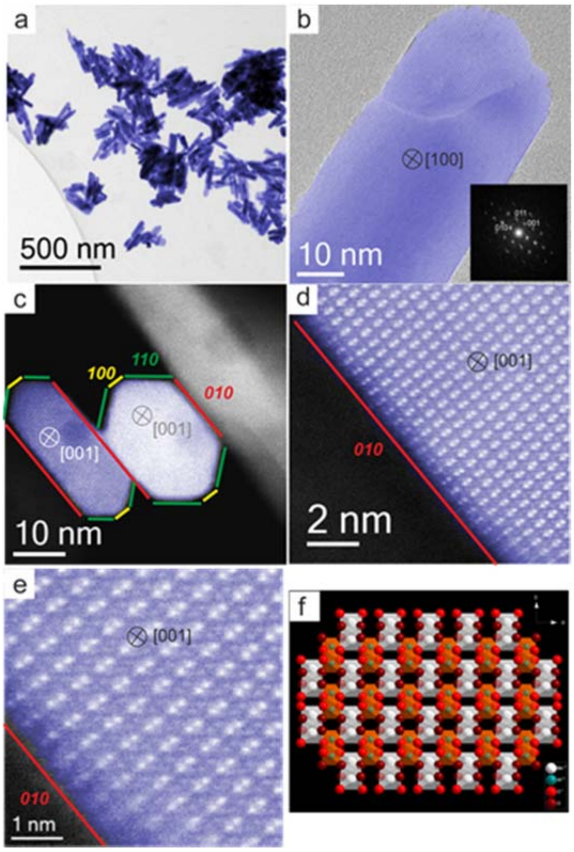


Figure 1: *(S)TEM analysis of the MnWO$_4$ powder catalyst: a) Overview TEM micrograph of the MnWO$_4$ nanorods; b) HRTEM image of one nanorod particle viewed along [100]. The inset denotes the power spectra recorded on either side of the defect; c) HAADF-STEM image of condensed [001] orientted MnWO$_4$ nanorods. The surface termination was identified by phase analysis of corresponding HR-HAADF-STEM images; d) and e) HR-HAADF-STEM images of (c); f) Schematic representation of the crystal structure of MnWO$_4$ viewed along [001].*

The system is in addition to its potential applicability (patent pending, publications awaiting IP clearance) of high scientific value, as it comprises for the first time the possibility to study catalytic reactivity in an array of selective oxidations as function of a structural parameter (aspect ratio) for a series of chemically and structurally identical systems.

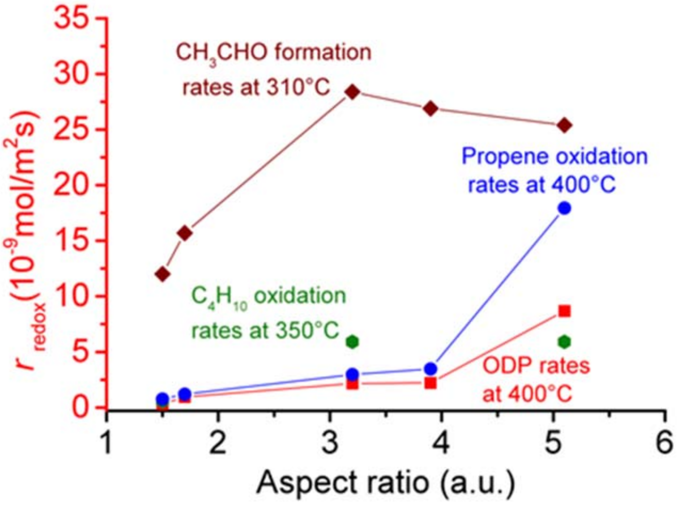


Figure 2: *Catalytic performance of the* $MnWO_4$ *powder system. A family of 5 compounds with different aspect ratios was investigated in several typical oxidation reactions. Conditions were as follows: ODP and propene oxidation:* $C3:O_2:N_2=10:5:85$, *W/F=1.8 g·s/ml; Ethanol oxidation:* $C_2H_5OH:O_2:N_2=4:8:85$, *W/F=0.4 g·s/ml; Butane oxidation:* $C4:O_2:H_2O:N_2=2.2:20:3:74.8$, *W/F= 1.67-2.0 g·s/ml.*

Figure 2 exemplifies the kind of information that can be obtained. Its correlation with extensive analytical investigation is currently underway. Our current working hypothesis is that structural OH groups play a critical role in explaining the performance. These are incorporated during the hydrothermal synthesis explaining the pronounced “chemical memory” effect of the system when comparing thermal and hydrothermal synthesis.

The data reveal that the system carries the potential to unravel the cooperation of acid-base and redox reactivity of a dynamical surface oxide in selective oxidation.

3.2 Chemical Electron Microscopy

The department AC has a long tradition in the development and exploitation of *in-situ* spectroscopic and diffraction techniques. We are therefore very well aware of the fact that catalysts are dynamic materials whose active centres are formed or transformed under reaction in response to the chemical potential[2] of the surrounding gas phase. In order to contribute to a mechanistic understanding of working catalysts, electron microscopy has to go beyond the conventional investigation of samples in vacuum of still poorly known composition and reactivity. We started to develop and implement methods for real-space and direct structural observation of catalysts under relevant catalytic conditions. Our approach can be summarized by the term “Chemical electron microscopy”. It stands[6] for analytical electron microscopy with a strong focus on the chemical state of the investigated materials by spectroscopic analysis and especially, under consideration of catalytically relevant dynamic processes.

Several examples of its application in studying mesoscopic and nanoscopic phenomena of chemical reactions are given in section 4.2. Here we present a combined study of the redox dynamics of Cu. This set of phenomena exemplifies the multi-scale nature of catalytic processes. Its combination with NAP XPS and advanced electron spectroscopy is exemplified in the oral presentation of the department AC (*Mark T. Greiner*). Here a brief account of the microscopic studies will be given.

During *in-situ* SEM investigation of Cu substrates in ethylene epoxidation and copper catalysed CVD growth[7] of graphene, we observed the redox dynamics of copper. At chemical potentials where copper oxides are metastable against copper metal plus diluted oxygen, rapid and extensive mass transport occurs that is driven by the mobility of Cu atoms along a reducing gradient of the chemical potential. In a gas mixture of hydrogen plus oxygen at mBar pressure we observe the formation of islands of Cu_2O on the surface of the polycrystalline Cu foil, which subsequently get reduced back to Cu. On the basis of the recorded images, we can analyse the formation of oxide domains and their subsequent reduction, as well as the periods in the red-ox cycling. The observed dynamics vary strongly with the H_2:O_2 ratio, pressure and temperature. The definition of static average surface structures becomes impossible under such conditions that are easily attained under practical application conditions of Cu catalysts.

In order to find out, if nanostructured isolated Cu particles show a similar red-ox structural dynamic behaviour and to investigate the effect of size of Cu domains, we conducted experiments under similar conditions in the *in-situ* TEM holder. Besides offering a higher spatial resolution and additional analytical tools (diffraction, spectroscopy), the *in-situ* experiments in the TEM can currently be conducted at higher pressures than in the ESEM. First experiments revealed that similar red-ox dynamics occur on the nanometre scale. Indeed, the particles oscillate between reduced and oxidized forms of copper. At present, we are investigating parameters that influence the dynamics and try to understand the propagation of phase boundaries and the role these redox-dynamics play in generating catalytic active species and sites. Certainly, these first observations in our *in-situ* set-up demonstrate that some of the assumptions that were published in the catalysis literature on the basis of TEM observations made in vacuum have to be revised.

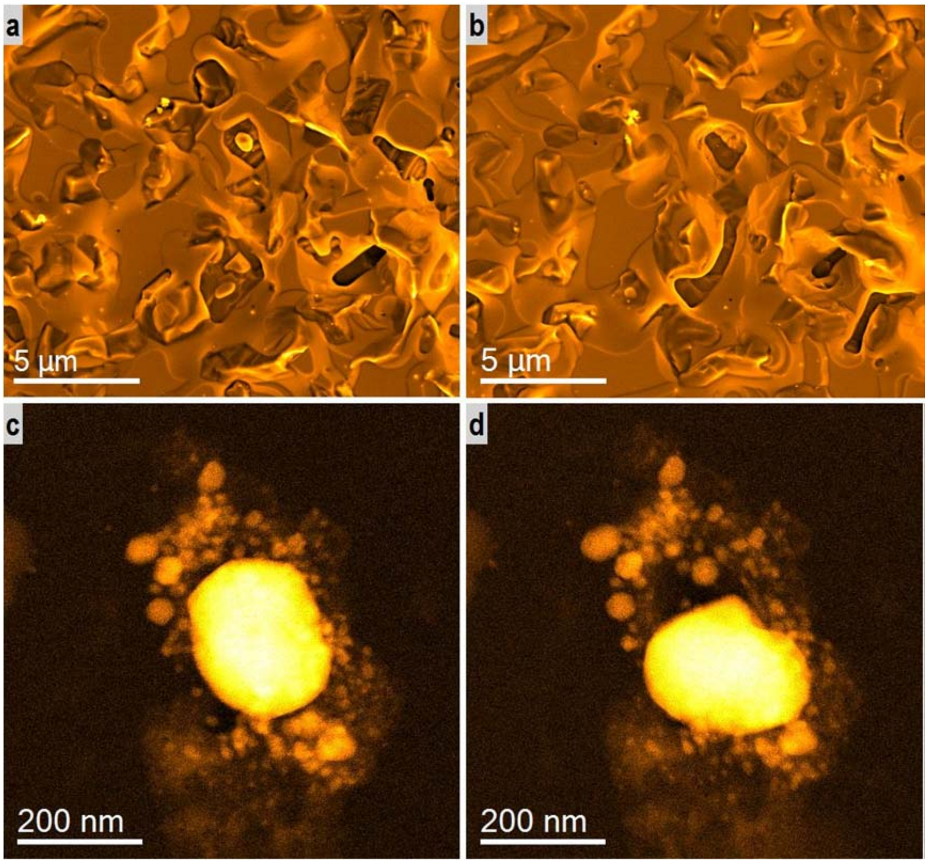


Figure 3: *(a) and (b) show the aspect of a copper surface in a* H_2/O_2 *(20:1) atmosphere at 0.2 mbar and 650 °C. Image (b) was recorded 8 minutes after image (a). (c) and (d) images recorded by in-situ STEM show dynamic shape changes caused by oxidation and reduction cycles. Images (c) and (d) were recorded with an interval of 3s*

4. Progress of the Research Activities

4.1 Selective Oxidation (Annette Trunschke)

We perform on a series of systems fundamental studies dealing with the activation of light alkanes in oxidation reactions at the surface of solid oxide catalysts. A generic key difficulty in catalytic oxidation arises from the chemical reactivity of reaction intermediates and/or the desired unsaturated or oxygenated target product, which is generally higher than that of the hydrocarbon substrate. Selectivity, i.e., avoiding the formation of the undesired thermodynamically most favourable product CO_2, is, consequently, the major challenge.[2] Fundamental principles of oxidation catalysis have been proposed, essentially based on comprehensive experimental studies performed in the last thirty years on the oxidation of olefins. However, the predictive power of these guidelines is not satisfying. New experimental approaches are needed that go beyond relations between crystallographic phase composition of structurally very complex catalysts and reactivity lacking causality.

Our approach includes controlled synthesis of well-defined oxide materials,[8] kinetic analysis of complex reaction networks,[9] and the investigation of solid-state and surface properties of the catalyst under operation. We reduce complexity by studying only pure phases that represent functional models of well-performing catalysts including alkaline earth oxides in the oxidative coupling of methane,[10] the "M1 phase" of MoVTeNb oxide in ethane and propane oxidation,[3b, 8a, 9] and vanadyl pyrophosphate $(VO)_2P_2O_7$ in oxidation of *n*-butane.[3b] The bulk catalysts are compared with binary oxides and metal oxide monolayers supported for example on meso-structured silica as inert carrier as well as molecular complexes that contain differently coordinated oxygen atoms. One highlight resulting from the combined results of our approach is the finding that "phase cooperation" is a non-necessary and possibly even detrimental property of oxide systems. Homogeneous and phase-pure compounds prove to be well-performing and superior catalysts over mixture of phases exhibiting typically severe deficits in performance stability.

4.1.1 Pure MgO as Model Catalyst in Oxidative Coupling of Methane

Pure nano-structured MgO catalysts with varying primary particle size, shape and specific surface area were prepared.[10a] The initial activity of MgO in the OCM reaction was found to be structure-sensitive. Kinetic studies reveal the occurrence of two parallel reaction mechanisms and a change in the contribution of these pathways to the overall performance of the catalysts with time on stream. The initial performance of freshly calcined MgO is governed by a surface-mediated coupling mechanism involving direct electron transfer between methane and oxygen at structural defects (steps) on the surface of MgO. The water formed in the OCM reaction causes sintering of the MgO particles and loss of active sites by degradation of structural defects, which is reflected in decreasing activity of MgO with time on stream.

The catalysts in the dehydroxylated state before the reaction and after catalysis have been studied by infrared and photoluminescence spectroscopy.[10a] The abundance of structural defects, in particular mono-atomic steps, correlates with the initial rates of both methane consumption and C_{2+} hydrocarbon formation (Figure 4). Infrared spectroscopy evidences strong polarization of C-H bonds due to adsorption of methane on dehydroxylated MgO surfaces that contain a high number of mono-atomic steps. It is postulated that these sites effectively promote intermolecular charge transfer between adsorbed methane and weakly adsorbed oxygen that leads to the dissociation of one C-H bond in the methane molecule and simultaneous formation of a superoxide species. Heterolytic splitting of C-H bonds in the presence of oxygen at the surface of dehydroxylated MgO already at room temperature has been proven by the appearance of an EPR signal associated with superoxide species that are located in close vicinity to a proton.

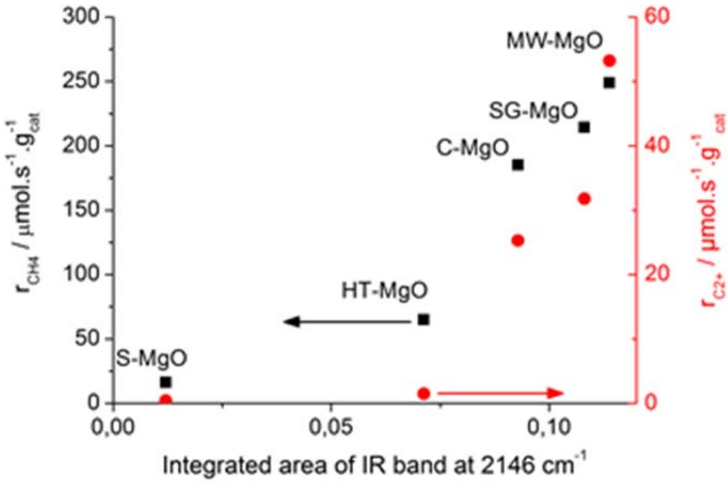


Figure 4: *Rate of methane consumption and* C_{2+} *formation at t=0 measured at T=1023 K, applying a feed composition of* $CH_4/O_2/N_2=3/1/1$, *and a contact time of 0.033 g·s·ml*$^{-1}$ *plotted versus the integrated area of the CO adsorption peak at 2146 cm*$^{-1}$ *that indicates the abundance of mono-atomic steps.*

4.1.2 Synthesis of Mixed Oxides

MoVTeNb M1 oxide is available via different synthesis routes. Hydrothermal synthesis benefits from kinetic control that facilitates formation of the metastable phase. We developed an analytical autoclave that enables the synthesis of comparatively large batches of oxides according to a new concept that implies a guided synthesis based on spectroscopic information obtained online.[8b] The synthesis is performed automated according to a pre-assigned sequence of reaction steps. The reaction parameters, such as temperature, pressure, power intake of the stirrer, and pH are measured and recorded. Reactants can be fed into the autoclave at reaction temperature by using HPLC pumps.

In situ Raman spectroscopy was applied to investigate the speciation of molybdates under hydrothermal conditions in aqueous solutions in the temperature range between 20°C and 200 °C and at pH values between 7 and 1 in this autoclave.[8b] The nature and abundance of molecular and supra-molecular species differs significantly compared to the distribution of species under ambient conditions at the same pH. The structural type of the solid phase formed through addition of vanadyl sulfate under hydrothermal conditions is sensitively controlled by the nature of the molecular precursor, which is adjusted by the pH. The results clearly demonstrate the power of in situ spectroscopy as a tool to improve our understanding of the inorganic reactions occurring under hydrothermal conditions.

4.1.3 Kinetic Studies of M1 Catalysts

MoVTeNb oxide catalysts exclusively composed of the M1 phase were studied in the oxidation of propane to acrylic acid applying a broad range of reaction conditions.[9a] The reactivity of MoVTeNb M1 oxide was compared with the reactivity of a M1 phase that contains only Mo and V at the metal positions of the crystal structure.[8a]. Analysis of the three-dimensional experimental parameter field measured in fixed bed reactors revealed that the complexity of the reaction network is reduced compared to less-defined catalysts due to phase purity and homogeneity. The oxidative dehydrogenation of propane to propene followed by allylic oxidation of propene comprises the main route to acrylic acid. The oxygen partial pressure was identified as an important process parameter that controls the activity in propane oxidation over phase-pure M1 without negative implications on the selectivity. Auxiliary steam increases activity and selectivity of M1 by changing the chemical natures of the active sites and by facilitating acrylic acid desorption. The M1 phase that contains only Mo and V produces acrylic acid, but shows low selectivity.

4.1.4 Surface Dynamics: NAP-XPS

The catalyst surface changes dynamically and reversibly when the feed composition is varied, but only in the outermost surface layer in a depth of around one nanometer.[3b, 9a] Synchrotron based near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) has demonstrated that MoVTeNb M1 oxide is a self-supported monolayer catalyst. The addition of steam causes enrichment in V and Te on the surface at the expense of Mo. Switching on and off the steam changes the surface composition reversibly. In addition, surface vanadium becomes more oxidized in presence of steam. These changes correlate with the abundance of acrylic acid detected in the in situ experiment. Such a dynamic redox behaviour was not observed for the M1 phase that contains only Mo and V. MoV M1 oxide produces acrylic acid as well, but the selectivity to undesired products CO and CO_2 is much higher compared to MoVTeNb M1 oxide. The detected high V concentration at the MoV M1 is likely to be responsible for consecutive reactions in which acrylic acid is further oxidized to carbon oxides.

In summary, our results clearly show a clear yet indirect impact of the crystalline bulk structure on surface composition and reactivity of Mo-based mixed oxides in selective oxidation of propane. The oxide surface is significantly reconstructed under working conditions and differs from the bulk in composition and in oxidation state of V. The selective MoVTeNb oxide catalyst features dynamic site isolation due to segregation of Te, and is characterized by redox dynamics compared to the unselective catalysts composed of the same crystal structure. The experiments illustrate critical relations between solid-state and surface dynamics in catalysis.

4.1.5 Semiconducting Properties of Mixed Oxide Catalysts

The electronic structure of the selective oxidation catalysts MoVTeNb M1 oxide and vanadyl pyrophosphate were investigated by conductivity measurements applying the microwave cavity perturbation technique in combination with NAP-XPS, soft X-ray absorption, and resonant photoelectron spectroscopy under operation.[3b] The presence of band bending and hence the formation of a high surface potential barrier, which electrons have to overcome on their way from the bulk to the surface, could be necessary to terminate the bulk surface charge transfer, limit the formation of active oxygen species on the surface and finally promote high selectivity to acrylic acid, while suppressing its total oxidation to CO_2. The surface potential barrier and the limited bulk surface charge transfer would also explain the extraordinary stability of the MoVTeNb M1 oxide bulk phase under reaction conditions. A high V^{5+}/V^{4+} ratio can increase the surface barrier height to such an extent, that the bulk–surface electron transport is impeded with implications on the reduction of gas phase oxygen and selectivity to the desired product as discussed above.

4.2 Electron Microscopy (Marc G. Willinger)

4.2.1 Local Chemical Information from Electron Energy-loss Spectrometry

In the microscope we are collecting structural information at high-resolution and combine it with simultaneously obtained spectroscopic information. On the basis of well-prepared samples and reproducible experimental conditions[4b], we are able to explain properties that are observed at the meso-scale. One example is the study of the electrochemical degradation of multi-walled carbon nanotubes (MWCNTs) under conditions of the oxygen evolution reaction in acidic media.[4] The loss of structural order due to the accumulation of defects can be seen in the HRTEM images. They give rise to a change in the electronic structure as can be seen in the energy-loss near-edge structure (ELNES) of the carbon K-edge. The combination of high-resolution imaging and electron energy-loss spectroscopy (EELS) provided key insight about the degradation mechanism and confirmed the formation of a self-limiting, highly stable surface oxide that kinetically hinders further corrosion of the tubes.[4]

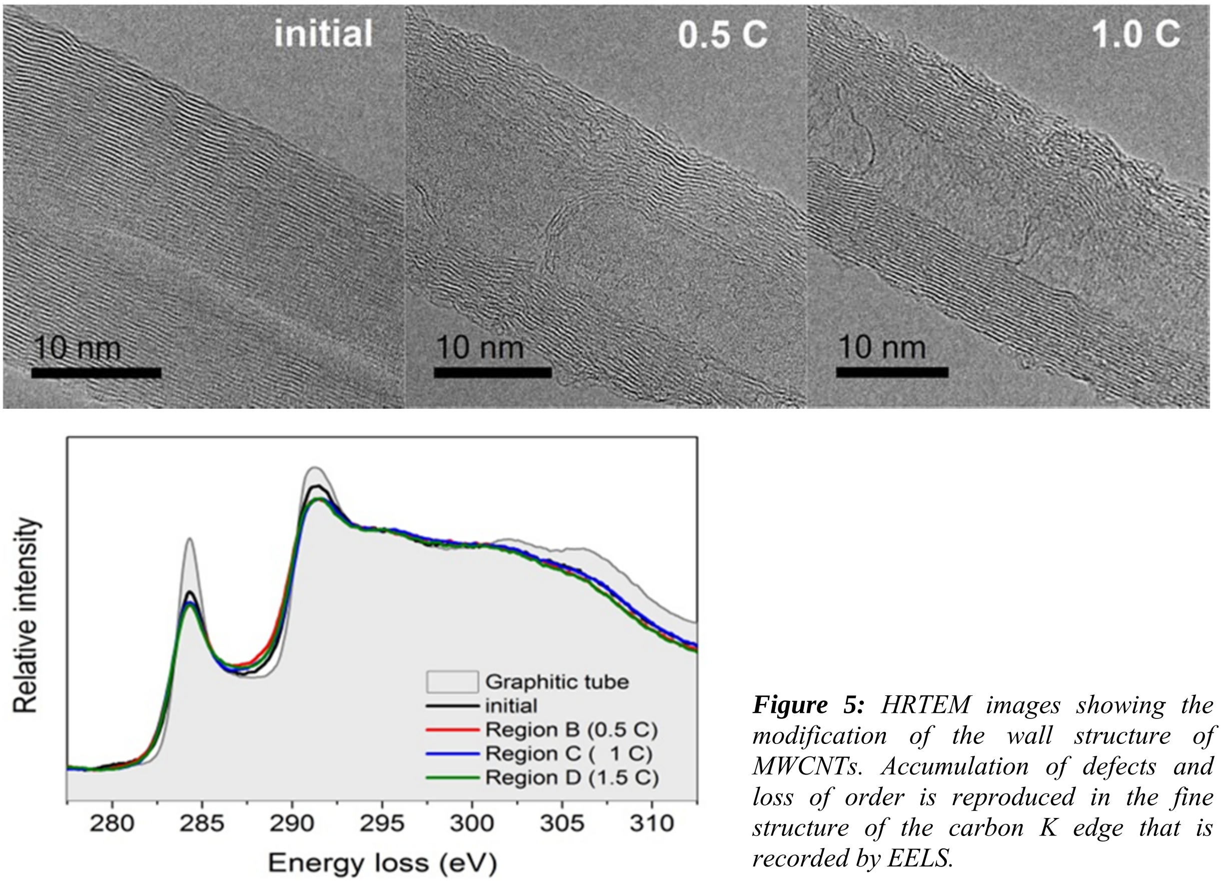


Figure 5: *HRTEM images showing the modification of the wall structure of MWCNTs. Accumulation of defects and loss of order is reproduced in the fine structure of the carbon K edge that is recorded by EELS.*

4.2.2 Surface Imaging and Spectroscopy

Using combinations of analytical techniques, we try to identify the role that different components of a catalyst play in a catalytic reaction. Similarly, we try to understand the effect of added promoters. We thus need to be able to detect the relevant species and distinguish them from eventually present spectator phases that do not contribute to the modification of the catalytic performance. The example shown here is the case of a carbon-supported platinum catalyst for fuel cell applications. We were interested in the effect of a tungsten modification of the carbon support that resulted in improved electrochemical stability and reduced loss of platinum. Using a combination of surface sensitive near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and high-resolution imaging we were able to identify the relevant species and thus understand the effect of the modification. It was found that atomic W species are decorating the surface of the Pt particles and furthermore, form bridges between platinum and carbon. Tungsten modification thus plays a dual role and gives rise to an improved stability of the Pt surface against oxidation, and to a stronger anchoring of the Pt particles on the support. As a consequence, the activity of the platinum particles was slightly reduced, while the overall stability of the catalyst was greatly improved.[5]

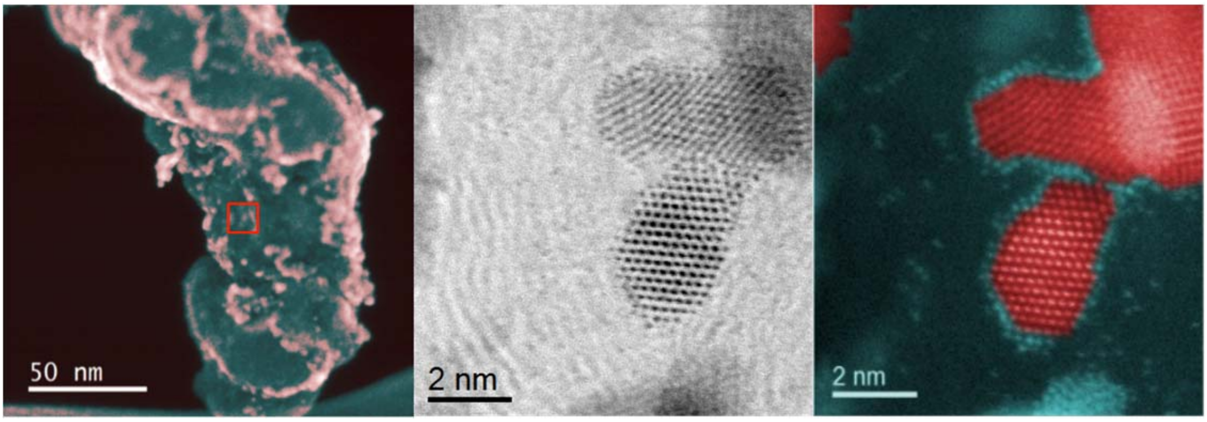


***Figure 6**: Secondary electron image of the W-modified Pt/C catalyst. High resolution annular bright field (ABF) and high angle annular dark field (HAADF) reveal the presence of atomic W species that are sitting at defect sites on the carbon support and are distributed over the surface of Pt particles.*

4.2.3 µ-Reactors: Enabling a Close Coupling of Ex-situ Catalytic Testing with High-resolution TEM Analysis at Identical Location

We continued our development of TEM-grid micro-reactors for ambient (AMBITEM) and high (HITEM) pressure catalysis. The reactors allow a decoupling of the catalytic reaction from the imaging process. In addition, imaging at identical location before and after experiments in the micro–reactor allows following morphological, structural and chemical changes of precursors and catalytically active materials at high resolution. Transport of the sample between the TEM and the micro-reactors is enabled via vacuum transfer holders and glove box without contact to ambient environment. Hence, restrictions with respect to pressure, atmosphere and electron beam are omitted. In order to elucidate the pitfalls of these new kinds of reactors, we first focused on CO oxidation and methanol synthesis, which were studied in the AMBITEM and HITEM, respectively. Although a catalytic conversion can be traced, the proper handling of the TEM grid during transfer and the cleanliness of the gases and reactors are still important factors that have to be considered in the future.

4.2.4 CVD Growth of Graphene

Due to the high sensitivity of the secondary electron signal to changes at the catalyst surface, we are able to visualize the formation of single atom thick sheets of carbon, i.e. the growth of graphene on the surface of metal catalysts. In fact, we are able to distinguish up to 8 carbon layers by the changes in contrast obtained in our ESEM instrument. In comparison with NAP-XPS on the graphene-substrate interaction, we demonstrated that different degrees of coupling and oxygen intercalation between graphene and the metal substrate[7b] can be detected as a variation in contrast.

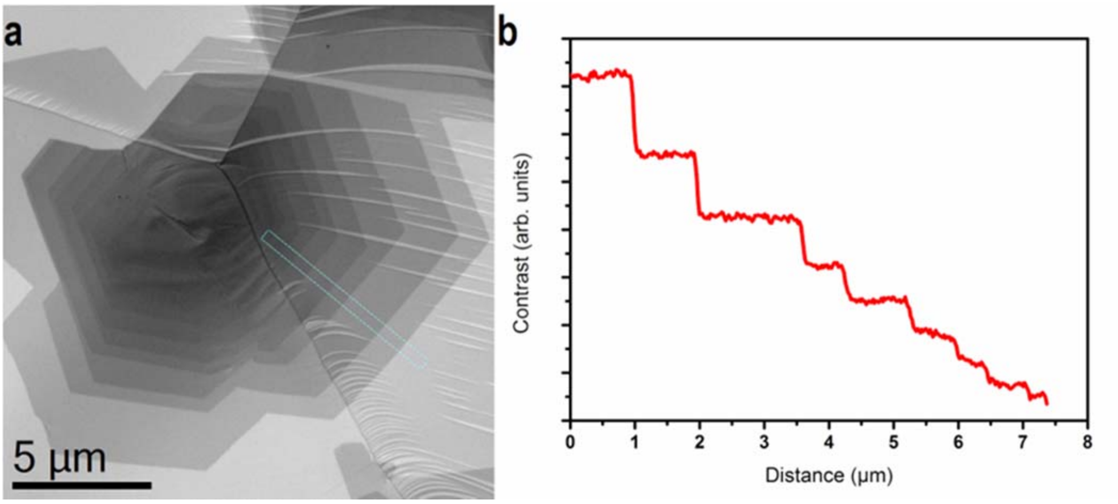


Figure 7: *The stacking of graphene sheets can be detected in the ESEM through the stepwise change in contrast. Up to 8 layers of carbon can be identified by their contrast.*

Understanding the growth mechanism and stacking order of thin carbon sheets is a pre-requisite for large-scale production of extended, high quality graphene via metal catalyzed chemical vapour deposition. *In-situ* scanning electron microscopy provides a unique and flexible tool[7a] for real-time visual observation of graphene growth under relevant conditions.

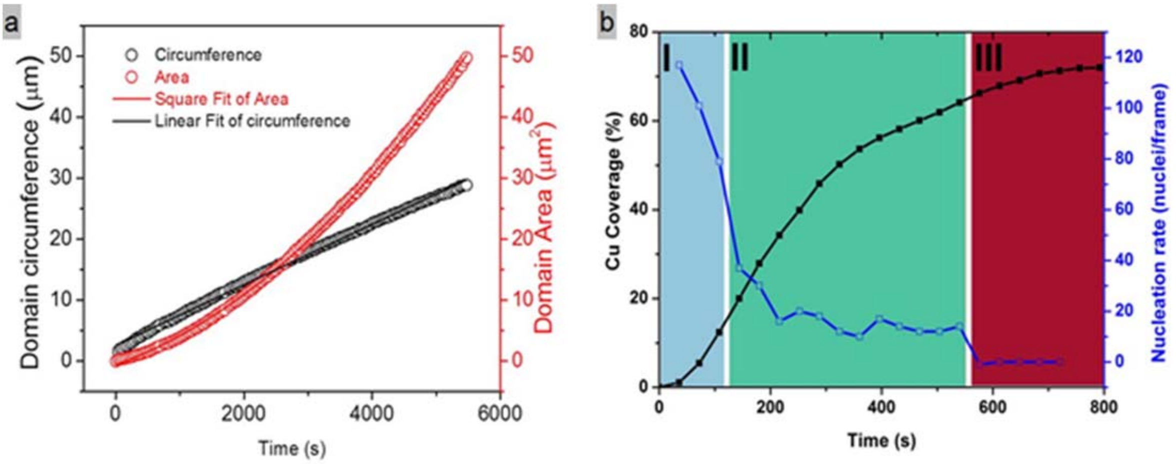


Figure 8*: Growth curves abstracted from the recorded videos reveal linear growth in the case of the highly active Pt substrate, while growth is only linear in the initial phase on copper. With increasing coverage of the copper surface, growth slows down due to the slow generation of feedstock carbon atoms resulting from the low catalytic activity of Cu.*

We are presently using the combined results from these studies to generate large-area high quality graphene systems as windows for the electrochemical in-situ XPS studies reported in section 4.3.

4.3 Electron Spectroscopy and Adsorption (Axel Knop-Gericke)

4.3.1 Coin Metal Redox Chemistry

The epoxidation of ethylene over copper was studied by in situ photoelectron spectroscopy and in situ electron microscopy, since is of fundamental interest to compare the surface chemistry of Cu and Ag with respect to the activation of oxygen. It was shown, that there exist a range of conditions in which epoxidation can be achieved at low temperatures (T<180°C) with relatively high selectivity (25%). The conditions where this activity is observed coincide with the conditions for which a phase transition between Cu_2O and CuO occurs. Under these conditions Cu^{1+} and Cu^{2+} are expected to exhibit a „bi-stability“, such that the oxidation state of the copper centers on the catalyst’s surface can easily flip back and forth between +1 and+2.

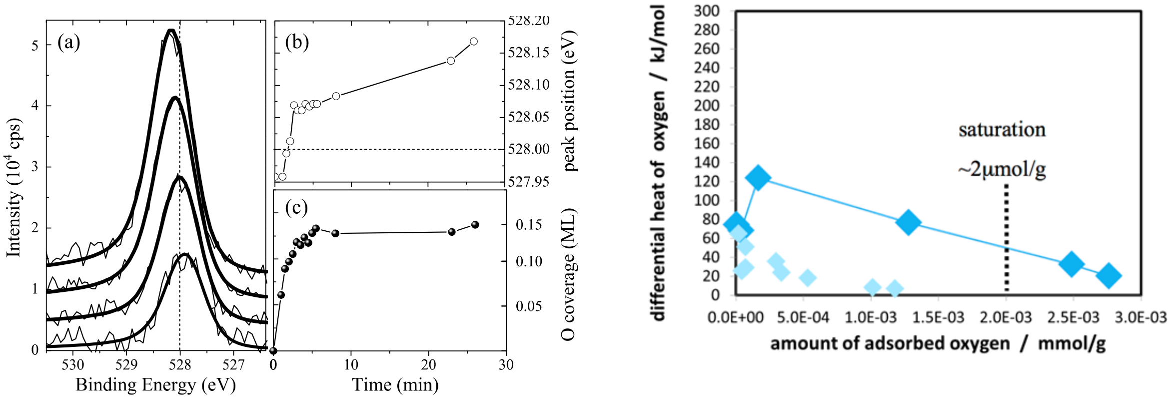


Figure 9: *(left) Short time scale dynamics of oxygen reconstruction on an Ag(111) surface probed by in situ XPS (~10^{-4} mbar O2 and 428 K). The O1s spectra shown were measured after 1, 2, 7, and 23 mins. data from [5]. (right) The multi time scale dynamics of oxygen reconstruction and O_{elec} formation on silver powders revealed through micro-calorimetry. Dark blue colored diamond symbols show oxygen adsorption on a clean surface and light blue color diamond symbols show oxygen adsorption on a surface pre-covered in oxygen.*

Silver[11] is the only metal capable of selectively epoxidizing ethylene in the industrial process. It does not form any stable oxides under reaction conditions and should this be present in its metallic state. It holds, however, several types of atomic oxygen. A predominant hypothesis is that O_{nucl} is bound in surface reconstruction and O_{elec} is unreconstructed atomic oxygen. To test this hypothesis we performed a joint experimental and theoretical study of single crystals, (111) and (110), and powders, <45 µm, under oxygen chemical potentials relevant for epoxidation. By combining in situ XPS/NEXAFS measurements with calculated spectra we were able to show for the first time the unreconstructed atomic oxygen has a binding energy of 527.9 eV and does not account for O_{elec}. Furthermore, unreconstructed atomic oxygen persists only at low oxygen coverage, giving rise to the short time scale dynamics seen in Figure 9. Within minutes of O_2 exposure (~10^{-4}mbar O_2 and 428 K) the single crystals become saturated in unreconstructed atomic oxygen, at which point surface reconstructions precipitate, giving rise to E_b=528.1 eV. Though not shown in the O1s spectra, O_{elec} is formed in a much slower process, only appearing after hours of O_2 exposure at these oxygen chemical potentials. Microcalorimetry measurements show, that O_{elec} can be seen to accumulate until reaching the saturation coverage of 2µmol/g. Exposing this oxygen-saturated surface to vacuum and then re-adsorbing oxygen reveals that the reconstructed and unreconstructed atomic oxygen are bound irreversibly but O_{elec} is bound reversibly.

Au nanoparticles (NP) on oxygen-free support (HOPG, functionalized CNTs, Au foil) were studied under conditions of CO oxidation by means of near ambient pressure –XPS (NAP-XPS) measurements. The results support the assumption, that the size reduction and the oxidation of the NP are not sufficient[12] to activate Au. To complement our results with the conjecture of the essential nature of a perimeter to an oxide surface, Au NP supported on transition metal oxides were synthesized by two different methods. It was shown that the catalytic performance is related not only to the formation of metal-oxide contact interface but in addition to the formation of a support overlayer inducing a strong metal support interaction by charge transfer processes.

4.3.2 Graphene Growth

The growth of mono layer graphene (MLG) was studied in the framework of the GRAFOL project. Combining the in situ capabilities of NAP-XPS with environmental scanning electron microscopy (ESEM, see section 4.2) and Monte Carlo simulations revealed that MLG growth on Ni is strongly affected by the presence of carbon atoms in the near surface region[13] of the catalyst. Epitaxial growth at low temperature is self-limiting because the small amount of dissolved carbon in the underlying sub- and sub-subsurface layers is readily depleted. On the other hand, high concentrations of dissolved carbon weaken the interaction of the growing graphene with the Ni leading to the loss of epitaxy and formation of rotated graphene and even multi-layer growth. In contrast, because of the small carbon solubility, MLG growth on Cu is easier to control[7b]. However, compared to Ni MLG interaction with the substrate is weak which allows for kinetically driven oxygen intercalation independent of the gas pressure and may be used for facilitated MLG transfers to other substrates. Cu was also found to be a promising catalyst for 2-dimensional h-BN films for a potential utilization as dielectric, support, or barrier layers in conjunction with graphene [14].

4.3.3 In-situ Electrochemical Studies

The oxygen evolution reaction (OER) on Iridium based catalysts was studied using sputtered metallic iridium films as a well-defined material. We developed a PEM-based, batch-like two-electrode cell to spectroscopically monitor oxygen-evolving catalysts' surfaces[15]. To allow for the diffusion of reactant molecules to the working electrode surface and the application of a potential, the OER-catalyst needs to be both water-permeable and conductive. These requirements are met by the sputtered film with a mud-crack type structure. During oxygen evolution, an oxidation of the initially metallic iridium was observed by photo electron spectroscopy. To help the identification of the present species and their dynamics, a variety of reference materials are currently studied by experiment and theory.

Thin film IrO_x catalysts prepared by the classical thermal decomposition of Ir precursor (spin coating of substrates with Ir acetate ethanol solution and calcination at 250, 350, 450 or 550°C for 15 min) were evaluated[16]. XRD analysis of Ir oxide thin films demonstrated that films calcined at 250°C were amorphous, although the precursor decomposed already at this temperature. To minimize the content of Ir in OER catalysts, we prepared core-shell $IrNi@IrO_x$ nanoparticles supported on carbon and on more corrosion resistant Sb-doped SnO_2 (ATO) for long-term stability[17] The activity and stability of oxidized $IrNiO_x$/meso-ATO electrocatalysts were assessed in OER in comparison with IrO_x/C and IrO_x/commercial-ATO reference materials). $IrNiO_x$/meso-ATO calcined at T≤ 300°C (and particularly the one at 180°C) were the most active catalysts; meanwhile their long-term stability were also excellent.

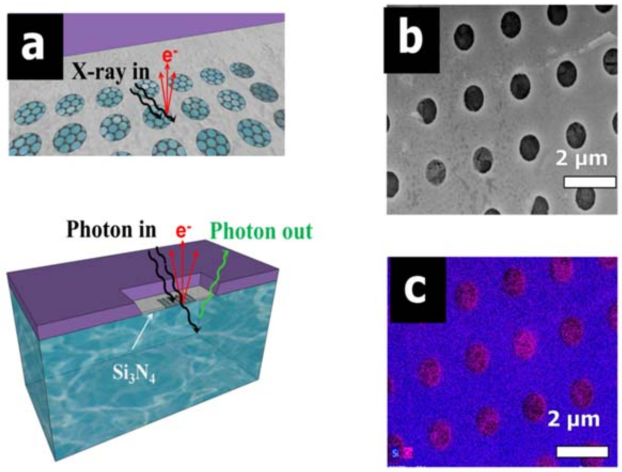


Figure 10: *a) BLG membrane schematic b) SEM and c) EDX of the membrane after Co electrodeposition.*

In order to study the interface between electrodes and electrolytes by XPS in ambient conditions we implemented the use of an electron transparent membrane based on graphene (see also section 4.2) to separate the vacuum measurement chamber from a cell filled with liquid. The graphene is supported on a thin Si_3N_4 film with a 40 x 40 array of holes of 1 µm diameter as shown in Figure 10. This cell allows the detection of photo- and Auger electrons generated near the solid/liquid interface. Furthermore, XAS can be performed in total electron yield (TEY) and in fluorescence yield (FY) modes. The performance of this cell was first demonstrated in the in situ study of the electrochemical deposited Cobalt on graphene. It was shown, that Cobalt anchors on graphene via carbonyl-like species. Furthermore, we observed that the covalent bonding between graphene and Cobalt promotes the reduction of Co^{3+} to Co^{2+}, which is believed to be active site of the catalyst.

4.4 Electrochemistry (Sébastien Cap)

The principal aim of the electrochemistry group is to study physicochemical processes that are involved in energy storage systems. More specifically, we are systematically varying the structural (topography, allotropes) and electronic properties (doping, surface chemical functionalization) of solid-state materials, followed by a comprehensive characterization of their consequent functional properties. This methodology aims to derive structure-function relations based upon causality (known structural origin of a function) to be used in development concepts based upon understanding rather than on empirical variations.

4.4.1 Electrochemical Stability and Dynamic Properties of Si-based Anode Materials

Since its first introduction onto the market in the 1980s by Sony, graphite-based anodes for lithium ion batteries were, and remain today, the prevailing battery concept due to their outstanding electrochemical stability. Today, efforts are being made to design anode materials based on silicon, as this element reversibly alloys with lithium at low potential (vs Li/Li^+) with a specific charge capacity exceeding the one of carbonaceous materials by one order of magnitude. However, silicon-based materials have a poor cycling stability, which is speculated to be related to two distinct degradation mechanisms, see Poster AC 5.1 for details. The current research aims at characterizing the electrochemical stability and the dynamic capability of Si-based anodes by systematically varying the structure and the surface electronic properties of the substrate with a particular focus on the charge storage location and charging-discharging mechanism. In pursuit of this specific research, our group has developed a model anode, which is composed of multiple nano-metric thin film layers of material deposited in a single batch process by a dedicated LP-CVD reactor. Figure 11 shows

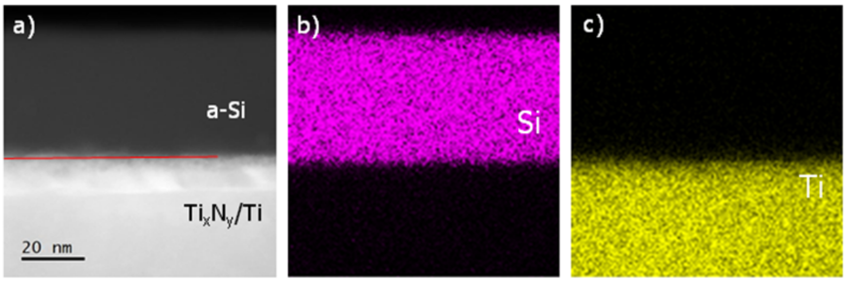


Figure 11: *a) TEM image: cross section of a model electrode formed of Ti/TiN/a-Si. Elemental mapping of b) Si and c) Ti of the anode cross section.*

a TEM image and associated elemental mapping of Si and Ti of the layered model electrode cross section. Here, a low roughness Ti disc is used as current collector and silicon is deposited on a blocking layer of TiN which prevents the formation of silicides.

We have further deposited silicon nano-droplets on various carbonaceous materials exhibiting various structural geometries and surface functional groups. Preliminary results indicate that the Si-based anode deposited by the LP-CVD method shows superior stability compared to the "classical" graphite/Si-nanoparticle composite, and that the interfacial chemistry significantly affects the electrochemical stability of the electrode.

4.4.2 Investigation of Charge Transport at Interfaces Using the Contact-free and In-situ Microwave Cavity Perturbation Technique

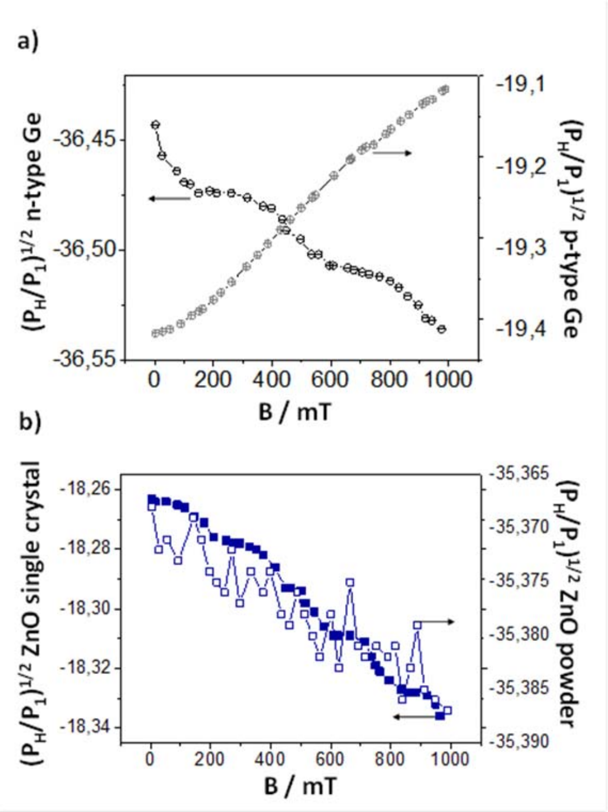


Figure 12: *Microwave Hall effect: investigation of benchmark systems in an external magnetic field (B) a) n- and p-type germanium crystals and b) ZnO*

Charge transport at interfaces plays a decisive role in materials science, for example in energy storage devices and in heterogeneously catalyzed reactions, such as the activation of hydrocarbons. The aim of our research is: 1) to investigate the kinetics and the thermodynamics of charge transport across interfaces under reaction conditions, and 2) to understand their relevance for the catalytic activity and selectivity towards the desired reaction products. As an example of our activity (see Poster AC 5.3) we compare catalysts with various selectivities in alkane oxidation reactions with and without steam over vanadyl pyrophosphate (VPP), $MoVTeNbO_x$ (M1 phase) and V_2O_5 catalysts using concepts[3,18] from semiconductor physics. We demonstrated that more selective catalysts have similar behavior to gas sensor materials, with dynamic charge transfer occurring between the bulk and the interface. In contrast, no significant changes were observed for the less selective catalyst (V_2O_5). Based on these results, we have suggested that the surface potential barrier can be a reasonable descriptor for catalyst selectivity. Our latest achievements include the development of instrumentation for a contact-free and *in situ* method to quantify charge carrier concentrations and determine carrier mobilities. The method is based on the Microwave Hall Effect (MHE) and can differentiate between electrons and holes as charge carriers. Figure 12 shows results from typical MHE experiments obtained with n- and p-type germanium single crystals and ZnO powder as a function of the external magnetic field (B). Recently, the MHE setup has been extended to perform elevated temperature measurements and is currently in the last phase of validation. The synergy of the microwave cavity based techniques available in our group, *i.e.*, EPR, MCPT, and MHE, offers a unique set of tools to characterize the charge transport across interfaces of thermally activated heterogeneous catalysts under relevant reaction conditions.

4.5 Carbon Chemistry (Saskia Buller, Sylvia Becker née Reiche)

The aim here is the knowledge-based development of advanced electrode materials consisting of a structured carbon backbone for electrical conductivity with additional functional groups incorporated by the monomeric units used that have the ability to anchor the catalytically active metal component and stabilize even small metal clusters. The work is focused on electrode materials for OER in water electrolysis. Furthermore, we develop concepts of functional carbon materials for battery applications. Besides spectroscopic techniques we use catalytic test reactions for verification of the nature and accessibility of the functional groups.

4.5.1 Functionalized Carbon Materials – Synthesis and Characterization

The carbon synthesis strategy of the group is based on the use of molecular precursors and controllable condensation reactions in liquid phase. The model precursor of this bottom-up approach is glucose. By hydrothermal treatment the glucose converts into carbonaceous materials highly functionalized by oxygen functional groups. The distribution of the oxygen functional groups, as well as the morphology of the carbonaceous product, is controlled[19] by process parameters, in particular the pH. For lower initial synthesis pH, i. e. pH 0, extended carbonaceous structures were confirmed by Raman spectroscopy, whereas for $pH > 3$ furanic structural entities from the 5-hydroxymethyl furfural intermediate remained the dominant structural motive of the carbon. The high number of functional groups leads to intrinsic binding properties that allow the preparation of functional disc electrodes by pressing and thermal annealing to 900°C. Hence, the general used concept of drop coated glassy carbon discs for electrochemical testing can be replaced by carbon based disc electrodes of controllable structure and functionalization. In the absence of Nafion, material-only properties can be studied for further fundamental understanding of electrochemical processes. The macroscopic dimension of the bulk electrode allows quantitative analytical investigations after electrochemical testing.

For further variation of the functionalization i. a. nitrogen containing precursors are applied. Post-functionalization techniques such as plasma treatment, electrochemical oxidation and (hydro)thermal treatments in active gases/solvents complete the methodical variety for the introduction of desired surface termination for the stabilization of catalysts. In order to distinguish differently functionalized carbon materials by Raman spectroscopy, a fitting procedure was developed based on MWCNTs. The theory-derived fit resulted in accurate ratios of the ideal graphitic lattice vibrations (G-Band) and lattice vibrations induces by defects/functional groups (D- and D’-Band). Supported by further characterization techniques such as microscopy, XPS and thermal analysis the type and quantity of functionalization of graphitic carbon materials can be derived.

This quantitative approach is superior to the commonly used empirical 5-component fit and allows for the first time a rational account of chemical modification of nano-carbons on the average electronic structure of the sp2 network of the sample as probed by phonon part of the RAMAN spectrum.

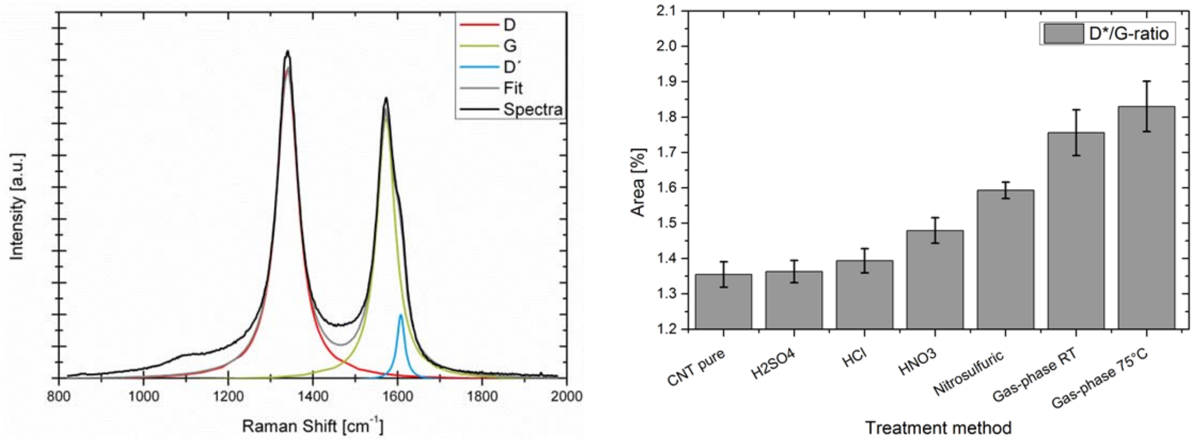


Figure 13: *MWCNT Raman spectra fitted by theory based process (left). D*/G-ratio for different functionalization techniques. D* corresponds to sum of peak areas of D- and D´-Bands (right). The unaccounted intensity arises from molecular species representing carbon not connected to the conducting* sp^2 *network of the sample.*

4.5.2 Metal Deposition

We further studied options of anchoring metals on structured carbon materials. We assume that for oxygen activation in the process of water splitting small cluster rather than single atoms are relevant for the active site. A close contact of catalytic active species to electric conductive carbon support is essential for high activity and stability of the materials. Therefore we applied direct synthesis of nanostructures on the support in variance to the commonly used pre-fabrication techniques within micelles to achieve different complexities of the deposited central atom. Besides oxidic aggregates Au nano-particles as model systems (in collaboration with UDE and MAXNET Energy) are prepared to study in detail the nature of the interacting carbon structure (see also example in section 4.2). Atomic layer deposition (ALD), wet impregnation and adsorption of colloids were applied. We focused on deposition of manganese oxides (MANGAN project) to draw on the expertise and methodical toolbox developed for photosystem II (department *Wolfgang Lubitz,* MPI CEC). We synthesized different pre-treated multi-walled carbon nanotubes and studied the influence of functional groups and defects on the surface on the stability of the impregnated manganese oxides. The HTC carbon systems described above were used to form binder-free free-standing electrically conducting systems. With respect to the localization of Mn oxide clusters it turned out that for wet impregnation defects in the structure have a stabilizing effect rather than the functional groups itself that are essential for the oxide structures arising from ALD.

4.6 Catalysis for Chemical Energy Conversion (Kevin Kähler)

Electro-catalytic H_2 production is often discussed as a key technology to store the fluctuating renewable energies. Numerous techniques to store the hydrogen have been suggested[1, 20] including the generation of NH_3 and CH_3OH, which are investigated in the catalytic technology group. Both substances offer the advantage of high H_2 contents and are easy to store as they are condensable.

4.6.1 Analysis of Exhaust Gases of Steel Mill Plants

Besides the electro-catalytic generated H_2 as potential feed, the capability of industrial exhaust gases as potential feed gases for ammonia and methanol synthesis is determined in the catalytic technology group. An extensive analysis of real exhaust gases from steel mill plants is performed for all kind of trace components including metals, sulfur-, nitrogen-, and chlorine-containing compounds, polycyclic aromatic hydrocarbons, and BTEX-aromatics, as well as for gaseous components (*HÜGAPROP*). Exhaust gas analysis for blast furnace gas, coke oven gas, and converter gas was already performed. As the composition of the exhaust gases depends on the production conditions as well as the raw materials and is time dependent, a detailed analysis over longer time period is mandatory. That is why the catalytic technology group constructed a mobile high-end gas analysis laboratory housed in a container to analyze the steel mill gases directly on-site. The container is equipped with a new generation PTR-IMR-TOF-MS for high performance analysis and reactors for gas purification and catalytic testing in methanol synthesis. The laboratory is expecting its first filed deployment during the day of the visit of the Fachbeirat.

4.6.2 Methanol Synthesis-technical Aspects

To elucidate the influence of impurities of the exhaust gases, systematic reactivity and stability studies in methanol synthesis were started. Feed gases consist of CO_2, H_2, and additionally trace components, like benzene as a representative of BTEX-aromatics. An industrial $Cu/ZnO/Al_2O_3$ catalyst is used. The reactor applied houses sufficient catalyst to determine the productivity by gravimetric analysis of condensate and high-precision GC product analysis (higher oxygenates). Figure 14 (A) shows the reaction rate of methanol production over a time period of 230 h in a stability test. The reaction rate stays in the same order of magnitude compared to benzene-free feed gas, which is represented in the first data point. Drops in the reaction rate after 50 and 165 h are caused by a decrease in the instrument pressure due to sample taking. A further purification step of the steel mill gases from BTEX aromatics does not seem to be necessary, as the impurities do not affect stability and activity of the technical catalyst.

4.6.3 Ammonia Synthesis

Ammonia synthesis represents an additional way to store hydrogen produced with renewable energy sources. Nevertheless, the ammonia synthesis catalyst is particularly prone for deactivation as only around 5% of the surface of a technical ammonia synthesis catalyst would actively dissociate di-nitrogen[1]. Oxygenate impurities for example act as catalyst poisons[1]. The development of catalysts with higher density of active sites may help to enhance the operation time of a technical catalyst. Figure 14 (B) shows the effluent mole fraction of ammonia in steady state during ammonia synthesis at 90 bar over an industrially used Fe-based catalyst in comparison to a $MgFe_2O_4$ catalyst synthesized from a layered double hydroxide precursor prepared by the group of *Malte Behrens* (UDE). Both catalysts show high stability in ammonia synthesis. At 425 °C industrially established multiple promoted Fe catalyst (8.7 $\mu mol \cdot g_{cat}^{-1} \cdot s^{-1}$) achieves only a less than 4-fold higher activity compared to the unpromoted model catalyst (2.3 $\mu mol \cdot g_{cat}^{-1} \cdot s^{-1}$). Therefore, the $MgFe_2O_4$ system is a promising starting point for further catalyst development. The key point here is the circumvention of the high-temperature melting process of the iron oxide precursor by low-temperature self-organisation of layered iron-oxihydroxide precursor supported on a mineral carrier. Such a "green" synthesis allows studying the interplay of morphology and promoter chemistry in the formation of the active iron species. This is currently underway also in collaboration with *Serena DeBeer* (*department Frank Neese*) performing XAS and XES analysis on the iron edges. To allow for this, a special reactor was constructed allowing the disassembly of the catalyst inside a glove box without contact to the ambient for ex-situ characterization methods. This may help to elucidate whether surface, subsurface, or bulk nitride species are generated during the reaction, as the active phase of the Fe-based catalyst under industrially used conditions is still unclear[2]. The very low conversion in ammonia synthesis at mbar pressure precludes direct in-situ analysis and the extreme air-sensitivity of the activated catalysts represents a major hurdle in getting insight into the chemistry of the active form of ammonia iron[21].

4.6.4 Oxidative Dehydrogenation of Ethyl Benzene

For the investigations of the oxidative dehydrogenation (ODH) of ethylbenzene forming styrene, a kinetic flow set-up was constructed in the catalytic technology group. ODH is an energy saving candidate for the synthesis of styrene. Additionally, ODH is employed for the characterization of carbon materials, which are produced in the "carbon synthesis and application" group in the institute. Carbon materials are active in the ODH reaction[22]. Di-carbonyl surface functional groups that can be modified by additional dopants such as nitrogen are assigned[23] to be the active sites. An extensive characterization and correlation to activity data can shed light into this assignment. If the structure-activity relation is identified, the ODH of ethyl benzene can outstandingly supplement the existing characterization methods for carbon materials.

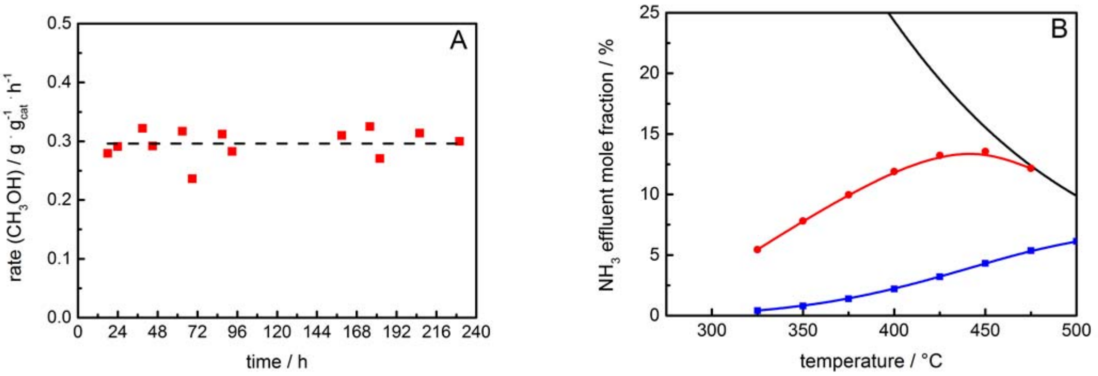


Figure 14: *(A) Methanol synthesis measurement at 250 °C and 15 bar in* $H_2/CO_2/(500$ *ppm* C_6H_6 *in* $N_2)$ *feed gas with ratio of 3:1:0.35, and a GHSV of 4800* h^{-1}*. First data point is recorded in* C_6H_6*-free feed gas. (B) Ammonia synthesis measurement at 325 – 500 °C and 90 bar in 75%* H_2/N_2 *with a HSV of 2.28* $h^{-1} \cdot g_{cat}^{-1}$ *over an industrially used Fe-based catalyst (red) and an* $MgFe_2O_4$ *model catalyst (blue). Maximum* NH_3 *concentrations in thermodynamic equilibrium are additionally shown (black).*

4.6.5 Methanol Synthesis-fundamental Insights (Elias Frei)

The Cu/ZnO contact within the Cu/ZnO/Al_2O_3 system is widely accepted to be an important part of the catalyst and often considered as "synergism". In the previous Fachbeirat report (2014), ZnO was identified as key component for the conversion of CO_2 into CH_3OH, proven on a Cu/MgO catalyst (active for CO but inactive for CO_2 conversion). The impregnation of CuMgO with ZnO leads instantly to activity for CO_2 hydrogenation to CH_3OH, that is comparable[24] to that of high performance Cu/ZnO/Al_2O_3 catalysts. To follow up these findings[25], we investigated the role of ZnO decoupled from Cu, on powdered model systems of nano-crystalline ZnO (co-precipitated Zn-hydroxy-carbonate, calcined at 603 K) optionally doped with 3 mol% Mg^{2+}, Al^{3+} and Ga^{3+}. The dopants were already part of the metal salt solutions during the co-precipitation process and consequently part of the ZnO lattice. Due to the semi-conducting properties of ZnO (direct band gap, 3.3 eV) the optoelectronic characterization is of particular interest. With diffuse reflectance UV-vis spectroscopy optical band gaps of the supports were estimated. It was found that Mg^{2+} increased the apparent optical band gap of ZnO, whereas Al^{3+} and Ga^{3+} led to a decrease of the optical band gap (see Figure 15a). Ga^{3+} and Al^{3+} form defect states in the band gap as expected for trivalent ions in n-type semiconductors while Mg^{2+} makes ZnO more insulating. Using the microwave cavity perturbation technique (see section 4.4) the conductivities of the ZnO systems in inert (N_2), reducing (5.2 vol% H_2 in N_2) and oxidizing (5.2 vol% O_2 in N_2) gas environments were measured at 230 °C (Figure 15b).

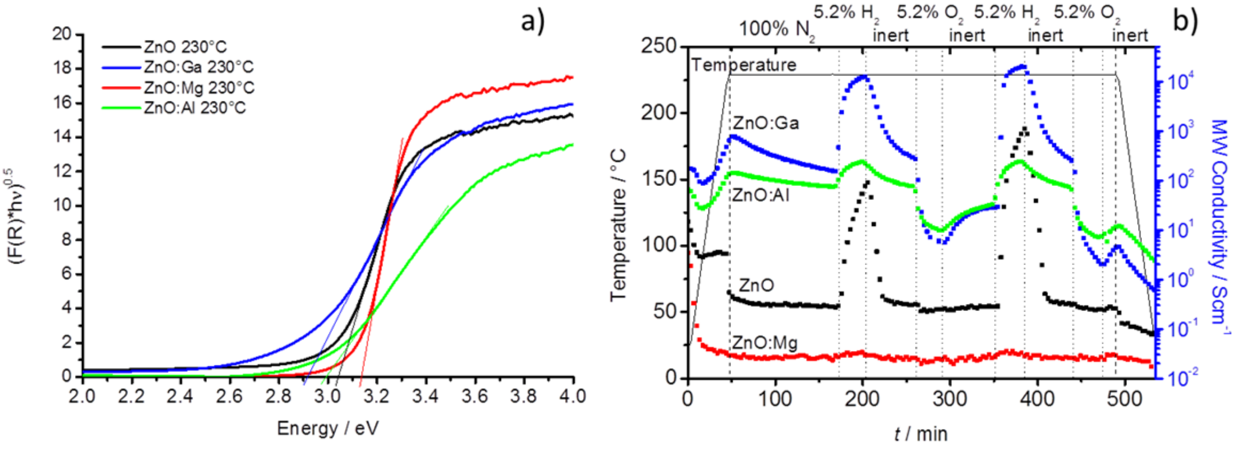


Figure 15: *Determination of the optoelectronic properties of ZnO, with and without dopant. Tauc-plot for band gap estimation from UV/Vis spectra (a). Microwave conductivity measurements in different gas atmospheres at elevated temperatures (b).*

The results show that the conductivity behavior is strongly modified by the different dopants and is consistent with the trends observed for the optical band gap measurements. The n-type character of ZnO, with electrons as majority charge carriers, explains the increase in conductivity with hydrogen exposure (donation of electrons) and a decrease with oxygen exposure (consumption of electrons). Electron paramagnetic resonance (EPR) measurements support the microwave conductivity results and reveal a stronger resonance at *g* values of 1.963 for Al^{3+} and Ga^{3+} doped ZnO in contrast to undoped or Mg^{2+} doped ZnO. To investigate the catalytic impact of the electronic properties, the ZnO:M samples were impregnated with Cu and tested in the reverse water gas shift (RWGS) and methanol reaction. Interestingly, the activities of the ZnO:M/Cu systems are different, but staggered according to the optoelectronic properties of the samples, e.g. ZnO:Al/Cu was much more active than ZnO:Mg/Cu. The determined apparent activation energies confirm these findings and give further experimental evidence that the $Cu/ZnO/Al_2O_3$ system might be dominated by the optoelectronic influence of the doped ZnO and less by Cu.

A 148-day time-on-stream (TOS) study clarifies the importance of the different constituents of an industrial relevant $Cu/ZnO/Al_2O_3$ methanol catalyst.

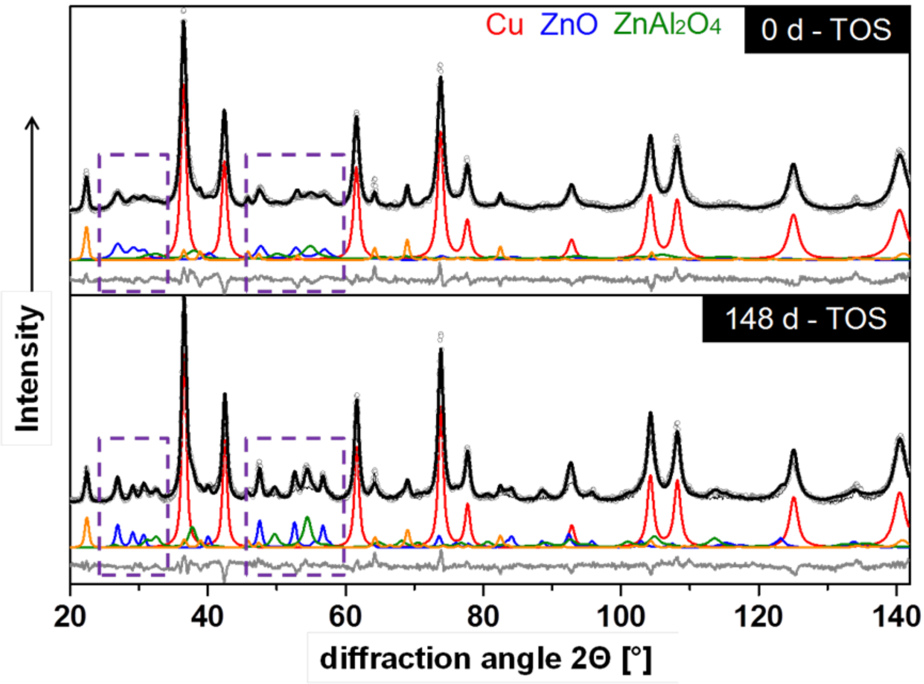


Figure 16: *ND patterns (grey circles) after the first contact to the reaction feed (0 days) and after 148 days TOS. The Rietveld fits (black line), the relevant phases (Cu, ZnO,* $ZnAl_2O_4$*) and the difference of the pattern and the fit (thin grey line) are shown. The orange curve is referred to graphite as a binder and necessary for the fit. The dashed boxes highlight regions of important changes.*

Figure 16 shows the Rietveld fitted neutron diffraction patterns[4f] of the 0 days and 148 days TOS samples. All detected structural changes occur with the Zn-containing phases. The crystallographic changes are paralleled by a loss in specific surface area and catalytic activity. The Cu phase stays almost unaffected during 148 days TOS. It seems that the ZnO dynamics controls the deactivation process of the catalyst and consequently the catalytic performance. It is thus the defect structure (that may be modified by dopants such as part of the structural promoter Al^{3+}) that controls the synergy in the ternary catalyst. The high specificity of the synergy to ZnO with respect to other oxide systems may thus be explained by the relative ease with which the electronic structure of ZnO may be doped under the conditions prevailing in methanol synthesis.

4.7 Theory Support (Klaus E. Hermann)

The activities of this team have focused on applications of density-functional theory (DFT), on theoretical electron and photon spectroscopy (near-edge X-ray, NEXAFS and infrared, IR), and on bulk as well as surface crystallography. The results of collaborations with all groups of the department have proven to be valuable asset. Here we mention only support for the interpretation of structure-reactivity relationships based on core electron and vibrational spectra (NEXAFS, IR, Raman) of vanadium oxo-peroxo species[26], $K[VO(O_2)Hheida]$. More recently, we have started to study energetics and thermodynamic behavior (with Travis E. Jones) of differently terminated $MnWO_4$ surfaces. Discussions of the interpretation of core excitation spectra (XAS) recorded for nitrogen doped carbon nanotubes[23b] and the evaluation of crystallographic shapes of metal and oxide particles as well as calculations of the relative stability of differently terminated $MnWO_4$ (010) and (011) surfaces in connection with corresponding electron microscopic images complete the activities of the group.

In addition, the theory support team studied various subjects not immediately connected with experimental work in the department but also in collaboration with external groups. This includes work on theoretical NEXAFS spectra of large coordination networks involving pyridine based Cu-T4PT species at the Cu(111) surface considered as molecular switching devices, of cis- and trans-stilbene adsorbates to identify switching behavior and of the C 1s fine structure of molecular anthracene. Other interests concern reconstruction mechanisms of the Si(100) surface where model reconstruction paths have been evaluated using molecular dynamics and DFT and the dynamics of molecular machines such as the muscle-like [c2]daisy chain. Further, the 2nd edition of the book “Crystallography and Surface Structure” by K. Hermann[8] increasing the present edition by about 50% will be completed by December 2015. Finally, code development on the Balsac software (surface structure analyzer) has been continued with a major upgrade to the new version 4.0. This package is used quite frequently by the theory support team for the design and analysis of complex crystal surface structures but also distributed commercially outside the institute by the MPG.

5. Future Developments

The department AC will further consolidate its activities directed towards understanding the nature of active systems in the selective heterogeneous catalysis of oxidation (water, hydrocarbons) and reductions (CO_2, N_2). The search for mechanisms of how catalyst precursors activate in the chemical potential of reactants into active systems will be a core target. If this pathway continues to be a generic sign of catalytic materials, then we need considerations of how we can incorporate catalyst dynamics into kinetic equations of catalytic processes. Likewise, we have to fill our toolbox of synthetic methods for creating precursors that undergo the transformation into dynamical states without rapid deactivation in a most effective way (activation period of the catalyst).

On the methodical side we wish to complete the development of the contactless measurement of charge carrier dynamics. The completion and initial operation of the EMIL project with the CAT beamline and the implementation of the Joint Lab at HZB-BESSY will keep us occupied. We seek support from the Fachbeirat for our combined activities on the development of “chemical electron microscopy” to be ready with commercial implementations when the new microscopy laboratory at MPI CEC comes into operation. As multiple rapid technological developments characterize this field we may have to put forward additional proposals (for a target preparation system and for novel camera detectors with greatly enhanced temporal resolution without sacrificing dynamic sensitivity ranges). On the personnel side we have agreed to send *Marc G. Willinger* to the MPI for colloid science (*Markus Antonietti*) to support the creation of a competence group for electron microscopy that can apply immediately the results from the chemical electron microscopy development. He will take his Habilitation with the results generated. When the microscopy group moves to MPI CEC, *M. G. Willinger* will come back to the department and take on the leadership of the microscopy facility.

The evolution of the activities at MPI CEC that are limited by space and the only temporal existence of the group there will continue to be a focal effort of the whole department. The process was supported by the organisational homogenization between the two parts of the department described in section 2 of this report. We will extend our activities in electrochemistry as joint effort for the whole department and we will execute the projects MANGAN and CARBONTOCHEM in addition to our participation in the MAXNET Energy. The implementation of the Joint Lab MPG-JARA (in Aachen) dealing with the creation of an in-situ magnetic resonance facility and the installation of a MPG research group with tenure track to a W3 position in RWTH Aachen will be an important additional step in extending the network of collaborations. This activity being positively decided by the Perspective Commission of the CPTS section carries besides its value for the MPI CEC also some political relevance for the relation of MPG with places of excellence in Germany.

The department AC actively takes part (with *Elias Frei*) in pursuing the inter-FHI project „CO_2 activation“ where it has several activities related to methanol synthesis but also more general in CO_2 activation over metal oxides. In particular, the effects of electronically modified ZnO (doped, partly reduced) and of Cr_2O_3 on CO_2 reduction are studied. Activities comprise model experiments at the CP departments (with *Shamil Shaikhutdinov*) to which the AC department synthesizes and tests polycrystalline performance analogues. In addition, with the PC department (*Julia Stähler*) fundamental studies on the charge carrier dynamics and the electronic structure are performed using TR photoemission and THz spectroscopy under reaction conditions. The TH department conducts extensive theoretical studies on the effect of doped oxides on CO_2 activation in extension to their work on OCM of such systems. In order to complement these activities the AC department synthesizes samples with the chemical composition adopted in the models of the TH department (with *Sergey Levchenko*) and performs reactivity studies as well as the analysis of the (doped) electronic structure.

The speciation of oxo-ions in aqueous solution is of fundamental relevance for planning the synthesis of oxides in particular under hydrothermal conditions. We have initiated collaboration with the MP department (*Gert von Helden*) in determining the species distribution of relevant solutions by mass spectrometry with advanced ionisation techniques and vibrational spectroscopy using the FHI FEL. First experiments reveal surprising insight into the species distribution of molybdates being at variance with commonly used assignments derived from RAMAN spectroscopy and conductivity data.

The collaboration with the Molecular Chemistry department in MPI CEC (with *Dimitrios Manganas*) concerning the development of theory for assigning the molecular structure of reactive vanadium species is being extended into a generalized methodology. The combination of several observable spectroscopic properties (UV-Vis, NEXAFS and RAMAN) with calculation of each of these species followed by a regression of computed multi-method observable properties for several hypothetical structural models against precision experimental data allows unprecedented precision in the exclusion of hypothetical structures as active species. The method was developed for a set of monolayer vanadium species and is being extended to other systems where the determination of the local geometry does not lead to conclusive results from single experimental or theoretical analysis.

[1] R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *Early View*.

[2] R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *54*, 3465-3520.

[3] aC. Heine, M. Hävecker, A. Trunschke, R. Schlögl, M. Eichelbaum, *Phys. Chem. Chem. Phys.* **2015**, *advanced article*; bM. Eichelbaum, M. Hävecker, C. Heine, F. Rosowski, A. Trunschke, R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *54*, 2922-2926; cC. Heine, M. Hävecker, E. Stotz, F. Rosowski, A. Knop-Gericke, A. Trunschke, M. Eichelbaum, R. Schlögl, *J. Phys. Chem. C* **2014**, *118*, 20405-20412.

[4] aK. Mette, S. Kühl, A. Trasov, H. Düdder, K. Kähler, M. Muhler, R. Schlögl, M. Behrens, *Catal. Today* **2015**, *242* 1010-1110; bT. Lunkenbein, J. Schumann, M. Behrens, M. G. Willinger, *Angew. Chem. Int. Ed.* **2015**, *Early View*; cS. Kühl, J. Schumann, I. Kasatkin, M. Hävecker, R. Schlögl, M. Behrens, *Catal. Today* **2015**, *246*, 92-100; dA. Tarasov, H. Düdder, K. Mette, S. Kühl, K. Kähler, R. Schlögl, M. Muhler, M. Behrens, *Chem. Ing. Tech.* **2014**, *86*, 1916-1924; eJ. Schumann, T. Lunkenbein, A. Tarasov, N. Thomas, R. Schlögl, M. Behrens, *ChemCatChem* **2014**, *6*, 2889-2897; fT. Kandemir, I. Kasatkin, F. Girgsdies, S. Zander, S. Kühl, M. Tovar, R. Schlögl, M. Behrens, *Top. Catal.* **2014**, *57*, 188-206; gM. B. Fichtl, J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler, O. Hinrichsen, *Angew. Chem. Int. Ed.* **2014**, *53*, 7043-7047; hS. Zander, E. L. Kunkes, M. E. Schuster, J. Schumann, G. Weinberg, D. Teschner, N. Jacobsen, R. Schlögl, M. Behrens, *Angew. Chem. Int. Ed.* **2013**, *52*, 6536-6540.

[5] F. Bisti, G. Profeta, H. Vita, M. Donarelli, F. Perrozzi, P. M. Sheverdyaeva, P. Moras, K. Horn, L. Ottaviano, *Physical Review B* **2015**, *91*.

[6] D. S. Su, B. Zhang, R. Schloegl, *Chemical Reviews* **2015**, *115*, 2818-2882.

[7] aZ.-J. Wang, G. Weinberg, Q. Zhang, T. Lunkenbein, A. Klein-Hoffmann, M. Kurnatowska, M. Plodinec, Q. Li, L. Chi, R. Schloegl, M.-G. Willinger, *Acs Nano* **2015**, *9*, 1506-1519; bR. Blume, P. R. Kidambi, B. C. Bayer, R. S. Weatherup, Z.-J. Wang, G. Weinberg, M.-G. Willinger, M. Greiner, S. Hofmann, A. Knop-Gericke, R. Schlögl, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25989-26003.

[8] aT. Lunkenbein, F. Girgsdies, A. Wernbacher, J. Noack, G. Auffermann, A. Yasuhara, A. Klein-Hoffmann, W. Ueda, M. Eichelbaum, A. Trunschke, R. Schloegl, M. G. Willinger, *Angewandte Chemie-International Edition* **2015**, *54*, 6828-6831; bJ. Noack, F. Rosowski, R. Schlögl, A. Trunschke, *Z. Allg. Anorg. Chem.* **2014**, *640*, 2730-2736.

[9] aR. N. d'Alnoncourt, L.-I. Csepei, M. Haevecker, F. Girgsdies, M. E. Schuster, R. Schloegl, A. Trunschke, *Journal of Catalysis* **2014**, *311*, 369-385; bK. Amakawa, Y. V. Kolen'ko, R. Schlögl, A. Trunschke, *ChemCatChem* **2014**, *6*, 3338-3341.

[10] aP. T. Schwach, A; Schlögl, R., *Journal of Catalysis* **2015**, *accepted*; bK. Kwapien, J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke, R. Schlogl, *Angewandte Chemie-International Edition* **2014**, *53*, 8774-8778.

[11] aT. Jones, T. C. R. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl, S. Piccinin, *Phys. Chem. Chem. Phys.* **2015**, *accepted*; bT. E. Jones, T. C. R. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl, S. Piccinin, *Phys. Chem. Chem. Phys.* **2014**, *16*, 9002-9014; cA. Indra, M. Greiner, A. Knop-Gericke, R. Schlögl, D. Avnir, M. Driess, *ChemCatChem* **2014**, *6*, 1935-1939; dL. Cheng, C. Yin, F. Mehmood, B. Liu, J. Greeley, S. Lee, B. Lee, S. Seifert, R. E. Winans, D. Teschner, R. Schlögl, S. Vajda, L. A. Curtiss, *ACS Catal.* **2014**, *4*, 32-39.

[12] aD. Wang, A. Villa, D. S. Su, R. Schlögl, *ChemCatChem* **2013**, *5*, 2717-2723; bA. Y. Klyushin, T. C. R. Rocha, M. Hävecker, A. Knop-Gericke, R. Schlögl, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7881-7886.

[13] R. S. Weatherup, H. Amara, R. Blume, B. Dlubak, B. C. Bayer, M. Diarra, M. Bahri, A. Cabrero-Vilatela, S. Caneva, P. R. Kidambi, M.-B. Martin, C. Deranlot, P. Seneor, R. Schloegl, F. Ducastelle, C. Bichara, S. Hofmann, *Journal of the American Chemical Society* **2014**, *136*, 13698-13708.

[14] P. R. Kidambi, R. Blume, J. Kling, J. B. Wagner, C. Bähtz, R. S. Weatherup, R. Schlögl, B. C. Bayer, S. Hofmann, *Chem. Mater.* **2014**, *26*, 6380-6392.

[15] R. Arrigo, M. Hävecker, M. E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schlögl, *Angew. Chem. Int. Ed.* **2013**, *52*, 11660-11664.

[16] T. Reier, D. Teschner, T. Lunkenbein, A. Bergmann, S. Selve, R. Kraehnert, R. Schlögl, P. Strasser, *J. Electrochem. Soc.* **2014**, *161*, F876-F882.

[17] aN. Hong Nhan, H.-S. Oh, T. Reier, E. Willinger, M.-G. Willinger, V. Petkov, D. Teschner, P. Strasser, *Angewandte Chemie-International Edition* **2015**, *54*, 2975-2979; bH. N. Nong, L. Gan, E. Willinger, D. Teschner, P. Strasser, *Chemical Science* **2014**, *5*, 2955-2963.

[18] C. Heine, M. Hävecker, M. Sanchez-Sanchez, A. Trunschke, R. Schlögl, M. Eichelbaum, *J. Phys. Chem. C* **2013**, *117*, 26988-26997.

[19] S. Reiche, N. Kowalew, R. Schlögl, *ChemPhysChem* **2014**, *16*, 579-587.

[20] R. Schlögl, in *Chemical Energy Storage* (Ed.: R. Schlögl), DeGruyter, **2012**.

[21] T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens, R. Schlögl, *Angew. Chem. Int. Ed.* **2013**, *52*, 12723-12726.

[22] aS. Wu, G. Wen, J. Wang, J. Rong, B. Zong, R. Schlögl, D. S. Su, *Catal. Sci. Technol.* **2014**, *4*, 4183-4187; bR. Schlögl*, Vol. 56* (Eds.: B. C. Gates, F. C. Jentoft), Elsevier Inc., **2013**, pp. 103-185; cJ. J. Delgado, X. Chen, B. Frank, D. S. Su, R. Schlögl, *Catal. Today* **2012**, *186*, 93-98.

[23] aS. Reiche, R. Blume, X.-C. Zhao, D. S. Su, E. Kunkes, M. Behrens, R. Schlögl, *Carbon* **2014**, *77*, 175-183; bR. Arrigo, M. E. Schuster, S. Abate, S. Wrabetz, K. Amakawa, D. Teschner, M. Freni, G. Centi, S. Perathoner, M. Hävecker, R. Schlögl, *ChemSusChem* **2014**, *7*, 1; cO. Khavryuchenko, B. Frank, A. Trunschke, K. Hermann, R. Schlögl, *J. Phys. Chem. C* **2013**, *117*, 6225-6234.

[24] E. L. Kunkes, F. Studt, F. Abild-Pedersen, R. Schloegl, M. Behrens, *Journal of Catalysis* **2015**, *328*, 43-48.

[25] J. Schumann, M. Eichelbaum, T. Lunkenbein, N. Thomas, M. C. Alvarez Galvan, R. Schloegl, M. Behrens, *Acs Catalysis* **2015**, *5*, 3260-3270.

[26] L. L. Sun, K. E. Hermann, J. Noack, O. Timpe, D. Teschner, M. Haevecker, A. Trunschke, R. Schloegl, *Journal of Physical Chemistry C* **2014**, *118*, 24611-24622.

6. Publications of the Department of Inorganic Chemistry[1]

2013 (late publications)

Amakawa, K., L. Sun, C. Guo, M. Hävecker, P. Kube, I.E. Wachs, S. Lwin, A.I. Frenkel, A. Patlolla, K. Hermann, R. Schlögl and A. Trunschke: How Strain Affects the Reactivity of Surface Metal Oxide Catalysts. Angewandte Chemie International Edition **52** (51), 13553-13557 (2013).

Amakawa, K., L. Sun, C. Guo, M. Hävecker, P. Kube, I.E. Wachs, S. Lwin, A.I. Frenkel, A. Patlolla, K. Hermann, R. Schlögl and A. Trunschke: Der Einfluss von strukturellen Spannungen auf die Reaktivität von getragenen Metalloxidkatalysatoren. Angewandte Chemie **125** (51), 13796-13800 (2013).

Behrens, M. and R. Schlögl: How to Prepare a Good Cu/ZnO Catalyst or the Role of Solid State Chemistry for the Synthesis of Nanostructured Catalysts. Zeitschrift für anorganische und allgemeine Chemie **639** (15), 2683-2695 (2013).

Buchwald, D.K., J. Renn and R. Schlögl: A note on Einstein's Scratch Notebook of 1910-1913. In: Physics as a Calling, Science for Society: Studies in Honour of A. J. Kox. (Eds.) A. Maas and H. Schatz. University Press, Leiden, 81-88 (2013). ISBN 978-90-8728-198-4.

Demuth, D., R.W. Fischer, H.-J. Freund and M. Baerns: Katalyse - moderne Alchemie? Chemie-Ingenieur-Technik **85** (12), 1807-1814 (2013).

Frank, B., T.P. Cotter, M.E. Schuster, R. Schlögl and A. Trunschke: Carbon Dynamics on the Molybdenum Carbide Surface during Catalytic Propane Dehydrogenation. Chemistry - A European Journal **19** (50), 16938-16945 (2013).

Gruber, M. and K. Hermann: Elementary steps of the catalytic NO_x reduction with NH_3: Cluster studies on reaction paths and energetics at vanadium oxide substrate. The Journal of Chemical Physics **139** (24), 244701 (2013). OPEN ACCESS

Guiet, A., T. Reier, N. Heidary, D. Felkel, B. Johnson, U. Vainio, H. Schlaad, Y. Aksu, M. Driess, P. Strasser, A. Thomas, J. Polte and A. Fischer: A One-Pot Approach to Mesoporous Metal Oxide Ultrathin Film Electrodes Bearing One Metal Nanoparticle per Pore with Enhanced Electrocatalytic Properties. Chemistry of Materials **25** (23), 4645-4652 (2013).

Heine, C., M. Hävecker, M. Sanchez-Sanchez, A. Trunschke, R. Schlögl and M. Eichelbaum: Work Function, Band Bending, and Microwave Conductivity Studies on the Selective Alkane Oxidation Catalyst MoVTeNb Oxide (Orthorhombic M1 Phase) under Operation Conditions. The Journal of Physical Chemistry C **117** (51), 26988-26997 (2013).

Johnson, B., F. Girgsdies, G. Weinberg, D. Rosenthal, A. Knop-Gericke, R. Schlögl, T. Reier and P. Strasser: Suitability of Simplified $(Ir,Ti)O_x$ Films for Characterization during Electrocatalytic Oxygen Evolution Reaction. The Journal of Physical Chemistry C **117** (48), 25443-25450 (2013).

Kandemir, T., M.E. Schuster, A. Senyshyn, M. Behrens and R. Schlögl: The Haber-Bosch Process Revisited: On the Real Structure and Stability of "Ammonia Iron" under Working Condition. Angewandte Chemie International Edition **52** (48), 12723-12726 (2013).[1]

---

[1] OPEN ACCESS = Gold open access publication

Kandemir, T., M.E. Schuster, A. Senyshyn, M. Behrens and R. Schlögl: Über die Realstruktur von “Ammoniakeisen” und ihre Stabilität während des Haber-Bosch-Verfahrens. Angewandte Chemie **125** (48), 12955-12959 (2013).

Kristiansen, P.T., T. Rocha, A. Knop-Gericke, J.H. Guo and L.C. Duda: Reaction cell for *in situ* soft x-ray absorption spectroscopy and resonant inelastic x-ray scattering measurements of heterogeneous catalysis up to 1 atm and 250 °C. Review of Scientific Instruments **84** (11), 113107 (2013).

Majoulet, O., C. Salameh, M.E. Schuster, U.B. Demirci, Y. Sugahara, S. Bernard and P. Miele: Preparation, Characterization, and Surface Modification of Periodic Mesoporous Silicon-Aluminum-Carbon-Nitrogen Frameworks. Chemistry of Materials **25** (20), 3957-3970 (2013).

Moser, M., C. Mondelli, A.P. Amrute, A. Tazawa, D. Teschner, M.E. Schuster, A. Klein-Hoffmann, N. López, T. Schmidt and J. Pérez-Ramírez: HCl Oxidation on IrO_2-Based Catalysts: From Fundamentals to Scale-Up. ACS Catalysis **3** (12), 2813-2822 (2013).

Ocon, J.D., T.N. Tuan, Y. Yi, R.L. de Leon, J.K. Lee and J. Lee: Ultrafast and stable hydrogen generation from sodium borohydride in methanol and water over Fe-B nanoparticles. Journal of Power Sources **243**, 444-450 (2013).

Schlögl, R.: Author Profile Robert Schlögl. Angewandte Chemie International Edition **52** (50), 13140-13141 (2013).

Schlögl, R.: Autoren-Profil Robert Schlögl. Angewandte Chemie **125** (50), 13378-13379 (2013).

Schlögl, R.: Carbon in catalysis. Advances in Catalysis **56**, 103-185 (2013).

Schlögl, R. and J.W. Niemantsverdriet: Surface Inorganic Chemistry and Heterogeneous Catalysis. (Comprehensive Inorganic Chemistry II, Vol. 7). Elsevier, Oxford (2013). ISBN 978-0-08-096529-1.

Schomäcker, R., S. Arnd, B. Beck, S. Mavlyankariev, R. Horn, R. Schlögl, U. Simon, H. Schubert, A. Berthold, O. Görke, A. Urakawa, S. Jaso, H. Godini and G. Wozny: Oxidative Coupling of Methane - Still a Challenge for Catalyst Development and Reaction Engineering. In: Proceedings of the New Technologies and Alternative Feedstocks in Petrochemistry and Refining. (Ed.) S. Ernst. DGMK, Hamburg, 111-112 (2013). ISBN 978-3-941721-32-6.

Starr, D.E., H. Bluhm, Z. Liu, A. Knop-Gericke and M. Hävecker: Application of Ambient-Pressure X-ray Photoelectron Spectroscopy for the In-situ Investigation of Heterogeneous Catalytic Reactions. In: In-situ Characterization of Heterogeneous Catalysts. (Eds.) J.A. Rodriguez, J.C. Hanson and P.J. Chupas. Wiley-VCH, Weinheim, 315-343 (2013). ISBN 978-1-118-00016-8.

Toghan, A., R. Arrigo, A. Knop-Gericke and R. Imbihl: Corrigendum to “Ambient pressure X-ray photoelectron spectroscopy during electrochemical promotion of ethylene oxidation over a bimetallic Pt–Ag/YSZ catalyst”. Journal of Catalysis **302**, 92-92 (2013).

Zheng, Z., X. Huang, M. Schenderlein, D. Borisova, R. Cao, H. Moehwald and D.G. Shchukin: Self-Healing and Antifouling Multifunctional Coatings Based on pH and Sulfide Ion Sensitive Nanocontainers. Advanced Functional Materials **23** (26), 3307-3314 (2013).

Habilitation

Behrens, M.: Materials Chemistry of Cu/ZnO-based Catalysts for Methanol Synthesis and Steam Reforming. Technische Universität Berlin 2013.

Doctoral Thesis

Farra, R.: Spectroscopic studies towards the understanding of CeO_2-based catalysts for chlorine production. Technische Universität Berlin 2013.

Schwarz, H.: Gas-Phase Methane Oxidation Investigated by Laser-Induced Fluorescence, Species Profile Measurements and Kinetic Reactor Simulations. Technische Universität Berlin 2013.

2014

Abate, S., R. Arrigo, S. Perathoner and G. Centi: Role of Feed Composition on the Performances of Pd-Based Catalysts for the Direct Synthesis of H_2O_2. Topics in Catalysis **57** (14-16), 1208-1217 (2014).

Amakawa, K., Y.V. Kolen'ko, R. Schlögl and A. Trunschke: The M1 Phase of MoVTeNbO as a Catalyst for Olefin Metathesis and Isomerization. ChemCatChem **6** (12), 3338-3341 (2014).

Armbrüster, M., R. Schlögl and Y. Grin: Intermetallic compounds in heterogeneous catalysis - a quickly developing field. Science and Technology of Advanced Materials **15** (3), 034803 (2014). OPEN ACCESS

Arrigo, R., M.E. Schuster, S. Abate, S. Wrabetz, K. Amakawa, D. Teschner, M. Freni, G. Centi, S. Perathoner, M. Hävecker and R. Schlögl: Dynamics of Palladium on Nanocarbon in the Direct Synthesis of H_2O_2. ChemSusChem **7** (1), 179-194 (2014).

Bairamov, F.B., E.D. Poloskin, A.A. Kornev, A.L. Chernev, V.V. Toporov, M.V. Dubina, C. Röder, C. Sprung, H. Lipsanen and B.H. Bairamov: Functionalization of nc-Si/SiO_2 semiconductor quantum dots by oligonucleotides. Semiconductors **48** (11), 1485-1489 (2014).

Bairamov, F.B., E.D. Poloskin, A.A. Kornev, A.L. Chernev, V.V. Toporov, M.V. Dubina, C. Röder, C. Sprung, H. Lipsanen and B.K. Bairamov: Resonant raman scattering in complexes of nc-Si/SiO_2 quantum dots and oligonucleotides. Technical Physics Letters **40** (11), 1035-1037 (2014).

Behrens, M., T. Lunkenbein and R. Weihrich: Festkörperchemie 2013. Nachrichten aus der Chemie **62** (3), 251-263 (2014).

Blume, R., P.R. Kidambi, B.C. Bayer, R.S. Weatherup, Z.-J. Wang, G. Weinberg, M.G. Willinger, M. Greiner, S. Hofmann, A. Knop-Gericke and R. Schlögl: The influence of intercalated oxygen on the properties of graphene on polycrystalline Cu under various environmental conditions. Physical Chemistry Chemical Physics **16** (47), 25989-26003 (2014). OPEN ACCESS

Busser, G.W., B. Mei, A. Pougin, J. Strunk, R. Gutkowski, W. Schuhmann, M.G. Willinger, R. Schlögl and M. Muhler: Photodeposition of Copper and Chromia on Gallium Oxide: The Role of Co-Catalysts in Photocatalytic Water Splitting. ChemSusChem **7** (4), 1030-1034 (2014).

Carrero, C.A., M. Kauer, A. Dinse, T. Wolfram, N. Hamilton, A. Trunschke, R. Schlögl and R. Schomäcker: High performance $(VO_x)_n$-$(TiO_x)_m$/SBA-15 catalyst for the oxidative dehydrogenation of propane. Catalysis Science & Technology **4** (3), 786-794 (2014). OPEN ACCESS

Carrero, C.A., R. Schlögl, I.E. Wachs and R. Schomäcker: Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts. ACS Catalysis **4** (10), 3357-3380 (2014).

Cheng, L., C. Yin, F. Mehmood, B. Liu, J. Greeley, S. Lee, B. Lee, S. Seifert, R. Winans, D. Teschner, R. Schlögl, S. Vajda and L. Curtiss: Reaction Mechanism for Direct Propylene Epoxidation by Alumina-Supported Silver Aggregates: The Role of the Particle/Support Interface. ACS Catalysis **4** (1), 32-39 (2014).

Düdder, H., K. Kähler, B. Krause, K. Mette, S. Kühl, M. Behrens, V. Scherer and M. Muhler: The role of carbonaceous deposits in the activity and stability of Ni-based catalysts applied in the dry reforming of methane. Catalysis Science & Technology **4** (9), 3317-3328 (2014).

Düdder, H., K. Kähler, B. Krause, K. Mette, S. Kühl, M. Behrens, V. Scherer and M. Muhler: Correction: The role of carbonaceous deposits in the activity and stability of Ni-based catalysts applied in the dry reforming of methane. Catalysis Science & Technology **4** (11), 4100 (2014).

Eder, D. and R. Schlögl: Nanocarbon-Inorganic Hybrids. De Gruyter, Berlin (2014). ISBN 978-3-11-026986-4.

Erini, N., R. Loukrakpam, V. Petkov, E.A. Baranova, R. Yang, D. Teschner, Y. Huang, S. Brankovic and P. Strasser: Ethanol Electro-Oxidation on Ternary Platinum-Rhodium-Tin Nanocatalysts: Insights in the Atomic 3D Structure of the Active Catalytic Phase. ACS Catalysis **4** (6), 1859-1867 (2014).

Fichtl, M.B., J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler and O. Hinrichsen: Counting of Oxygen Defects versus Metal Surface Sites in Methanol Synthesis Catalysts by Different Probe Molecules. Angewandte Chemie International Edition **53** (27), 7043-7047 (2014).

Fichtl, M.B., J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler and O. Hinrichsen: Counting of Oxygen Defects versus Metal Surface Sites in Methanol Synthesis Catalysts by Different Probe Molecules. Angewandte Chemie **126** (27), 7163-7167 (2014).

Flesch, R., N. Kosugi, A. Knop-Gericke and E. Rühl: 2s-Excitation and Photoionization of Neon Clusters. Zeitschrift für physikalische Chemie **228** (4-5), 387-403 (2014).

Frank, B.: Nanocarbon materials for heterogeneous catalysis. In: Nanocarbon-Inorganic Hybrids. (Eds.) D. Eder and R. Schlögl. De Gruyter, Berlin, 393-427 (2014). ISBN 978-3-11-026986-4.

Greiner, M., T. Rocha, B. Johnson, A. Klyushin, A. Knop-Gericke and R. Schlögl: The Oxidation of Rhenium and Identification of Rhenium Oxides During Catalytic Partial Oxidation of Ethylene: An In-Situ XPS Study. Zeitschrift für physikalische Chemie **228** (4-5), 521-541 (2014).

Guo, C., K. Hermann and Y. Zhao: Dynamics and Energetics of Reconstruction at the Si(100) Surface. The Journal of Physical Chemistry C **118** (44), 25614-25619 (2014).

Heenemann, M., F. Rosowski, R. Schlögl and M. Eichelbaum: Contact-free and in-situ: Electrical Conductivity of Oxidation Catalysts studied by Microwave Cavity Perturbation. In: Preprints of the DGMK-Conference "Selective Oxidation and Functionalization: Classical and Alternative Routes and Sources". DGMK, Hamburg, 41-44 (2014). ISBN 978-3-941721-44-9.

Heine, C., M. Hävecker, E. Stotz, F. Rosowski, A. Knop-Gericke, A. Trunschke, M. Eichelbaum and R. Schlögl: Ambient-Pressure Soft X-ray Absorption Spectroscopy of a Catalyst Surface in Action: Closing the Pressure Gap in the Selective n-Butane Oxidation over Vanadyl Pyrophosphate. The Journal of Physical Chemistry C **118** (35), 20405-20412 (2014).

Hetaba, W., S. Löffler, M.G. Willinger, M.E. Schuster, R. Schlögl and P. Schattschneider: Site-specific ionisation edge fine-structure of Rutile in the electron microscope. Micron **63**, 15-19 (2014).

Hill, L.J., N.E. Richey, Y. Sung, P.T. Dirlam, J.J. Griebel, E. Lavoie-Higgins, I.-B. Shim, N. Pinna, M.G. Willinger, W. Vogel, J.J. Benkoski, K. Char and J. Pyun: Colloidal Polymers from Dipolar Assembly of Cobalt-Tipped CdSe@CdS Nanorods. ACS Nano **8** (4), 3272-3284 (2014).

Hill, L.J., N.E. Richey, Y. Sung, P.T. Dirlam, J.J. Griebel, I.-B. Shim, N. Pinna, M.G. Willinger, W. Vogel, K. Char and J. Pyun: Synthesis of ferromagnetic cobalt nanoparticle tipped CdSe@CdS nanorods: critical role of Pt-activation. CrystEngComm **16** (40), 9461-9468 (2014).

Huang, X., M.G. Willinger, H. Fan, Z. Xie, L. Wang, A. Klein-Hoffmann, F. Girgsdies, C.-S. Lee and X.-M. Meng: Single crystalline wurtzite ZnO/zinc blende ZnS coaxial heterojunctions and hollow zinc blende ZnS nanotubes: synthesis, structural characterization and optical properties. Nanoscale **6** (15), 8787-8795 (2014).

Indra, A., M. Greiner, A. Knop-Gericke, R. Schlögl, D. Avnir and M. Driess: High Catalytic Synergism between the Components of the Rhenium Complex@Silver Hybrid Material in Alkene Epoxidations. ChemCatChem **6** (7), 1935-1939 (2014).

Jones, T.E., T. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl and S. Piccinin: Adsorbate induced vacancy formation on silver surfaces. Physical Chemistry Chemical Physics **16** (19), 9002-9014 (2014).

Kaichev, V.V., G.Y. Popova, Y.A. Chesalov, A.A. Saraev, D.Y. Zemlyanov, S.A. Beloshapkin, A. Knop-Gericke, R. Schlögl, T.V. Andrushkevich and V.I. Bukhtiyarov: Selective oxidation of methanol to form dimethoxymethane and methyl formate over a monolayer V_2O_5/TiO_2 catalyst. Journal of Catalysis **311**, 59-70 (2014).

Kandemir, T., I. Kasatkin, F. Girgsdies, S. Zander, S. Kühl, M. Tovar, R. Schlögl and M. Behrens: Microstructural and Defect Analysis of Metal Nanoparticles in Functional Catalysts by Diffraction and Electron Microscopy: The Cu/ZnO Catalyst for Methanol Synthesis. Topics in Catalysis **57** (1-4), 188-206 (2014).

Karpinsky, D.V., I.O. Troyanchuk, V. Sikolenko, V. Efimov, E. Efimova, M.G. Willinger, A.N. Salak and A.L. Kholkin: Phase coexistence in $Bi_{1-x}Pr_xFeO_3$ ceramics. Journal of Materials Science **49** (20), 6937-6943 (2014).

Karpinsky, D.V., I.O. Troyanchuk, V.V. Sikolenko, V. Efimov, E. Efimova, M.V. Silibin, G.M. Chobot and E. Willinger: Temperature evolution of the crystal structure of Bi_{1-x} Pr_x FeO_3 solid solutions. Physics of the Solid State **56** (11), 2263-2268 (2014).

Kidambi, P.R., R. Blume, J. Kling, J.B. Wagner, C. Baehtz, R.S. Weatherup, R. Schlögl, B.C. Bayer and S. Hofmann: In Situ Observations during Chemical Vapor Deposition of Hexagonal Boron Nitride on Polycrystalline Copper. Chemistry of Materials **26** (22), 6380-6392 (2014). OPEN ACCESS

Klokishner, S., O. Reu, G. Tzolova-Müller, R. Schlögl and A. Trunschke: Apparent Absorption Spectra of Silica Supported Vanadium-Titanium Oxide Catalysts: Experimental Study and Modeling. The Journal of Physical Chemistry C **118** (26), 14677-14691 (2014).

Klues, M., K. Hermann and G. Witte: Analysis of the near-edge X-ray-absorption fine-structure of anthracene: A combined theoretical and experimental study. The Journal of Chemical Physics **140** (1), 014302 (2014).

Klyushin, A., T. Rocha, M. Hävecker, A. Knop-Gericke and R. Schlögl: A near ambient pressure XPS study of Au oxidation. Physical Chemistry Chemical Physics **16** (17), 7881-7886 (2014). OPEN ACCESS

Kogler, M., E.-M. Köck, L. Perfler, T. Bielz, M. Stöger-Pollach, W. Hetaba, M.G. Willinger, X. Huang, M.E. Schuster, B. Klötzer and S. Penner: Methane Decomposition and Carbon Growth onY_2O_3, Yttria-Stabilized Zirconia, and ZrO_2. Chemistry of Materials **26** (4), 1690-1701 (2014). OPEN ACCESS

Kristiansen, P.T., M. Dahbi, T. Gustafsson, K. Edström, D. Newby, K.E. Smith and L.-C. Duda: X-ray absorption spectroscopy and resonant inelastic scattering study of the first lithiation cycle of the Li-ion battery cathode $Li_{2-x}MnSiO_4$. Physical Chemistry Chemical Physics **16** (8), 3846-3852 (2014). OPEN ACCESS

Kühl, S., A. Tarasov, S. Zander, I. Kasatkin and M. Behrens: Cu-Based Catalyst Resulting from a Cu,Zn,Al Hydrotalcite-Like Compound: A Microstructural, Thermoanalytical, and In Situ XAS Study. Chemistry - A European Journal **20** (13), 3782-3792 (2014).

Kurnatowska, M., M.E. Schuster, W. Mista and L. Kepinski: Self-Regenerative Property of Nanocrystalline $Ce_{0.89}M_{0.11}O_{2-y}$ (M = Pd, Rh) Mixed Oxides. ChemCatChem **6** (11), 3125-3131 (2014).

Kwapien, K., J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke and R. Schlögl: Sites for Methane Activation on Lithium-Doped Magnesium Oxide Surfaces. Angewandte Chemie International Edition **53** (33), 8774-8778 (2014).

Kwapien, K., J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke and R. Schlögl: Zentren der Methanaktivierung auf Oberflächen von Lithium-dotiertem MgO. Angewandte Chemie **126** (33), 8919-8923 (2014).

Lin, Y. and D.S. Su: Fabrication of Nitrogen-Modified Annealed Nanodiamond with Improved Catalytic Activity. ACS Nano **8** (8), 7823-7833 (2014).

Lips, K., D.E. Starr, M. Bär, T.F. Schulze, F. Fenske, S. Christiansen, R. van de Krol, S. Raoux, G. Reichardt, F. Schäfers, S. Hendel, R. Follath, J. Bahrdt, M. Scheer, G. Wüstefeld, P. Kuske, M. Hävecker, A. Knop-Gericke, R. Schlögl and B. Rech: EMIL: The Energy Materials In Situ Laboratory Berlin. In: Proceedings of the Photovoltaic Specialist Conference (PVSC). IEEE, Denver, CO, 0698-0700 (2014). ISBN 978-147994398-2.

Liu, J., L. Jiang, B.S. Zhang, J. Jin, D.S. Su, S. Wang and G. Sun: Controllable Synthesis of Cobalt Monoxide Nanoparticles and the Size-Dependent Activity for Oxygen Reduction Reaction. ACS Catalysis **4** (9), 2998-3001 (2014).

Liu, J., E. Rühl, A.P. Hitchcock, D.N. McIlroy, J.D. Bozek, T. Tyliszczak, A. Knop-Gericke, N.M. Boag and P.A. Dowben: Double Cation Formation from the Photo-Fragmentation of the closo-Carboranes. Zeitschrift für physikalische Chemie **228** (4-5), 421-436 (2014).

Maganas, D., P.T. Kristiansen, L.-C. Duda, A. Knop-Gericke, S. DeBeer, R. Schlögl and F. Neese: Combined Experimental and Ab Initio Multireference Configuration Interaction Study of the Resonant Inelastic X-ray Scattering Spectrum of CO_2. The Journal of Physical Chemistry C **118** (35), 20163-20175 (2014).

Maganas, D., M. Roemelt, T. Weyhermüller, R. Blume, M. Hävecker, A. Knop-Gericke, S. DeBeer, R. Schlögl and F. Neese: L-edge X-ray absorption study of mononuclear vanadium complexes and spectral predictions using a restricted open shell configuration interaction ansatz. Physical Chemistry Chemical Physics **16** (1), 264-276 (2014).

Maurin-Pasturel, G., J. Long, Y. Guari, F. Godiard, M.G. Willinger, C. Guerin and J. Larionova: Nanosized Heterostructures of Au@Prussian Blue Analogues: Towards Multifunctionality at the Nanoscale. Angewandte Chemie International Edition **53** (15), 3872-3876 (2014).

Maurin-Pasturel, G., J. Long, Y. Guari, F. Godiard, M.G. Willinger, C. Guerin and J. Larionova: Nanosized Heterostructures of Au@Prussian Blue Analogues: Towards Multifunctionality at the Nanoscale. Angewandte Chemie **126** (15), 3953-3957 (2014).

Maurin-Pasturel, G., J. Long, Y. Guari, F. Godiard, M.G. Willinger, C. Guerin and J. Larionova: Back Cover: Nanosized Heterostructures of Au@Prussian Blue Analogues: Towards Multifunctionality at the Nanoscale. Angewandte Chemie International Edition **53** (15), 4008-4008 (2014).

Maurin-Pasturel, G., J. Long, Y. Guari, F. Godiard, M.G. Willinger, C. Guerin and J. Larionova: Rücktitelbild: Nanosized Heterostructures of Au@Prussian Blue Analogues: Towards Multifunctionality at the Nanoscale. Angewandte Chemie **126** (15), 4088-4088 (2014).

Mayr, L., H. Lorenz, M. Armbrüster, S.A. Villaseca, Y. Luo, R. Cardoso, U. Burkhardt, D. Zemlyanov, M. Hävecker, R. Blume, A. Knop-Gericke, B. Klötzer and S. Penner: The catalytic properties of thin film Pd-rich $GaPd_2$ in methanol steam reforming. Journal of Catalysis **309**, 231-240 (2014).

Mayr, L., R. Rameshan, B. Klötzer, S. Penner and C. Rameshan: Combined UHV/high-pressure catalysis setup for depth-resolved near-surface spectroscopic characterization and catalytic testing of model catalysts. Review of Scientific Instruments **85** (5), 055104 (2014).

Mette, K., S. Kühl, H. Düdder, K. Kähler, A. Tarasov, M. Muhler and M. Behrens: Stable Performance of Ni-Catalysts in Dry Reforming of Methane at High Temperatures for an Efficient CO_2-Conversion into Syngas. ChemCatChem **6** (1), 100-104 (2014).

Mierwaldt, D., S. Mildner, R. Arrigo, A. Knop-Gericke, E. Franke, A. Blumenstein, J. Hoffmann and C. Jooss: In Situ XANES/XPS Investigation of Doped Manganese Perovskite Catalysts. Catalysts **4** (2), 129-145 (2014).

Monachino, E., M. Greiner, A. Knop-Gericke, R. Schlögl, C. Dri, E. Vesselli and G. Comelli: Reactivity of Carbon Dioxide on Nickel: Role of CO in the Competing Interplay between Oxygen and Graphene. The Journal of Physical Chemistry Letters **5** (11), 1929-1934 (2014).

Morselli, D., M. Niederberger, I. Bilecka and F. Bondioli: Double role of polyethylene glycol in the microwaves-assisted non-hydrolytic synthesis of nanometric TiO_2: Oxygen source and stabilizing agent. Journal of Nanoparticle Research **16** (10), 2645 (2014).

Nasani, N., Z.-J. Wang, M.G. Willinger, A.A. Yaremchenko and D.P. Fagg: In-situ redox cycling behaviour of Ni-$BaZr_{0.85}Y_{0.15}O_{3-\delta}$ cermet anodes for Protonic Ceramic Fuel Cells. International Journal of Hydrogen Energy **39** (34), 19780-19788 (2014).

Naumann d'Alnoncourt, R., L.-I. Csepei, M. Hävecker, F. Girgsdies, M.E. Schuster, R. Schlögl and A. Trunschke: The reaction network in propane oxidation over phase-pure MoVTeNb M1 oxide catalysts. Journal of Catalysis **311**, 369-385 (2014).

Naumann d'Alnoncourt, R., M. Friedrich, E.L. Kunkes, D. Rosenthal, F. Girgsdies, B.S. Zhang, L. Shao, M.E. Schuster, M. Behrens and R. Schlögl: Strong metal-support interactions between palladium and iron oxide and their effect on CO oxidation. Journal of Catalysis **317**, 220-228 (2014).

Noack, J., F. Rosowski, R. Schlögl and A. Trunschke: Speciation of Molybdates under Hydrothermal Conditions. Zeitschrift für anorganische und allgemeine Chemie **640** (14), 2730-2736 (2014).

Nong, H.N., L. Gan, E. Willinger, D. Teschner and P. Strasser: IrOx core-shell nanocatalysts for cost- and energy-efficient electrochemical water splitting. Chemical Science **5** (8), 2955-2963 (2014).

Ota, A., J. Kröhnert, G. Weinberg, I. Kasatkin, E.L. Kunkes, D. Ferri, F. Girgsdies, N. Hamilton, M. Armbrüster, R. Schlögl and M. Behrens: Dynamic Surface Processes of Nanostructured Pd_2Ga Catalysts Derived from Hydrotalcite-Like Precursors. ACS Catalysis **4** (5), 2048-2059 (2014).

Papaefthimiou, V., F. Tournus, A. Hillion, G. Khadra, D. Teschner, A. Knop-Gericke, V. Dupuis and S. Zafeiratos: Mixing Patterns and Redox Properties of Iron-Based Alloy Nanoparticles under Oxidation and Reduction Conditions. Chemistry of Materials **26** (4), 1553-1560 (2014).

Plodinec, M., A. Gajović, D. Iveković, N. Tomašić, B. Zimmermann, J. Macan, T. Haramina, D.S. Su and M.G. Willinger: Study of thermal stability of (3-aminopropyl) trimethoxy silane-grafted titanate nanotubes for application as nanofillers in polymers. Nanotechnology **25** (43), 435601 (2014).

Reiche, S., R. Blume, X.-C. Zhao, D.S. Su, E.L. Kunkes, M. Behrens and R. Schlögl: Reactivity of mesoporous carbon against water – An in-situ XPS study. Carbon **77**, 175-183 (2014).

Reier, T., D. Teschner, T. Lunkenbein, A. Bergmann, S. Selve, R. Kraehnert, R. Schlögl and P. Strasser: Electrocatalytic Oxygen Evolution on Iridium Oxide: Uncovering Catalyst-Substrate Interactions and Active Iridium Oxide Species. Journal of the Electrochemical Society **161** (9), F876-F882 (2014).

Ressnig, D., T. Corbiere, T. Lunkenbein, U. Braun, M.G. Willinger and M. Antonietti: Decomposition synthesis of tuneable, macroporous carbon foams from crystalline precursors *via in situ* templating. Journal of Materials Chemistry A **2** (42), 18076-18081 (2014). OPEN ACCESS

Rocha, T., M. Hävecker, A. Knop-Gericke and R. Schlögl: Promoters in heterogeneous catalysis: The role of Cl on ethylene epoxidation over Ag. Journal of Catalysis **312**, 12-16 (2014).

Rocquin, M., M. Henrion, M.G. Willinger, P. Bertani, M.J. Chetcuti, B. Louis and V. Ritleng: One-step synthesis of a highly homogeneous SBA-NHC hybrid material: En route to single-site NHC-metal heterogeneous catalysts with high loadings. Dalton Transactions **43** (9), 3722-3729 (2014). OPEN ACCESS

Sarmiento-Pérez, R., S. Botti, C.S. Schnohr, I. Lauermann, A. Rubio and B. Johnson: Local versus global electronic properties of chalcopyrite alloys: X-ray absorption spectroscopy and ab initio calculations. Journal of Applied Physics **116** (9), 093703 (2014).

Schlögl, R.: Systemverständnis für die erfolgreiche Umsetzung der Energiewende. Bunsen-Magazin **16** (6), 257-258 (2014).

Schumann, J., T. Lunkenbein, A. Tarasov, N. Thomas, R. Schlögl and M. Behrens: Synthesis and Characterisation of a Highly Active Cu/ZnO:Al Catalyst. ChemCatChem **6** (10), 2889-2897 (2014).

Schuster, M.E., D. Teschner, J. Popovic, N. Ohmer, F. Girgsdies, J. Tornow, M.G. Willinger, D. Samuelis, M.M. Titirici, J. Maier and R. Schlögl: Charging and Discharging Behavior of Solvothermal $LiFePO_4$ Cathode Material Investigated by Combined EELS/NEXAFS Study. Chemistry of Materials **26** (2), 1040-1047 (2014).

Schwarz, H., M. Geske, C.F. Goldsmith, R. Schlögl and R. Horn: Fuel-rich methane oxidation in a high-pressure flow reactor studied by optical-fiber laser-induced fluorescence, multi-species sampling profile measurements and detailed kinetic simulations. Combustion and Flame **161** (7), 1688-1700 (2014).

Shao, L., X. Huang, D. Teschner and W. Zhang: Gold Supported on Graphene Oxide: An Active and Selective Catalyst for Phenylacetylene Hydrogenations at Low Temperatures. ACS Catalysis **4** (7), 2369-2373 (2014).

She, G., X. Huang, L. Jin, X. Qi, L. Mu and W. Shi: SnO_2 Nanoparticle-Coated ZnO Nanotube Arrays for High-Performance Electrochemical Sensors. Small **10** (22), 4685-4692 (2014).

Smejkal, Q., U. Rodemerck, E. Wagner and M. Baerns: Economic Assessment of the Hydrogenation of CO_2 to Liquid Fuels and Petrochemical Feedstock. Chemie-Ingenieur-Technik **86** (5), 679-686 (2014).

Smith, M.A., A. Zoelle, Y. Yang, R.M. Rioux, N. Hamilton, K. Amakawa, P.K. Nielsen and A. Trunschke: Surface roughness effects in the catalytic behavior of vanadia supported on SBA-15. Journal of Catalysis **312**, 170-178 (2014).

Su, D.S.: Batteries/Supercapacitors: Hybrids with CNTs. In: Nanocarbon-Inorganic Hybrids. (Eds.) D. Eder and R. Schlögl. De Gruyter, Berlin, 297-318 (2014). ISBN 978-3-11-026986-4.

Su, D.S.: The Chemistry of Energy Conversion and Storage. ChemSusChem **7** (5), 1199-1200 (2014).

Sun, L., K. Hermann, J. Noack, O. Timpe, D. Teschner, M. Hävecker, A. Trunschke and R. Schlögl: DFT Studies and Experiments on Biocatalytic Centers: Structure, Vibrations, and Core Excitations of the K[VO(O_2)Hheida] Complex. The Journal of Physical Chemistry C **118** (42), 24611-24622 (2014).

Sun, X., R. Wang, B. Zhang, R. Huang, X. Huang, D.S. Su, T. Chen, C. Miao and W. Yang: Evolution and Reactivity of Active Oxygen Species on sp^2@sp^3 Core-Shell Carbon for the Oxidative Dehydrogenation Reaction. ChemCatChem **6** (8), 2270-2275 (2014).

Sun, Z., X. Huang, F. Liu, X. Yang, C. Rösler, R.A. Fischer, M. Muhler and W. Schuhmann: Amine-based solvents for exfoliating graphite to graphene outperform the dispersing capacity of N-methyl-pyrrolidone and surfactants. Chemical Communications **50** (72), 10382-10385 (2014).

Sun, Z., X. Huang, M. Muhler, W. Schuhmann and E. Ventosa: A carbon-coated TiO_2(B) nanosheet composite for lithium ion batteries. Chemical Communications **50** (41), 5506-5509 (2014).

Tarasov, A., H. Düdder, K. Mette, S. Kühl, K. Kähler, R. Schlögl, M. Muhler and M. Behrens: Investigation of Coking During Dry Reforming of Methane by Means of Thermogravimetry. Chemie-Ingenieur-Technik **86** (11), 1916-1924 (2014).

Tarasov, A., J. Schumann, F. Girgsdies, N. Thomas and M. Behrens: Thermokinetic investigation of binary Cu/Zn hydroxycarbonates as precursors for Cu/ZnO catalysts. Thermochimica Acta **591**, 1-9 (2014).

Tian, G.-L., M.-Q. Zhao, B. Zhang, Q. Zhang, W. Zhang, J.-Q. Huang, T.-C. Chen, W.-Z. Qian, D.S. Su and F. Wei: Monodisperse embedded nanoparticles derived from an atomic metal-dispersed precursor of layered double hydroxide for architectured carbon nanotube formation. Journal of Materials Chemistry A **2** (6), 1686-1696 (2014).

Umbach, T.R., M. Bernien, C.F. Hermanns, L. Sun, H. Mohrmann, K. Hermann, A. Krüger, N. Krane, Z. Yang, F. Nickel, Y.-M. Chang, K.J. Franke, J.I. Pascual and W. Kuch: Site-specific bonding of copper adatoms to pyridine end groups mediating the formation of two-dimensional coordination networks on metal surfaces. Physical Review B **89** (23), 235409 (2014).

Vilé, G., S. Wrabetz, L. Floryan, M.E. Schuster, F. Girgsdies, D. Teschner and J. Pérez-Ramírez: Stereo- and Chemoselective Character of Supported CeO_2 Catalysts for Continuous-Flow Three-Phase Alkyne Hydrogenation. ChemCatChem **6** (7), 1928-1934 (2014).

Wang, L., B. Zhang, X. Meng, D.S. Su and F.-S. Xiao: Hydrogenation of Biofuels with Formic Acid over a Palladium-Based Ternary Catalyst with Two Types of Active Sites. ChemSusChem **7** (6), 1537-1541 (2014).

Wang, L., J. Zhang, X. Wang, B. Zhang, W. Ji, X. Meng, J. Li, D.S. Su, X. Bao and F.-S. Xiao: Creation of Brønsted acid sites on Sn-based solid catalysts for the conversion of biomass. Journal of Materials Chemistry A **2** (11), 3725-3729 (2014).

Weatherup, R., H. Amara, R. Blume, B. Dlubak, B. Bayer, M. Diarra, M. Bahri, A. Cabrero-Vilatela, S. Caneva, P. Kidambi, M.-B. Martin, C. Deranlot, P. Seneor, R. Schlögl, F. Ducastelle, C. Bichara and S. Hofmann: Interdependency of Subsurface Carbon Distribution and Graphene-Catalyst Interaction. Journal of the American Chemical Society **136** (39), 13698-13708 (2014). OPEN ACCESS

Willinger, M.G., W. Zhang, O. Bondarchuk, S.K. Shaikhutdinov, H.-J. Freund and R. Schlögl: A Case of Strong Metal-Support Interactions: Combining Advanced Microscopy and Model Systems to Elucidate the Atomic Structure of Interfaces. Angewandte Chemie International Edition **53** (23), 5998-6001 (2014).

Willinger, M.G., W. Zhang, O. Bondarchuk, S.K. Shaikhutdinov, H.-J. Freund and R. Schlögl: Metall-Substrat-Wechselwirkung: Kombination von hochauflösender Mikroskopie und Modellsystemen, um die atomare Struktur von Grenzflächen aufzuklären. Angewandte Chemie **126** (23), 6108-6112 (2014).

Wowsnick, G., D. Teschner, I. Kasatkin, F. Girgsdies, M. Armbrüster, A. Zhang, Y. Grin, R. Schlögl and M. Behrens: Surface dynamics of the intermetallic catalyst Pd_2Ga, Part I - Structural stability in UHV and different gas atmospheres. Journal of Catalysis **309**, 209-220 (2014).

Wowsnick, G., D. Teschner, M. Armbrüster, I. Kasatkin, F. Girgsdies, Y. Grin, R. Schlögl and M. Behrens: Surface dynamics of the intermetallic catalyst Pd_2Ga, Part II - Reactivity and stability in liquid-phase hydrogenation of phenylacetylene. Journal of Catalysis **309**, 221-230 (2014).

Wu, S., G. Wen, J. Wang, J. Rong, B. Zong, R. Schlögl and D.S. Su: Nitrobenzene reduction catalyzed by carbon: does the reaction really belong to carbocatalysis? Catalysis Science & Technology **4** (12), 4183-4187 (2014). OPEN ACCESS

Xia, J., X. Huang, L. Liu, M. Wang, L. Wang, B. Huang, D. Zhu, J.J. Li, C.-Z. Gu and X. Meng: CVD synthesis of large-area, highly crystalline $MoSe_2$ atomic layers on diverse substrates and application to photodetectors. Nanoscale **6** (15), 8949-8955 (2014). OPEN ACCESS

Xie, Z., X. Huang and A. Taubert: DyeIonogels: Proton-Responsive Ionogels Based on a Dye-Ionic Liquid Exhibiting Reversible Color Change. Advanced Functional Materials **24** (19), 2837-2843 (2014). OPEN ACCESS

Xie, Z., X. Huang, M.-M. Titirici and A. Taubert: Mesoporous graphite nanoflakes via ionothermal carbonization of fructose and their use in dye removal. RSC Advances **4** (70), 37423-37430 (2014). OPEN ACCESS

Zhang, B., L. Shao, W. Zhang, X. Sun, X. Pan and D.S. Su: Interaction between Palladium Nanoparticles and Surface-Modified Carbon Nanotubes: Role of Surface Functionalities. ChemCatChem **6** (9), 2607-2612 (2014).

Zhang, B. and D.S. Su: Using electron beams to investigate catalytic materials. Comptes Rendus Physique **15** (2-3), 258-268 (2014).

Zhao, A., J. Masa, W. Xia, A. Maljusch, M.G. Willinger, G. Clavel, K. Xie, R. Schlögl, W. Schuhmann and M. Muhler: Spinel Mn-Co Oxide in N-Doped Carbon Nanotubes as a Bifunctional Electrocatalyst Synthesized by Oxidative Cutting. Journal of the American Chemical Society **136** (21), 7551-7554 (2014).

Zheng, A., Y. Chu, S. Li, D.S. Su and F. Deng: Insight into the activation of light alkanes over surface-modified carbon nanotubes from theoretical calculations. Carbon **77**, 122-129 (2014).

Zheng, Z., X. Huang and D. Shchukin: A cost-effective pH-sensitive release system for water source pH detection. Chemical Communications **50** (90), 13936-13939 (2014). OPEN ACCESS

Zhou, K., B. Li, Q. Zhang, J.-Q. Huang, G.-L. Tian, J.-C. Jia, M.-Q. Zhao, G.-H. Luo, D.S. Su and F. Wei: The Catalytic Pathways of Hydrohalogenation over Metal-Free Nitrogen-Doped Carbon Nanotubes. ChemSusChem **7** (3), 723-728 (2014).

Doctoral Thesis

Dölle, J.: Investigation of Si/C-based anodes for Li-Ion batteries. Technische Universität Berlin 2014.

Friedel, K.: Insights into the Acid-Base Properties of Functionalized Multiwall Carbon Nanotubes. Technische Universität Berlin 2014.

Heine, C.: The Electronic Structure of Vanadium Oxides as Catalysts in the Selective Oxidation of Small Alkanes. Technische Universität Berlin 2014. OPEN ACCESS

Schwach, P.: Oxidative activation of methane over MgO model catalysts. Technische Universität Berlin 2014.

Wolfram, T.: Trägereinfluss bei Vanadiumoxid-Katalysatoren zur selektiven Oxidation kurzkettiger Alkane. Technische Universität Berlin 2014.

Yi, Y.: Study on the degradation of carbon materials for electrocatalytic applications. Technische Universität Berlin 2014.

Master's Thesis

Dessal, C.: Synthesis and characterization of silica supported vanadium oxide catalysts for oxidative dehydrogenation of propane. University Strasbourg 2014

Macino, M.: A study of mesoporous silica dissolution. Freie Universität Berlin 2014.

Millet, M.-M.: Water oxidation photocatalysis : Mn-based co-catalysts on TaON. University Lyon 2014.

Thum, L.: Synthesis and characterisation of calcium oxide catalysts for the oxidative coupling of methane (OCM). Technische Universität Berlin 2014.

2015

Amakawa, K., J. Kröhnert, S. Wrabetz, B. Frank, F. Hemmann, C. Jäger, R. Schlögl and A. Trunschke: Active Sites in Olefin Metathesis over Supported Molybdena Catalysts. ChemCatChem, in press.

Arrigo, R., M.E. Schuster, Z. Xie, Y. Yi, G. Wowsnick, L. Sun, K. Hermann, M. Friedrich, P. Kast, M. Hävecker, A. Knop-Gericke and R. Schlögl: Nature of the N-Pd Interaction in Nitrogen-Doped Carbon Nanotube Catalysts. ACS Catalysis **5** (5), 2740-2753 (2015).

Behrens, M.: Coprecipitation: An excellent tool for the synthesis of supported metal catalysts - From the understanding of the well known recipes to new materials. Catalysis Today **246**, 46-54 (2015).

Blume, R., D. Rosenthal, P.D.J.-P. Tessonnier, H. Li, A. Knop-Gericke and R. Schlögl: Characterizing Graphitic Carbon with X-ray Photoelectron Spectroscopy: A Step-by-Step Approach. ChemCatChem, in press.

Bozzini, B., M. Amati, P. Bocchetta, S.D. Zilio, A. Knop-Gericke, E. Vesselli and M. Kiskinova: An in situ near-ambient pressure X-ray Photoelectron Spectroscopy study of Mn polarised anodically in a cell with solid oxide electrolyte. Electrochimica Acta **174**, 532-541 (2015).

Busser, G.W., B. Mei, P. Weide, P.C.K. Vesborg, K. Stührenberg, M. Bauer, X. Huang, M.G. Willinger, I. Chorkendorff, R. Schlögl and M. Muhler: Cocatalyst Designing: A Regenerable Molybdenum-Containing Ternary Cocatalyst System for Efficient Photocatalytic Water Splitting. ACS Catalysis **5** (9), 5530-5539 (2015).

Cardoso, C.S., Y.E. Licea, X. Huang, M.G. Willinger, B. Louis and M.M. Pereira: Improving textural properties of γ-alumina by using second generation biomass in conventional hydrothermal method. Microporous and Mesoporous Materials **207**, 134-141 (2015).

Ding, Y., X. Sun, L. Zhang, S. Mao, Z. Xie, Z.-W. Liu and D.S. Su: Entrapping an Ionic Liquid with Nanocarbon: The Formation of a Tailorable and Functional Surface. Angewandte Chemie International Edition **54** (1), 231-235 (2015).

Ding, Y., X. Sun, L. Zhang, S. Mao, Z. Xie, Z.-W. Liu and D.S. Su: Entrapping an Ionic Liquid with Nanocarbon: The Formation of a Tailorable and Functional Surface. Angewandte Chemie **127** (1), 233-237 (2015).

Eichelbaum, M., M. Hävecker, C. Heine, A.M. Wernbacher, F. Rosowski, A. Trunschke and R. Schlögl: The Electronic Factor in Alkane Oxidation Catalysis. Angewandte Chemie International Edition **54** (10), 2922-2926 (2015).

Eichelbaum, M., M. Hävecker, C. Heine, A.M. Wernbacher, F. Rosowski, A. Trunschke and R. Schlögl: Der elektronische Faktor in der Alkanoxidationskatalyse. Angewandte Chemie **127** (10), 2965-2969 (2015).

Engeldahl, B., M. Özaslan, R. Marschall, M. Rose, S. Kaluza, J. Titus and C. Sprung: Weimar 2015: Catalysing Tomorrow's Solutions. ChemCatChem **7** (12), 1794-1796 (2015).

Falcone, D., J. Hack, A. Klyushin, A. Knop-Gericke, R. Schlögl and R. Davis: Evidence for the Bifunctional Nature of Pt-Re Catalysts for Selective Polyol Hydrogenolysis. ACS Catalysis **5** (9), 5679-5695 (2015).

Ferreira dos Santos, C., P.S. Gomes, M.M. Almeida, M.G. Willinger, R.-P. Franke, M.H. Fernandes and M.E. Costa: Gold-dotted hydroxyapatite nanoparticles as multifunctional platforms for medical applications. RSC Advances **5** (85), 69184-69195 (2015).

Fichtl, M.B., D. Schlereth, N. Jacobsen, I. Kasatkin, J. Schumann, M. Behrens, R. Schlögl and O. Hinrichsen: Kinetics of deactivation on Cu/ZnO/Al$_2$O$_3$ methanol synthesis catalysts. Applied Catalysis A **502**, 262-270 (2015).

Greiner, M., T. Jones, B. Johnson, T. Rocha, Z.-J., Wang, M. Armbrüster, M.G. Willinger, A. Knop-Gericke and R. Schlögl: The oxidation of copper catalysts during ethylene epoxidation. Physical Chemistry Chemical Physics, in press.

Heine, C., M. Hävecker, A. Trunschke, R. Schlögl and M. Eichelbaum: The impact of steam on the electronic structure of the selective propane oxidation catalyst MoVTeNb oxide (orthorhombic M1 phase). Physical Chemistry Chemical Physics **17** (14), 8983-8993 (2015).

Horn, R. and R. Schlögl: Methane Activation by Heterogeneous Catalysis. Catalysis Letters **145** (1), 23-39 (2015).

Hu, P., M.E. Schuster, Z. Huang, F. Xu, S. Jin, Y. Chen, W. Hua, D.S. Su and X. Tang: The Active Sites of a Rod-Shaped Hollandite DeNO$_x$ Catalyst. Chemistry – A European Journal **21** (27), 9619-9623 (2015).

Huang, X., Z.-J. Wang, G. Weinberg, X.-M. Meng and M.G. Willinger: In-Situ Scanning Electron Microscopy Observation of Growth Kinetics and Catalyst Splitting in Vapor-Liquid-Solid Growth of Nanowires. Advanced Functional Materials, in press.

Huang, X., Y.-Q. Yu, J. Xia, H. Fan, L. Wang, M.G. Willinger, X.-P. Yang, Y. Jiang, T.-R. Zhang and X.-M. Meng: Ultraviolet photodetectors with high photosensitivity based on type-II ZnS/SnO$_2$ core/shell heterostructured ribbons. Nanoscale **7** (12), 5311-5319 (2015). OPEN ACCESS

Jones, T., T. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl and S. Piccinin: Insights into the electronic structure of the oxygen species active in alkene epoxidation on silver. ACS Catalysis, in press. OPEN ACCESS

Jones, T., T. Rocha, A. Knop-Gericke, C. Stampfl, R. Schlögl and S. Piccinin: Thermodynamic and spectroscopic properties of oxygen on silver under an oxygen atmosphere. Physical Chemistry Chemical Physics **17** (14), 9288-9312 (2015). OPEN ACCESS

Kast, P., M. Friedrich, F. Girgsdies, J. Kröhnert, D. Teschner, T. Lunkenbein, M. Behrens and R. Schlögl: Strong metal-support interaction and alloying in Pd/ZnO catalysts for CO oxidation. Catalysis Today, in press.

Kast, P., M. Friedrich, D. Teschner, F. Girgsdies, T. Lunkenbein, R. Naumann d'Alnoncourt, M. Behrens and R. Schlögl: CO oxidation as a test reaction for strong metal-support interaction (SMSI) in nanostructured Pd/FeO$_x$ powder catalysts. Applied Catalysis A **502**, 8-17 (2015).

Kondratenko, E.V., M. Schlüter, M. Baerns, D. Linke and M. Holena: Developing catalytic materials for the oxidative coupling of methane through statistical analysis of literature data. Catalysis Science & Technology **5** (3), 1668-1677 (2015). OPEN ACCESS

Kühl, S., J. Schumann, I. Kasatkin, M. Hävecker, R. Schlögl and M. Behrens: Ternary and quaternary Cr or Ga-containing ex-LDH catalysts - Influence of the additional oxides onto the microstructure and activity of Cu/ZnAl$_2$O$_4$ catalysts. Catalysis Today **246**, 92-100 (2015).

Kunkes, E.L., F. Studt, F. Abild-Pedersen, R. Schlögl and M. Behrens: Hydrogenation of CO$_2$ to methanol and CO on Cu/ZnO/Al$_2$O$_3$: Is there a common intermediate or not? Journal of Catalysis **328**, 43-48 (2015).

Law, Y.T., S. Zafeiratos, S.G. Neophytides, A. Orfanidi, D. Costa, T. Dintzer, R. Arrigo, A. Knop-Gericke, R. Schlögl and E.R. Savinova: In situ investigation of dissociation and migration phenomena at the Pt/electrolyte interface of an electrochemical cell. Chemical Science, in press. OPEN ACCESS

Lee, S., K. Schneider, J. Schumann, A.K. Mogalicherla, P. Pfeifer and R. Dittmeyer: Effect of metal precursor on Cu/ZnO/Al2O3 synthesized by flame spray pyrolysis for direct DME production. Chemical Engineering Science **138**, 194-202 (2015).

Lin, Y., S. Wu, W. Shi, B. Zhang, J. Wang, Y.A. Kim, M. Endo and D.S. Su: Efficient and highly selective boron-doped carbon materials-catalyzed reduction of nitroarenes. Chemical Communications **51** (66), 13086-13089 (2015).

Lunkenbein, T., F. Girgsdies, A.M. Wernbacher, J. Noack, G. Auffermann, A. Yasuhara, A. Klein-Hoffmann, W. Ueda, M. Eichelbaum, A. Trunschke, R. Schlögl and M.G. Willinger: Direct Imaging of Octahedral Distortion in a Complex Molybdenum Vanadium Mixed Oxide. Angewandte Chemie International Edition **54** (23), 6828-6831 (2015).

Lunkenbein, T., F. Girgsdies, A.M. Wernbacher, J. Noack, G. Auffermann, A. Yasuhara, A. Klein-Hoffmann, W. Ueda, M. Eichelbaum, A. Trunschke, R. Schlögl and M.G. Willinger: Direct Imaging of Octahedral Distortion in a Complex Molybdenum Vanadium Mixed Oxide. Angewandte Chemie **127** (23), 6932-6935 (2015).

Lunkenbein, T., J. Schumann, M. Behrens, R. Schlögl and M.G. Willinger: Formation of a ZnO Overlayer in Industrial Cu/ZnO/Al_2O_3 Catalysts Induced by Strong Metal-Support Interactions. Angewandte Chemie International Edition **54** (15), 4544-4548 (2015).

Lunkenbein, T., J. Schumann, M. Behrens, R. Schlögl and M.G. Willinger: Formation of a ZnO Overlayer in Industrial Cu/ZnO/Al_2O_3 Catalysts Induced by Strong Metal-Support Interactions. Angewandte Chemie **127** (15), 4627-4631 (2015).

Marichy, C., N. Donato, M. Latino, M.G. Willinger, J.-P. Tessonnier, G. Neri and N. Pinna: Gas sensing properties and p-type response of ALD TiO_2 coated carbon nanotubes. Nanotechnology **26** (2), 024004 (2015).

Martin, M.-B., B. Dlubak, R.S. Weatherup, M. Piquemal, H. Yang, R. Blume, R. Schlögl, S. Collin, F. Petroff, S. Hofmann, J. Robertson, A. Anane, A. Fert and P. Seneor: Protecting nickel with graphene spin-filtering membranes: A single layer is enough. Applied Physics Letters **107** (1), 012408 (2015).

Matveev, A.V., V.V. Kaichev, A.A. Saraev, V.V. Gorodetskii, A. Knop-Gericke, V.I. Bukhtiyarov and B.E. Nieuwenhuys: Oxidation of propylene over Pd(5 5 1): Temperature hysteresis induced by carbon deposition and oxygen adsorption. Catalysis Today **244**, 29-35 (2015).

Mette, K., S. Kühl, A. Tarasov, H. Düdder, K. Kähler, M. Muhler, R. Schlögl and M. Behrens: Redox dynamics of Ni catalysts in CO_2 reforming of methane. Catalysis Today **242, Pt. A**, 101-110 (2015).

Moser, M., G. Vilé, S. Colussi, F. Krumeich, D. Teschner, L. Szentmiklósi, A. Trovarelli and J. Perez-Ramirez: Structure and reactivity of ceria-zirconia catalysts for bromine and chlorine production via the gas-phase oxidation of hydrogen halides. Journal of Catalysis, in press.

Nong, H.N., H.-S. Oh, T. Reier, E. Willinger, M.G. Willinger, V. Petkov, D. Teschner and P. Strasser: Oxide-Supported $IrNiO_x$ Core-Shell Particles as Efficient, Cost-Effective, and Stable Catalysts for Electrochemical Water Splitting. Angewandte Chemie International Edition **54** (10), 2975-2979 (2015).

Nong, H.N., H.-S. Oh, T. Reier, E. Willinger, M.G. Willinger, V. Petkov, D. Teschner and P. Strasser: Oxide-Supported $IrNiO_x$ Core-Shell Particles as Efficient, Cost-Effective, and Stable Catalysts for Electrochemical Water Splitting. Angewandte Chemie **127** (10), 3018-3022 (2015).

Opitz, A.K., A. Nenning, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, J. Fleig and B. Klötzer: Enhancing Electrochemical Water-Splitting Kinetics by Polarization-Driven Formation of Near-Surface Iron(0): An In Situ XPS Study on Perovskite-Type Electrodes. Angewandte Chemie International Edition **54** (9), 2628-2635 (2015).

Opitz, A.K., A. Nenning, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, J. Fleig and B. Klötzer: Enhancing Electrochemical Water-Splitting Kinetics by Polarization-Driven Formation of Near-Surface Iron(0): An In Situ XPS Study on Perovskite-Type Electrodes. Angewandte Chemie **127** (9), 2666-2670 (2015).

Opitz, A.K., A. Nenning, S. Kogler, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, B. Klötzer and J. Fleig: Water Splitting on Model-Composite $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) Electrodes in H_2/H_2O Atmosphere. ECS Transactions 68 (8), 3333-3343 (2015).

Reiche, S., N. Kowalew and R. Schlögl: Influence of Synthesis pH and Oxidative Strength of the Catalyzing Acid on the Morphology and Chemical Structure of Hydrothermal Carbon. ChemPhysChem **16** (3), 579-587 (2015).

Schieder, M., T. Lunkenbein, C. Bojer, M. Dulle, J.v. Stein, G. Auffermann, T. Löbling, J. Schöbel, H. Schmalz and J. Breu: Selective Template Removal by Thermal Depolymerization to Obtain Mesostructured Molybdenum Oxycarbide. Zeitschrift für anorganische und allgemeine Chemie **641** (10), 1829-1834 (2015).

Schlögl, R.: Heterogeneous Catalysis. Angewandte Chemie International Edition **54** (11), 3465-3520 (2015).

Schlögl, R.: Heterogene Katalysatoren - fundamental betrachtet. Angewandte Chemie **127** (11), 3531-3589 (2015).

Schlögl, R.: The Revolution Continues: Energiewende 2.0. Angewandte Chemie International Edition **54** (15), 4436-4439 (2015).

Schlögl, R.: Energiewende 2.0. Angewandte Chemie **127** (15), 4512-4516 (2015).

Schlögl, R.: Von der Natur lernen: Chemische CO_2-Reduktion. In: Die Zukunft des Klimas: Neue Erkenntnisse, neue Herausforderungen: Ein Report der Max-Planck-Gesellschaft. (Eds.) J. Marotzke and M. Stratmann. Beck, München, 167-181 (2015). ISBN 978-3-406-66967-5.

Schumann, J., M. Eichelbaum, T. Lunkenbein, N. Thomas, M.C. Alvarez Galvan, R. Schlögl and M. Behrens: Promoting Strong Metal Support Interaction: Doping ZnO for Enhanced Activity of Cu/ZnO:M (M = Al, Ga, Mg) Catalysts. ACS Catalysis **5** (6), 3260-3270 (2015).
OPEN ACCESS

Schwach, P., N. Hamilton, L. Thum, T. Lunkenbein, R. Schlögl and A. Trunschke: Structure sensitivity of the oxidative activation of methane over MgO model catalysts: I. Kinetic study. Journal of Catalysis **329**, 560-573 (2015).

Schwach, P., N. Hamilton, L. Thum, T. Lunkenbein, R. Schlögl and A. Trunschke: Structure sensitivity of the oxidative activation of methane over MgO model catalysts: II. Nature of active sites and reaction mechanism. Journal of Catalysis **329**, 574-587 (2015).

S*elmani, A., M. Špadina, M. Plodinec, I. Delač Marion, M.G. Willinger, J. Lützenkirchen, H.D. Gafney and E. Redel:* An Experimental and Theoretical Approach to Understanding the Surface Properties of One-Dimensional TiO_2 Nanomaterials. The Journal of Physical Chemistry C **119** (34), 19729-19742 (2015).

Söllradl, S., M. Greiwe, V.J. Bukas, M.R. Buchner, M. Widenmeyer, T. Kandemir, T. Zweifel, A. Senyshyn, S. Günther, T. Nilges, A. Türler and R. Niewa: Nitrogen-Doping in ZnO via Combustion Synthesis? Chemistry of Materials **27** (12), 4188-4195 (2015).

Spiel, C., D. Vogel, R. Schlögl, G. Rupprechter and Y. Suchorski: Spatially coupled catalytic ignition of CO oxidation on Pt: Mesoscopic versus nano-scale. Ultramicroscopy, in press. OPEN ACCESS

Studt, F., M. Behrens, E.L. Kunkes, N. Thomas, S. Zander, A. Tarasov, J. Schumann, E. Frei, J.B. Varley, F. Abild-Pedersen, J.K. Nørskov and R. Schlögl: The Mechanism of CO and CO_2 Hydrogenation to Methanol over Cu-Based Catalysts. ChemCatChem **7** (7), 1105-1111 (2015).

Su, D.S., B.S. Zhang and R. Schlögl: Electron Microscopy of Solid Catalysts - Transforming from a Challenge to a Toolbox. Chemical Reviews **115** (8), 2818-2882 (2015).

Velasco Vélez, J., V. Pfeifer, M. Hävecker, R.S. Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl and A. Knop-Gericke: Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst. Angewandte Chemie, International Edition, in press.

Velasco Vélez, J., V. Pfeifer, M. Hävecker, R.S. Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl and A. Knop-Gericke: Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst. Angewandte Chemie, in press.

Villa, A., D. Wang, D.S. Su and L. Prati: New challenges in gold catalysis: bimetallic systems. Catalysis Science & Technology **5** (1), 55-68 (2015). OPEN ACCESS

Wang, Z.-J., G. Weinberg, Q. Zhang, T. Lunkenbein, A. Klein-Hoffmann, M. Kurnatowska, M. Plodinec, Q. Li, L. Chi, R. Schlögl and M.G. Willinger: Direct Observation of Graphene Growth and Associated Copper Substrate Dynamics by *in Situ* Scanning Electron Microscopy. ACS Nano **9** (2), 1506-1519 (2015).

Wen, G., J. Diao, S. Wu, W. Yang, R. Schlögl and D.S. Su: Acid Properties of Nanocarbons and Their Application in Oxidative Dehydrogenation. ACS Catalysis **5** (6), 3600-3608 (2015).

Willinger, E., V. Sinitsyn, S. Khasanov, B. Redkin, S. Shmurak and E. Ponyatovsky: Origin of "memory glass" effect in pressure-amorphized rare-earth molybdate single crystals. Journal of Solid State Chemistry **222**, 1-6 (2015).

Willinger, M.G., J. Polleux, M. Antonietti, H. Cölfen, N. Pinna and N. Nassif: Structural evolution of aragonite superstructures obtained in the presence of the siderophore deferoxamine. CrystEngComm **17** (21), 3927-3935 (2015). OPEN ACCESS

Wu, S., G. Wen, R. Schlögl and D.S. Su: Carbon nanotubes oxidized by a green method as efficient metal-free catalysts for nitroarene reduction. Physical Chemistry Chemical Physics **17** (3), 1567-1571 (2015). OPEN ACCESS

Xia, J., D. Zhu, L. Wang, B. Huang, X. Huang and X.-M. Meng: Large-Scale Growth of Two-Dimensional SnS_2 Crystals Driven by Screw Dislocations and Application to Photodetectors. Advanced Functional Materials **25** (27), 4255-4261 (2015).

Xie, Z.-L. and D.S. Su: Ionic Liquid Based Approaches to Carbon Materials Synthesis. European Journal of Inorganic Chemistry **2015** (7), 1137-1147 (2015).

Yang, X., Y.-B. Tang, X. Huang, H.T. Xue, W.P. Kang, W.Y. Li, T.-W. Ng and C.-S. Lee: Lithium ion battery application of porous composite oxide microcubes prepared via metal-organic frameworks. Journal of Power Sources **284**, 109-114 (2015).

Yi, Y., J. Tornow, E. Willinger, M.G. Willinger, C. Ranjan and R. Schlögl: Electrochemical Degradation of Multiwall Carbon Nanotubes at High Anodic Potential for Oxygen Evolution in Acidic Media. ChemElectroChem, in press.

Zhao, Y.-L., R. Zhang, C. Minot, K. Hermann and M.A.V. Hove: Revealing highly unbalanced energy barriers in the extension and contraction of the muscle-like motion of a [c2]daisy chain. Physical Chemistry Chemical Physics **17** (18), 18318-18326 (2015). OPEN ACCESS

Zheng, Z., X. Huang, M. Schenderlein, H. Moehwald, G.-K. Xu and D.G. Shchukin: Bioinspired nanovalves with selective permeability and pH sensitivity. Nanoscale **7** (6), 2409-2416 (2015). OPEN ACCESS

Zhong, X., L. Liu, Y. Jiang, X. Wang, L. Wang, G. Zhuang, X. Li, D. Mei, J.-g. Wang and D.S. Su: Synergistic Effect of Nitrogen in Cobalt Nitride and Nitrogen-Doped Hollow Carbon Spheres for the Oxygen Reduction Reaction. ChemCatChem **7** (12), 1826-1832 (2015).

Zhong, X., L. Liu, Y. Jiang, X. Wang, L. Wang, G. Zhuang, X. Li, D. Mei, J.-g. Wang and D.S. Su: Inside Cover: Synergistic Effect of Nitrogen in Cobalt Nitride and Nitrogen-Doped Hollow Carbon Spheres for the Oxygen Reduction Reaction. ChemCatChem **7** (12), 1722-1722 (2015).

Doctoral Thesis

Kast, P.: Structure-function relationship of Strong Metal-Support Interaction studied on supported Pd reference catalysts. Technische Universität Berlin 2015. OPEN ACCESS

Mette, K.: Development of Hydrotalcite-derived Ni Catalyst for the Dry Reforming of Methane at High Temperatures. Technische Universität Berlin 2015. OPEN ACCESS

Schumann, J.: Cu, Zn-based catalysts for methanol synthesis. Technische Universität Berlin 2015. OPEN ACCESS

Bachelor Thesis

Brennecke, D.: Einfluss der thermischen und mikrowellenunterstützten Alterung von kogefällten Methanolsynthesekatalysatoren. Beuth Hochschule für Technik Berlin 2015.

7. Invited Talks of the Members of the Department of Inorganic Chemistry

Malte Behrens

Nov 2013	Workshop on Nanomaterials for Energy Conversion and Storage, CENIDE, University of Duisburg-Essen, Duisburg, Germany *Catalysis for the Methanol Economy*
Dec 2013	Kolloquium, Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Kiel, Germany *Solid Catalysts for the Conversion of CO_2 to Methanol: New Insights into an Old Process*
Dec 2013	User Meeting, Helmholtz-Zentrum Berlin, Berlin, Germany *Surface and Bulk Analysis of Cu-Composite Catalysts for Methanol Synthesis Using Photons and Neutrons*
Jan 2014	Seminar, Department of Energy Conversion and Storage, DTU National Laboratory for Sustainable Energy, Technical University of Denmark, Copenhagen, Denmark *Catalytic Hydrogenation of CO_2 to Methanol: Status, Challenges and Perspectives for Sustainable Fuel Production*
Jan 2014	Seminar, Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany *Syngas-to-Methanol: New Insights into an Old Process*
Mar 2014	4th British-German Frontiers of Science Symposium 2014 (BRIGFOS), Potsdam, Germany *Catalyzing Sustainable Fuel Production: Development of Cu-Based Catalysts for the Hydrogenation of CO_2*
May 2014	5th Max-Planck LeadNet Meeting, Mainz, Germany *Catalytic Carbon Dioxide Conversion into Fuel*

Sébastian Cap

Jun 2015	Seminar, Research Department Plasmas with Complex Interactions, Ruhr-Universität Bochum, Bochum, Germany *Energy Storage Research at the FHI*

Maik Eichelbaum

Mar 2014	BASF Research Forum Europe, Antwerp, Belgium *Academia OR Industry? Academia AND Industry! Research at BasCat, the UniCat BASF JointLab in Berlin*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Charge Transport in a Working Oxidation Catalyst*

Elias Frei

Apr 2015	Colloquium, Inorganic Chemistry, Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany *The Role of Promoters in Industrially Relevant Methanol Catalysts*

May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *CO_2 Activities in the Department of Inorganic Chemistry*

Mark Greiner

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *The Behavior of Copper and its Oxides in Ethylene Epoxidation: Insights from Ambient-Pressure Photoemission*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Dynamics of Reactivity of Copper Interfaces*

Klaus Hermann

Nov 2013	Seminar, Max-Planck-Institut für chemische Energiekonversion, Mülheim an der Ruhr, Germany *Theoretical X-Ray Spectroscopy: DFT Cluster Studies for Systems of Catalytic Relevance*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Section of Surface and Catalytic Reactions for Energy Efficiency, Dallas, TX, USA *Structure and Reactivity of Oxygen in Particles of Catalytic Interest: DFT Studies on $K[VO(O_2)Hheida]$ and IR/Raman, NEXAFS Spectroscopy*
Mar 2014	Lecture, Department of Physics, Stockholm University, Stockholm, Sweden *Structural Properties of Surfaces: Single Crystals, Nanotubes and Moirons*
Apr 2014	DPG-Frühjahrstagung, Dresden, Germany *Structure and Reactivity of $K[VO(O_2)Hheida]$: DFT Studies on the Interpretation of IR and NEXAFS Spectra*
Apr 2014	Lecture, Shanghai Synchrotron Research Facility, Physics Department, Fudan University, Shanghai, China *Theoretical X-Ray Spectroscopy: DFT Cluster Studies for Systems of Catalytic Relevance*
May 2014	Lecture, Institute of Computational and Theoretical Studies, Hong Kong Baptist University, Hong Kong, China *Structure and Reactivity in Biocatalytic Centers: DFT Studies on Vanadium Oxo-Peroxo Species*
Jul 2014	11th International Conference on the Structure of Surfaces (ICSOS-11), Warwick, UK *Periodicity and Interference Lattices: Moirons at Graphene and Other Overlayers*
Dec 2014	Plenary Talk, International Workshop on Computational Science and Engineering (IWCSE 2014), Hong Kong, China *Computational Core Electron Spectroscopy: What Can We Learn?*
Feb 2015	Joint Colloquium, Mathematics and Physics Faculty, Hong Kong Baptist University, Hong Kong, China *Periodic Overlayers, Interference Lattices and Moiré Patterns: A Unified Theoretical Treatment*

Walid Hetaba

May 2015	Workshop, Joint Group Seminar AC-FHI-CEC, Max-Planck-Institut für chemische Energiekonversion, Mülheim an der Ruhr, Germany *Mapping Electronic Structure Using Advanced TEM and EELS*

Axel Knop-Gericke

Feb 2014	Winterschool/Compact course on “Characterization of Micro- and Nano-Materials”, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany *Near Ambient Pressure XPS: A Useful Tool to Study Heterogeneous Catalytic Processes*
Feb 2014	Workshop on Spectroscopy of Chemical Reactions in Gases and Plasmas, Helmholtz-Zentrum Berlin, Berlin, Germany *Dynamic Surfaces in Heterogeneous Catalysis Studied by near Ambient Pressure X-Ray Photoelectron Spectroscopy*
Jun 2014	Seminar, Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria *Near Ambient Pressure X-Ray Photoelectron Spectroscopy in Heterogeneous Catalysis and Electrochemistry: Status and Outlook*
Nov 2014	3rd International Ertl Symposium on Surface Analysis and Dynamics, Berlin, Germany *The Influence of Intercalated Oxygen on the Properties of Graphene on Polycrystalline Cu under Various Environmental Conditions*
Dec 2014	International Workshop on Surface Chemistry and Near-Ambient Pressure Photoemission: New Tools and New Paradigms, Synchrotron SOLEIL, Saclay, France *In-Situ Studies of Heterogeneous Interfaces Relevant to Catalysis and Energy Research: Status and Outlook*
Dec 2014	Tender X-Ray Workshop, Helmholtz-Zentrum Berlin, Berlin, Germany *Near Ambient Pressure X-Ray Photoelectron Spectroscopy in the Tender X-Ray Range*
May 2015	EMIL Seminar, Helmholtz-Zentrum Berlin, Berlin, Germany *The Electronic Structure of (Electro) Catalysts Surfaces Estimated by near Ambient Pressure X-Ray Photoelectron Spectroscopy*
May 2015	Workshop on Ambient Pressure X-ray Photoelectron Spectroscopy, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea *Ambient Pressure X-Ray Photoelectron Spectroscopy in Catalysis and Energy Research*
May 2015	Workshop, Joint Group Seminar AC-FHI-CEC, Max-Planck-Institut für chemische Energiekonversion, Mülheim an der Ruhr, Germany *The Electronic Structure of (Electro)Catalysts Surfaces*

Thomas Lunkenbein

Aug 2014	Workshop, Young Researcher Network (YRN), Mülheim an der Ruhr, Germany *Chemische Elektronenmikroskopie: Verzerrungen im Sauerstoffgitter von komplexen Metalloxiden*
May 2015	Seminar, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany *Beam Sensitive Mixed Metal Oxides in the Electron Microscope - A Chemical Analysis*
Jun 2015	ARM Owner Group 2nd User Meeting, Center for Electron Microscopy, Max Planck Institute for Solid State Research, Stuttgart, Germany *Direct Imaging of the Oxygen Sub-Lattice in Complex Mixed Metal Oxides*

Johannes Noack

Jan 2015	Seminar, University of Twente, Enschede, The Netherlands *In-Situ Raman Analysis: From Dissolved Metalate Species to Complex Metal Oxide Catalysts*

Tulio Rocha

Feb 2014	17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany *The Ag-O System in Catalysis: Simple Chemistry Meets Complex Physics*

Robert Schlögl

Oct 2013	Grundvorlesung, Technische Universität Berlin, Berlin, Germany *Heterogene Katalyse*
Nov 2013	100 Years of Ammonia Synthesis, BASF, Ludwigshafen, Germany *The Iron Catalyst - from its Understanding to Perspectives*
Nov 2013	Seminar, Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany *Functional Insights into Earth-Alkali Catalyzed OCM: Status and Perspectives*
Nov 2013	SFB 1073 Symposium, Atomic Scale Control of Energy Conversion, University of Göttingen, Göttingen, Germany *The Role of Electron Microscopy in Understanding Heterogeneous Catalytic Processes*
Nov 2013	Tag der Energiewirtschaft, IHK Berlin und Berlin Partner für Wirtschaft und Technologie, Berlin, Germany *Energiewende - wohin?*
Nov 2013	Unternehmertreff, Netzwerk ZENIT, Mülheim an der Ruhr, Germany *Energiewende - wohin?*
Feb 2014	Congress, E-World Energy & Water 2014, Essen, Germany *Energiespeicher – Ein Zustandsbericht*
Feb 2014	Leopoldina-Symposium “Energiespeicher - Der fehlende Baustein der Energiewende?”, Leopoldina, Halle, Germany *Chemical Energy Conversion - More Than Just “Storage”*

Feb 2014	Verkehrs- und energiepolitisches Forum, Embassy of Canada to Germany, Berlin, Germany *ESYS: Research Initiative of the National German Academies*
May 2014	35. Internationales Wiener Motorensymposium, Vienna, Austria *Synthetic Fuels: On the Way Towards Sustainable Fuels*
May 2014	Carl-Friedrich-Gauß-Kolloquium, Brunswick, Germany *Carbon: Too Valuable for Just Burning!*
May 2014	Centennial Shell Catalysis Conference, Amsterdam, The Netherlands *Catalysis and Energy - Future Challenges*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Catalysis and Energy*
May 2014	Workshop on Materials Challenges in Devices for Fuel Solar Production and Employment, International Centre for Theoretical Physics, Trieste, Italy *Solar Fuels: Key to Integration of Renewable Energies?*
Jun 2014	Graphitic Carbon Materials, Chemistry and Physics, Gordon Research Conference (GRC): From Fundamentals to Applications, Lewiston, ME, USA *Carbon: Nanostructures for Electro-Catalytic Design Concepts*
Jun 2014	Meeting, University of Virginia, Charlottesville, VA, USA *Mission of the Max Planck Society*
Jun 2014	RWE Regionalbeiratssitzung, Meerbusch, Germany *Energiewende 2.0 - Zur Zukunft fossiler Brennstoffe*
Jul 2014	20th International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-20), Berlin, Germany *Heterogeneous Catalysts for the Synthesis of Solar Fuels: Status and Perspectives*
Jul 2014	BasCat Eröffnung, Technische Universität Berlin, Berlin, Germany *Warum ist die Oxidationskatalyse immer noch schwierig?*
Jul 2014	Berliner Physikalisches Kolloquium, Physikalische Gesellschaft zu Berlin, Berlin, Germany *Energiewende 2.0*
Jul 2014	Joint EPS-SIF International School on Energy 2014, Varenna, Italy *Chemical Energy*
Sep 2014	Impulsvortrag, 3. Leopoldina Lecture, Hannover, Germany *Der Strombürger und das liebe Geld. Sozio-Ökonomische Aspekte der Energiewende*
Sep 2014	18th International Microscopy Congress (IMC), Prague, Czech Republic *Working Catalysts Observed by ESEM: The Meso-Scale*
Sep 2014	30th European Conference on Surface Science (ECOSS-30), Antalya, Turkey *Electron Spectroscopy of Working Catalysts*

Sep 2014	Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2014, Deutsche Gesellschaft für Kristallographie, Bonn, Germany *Catalysts at Work: Insights from Synchrotron and Neutron Experiments*
Sep 2014	International Gas Union Research Conference 2014, Copenhagen, Denmark *How Gas and Renewable Energies Create a New Business Model*
Sep 2014	ProcessNet-Jahrestagung und 31. DECHEMA-Jahrestagung der Biotechnologen 2014, Aachen, Germany *Chemische Energiekonversion: Nicht so einfach wie gedacht!*
Sep 2014	SLAC Workshop, Stanford University, Menlo Park, CA, USA *Catalysts at Work: The Multiple Roles of Dynamics*
Oct 2014	POF Evaluierung, Forschungszentrum Dresden-Rossendorf, Dresden, Germany *Energiewende aus der Sicht eines Chemikers: Energy Transformation from a Chemist's Viewpoint*
Nov 2014	Fakultätsseminar, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany *Energiewende 2.0*
Nov 2014	GDCh Kolloquium, Fachbereich Chemie, Technische Universität Darmstadt, Darmstadt, Germany *Energiewende aus der Sicht eines Chemikers: Energy Transformation from a Chemist's Viewpoint*
Nov 2014	Lecture, Berlin International Graduate School of Natural Sciences and Engineering, Technische Universität Berlin, Berlin, Germany *Catalysts at Work: Characterization*
Nov 2014	Lionsclub Mülheim/Ruhr, Mülheim an der Ruhr, Germany *Energiewende 2.0*
Dec 2014	2014 Fall MRS Meeting and Exhibit, Materials Research Society, Boston, MA, USA *Dynamics of Catalysts*
Dec 2014	GDCh Kolloquium, Westfälische Wilhelms-Universität Münster, Münster, Germany *Dynamics of Catalysts*
Dec 2014	Vollversammlung, acatech, Berlin, Germany *Energiewende: Vom Kleinen zum Großen*
Jan 2015	3rd International Symposium on Chemistry for Energy Conversion and Storage (ChemEner2015), Berlin, Germany *Sustainable Energy Systems: Remarks on Critical Bottlenecks*
Jan 2015	Neujahrsempfang, Leopoldina, Halle, Germany *Energiesysteme der Zukunft*
Feb 2015	Chemical Reactions at Surfaces, Gordon Research Conference (GRC), Ventura, CA, USA *Dynamics of Catalysts – How Easy Form Active Sites?*

Feb 2015	INNOspace/acatech-Workshop “Was leistet die Raumfahrt für die Energiewende”, Bonn, Germany *Strategische Forschungsagenda 2015 – Energie und Raumfahrt: Passt das?*
Feb 2015	LCLS-II Scientific Opportunities Workshop, Chemistry Workshop, SLAC, Stanford University, Menlo Park, CA, USA *Dynamics of Catalysts – Opportunities for LCLS II*
Mar 2015	48. Jahrestreffen Deutscher Katalytiker, Weimar, Germany *Dynamics of Catalysts: Selective Oxidation as Challenge*
Mar 2015	79. Jahrestagung der DPG und DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Berlin, Germany *Grenzflächen und Grenzgänge: Surface Science and the Energy Transformation*
Mar 2015	150 Jahre BASF, Ludwigshafen, Germany *Energy Transformation: Herterogeneous Catalysis from a Fundamental Perspective*
Mar 2015	International Winterschool on Electronic Properties of Novel Materials (IWEPNM), Kirchberg, Austria *Growth of Graphene: In-Situ Observations and Chemical Considerations*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Activities in UNICAT*
May 2015	International SFB FOXSI Symposium, Functional Oxide Surfaces and Interfaces, Vienna, Austria *Dynamics of Metal Oxide Terminations*
May 2015	Seminar, Max-Planck-Institut für Plasmaphysik, Garching, Germany *Energiewende 2.0*
Jun 2015	Irsee VII Symposium, Kloster Irsee, Irsee, Germany *Structure-Function Correlations in Selective Oxidation: An Experimental Approach*
Jun 2015	Jubiläumsfeier, 25 Jahre Fraunhofer UMSICHT, Oberhausen, Germany *Fraunhofer UMSICHT: Mit Energie in die Zukunft*
Jul 2015	17th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC17), Utrecht, The Netherlands *Catalytic Performance and Structural Dynamics of Solid Systems*
Jul 2015	Festveranstaltung zur Verleihung der Ehrendoktorwürde von Prof. Klaus Müllen, University of Ulm, Ulm, Germany *Kohlenstoff: Chemie für Organiker und Anorganiker*
Jul 2015	Principal Investigators' Meeting, Catalysis Science, U.S. Department of Energy, Annapolis, MD, USA *Benchmarking and Standardization of Electro- and Chemo-Catalysts: Basic Considerations and Experimental Procedures*
Jul 2015	Workshop, The Theory and Practice of Catalysis, Telluride Science Research Center, Telluride, CO, USA *Structure Function Relation in Selective Oxidation Catalysis*

Aug 2015	5. Sitzung der Expertengruppe Power-to-Gas, Oberhausen, Germany *Synthetic Fuels: On the Way Towards Sustainable Fuels*
Aug 2015	EuropaCat-XII “Catalysis: Balancing the use of fossil and renewable resources”, Kazan, Russia *Generation of Solar Hydrogen and its Use in* CO_2 *Reduction*
Sep 2015	12. BMBF-Forum für Nachhaltigkeit, Bonn, Germany *Nachhaltig Wirtschaften und Energiewende*
Sep 2015	Summerschool Trifels 2015, Graduate School of Energy Science and Engineering, Technische Universität Darmstadt, Darmstadt, Germany *Energie im Fokus*

Andrey Tarasov

Sep 2015	Rubotherm Seminar, Ruhr-Universität Bochum, Bochum, Germany *Anwendung der TGA für Untersuchung der Katalytischen* CO_2 *Umwandlung. (Methanol Synthese, Trockenreformierung)*
Sep 2015	Workshop, Methoden der Charakterisierung von Katalysatoren, University of Duisburg-Essen, Duisburg, Germany *Thermal Analysis as a Guide for Studying Cu and Ni Catalytic Materials*

Annette Trunschke

Nov 2013	Catalysis Talks @ Heufeld, Clariant AG, Heufeld, Germany *Selective Oxidation of Alkanes over Mixed Metal Oxide Catalysts*
Feb 2014	Workshop, Redox Flow Batteries, Düsseldorf, Germany *All-Vanadium Redox Flow Batteries – Fundamental Research*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Synthesis of Complex Transition Metal Oxides*
Jan 2015	Seminar, University of Twente, Enschede, The Netherlands *The Activation of Light Alkane Molecules over Metal Oxide Catalysts*
Feb 2015	Colloquium, Leibniz Institute for Catalysis, Rostock, Germany *From Molecular Precursors to Nanostructured Metal Oxide Catalysts*
May 2015	Workshop, Joint Group Seminar AC-FHI-CEC, Max-Planck-Institut für chemische Energiekonversion, Mülheim an der Ruhr, Germany *Active Sites in Selective Oxidation of Light Alkane Molecules*

Juan Velasco Vélez

Apr 2014	Seminar, ALBA Synchrotron, Universitat Autònoma de Barcelona, Barcelona, Spain *Overcoming the “Pressure Gap” in X-Ray Spectroscopy: From UHV to Liquid*
Aug 2014	Seminar, Department of Physics, Tamkang University, New Taipei City, Taiwan *In-Situ X-Ray Spectroscopy at Electrified Electrodes*

Marc Georg Willinger

Dec 2013	Seminar, Institute of Condensed Matter Physics (IPMC), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland *Investigations of Dynamics in Metallic Systems and the CVD Growth of Graphene by In-Situ Electron Microscopy*
Apr 2014	BioMineralix, Meeting on the EC FP7 COST Action TD0903 on Biomineralization, Granada, Spain *Electron Microscopic Insight into Twisted Crystals*
Jul 2014	5th International Conference on Advanced Nano Materials (ANM2014), Aveiro, Portugal *In-Situ Observation of Graphene Growth Dynamics by Environmental Scanning Electron Microscopy*
Oct 2014	Seminar, Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam-Golm Science Park, Potsdam, Germany *Electron Microscopy for Catalysis*
Jan 2015	Seminar, Laboratory of Physics of Complex Matter (LPMC), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland *In-Situ Observation of Graphene Growth Dynamics by Environmental Scanning Electron Microscopy*
Feb 2015	Symposium: Advanced Materials Analysis by latest STEM Technologies, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany *Direct Imaging of Octahedral Distortion in a Complex Molybdenum Vanadium Mixed Oxide*
Feb 2015	Workshop über Metall-Metalloxid-Komposite für Sensorik und Katalyse, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany *In-Situ Observation of the Dynamics of Metal Catalysts During Graphene Growth by Environmental SEM*
Apr 2015	3rd Croatian Microscopy Congress, Zadar, Croatia *In-Situ Observation of Graphene Growth Dynamics by Environmental Scanning Electron Microscopy*
Apr 2015	Jornadas CICECO 2015, Nanotechnology … From the Lab to the Industry, University of Aveiro, Aveiro, Portugal *The Dynamics of Metal Catalysts During CVD Graphene Growth Investigated by In-Situ Scanning Electron Microscopy*
May 2015	Workshop, Joint Group Seminar AC-FHI-CEC, Max-Planck-Institut für chemische Energiekonversion, Mülheim an der Ruhr, Germany *Chemical Electron Microscopy*
Jun 2015	ARM Owner Group 2nd User Meeting, Center for Electron Microscopy, Max Planck Institute for Solid State Research, Stuttgart, Germany *Chemical Electron Microscopy in Heterogeneous Catalysis*
Jun 2015	Lecture, Institut für Chemische Reaktionstechnik, Technische Universität Hamburg-Harburg, Hamburg, Germany *Electron Microscopy*

Sabine Wrabetz

May 2015	21. Kalorimetrietage in Braunschweig, Brunswick, Germany *New Insights on Active Sites of Key Catalyst Materials Using Microcalorimetry at Close to the Reaction Conditions*
May 2015	Lecture Series: Modern Methods in Heterogeneous Catalysis, Technische Universität Hamburg-Harburg, Hamburg, Germany *Adsorption Microcalorimetry: Basics and Applications in Heterogeneous Catalysis*

Department of Chemical Physics **Director: H.-J. Freund**

Staff scientists:

Markus Heyde	(Habilitation)
Helmut Kuhlenbeck	(Habilitation)
Swetlana Schauermann	(Habilitation, left on 01/04/2015)
Shamil Shaikhutdinov	
Martin Sterrer	(Habilitation, left on 09/01/2014)
Thomas Schmidt	

Guest scientists, staying for at least six months:

Miguel Ruiz Oses	*until 03/31/2015*	Heloise Tissot	*until 12/31/2015*
Ewa Madej	*until 04/30/2015*	Franzisco Ivars	*until 01/31/2016*
Casey O'Brien	*until 05/31/2014*	Zongfang Wu	*until 03/03/2016*
Quishi Pan	*until 05/31/2015*	Helder Marchetto	*until 04/30/2016*
Xin Yu	*until 12/31/2014*	Laxman Kankate	*until 05/31/2016*
Yichi Fujimori	*until 08/31/2015*	Mauricio Prieto	*until 06/14/2016*
Damien Cornu	*until 09/30/2015*	Dietrich Menzel	
Leandro Pascua	*until 10/31/2015*	Wolf-Dieter Schneider	
Eberhard Umbach			

Scientists (temporary) paid from external funds:

Hendrik Bluhm	*AvH Awardee*	William Kaden	*until 11/06/2014, AvH Fellow*
Kristen Burson	*AvH Fellow*		
Florencia Calaza	*until 09/30/2015, AvH Fellow*	Mikolaj Lewandowski	*A. Mickiewicz University*
Yi Cui	*until 06/30/2015, AvH Fellow*	Hrvoje Petek	*AvH Awardee*
		Thomas Risse	*FU Berlin*
Andrew Gellman	*Carnegie Mellon University*	Jan Seifert	*DFG*
		Evan Spadafora	*ERC*
Ahmed Ghalgaoui	*until 11/30/2014, ERC Struboli*	Sefik Süzer	*AvH Fellow*
		Geoff Thornton	*AvH Awardee*
Weixin Huang	*AvH Fellow*	Gregory Yablonsky	*St. Louis University*
Julius Jellinek	*AvH Awardee*		

Graduate students:	20 (6 students paid from external funds) 1 IMPRS students
Trainees:	0
Diploma students:	0
Technicians:	11
PP&B Group:	Heinz Junkes (group leader) 4 Technicians, 2 Trainee, 1 Master student, 1 Bachelor student
Crystal Preparation Laboratory:	2 Technicians

Recent Developments in the Department of Chemical Physics

Director: Hans-Joachim Freund

1. General Remarks

Since the last visit of the Fachbeirat the following changes occurred among the staff members of the department.

The collaborations with two MPG partner groups were established:

- MPG Partner Group *("Atomic design of supported metal clusters for advanced catalysis")* with Prof. Junling Lu, Department of Chemical Physics, University of Science and Technology of China (USTC), P.R. China
- MPG Partner Group *("The Surface Science approach towards Artificial Photosynthesis: Tailoring oxides photocatalytic properties through doping and nanoparticles")* with Dr. Fernando Stavale, Experimental Physics Department, Brazilian Center for Physics Research, Brazil

Dr. Markus Heyde finished the habilitation at Humboldt University Berlin in 2015.

Dr. Martin Sterrer left the department to become Professor of Physics at University of Graz / Austria. The activities will be continued within Dr. Markus Heyde´s group.

Dr. Swetlana Schauermann left the department to become Professor of Physical Chemistry at Kiel University (CAU) / Germany.

A number of Postdoctoral Associates have left the group to higher academic positions. Among them are:

- Dr. William Kaden (University of Central Florida /USA)
- Dr. Yi Cui (SINANO, Chinese Academy of Science /China)
- Dr. Florencia Calaza (National University of the Littoral /Argentina)

Honors and Awards:

Hans-Joachim Freund

- Gaede-Langmuir Award of the American Vacuum Society (2014)
- Michel Boudart Award for the Advancement of Catalysis, sponsored by the Haldor Topsøe Company and administered by the North American Catalysis Society and the European Federation of Catalysis Societies (2015)
- ERC Advanced Grant 2014/15 "Crystalline and vitreous silica films and their interconversion"

- Bunsen-Denkmünze, Deutsche Bunsen-Gesellschaft für Physikalische Chemie (2015)

Wolf-Dieter Schneider

- Rudolf-Jaeckel-Prize of the German Vacuum Society (DVG) (October 2014)

Members of the department have been involved in a number of other activities:

Hans-Joachim Freund

- Member, European Research Council (ERC) Identification Committee (since 2014)
- Member, Advisory Board of the 17th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC17)
- Member, Board of Trustees of the Stiftung Alfried Krupp Kolleg Greifswald (since 2014)
- Series Editor, Springer Series in Surface Science (since 2014)
- Member, Editorial Board, "Catalysis Reviews – Science and Engineering" (since 2015)
- Officer, Member of the Scientific Council of the Chemistry Division, European Academy of Sciences (since 2015)
- Member, International Advisory Board, iChEM, Collaborative Innovation Center of Chemistry for Energy Materials (since 2015)

Wolf-Dieter Schneider

- Associate Editor, Frontiers in Condensed Matter Physics (since 2013)
- Panel moderator for the panel PE4-Physical and Analytical Chemical Sciences in the 2015 evaluation of completed ERC funded projects

The following events have been organized by the department:

- Department Workshop, Ringberg (2014)
- 18th Rideal Conference, Berlin (with Dr. Martyn Twigg) (2015)
- Colloquium and workshop in honor of Prof. Dietrich Menzel, Garching (with Peter Feulner and Johannes Barth) (2015)

Within the Department of Chemical Physics there are at present seven working groups:

1. Spectroscopy
   Helmut Kuhlenbeck
2. Structure and Reactivity
   Shamil Shaikhutdinov

3. Scanning Probe Microscopy
   Markus Heyde
   consultant: Wolf-Dieter Schneider
4. Magnetic Resonance
   Thomas Risse, FU Berlin (part time)
5. Catalysis/Laser Spectroscopy
   Martin Sterrer (until June 2014)
6. Molecular Beam
   Swetlana Schauermann (until April 2015)
7. Spectro-Microscopy (SMART)
   Thomas Schmidt
   consultants: Dietrich Menzel, Eberhard Umbach

During the last two years we have continued to concentrate on structure and reactivity studies of oxide surfaces and ultrathin films, electronic structure, and adsorption and reaction on metal and oxide nanoparticles and instrumentation developments in the Department of Chemical Physics. There are several collaborations with three Departments in the institute. Those include activities on nanoparticle oxide interfaces with the Department of Inorganic Chemistry, the Department of Physical Chemistry, and the Theory Department. The Department has also participated in a number of projects funded from outside sources, which are listed below.

A particular project of importance has been the “Cluster of Excellence” (CoE), “Unifying Concepts in Catalysis” (UniCat) funded by the DFG. The Department continues to represent the Institute in the Board of the CoE. Another important project for the Department has been the successful installation of another collaborative research centre (SFB 1109 “Understanding of Metal Oxide/ Water Systems at the Molecular Scale: Structural Evolution Interfaces, and Dissolution”) together with the three Berlin Universities.

The institute has applied as an associate member to the Einstein Center within the Berlin universities. The evaluation has been in favour. We are awaiting the final decision.

The complete list of collaborations encompasses:

- Collaboration H.-J. Freund, S. Shaikhutdinov:
  COST Action CM1104: “Reducible oxide chemistry, structure and functions”

- Collaboration H.-J. Freund, M. Sterrer, S. Shaikhutdinov:
  SFB 1109: “Understanding of Metal Oxide / Water Systems at the Molecular Scale: Structural Evolution, Interfaces, and Dissolution”
- Collaboration H.-J. Freund and T. Risse:
  Center of Excellence, UniCat, Teilprojekt D1: “Activation of methane“
  Center of Excellence, UniCat, Teilprojekt D2: “Chemical activation of carbon oxides“
- Collaboration H.-J. Freund and M. Asscher, Hebrew University, Jerusalem:
  *G.I.F. Grant: I-1236: “*Anchoring metal particles on oxide support surfaces towards sinter resistant catalysts”

Further collaborations include:

- Collaboration with Austria:
  H.-J. Freund, M. Heyde, S. Shaikhutdinov and M. Sterrer, University of Graz, Graz

- Collaboration with Brazil:
  H.-J. Freund and M. Schmal, Universidade Federal do Rio de Janeiro (UFRJ), Rio de Janeiro
  H.-J. Freund and F. Stavale, The Brazilian Center for Physics Research, Centro Brasileiro de Pesquisas Fisicas (CBPF), Rio de Janeiro

- Collaboration with China:
  H.-J. Freund, M. Heyde and H. Gao, Chinese Academy of Sciences, Beijing
  H.-J. Freund, S. Shaikhutdinov and W. Huang, University of Science and Technology of China, Chinese Academy of Sciences, Hefei

- Collaboration with Finland:
  H.-J. Freund, M. Heyde and H. Häkkinen, Nanoscience Center, University of Jyväskylä, Jyväskylä
  S. Schauermann and K. Honkala, University of Jyväskylä, Jyväskylä

- Collaboration with France:
  S. Shaikhutdinov, J. Goniakowski and C. Noguera, Sorbonne Universités (UPMC), Paris
  H. Junkes and R. Lange, ITER Organisation

- Collaboration within Germany:
  H.-J. Freund, M. Heyde and N. Nilius, University of Oldenburg, Oldenburg
  H.-J. Freund, M. Heyde, S. Shaikhutdinov, S. Schauermann, H. Kuhlenbeck and J. Sauer, Humboldt-Universität zu Berlin, Berlin

H.-J. Freund, H. Kuhlenbeck und V. Staemmler, Universität Bochum

- Collaboration with Hungary:
  H.-J. Freund and F. Solymosi, University of Szeged, Academy of Sciences, Szeged
- Collaboration with Italy:
  H.-J. Freund, M. Heyde, S. Shaikhutdinov and G. Pacchioni, Università degli Studi Milano-Bicocca, Milano
- Collaboration with Japan:
  H.-J. Freund and K. Asakura, Catalysis Research Center, Hokkaido University, Sapporo
- Collaboration with South Korea:
  H.-J. Freund and J.Y. Park, Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon
- Collaboration with Spain:
  S. Schauermann and K. Neyman, University of Barcelona, Barcelona
- Collaboration with the UK:
  S. Shaikhutdinov and M. Bowker, School of Chemistry, Cardiff University, Cardiff
  T. Risse and G. Thornton, University College London, London
  H. Kuhlenbeck and D.P. Woodruff, University of Warwick, Coventry
- Collaborations with the USA:
  H.-J. Freund, H. Kuhlenbeck and P.S. Bagus, University of North Texas, Denton
  H.-J. Freund, H. Kuhlenbeck and E. Bauer, Department of Physics, Arizona State University, Tempe
  H.-J. Freund, H. Kuhlenbeck and C.J. Nelin, consultant, Austin, Texas
  H.-J. Freund, M. Sterrer und H. Petek, University of Pittsburgh, Pittsburgh
  H.-J. Freund and J.C. Hemminger, School of Physical Sciences, University of California, Irvine
  H.-J. Freund, M. Heyde and S.T. Oyama, Virginia Polytechnic Institute and State University, Blacksburg
  H.-J. Freund and P.C. Stair, Northwestern University, Evanston
  H. Junkes and M. Davidsaver, Brookhaven National Laboratory, New York
  H. Junkes and S.B. Webb, Oak Ridge National Laboratory, Tennessee
  H. Junkes and A. Johnson, APS, Argonne National Laboratory, Argonne

H. Junkes and M. Shankar, SLAC, Stanford
S. Schauermann and A. Gellman, Carnegie Mellon University, Pittsburgh
H.-J. Freund and I. Wachs, Lehigh University, Bethlehem, Pennsylvania

The department has associated with it the PP&B group, and the Crystal Preparation Laboratory.

The following research highlights include results of research projects as well as on instrumental developments:

- A long-standing controversy concerning the surface termination of V_2O_3 (0001) has been solved. A combination of LEED I/V, STM and ion scattering revealed that the surface is vanadyl terminated as opposed to the so-called O_3-termination (Phys. Rev. Lett. **114**, 216101 (2015)). The work has been carried out in collaboration with Joachim Sauer´s group (HU Berlin).
- A new route to CO_2 activation on a metal-insulator-metal system by electron shuttling between an Au nanoparticle and a silver substrate, separated by a MgO(100) monolayer. CO_2 reacts spontaneously to form an oxalate ($C_2O_4^{2-}$) species imaged at the rim of the nanoparticle and characterized with IR spectroscopy. The oxalate reversibly forms CO_2 after heating (Angew. Chem. Int. Ed. **54**, in press (2015), DOI: 10.1002/ange.201501420). The work has been performed in collaboration with a theory group in Jyväskyla/Finnland (Häkkinen).
- On insulating CaO(100) overlayers on Mo(001) electron transport has been shown to be a hopping mechanism accompanied by strong surface phonon-polariton excitation as reflected by an oscillatory signature on the differential conductance spectra of the system. The Fuchs-Kliewer phonons show novel spatial dependence and become softer around lattice irregularities (Phys. Rev. Lett. **114**, 0168041-018045 (2015)). The work has been carried out in collaboration with Gianfranco Pacchioni´s group.
- For the first time we have been able to investigate the changes in the quantum structure of an individual supported Au nanoparticle upon adsorption by manipulating the adsorbed molecules. Physisorbed and chemisorbed molecules located at the rim of the particle, lead to opposing effects for the effective electron mass deduced from the observed quantum states (Phys. Rev. Lett., **115**, 036804 (2015)). In general chemical reactivity on clean and chemically modified surfaces supporting metal particles have remained in the focus of the Department.

- Using a combination of aberration corrected TEM and STM on Pt/Fe_3O_4(111) models for a strong metal support interaction state, it has been possible to prove the encapsulation and the migration of the covering oxide from the support. This study resulted from collaboration between the AC and the CP departments (Angew. Chem. Int. Ed. **53**, 5998-6001 (2014)).
- Ultrathin oxide films (ZnO, FeO) grown on a number of metallic substrates have been investigated with respect to structure and reactivity at the oxide metal interface. Those studies have turned out to be considerably more relevant to general catalysis than originally thought. It is of importance to consider the films transformation under the given chemical potential as exemplified by the FeO(111) film on Pt(111). The work performed in collaboration with theory groups in Milano (Pacchioni/Giorgdano) and in Paris (Noguera/Goniakowski) shows the importance of considering the restructured FeO_{2x} film as opposed to the FeO film (ChemCatChem **7**, 2620-2627 (2015); Catal. Lett. **144**, 648-655 (2015)).
- Water adsorption on oxide surfaces has become a topic of specific attention, as we have methods available, which avoid destruction of the adsorbate during measurements, i.e. single crystal micro-calorimetry and IR spectroscopy. Novel and unexpected structures have been found on CaO (100) (J. Phys. Chem. **6**, 1204-1208 (2015)) in collaboration with the TH Department) and on Fe_3O_4(111) in collaboration with Joachim Sauer's group (P. Dementyev *et al.*, Phys. Chem. Chem. Phys., submitted (2015)).
- The bi-layer silica film remains to be another important focus of the entire Department with respect to a number of aspects: Doping with Al (substitution of Si) to form two-dimensional zeolites. Doping (substitution of Si) with transition metals such as Fe and Ti (J. Phys. Chem. C **119**, 15443-15448 (2015), DOI: 10.1021/acs.jpcc.5b04291), which, led to unexpected structures (layered clay structures (nontronile in the case of Fe)). Those studies are carried out in collaboration with Joachim Sauer´s group. LEEM/PEEM studies indicate that on the mesoscale the bi-layer film exhibits larger holes, which render the film into a membrane (H.W. Klemm *et al.*, Surf. Sci. in press (2015), DOI: 10.1016/j.susc.2015.05.017). This allows for a new class of experiments where we investigate the diffusion and reaction of molecules in constrained space. First examples have been reported (J. Phys. Chem. C **118**, 29034-29042 (2014)).

- Metal deposits on the silica film (both crystalline and vitreous) have been studied as a function of the size of the metal atoms. STM and x-ray photoemission reveal the position of the metal atom with respect to the film (Phys. Rev. B **89**, 1154361-1154368 (2015)). Those studies indicate the necessity to carefully analyze core level binding energies with respect to initial and final state effects. Theory support came from Gianfranco´s group, as well as Conny Nelin and Paul Bagus.
- Characterization of oxide transformation has been investigated using LEEM/XPEEM and EELS studies (J. Chem. Phys. C **118**, 29068-29076 (2014); Surf. Sci. **641**, 30-36 (2015)).
- Molecular beam studies primarily aimed at the competitive hydrogenation of C-C double bonds against C-O double bonds using acrolein and isophorone as model systems on Pd single crystals in comparison to oxide supported Pd nanoparticles (K.-H. Dostert et al., J. Am. Chem. Soc. submitted (2015); J. Phys. Chem. C **118**, 27833–27842 (2014)). Remarkable selectivities are observed between single crystals and supported nanoparticles.
- Instrument development played an important role in the activities of the Department: The SMART II instrument has now been fully characterized by ray tracing and is under construction, after we had realized that we need to exclude e-e-repulsion upon synchrotron radiation exposure. The high field EPR experiment has been finally published (Rev. Sci. Instrum. **85**, 0839031-083903110 (2014)) and crucial experiments to reproduce the high-resolution EPR spectra of color centers are being reproduced. An instrument to combine Temperature Programmed Desorption with Scanning Probe Microscopy has been setup.

2. Progress Reports

In the following, results from the various groups obtained during the last two years are summarized:

2.1 Spectroscopy Group

Members: E. Davis[d]*, F. Feiten*[d]*, H. Kuhlenbeck*[a]*, M. Naschitzki*[b]*, X. Song*[d]*, W. Wachsmann*[b]*, Z. Wu*[c]

In the last ~2 years an experiment for action spectroscopy of deposited clusters and solid surfaces was constructed and TDS+XPS+STM studies of V+Ti mixed oxide layers on $TiO_2(110)$ and methanol adsorption hereon were performed.

2.1.1 Setup of an Experiment for Action Spectroscopy of Surfaces and Deposited Clusters

Action spectroscopy experiments are often performed to measure a vibrational spectrum of small aggregates in the gas phase. The first step of such an experiment is the production of cold aggregates and their decoration with rare gas atoms. These decorated aggregates are guided through an area which is illuminated with variable energy infrared light. The rare gas atoms desorb when the light is in resonance with a vibrational level of the aggregates due to the energy absorbed by the system. By detection of the rare gas pressure as a function of the infrared energy a vibrational spectrum of the aggregates is obtained. In many cases the measured spectrum is compared with spectra computed for different structures in order to identify the structure of the aggregates.

We have constructed a system which applies this experimental technique to solid surfaces. The main components of this system are a sensitive mass spectrometer to detect rare gas atoms desorbing from the sample and a low-temperature STM/AFM to (1) image the surface structure and (2) to monitor the rare gas atoms on the surface and to identify areas from which these atoms are desorbed by the action of the infrared radiation. The scientific problems that may be treated with this method include the following:

a.) Vibrational spectra of deposited aggregates.

This includes pure metal clusters, mixed metal clusters as well as dielectric clusters. Especially for metal aggregates vibrational spectra may not easily be measured with standard techniques due to the small absorption cross section. The structural information which may be derived from the vibrational data is relevant for catalytic reactions involving the aggregates. Spectra of pure metal clusters with heavy atoms like gold cannot be measured with the free electron laser at present - an extension of the energy range to lower energies would make such vibrations accessible.

b.) Vibrational spectra of atoms dissolved in clusters.

Such atoms may just act as catalytic modifiers or they may take actively part in the reaction as educts or products. At present, experiments are planned to measure vibrational spectra of hydrogen in palladium clusters. It has been shown (see, e.g., Acc. Chem. Res. **46**, 1673 (2013)) that dissolved hydrogen drives hydrogenation reactions. Depending on

---

key:
[a] Team Leader, [b.] Technician, [c.] Postdoc, [d] PhD student, [e] Consultant

the hydrogen concentration different phases with different reactivity are to be expected and the vibrational spectra are suitable handles to differentiate between them. Other embedded atoms like carbon, oxygen, etc. should also be detectable. The vibrational data may be employed to identify the sites where the atoms are located in the cluster lattice.

c.) Vibrational spectra of impurities and defects at an oxide surface.
Using the STM/AFM it may be possible to detect IR-induced desorption of rare gas atoms in a laterally resolved way, which would permit to identify localized sites like dopants, point defects and impurities which absorb infrared radiation and to get information about the vibrational properties of these sites. Such sites may be relevant for catalytic reactions and therefore knowledge of their properties is important.

2.1.2 XPS+STM+TPD Study of V+Ti Mixed Oxide Layers and Methanol Adsorption Hereon

V+Ti mixed oxide layers were grown on rutile $TiO_2(110)$ with a Ta+Ti mixed oxide layer between the mixed oxide overlayer and the $TiO_2(110)$ substrate. The Ta+Ti mixed oxide layer has the task to block the diffusion of vanadium into the $TiO_2(110)$ bulk. The aim of these studies was to learn about the modification of the reactivity of the $TiO_2(110)$ surface by the vanadium atoms. Their concentration was typically in the range of just a few percent in order to suppress the agglomeration of vanadium-based aggregates.

The V+Ti mixed oxide systems are highly reducible. Annealing in UHV produces the (1x2) reconstruction known for heavily reduced $TiO_2(110)$ already at relatively low temperature. This is probably related to the high reducibility of the vanadium ions in the TiO_2 lattice which are transformed from V^{4+} into V^{3+} already by a mild annealing. The vanadium atoms are situated below the surface under such conditions and do not modify the surface reactivity notably, except that they are the indirect reason for the presence of many oxygen vacancies at the surface.

The situation is somewhat different when the annealing is performed under oxidizing conditions. Under such conditions even the reactivity of pure $TiO_2(110)$ gets somewhat complex - formaldehyde forms on surface structures resulting from the oxidation of reduced Ti ions. The TPD spectra depend on the oxidation conditions since the structures formed at the surface depend on them. Under oxidizing conditions vanadium atoms modify the reactivity of the surface in two ways: (1) oxygen vacancies with their well-known reactivity are present even under (not too) oxidizing conditions due to the high reducibility of the oxide and (2) near-surface vanadium or vanadium at the surface modifies the reactivity of the surface structures produced by the oxidation of reduced metal ions, which leads to a modified reactivity. Structural data (STM) have been obtained but calculations may be required to understand the microscopic processes at the surface.

2.2 Structure and Reactivity Group

Members: Y. Cui[c]*, E. Emmez*[d]*, H. Härtel*[b]*, B.-H. Liu*[d]*, Q. Pan*[c]*, S. Shaikhutdinov*[a]*, H. Tissot*[c]*, X. Weng*[d]*, X. Yu*[c]*, K. Zhang*[d]

In the last years, the group has continued studies on preparation of silicate films modified with other metals in attempts to fabricate model systems well-suited for experimental and theoretical studies of chemical reactions on surfaces of sheet silicates and related materials. Another project was aimed at understanding CO oxidation over transition metal oxide thin films, in particular at interfaces between an oxide film and a metal support. The latter is strongly related to the strong metal-support interaction (SMSI) effects, often observed for metal particles supported on reducible oxides.

2.2.1 Ultra-thin Silicate Films on Metals

The structural motif of well-ordered silica films fabricated on metals is a layer of corner-sharing [SiO_4] tetrahedra. The films can be grown either as a monolayer, strongly bound to a metal support (on Mo(112) and Ru(0001) surfaces), or as a weakly bonded bilayer (on Ru(0001) and Pt(111)). The experimental results, complemented by DFT calculations of Sauer and coworkers (HU Berlin), showed that introduction of Al into the bilayer silicate framework results in aluminosilicate films which upon hydroxylation expose surfaces resembling that of highly acidic zeolite cavities. A very different picture is observed for films modified by transition metals. Doping a bilayer silicate film with Fe produced a layered (silicate-iron oxide) structure that can be considered as a monolayer of Nontronite (the Fe-rich clay mineral). Also in the case of Ti-silicate films, experimental results are in nice agreement with a structural model proposed by DFT, where the film consists of a silicate monolayer on top of a monolayer formed by [TiO_6] octahedra. Similar structures are known for naturally occurring phyllosilicates.

Reactivity studies on such silicate films revealed that reactions may, in fact, occur not only on the silicate surface, but also on a metal surface underneath a film via intercalation by ambient gas molecules (e.g., CO, H_2, O_2) of the interface between the silicate and the metal. In particular, we found that, at elevated O_2 pressures (10^{-5} - 10 mbar) and temperatures (450 -

923 K), the silicate films stay essentially intact, while O_2 molecules readily penetrate the film and dissociate on the underlying Ru surface. The silicate layer does however strongly passivate the Ru surface towards RuO_2(110) oxide formation that readily occurs on bare Ru(0001) under the same conditions. The results indicate considerable constraint for oxidation reactions on metal surfaces in the confined space at the interface. Such metal-supported bilayer silicate films, which combine an ultrathin "membrane" and a chemically active metal surface underneath, could become interesting hybrid materials in catalysis.

2.2.2 CO Oxidation on Transition Metal Oxide/Metal Support Interfaces

Recently, we had shown that ultrathin oxide films of transition metals (TMO) grown on a metal support or those, natively formed on the noble metal surfaces under realistic pressure conditions, may show high reactivity in CO oxidation at low temperatures. It was found that the oxygen binding energy may serve as a good descriptor for reactivity of TMO ultrathin films. In continuation of this work, we extended such studies to a sub-monolayer coverage regime, exposing TMO/metal support interfaces. More specifically, we studied CO oxidation on FeO(111) films on Pt(111) at both ultra-high vacuum (UHV) and near-atmospheric pressure conditions. The FeO(111) bilayer islands were inert towards CO_2 formation. In contrast, the FeO_{2-x} trilayer structure, which can only be formed at high oxygen pressures, showed substantial CO_2 production reaching a maximum at ~ 40% coverage at both, UHV and realistic, pressure conditions. The results provide compelling evidence that the $FeO_{2-x}\,/\,Pt(111)$ interface is the most active in CO oxidation. Tis finding is in contrast to report in literature. Corroborated by DFT calculations performed Goniakowski, Noguera (from Uni. Paris), Giordano, and Pacchioni (from Uni. Milano), we showed that strong binding of CO to Pt favours the reaction at the FeO_{2-x}/Pt interface as compared to the FeO_{2-x}/FeO, both possessing weakly bound oxygen species, thus giving a rationale to the reactivity enhancement observed in systems exposing metal/oxide boundaries. In addition, oxygen diffusion from the interior of an FeO_{2-x} island to the active edge sites may be effective for the oxygen replenishment in the CO oxidation catalytic cycle. In the case of closed films, weak adsorption of CO on oxide surfaces levels out the (negligible) role of CO adsorption characteristics, thus rendering the oxygen binding energy as the decisive parameter.

2.2.3 Strong Metal-support Interaction between Pt and Iron Oxides

Strong metal-support interaction (SMSI) is often observed for metal particles supported on reducible oxides and is mostly discussed in terms of encapsulation of the metal by the oxide.

Our previous studies on Pt/Fe_3O_4(111) planar model catalysts showed Pt encapsulation by a FeO(111) monolayer upon vacuum annealing at elevated temperatures. Whether the SMSI effects are structure sensitive, i.e. dependent on the surface structure of the oxide support, remains poorly understood. To address this issue, we performed comparative studies of nucleation, growth and thermal stability of Pt deposited on Fe_3O_4(111) and Fe_3O_4(001) surfaces. First, we developed fabrication of the Fe_3O_4(001) films on a Pt(100) substrate. The results showed that oxide surface termination could be tuned by a Fe buffer layer that had to be deposited to grow iron oxide in (001) orientation. Pt ad-atoms strongly interact with the $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstructed Fe_3O_4(001) surface and adsorb mono-atomically on the so-called "narrow" sites. Metal sintering sets in only above 700 K, resulting in cuboid Pt nanoparticles exposing primarily (100) and (110) facets. Concomitantly, CO adsorption on Pt is fully suppressed as a result of SMSI. The results provided strong evidence that the Pt nanoparticles on Fe_3O_4(001) are encapsulated by an FeO(111) layer in the same manner as observed for hemispherical Pt particles on Fe_3O_4(111). The comparison suggests that the SMSI effect via encapsulation is insensitive to the surface structure of oxide, although the latter strongly affects the particle morphology.

2.3 Scanning Probe Microscopy Group

Members: S. Beeg[d], C. Büchner[d], K. Burson[c], M. Heyde[a], B. Kell[b], L. Li[d], L. Liu[d], A.L. Lewandowski[d], L.E. Pascua[d], M. Ruiz Oses[d], C. Stiehler[d], S. Stuckenholz[d], G. Thielsch[b], W.-D. Schneider[e]

The main focus in our group is combining atomically resolved structures with spectroscopic measurements at the atomic scale. We have recently implemented a temperature programmed desorption (TPD) experiment within one of our low temperature ultrahigh vacuum (UHV) scanning probe microscope (SPM) machines. We continued to study the adsorption behavior of small molecules on oxide supported metal clusters originally started by the group of N. Nilius. Still another ongoing topic in our group is the detailed characterization of the bilayer silica film structure as well as its physical and chemical properties. We have made progress to transfer the silica film system from a pure model system towards application. To this end, we have employed a recently purchased high resolution environmental cell fast scanning atomic force microscope (AFM).

2.3.1 Temperature Programmed Desorption Combined with a Scanning Probe Microscope

Local real space structural and spectroscopic analysis of our samples are possible with our combined high-resolution non-contact atomic force microscope (nc-AFM) and scanning tunneling microscope (STM). The scanning probe measurements should ideally be accompanied by reactivity studies, since a detailed understanding of the structure-reactivity relationship of the samples is desired. To complement the SPM sample characterization a new TPD setup was designed and integrated into the existing UHV chamber. With the now multi-technique apparatus a comprehensive characterization of surfaces can be achieved. Structural analysis in real space, on the atomic scale and reactivity measurements can now be obtained of the identical sample surface.

For the extension of our high-end SPM to a multi-technique apparatus several challenges had to be faced. For the desired desorption experiments, e.g. with CO, low sample temperatures ($T < 20$ K) have to be reached. A liquid He-cooled manipulator was integrated into the setup that is able to pick up the portable samples used for microscopy while providing excellent thermal coupling. A quadrupole mass spectrometer was equipped with a custom built quartz glass cup for a higher signal/background ratio of the desorbing species. The setup was developed to perform TPD studies up to temperatures of 1200 °C in the future.

CO desorption from the MgO(001) surface, as a prototype for molecule desorption from oxide surfaces, has been experimentally studied in the department and elsewhere in the past. Recent theoretical studies on the topic, e.g. from J. Sauer's group sum up varying results for desorption energies of this system from theory and experiment. While the system has already been addressed experimentally, open questions still remain. For this reason, CO desorption of thin MgO films supported on Mo(001) surfaces was chosen for the first tests of the apparatus. CO desorption measurements of bulk MgO(001) from H. Kuhlenbecks' group in our department and of B. D. Kay's research group studying Mo(001) supported thin MgO films could be confirmed with our new TPD setup. Additionally, STM images of the same sample surfaces, before and after TPD measurements, can now be provided. So far, we observed mostly unchanged structures of the samples in the STM after the TPD measurements.

After the successful test phase of this multi-technique setup the application to other projects in the group are planned in the future.

2.3.2 CO_2 Activation at Oxide-supported Au Nanoclusters Induced by Electron Transfer Processes (in Collaboration with the Catalysis/Laser Spectroscopy Group)

Based on long-time department experiences in preparation, one of the best-suited model systems for heterogeneous catalysis could be exploited to activate CO_2 into useful chemicals. Therefore, Au clusters containing between 200-300 atoms have been deposited onto 2 ML MgO ultrathin films grown epitaxially on a Ag(001) support. As already intensively investigated in the department before, an enhanced chemical reactivity of this metal-oxide system is attributed to excess charges shuttled from the underlying support, resulting in a two-dimensional cluster growth. By adsorbing gas phase CO_2 to the model surface, a localization of molecules is exclusively observed at the cluster perimeter in STM, in agreement with the high localization of extra electrons. In combination with infrared reflection absorption spectroscopy and thermal desorption spectroscopic measurements performed in another group of the department as well as density functional calculations performed in the H. Häkkinen group, the two-step reaction taking place at the Au clusters could be clearly identified/disentangled: (i) CO_2 chemisorbs at the cluster rim and transforms into carboxylate (CO_2^-) via electron transfer from the nanoparticle. (ii) Subsequently, it reacts with another neutral CO_2 molecule to form oxalate ($C_2O_4^{2-}$). By heating molecule-cluster hybrids to about 50°C, the final reaction products desorb as CO_2 from the surface and the electrons are shuttled back to the nanostructures. The activation process is fully reversible and renders the investigated metal-oxide system to be a perfect model to investigate catalytic surface reactions.

2.3.3 Influence of Adsorption on the Quantum Well States of Nanoparticles

(in collaboration with N. Nilius and W.-D. Schneider)

Focus of our research on this experiment was the controlled perturbation of nano-sized electronic systems, formed by the quantum well states (QWSs) of an individual Au nanoparticle. For this purpose, energy position and symmetry of QWSs in pristine Au islands have been probed by STM conductance spectroscopy. The experiment was repeated after exposing the system to molecular adsorbates, either to isophorone as weakly interacting organic species or to CO_2 as electron-accepting entity. Both molecules were found to bind along the periphery of the Au clusters and indeed triggered shifts in the QWS energies. After isophorone exposure, the QWSs moved together in energy and the state-dispersion became flatter, while CO_2 adsorption increased the energy gaps between adjacent levels and resulted in a steeper dispersion. The observed trends can be explained with the anticipated interaction mechanism between molecular species and Au islands. Isophorone essentially polarizes the Au electron gas, which enlarges the available confinement volume and pushes the QWSs together. In contrast, CO_2 binds to the Au boundary via charge transfer followed by electrostatic interactions. The ring of CO_2^- anions around the Au island exerts repulsive forces on the electron gas, which in turn decreases the accessible confinement volume and moves the QWSs apart. Our experiments demonstrate that the interaction between a quantized electronic system and adsorbed molecules can indeed be probed at the single-particle level with STM. Such studies will be able to shed light on charge-transfer processes occurring in catalytic reactions on the supported metal-nanoparticles.

2.3.4 Silica Film Structures from Crystalline to Amorphous Ring Networks

Over the last years, atomically resolved STM and nc-AFM images of vitreous silica bilayer prepared on a Ru(0001) support were presented from our group. With these studies of the silica film, we have finally verified the atomic glass network, also known as random network theory, postulated by W. H. Zachariasen more than 80 years ago. The film structure resembles the original 2D drawings in all of its details. The availability of real-space data allows for a clear assignment of atomic sites. The position of oxygen and silicon atoms can be determined, the prominent ring structures, and their distribution and local neighborhood can be directly assessed. The film exhibits a complex ring network with a log-normal ring size distribution. By further analyzing the sizes of neighboring rings, characteristic arrangements of rings within the amorphous structure have been identified and their relative prevalence has been quantified. Results indicate that geometric strain plays an important role in determining ring cluster configurations within two dimensional amorphous network structures. Ring neighborhoods have also been analyzed within crystalline silica structures by considering grain boundaries and characteristic defects. Boundaries consisting of combinations of two five membered ring for each eight-member ring and boundaries consisting of equal numbers of five- and seven-membered rings are the most common. These boundaries can be understood by considering strain and interaction with the underlying substrate.

2.3.5 Universal Features of 2D Random Networks

We have identified common structural motifs among 2D random networks by analyzing a variety of atomic scale, molecular scale, and macro-scale 2D random networks. Both theoretically predicted and experimentally observed networks were considered. Similar 2D ring arrangements and typical ring combinations, such as the Stone Wales defect, are observed across systems with diverse length scales. Quantitative analysis was performed using ring statistics and pair correlation functions. Good agreement is found between observed distributions and the prediction by J. F. Shackelford and B. D. Brown that a lognormal ring size distribution is inherent to all amorphous networks. Furthermore, we compared crystalline-vitreous transition region characteristics in bubble rafts and the amorphous silica network structure. The structural changes across the transition region were studied by computing ring statistics for narrow image slices. In both cases, this evaluation revealed that five- and sevenfold rings occur closer to the crystalline phase than four-, eight-, and nine-membered rings.

2.3.6 Silica Films for Applications

Silica films have many potential applications ranging from nanoelectronics, to battery technologies, to model catalysis. As a proof of principle that the silica films are sufficiently robust for potential applications, silica has been transferred out of ultra-high vacuum, subjected to a variety of treatments, and examined both with ambient and liquid AFM. We find that the silica film is robust against a number of liquid treatments with common solvents including ethanol, water, and acetone as confirmed by low energy electron diffraction (LEED) and Auger electron spectroscopy. The stability of the silica film is indicated by the observation of certain structural features observed in UHV, ambient, and liquids. Specifically, in films of 1.7 monolayer silica, holes to the substrate with diameters on the order of 5-10 nm are observed by SPM in both UHV and liquids. In addition, the samples have been reintroduced to UHV after liquid treatments to confirm the stability of the film structure.

2.3.7 Photoluminescence from ZnO-Films

(in collaboration with N. Nilius)

Using a specifically designed STM that is able to probe the optical response of nanometer-sized areas on the surface, we have analyzed the local luminescence properties of ZnO thin films prepared on Au(111). Depending on the O_2 chemical potential, the ZnO growth can be reproducibly switched between a layer-by-layer (high μ_{O2}) and a 3D mode (low μ_{O2}). In both cases, the luminescence is characterized by a prominent band-recombination peak at 373 nm. In addition, several defect-mediated optical transitions have been identified and linked to the occurrence of Zn and O vacancies in the wurtzite lattice. Substituting small amounts of lattice oxygen with nitrogen leads to a drastic increase of the O-vacancy related emission peak. This finding suggests that O vacancies preferentially develop in the N-doped ZnO, as they are able compensate for the deviating charge state of the trivalent nitrogen impurities. The preparation of Ag nanoparticles on the ZnO films enabled us to study coupling processes between ZnO excitons and Ag plasmons. Indeed, both optical excitations could be clearly identified in our optical spectra, however the mutual coupling turned out to be weak, most likely because of the small contact area between Ag and ZnO at the interface.

2.3.8 Surface Phonon-Polariton Mediated Electron Transport through CaO Thin Films

(in collaboration with N. Nilius and W.-D. Schneider)

Scanning tunneling microscopy has developed into a powerful tool for the characterization of conductive surfaces, for which the overlap of tip and sample wavefunctions determines the image contrast. On insulating layers, as the CaO thin film grown on Mo(001) investigated here, direct overlap between initial and final states is not enabled anymore and electrons are transported via hopping through the conduction-band states of the oxide.

In this case, the carrier transport is accompanied by strong surface phonon-polariton excitations, reflected by an oscillatory signature on the differential conductance spectra of the system. These local phononic excitations tentatively assigned to Fuchs-Kliewer phonons induced by inelastically tunneling electrons show a characteristic spatial dependence and become softer around lattice irregularities in the oxide film, such as dislocation lines. Our work demonstrates that new physical phenomena become evident in STM/STS experiments on thin dielectric films with increasing thickness, where the dominant electron transport changes from a tunneling to a hopping regime.

2.4 Magnetic Resonance Group

Members: D. Cornu[c]*, W. Hänsel-Ziegler*[b]*, L. Kankate*[c]*, T. Risse*[a]

The activities of the magnetic resonance group focus on the development of an ultrahigh vacuum compatible high-field electron paramagnetic resonance (EPR) experiment operating at 95 GHz which increases the spectral resolution of EPR spectroscopy by a factor of ten as compared to the currently available apparatuses operating at X-band (9.5 GHz). The core of this machine is a commercial high-field EPR spectrometer (Bruker), which is integrated into a multi-technique apparatus including STM and IR to allow for a comprehensive characterization of the surfaces. The crucial step to adapt the high field spectrometer to UHV conditions was the development of a stable UHV compatible Fabry-Perot resonator, in which the planar metal single crystal surface, used as a substrate to grow well-defined oxide films serves as one of the mirrors of the Fabry-Perot resonator. The microwave radiation is coupled into the resonator through a rectangular hole in the second, opposing, concave mirror by means of a coupling antenna made out of a 60 μm thick Au wire. The sealing of the hole in the latter mirror to allow for experiments under UHV conditions is achieved by a sapphire window, which is glued inside the waveguide directly on the backside of the coupling hole of the concave mirror.

The machine was used to investigate paramagnetic point defects on single crystalline MgO(001) films grown on Mo(001). From experiments at X-band it is known that preparation of MgO films by reactive deposition of Mg onto a Mo(001) surface at room temperature results in paramagnetic centers located in the bulk of the film. Heating the system to 1000 K can destroy these bulk centers, while subsequent electron bombardment of the annealed film creates new paramagnetic color centers, which were shown to be mostly located in the domain boundaries of the film. The W-band EPR spectra of 30 ML thick MgO(001) films prepared at room temperature show a doublet of lines with maximal splitting if the magnetic field is oriented along <110> equivalent direction of the MgO film, while the doublet collapses into a single line in case the field is aligned with a <100> equivalent direction. The signals observed in W-band EPR correspond to bulk centers, which is in line with the observations at X-band. However, at X-band only a single, isotropic line is observed. This is consistent given the fact that a g-tensor anisotropy induced splitting of 12 G in W-band corresponds to 1.2 G splitting at X-band being much lower than the observed line width (6 G). This clearly demonstrates the ability of W-band EPR spectroscopy to provide additional information on the nature of the underlying centers not available from investigations at X-band. The collapse of the two lines with the magnetic field being oriented along the <100> direction is a direct consequence of the g-tensor orientation. To account for this behavior the principal components of the g-tensor have to be aligned with the <110> directions of the film. This is in contrast to expectations for electron centers being located in domain boundaries of the film shown to run along the <100> directions of the film. In contrast, it is suggesting that the unpaired electron is trapped at sites, which have a local symmetry corresponding to kinks of the domain boundaries. This is well in line with expectations based on theoretical calculations showing that the stability of trapped electrons increases at such sites.

As mentioned above electron bombardment of the film leads to the formation of a single line at X-band with a somewhat increased line width (8 G) and slightly asymmetric line shape. In comparison to that the W-band signal shows a broad (about 50 G) and very asymmetric line shape with a broad low field maximum and a sharp high field minimum. This line shape clearly indicates that the signal is made up by a variety of paramagnetic centers characterized by different local environments and hence different g-values. Hence, these results clearly show that the similar signals observed at X-band for the two scenarios is not sufficient to conclude that the underlying paramagnetic centers are the same, too. The experiments at W-band clearly show, that there are significant differences between the two situations. While the signal observed for the pristine films grown at room temperature is indicative for paramagnetic centers with a well-defined local environment, electron bombardment results in an inhomogeneous distribution of trapped electron centers in the domain boundaries of the MgO films.

2.5 Catalysis/Laser Spectroscopy Group

Members: F. Calaza[c], Y. Fujimori[c], A. Ghalgaoui[c], W. Kaden[c], S. Pomp[d], P. Seidel[d], M. Sterrer[a]

Our group runs several surface science experiments equipped with analytical tools such as X-ray photoelectron spectroscopy (XPS), infrared reflection-absorption spectroscopy (IRAS), temperature-programmed desorption (TPD), and scanning tunneling microscopy (STM) that allow the electronic, vibrational, and structural properties of model catalysts to be determined. We investigate adsorption and reaction phenomena on single-crystalline metal surfaces, thin oxide films, and oxide-supported metal particles at various degrees of chemical complexity – from ultrahigh-vacuum via elevated pressure and ambient conditions to solid-liquid interfaces. Our UHV-based methods are complemented by polarization-modulation IRAS (PM-IRAS), sum-frequency generation (SFG), electrochemical STM (EC-STM) and cyclic voltammetry (CV) as in-situ techniques for studying the complex interfaces.

2.5.1 CO_2 Activation

Our group has been involved in two projects related to CO_2 activation by charge transfer on Au surfaces, where our combined IRAS, XPS and TPD studies provided essential information about the chemical state of adsorbed CO_2. In collaboration with the group of Hrvoje Petek (University of Pittsburgh, USA), we studied CO_2 adsorption on an Au(111) surface modified by 1,4-phenylene-diisocyanide (PDI) chains and identified three different CO_2 species on this surface: chemisorbed CO_2 anions on Au adatoms, physisorbed CO_2 trapped between the PDI chains, and solid-like 2D CO_2 islands. Together with the STM data of Petek´s group, the results could be explained in terms of a seeding effect of $CO_2^{\delta-}$, which promotes the nucleation and growth of 2D CO_2 clusters.

2.5.2 Polyalcohol Chemistry on Metals and Metal-oxide Model Surfaces

Glycerol, which is the major byproduct in biodiesel production, is of industrial interest as it may serve as feedstock for a variety of chemical products. The search for new processes for its upgrade is reflected by the increasing number of applied catalysis work published during the last decade. By contrast, surprisingly little work about the fundamental interaction of glycerol with catalytic surfaces is available. Our group started the investigation of glycerol chemistry on clean and oxygen-covered Pd(111) and Au(111) single-crystal model surfaces. When the polyalcohol is adsorbed on the metallic Pd surface, it primarily decomposes into H_2 and CO, thus presenting promising results for its use in reforming reactions. On the other hand, on the Au(111) surface it interacts very weakly showing no decomposition. In the presence of chemisorbed oxygen or surface oxides, the interaction with both surfaces can be tuned towards different products (Pd showing more aldehyde production by selective oxidation). Chemisorbed oxygen leads to a strong enhancement of the reactivity of Au(111), where formation of carboxylates as intermediates towards total combustion was observed. These latter results are of interest to understand the mechanistic processes of selective catalytic oxidation of glycerol. Results from IR spectroscopy upon adsorption of the molecule at low temperatures show that its adsorption geometry and the cleavage of specific intra/intermolecular hydrogen bonds are key parameters dictating the decomposition pathways observed for the polyalcohol at higher temperatures. Further elucidation of this interaction is being investigated in collaboration with Alexandre Tkatchenko’s group (TH) by studying different adsorption structures by DFT and MD simulations and comparing calculated infrared spectra with our experimental results.

For the case of upgrading glycerol to 1,2-propylene glycol, the process goes through two steps, the dehydration to acetol followed by its hydrogenation to the final product. Even though precious metals are commonly used in hydrogenation reactions, it was found that some oxides perform also quite well, one of them being ceria. Thus, it is of our interest to study the interaction of this intermediate, namely acetol, with the surface of metals and ceria to elucidate the adsorption and reaction pathways both, under UHV conditions and at close to ambient pressure. We use our in-house PM-IRAS set-up to follow vibrational features of adsorbed intermediates from UHV up to ambient pressures, and combine this with results from NEXAFS and ambient pressure XPS studies (Dr. Hendrik Bluhm, LBNL, Berkeley, USA). Acetol interaction with the metal single crystals, Ru(0001) and Pd(111), shows Pd is more active than Ru towards decomposition of Acetol. We observed that adsorption of intact acetol molecules is possible at ambient pressure and that this can be related to the presence of coadsorbed carbon and/or oxygen.

In the case of ceria, $CeO_2(111)$ films grown on top of a Ru(0001) single crystal are used as model catalysts for acetol hydrogenation. The interaction of H_2 with the pristine oxide at ambient pressures (for activating the H_2 molecule) is currently under investigation and some preliminary results by TPD, XPS and PM-IRAS show an intricate relation between hydroxyl formation, Ce oxidation state and possible uptake of H atoms inside the oxide film. In order to learn more about the role of different hydrogen species, their distribution in/on the CeO_2 films is studied with nuclear reaction analysis (in collaboration with Dr. Markus Wilde, The University of Tokyo, Japan).

2.5.3 Hydroxylation of Oxide Surfaces

We continued our investigations of the hydroxylation of oxide surfaces and the influence of hydroxyls on the properties of metal nanoparticles with CaO(001)/Mo(001) and SiO_2/Ru(0001) thin films. Our combined IRAS and XPS study about water interaction with CaO(001) from UHV to elevated pressure allowed several different hydroxyl species on the surface to be identified and attributed to single, dissociated water molecules, small water/hydroxyl cluster and chains (together with the LT-STM group, Niklas Nilius, and Sergey Levchenko, TH), disordered and $Ca(OH)_2$-like structures. Furthermore, the influence of interfacial hydroxyls on the amorphous-to-crystalline ice transition has been revealed and studies of the CaO film thickness dependence showed that water dissociation is strongly limited on thin films due to the Mo-doping effect.

Together with Shamil Shaikhutdinov´s group we studied the hydroxylation of silica thin films, in particular the hydroxylation enhancement by electron bombardment of adsorbed water ice. We subsequently investigated and compared the nucleation of Pd on hydroxylated and non-hydroxylated silica thin films and found that the previously identified diffusion of Pd atoms through the pores of the silica film can be manipulated via hydroxylation.

2.5.4 Solid-Liquid Interfaces

We have completed the set-up of the new SFG spectrometer and the construction of a UHV preparation chamber with transfer option for electrochemical studies. In a first project we have investigated and compared the adsorption of 1,4-phenylene-diisocyanide (PDI) from solution and UHV on Au(111) and FeO-supported Au nanoparticles using SFG and STM. Our studies revealed different adsorption geometries of PDI depending on the preparation conditions as well as a strong restructuring of Au(111) at high PDI concentration in the solution. Iron oxide thin films grown on Pt(111) have been investigated under electrochemical conditions with CV and EC-STM. We have determined the potential range where the films are stable in electrolyte solution and performed first successful electrochemical experiments with catechol, hydrochinone and aminophthalic acid on FeO(111)/Pt(111).

2.6 Molecular Beam Group

Members: S. Attia[d]*, C. O´Brien*[c]*, P. Dementyev*[d]*, K.-H. Dostert*[d]*, J. Hartmann*[b]*,
F. Ivars Barceló*[c]*, F. Mirabella*[d]*, ,S. Schauermann*[a]*, J. Seifert*[c]*, E. Spadafora*[c]

The activities of the molecular beam group focus on atomistic-level understanding of heterogeneously catalyzed reactions including mechanisms, kinetics and thermodynamics of elementary surface processes. The main focus lies on finding detailed correlations between the structural properties of nano-sized supported catalysts and activity and selectivity of surface reactions. A variety of surface science methods - multi-molecular beam techniques, single crystal adsorption calorimetry (SCAC) and infrared reflection absorption spectroscopy (IRAS) – is employed in these studies in order to address both kinetic and thermodynamic aspects of interaction of gas phase molecules with model well-defined surfaces.

In the last two years, three topics were addressed in these studies including chemoselective partial hydrogenation of multi-unsaturated hydrocarbons, interaction of water with oxide surfaces and CO_2 activation over $Fe_3O_4(111)$. Moreover, a new UHV apparatus has being built up for investigation of enantioselective reactions on chirally modified model surfaces with the scope of the by ERC funded project ENREMOS.

2.6.1 Water Interaction with Oxide Surfaces: a Microcalorimetric and Spectroscopic Study on $Fe_3O_4(111)$ and $Fe_3O_4(100)$

There is rather limited atomistic understanding of water/iron oxide(s) interaction mostly due to the fact that it has been commonly addressed by the intruding methods, such as e.g. temperature programmed desorption (TPD) or photoelectron spectroscopy (PES), which themselves can strongly affect the result. Particularly for magnetite (Fe_3O_4), there is a limited knowledge on the nature of the surface species formed upon water adsorption and dissociation. Even though infrared vibrational spectroscopy of adsorbed water layers on well-defined model Fe_3O_4 surfaces provides some evidences for the formation of hydroxyl groups in the past, the spectra reveal rather high complexity and are not fully understood. Particularly, it is not clear if the simplest model suggesting formation of two individual hydroxyl groups upon dissociation of one water molecule – usually discussed in the literature – is valid.

In the last two years, we carried out the first direct calorimetric measurement of energetics of water interaction with well-defined model Fe_3O_4(111) and Fe_3O_4(100) surface grown on Pt(111) or Pt(100 to directly measure water adsorption and dissociation energies as a very detailed function of surface coverage. Complementary, we employed infrared reflection adsorption spectroscopy (IRAS) in combination with molecular beam techniques to identify the nature of the surface species formed upon water adsorption and to find detailed correlations between the adsorbates' structures and the energetics of their formation.

It was shown that water dissociation energy on Fe_3O_4(111) is considerably higher than all previously reported values obtained by the indirect desorption-based methods. By employing IRAS on isotopically labeled water and Fe_3O_4, we experimentally prove that the generally accepted simple model of water dissociation to form two individual OH groups is not correct. By combing experimental observations and theoretical calculations carried out in the group of Prof. J. Sauer (HU, Berlin), we show that OH groups formed upon water dissociation build a very stable complex with molecular water. We could unambiguously rule out formation of two individual spatially separated OH groups upon water dissociation. Calculated spectroscopic vibrational signatures and formation energy of an OH-water complex were found to be in excellent agreement with the experimental data.

The adsorption behavior of water on Fe_3O_4(100) was found to be similar to Fe_3O_4(111) but the adsorption energies exhibit somewhat lower values. Currently, we investigate water interaction with Fe_3O_4(100) by vibrational spectroscopy to identify the nature of the surface species formed upon water adsorption and dissociation on this surface.

2.6.2 Chemoselective Partial Hydrogenation of α,β-unsaturated Ketons over Pd Model Catalysts Supported on $Fe_3O_4(111)/Pt(111)$

Chemoselective partial hydrogenation of α,β-unsaturated ketones and aldehydes represents an important class of reactions resulting in a broad class of valuable intermediates for practically-relevant processes such as, e.g., unsaturated alcohols. Generally, thermodynamics favors hydrogenation of the C=C bond in these compounds to form the unwanted product, i.e., saturated aldehydes or ketones. Therefore, chemoselective hydrogenation of the C=O bond requires manipulation of kinetic effects by means of a suitable catalyst. This represents a challenging problem and asks for fundamental studies. While a variety of powdered supported metal catalysts, including Pt, Pd, Rh, Ni, Cu, Ag, and Au have been already investigated to understand and improve the activity and selectivity of this reaction, a deep fundamental understanding of this reaction and the parameters governing its activity and selectivity toward unsaturated alcohol formation is still missing.

In the last two years, we carried out a detailed mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) and Pd nanoparticles supported on an oxide support – under well-defined UHV conditions. Being the smallest α,β-unsaturated aldehyde, acrolein was chosen as a simple proxy to investigate the selective hydrogenation chemistry at the atomistic level. In previous studies on powdered supported Pd catalysts, acrolein was reported to be hydrogenated almost exclusively on the C=C bond forming propanal. In our studies, we showed for the first time that selective hydrogenation of the C=O bond in acrolein with nearly 100% selectivity is possible over Pd(111). However, this process requires a very distinct modification of the Pd(111) surface with a spectator species that turns the metal surface selective towards unsaturated alcohol formation. This spectator species is formed from acrolein during the initial stages of surface reaction and builds up a densely packed overlayer. By applying a combination of pulsed multi-molecular beam experiments and *in situ* infrared reflection-absorption spectroscopy (IRAS) we were able to identify the chemical nature of the spectator and the reactive surface intermediate and for the first time experimentally follow the simultaneous evolution of the reactive intermediate on the surface and formation of the product in the gas phase. With this study it has been possible to directly identify the reaction intermediate that leads to the formation of the unsaturated alcohol as a final product and obtain atomistic-level insights into the chemoselective hydrogenation chemistry of acrolein. Spectator species were found to play an important role in governing chemoselectivity – the observation that might be of great interest for development of new selective powdered catalysts such as e.g. ligand-modified nanoparticles.

2.6.3 CO_2 Activation over $Fe_3O_4(111)$In this project, we apply a combination of molecular beam techniques and infrared reflection-absorption spectroscopy in order to monitor the evolution of the surface species formed upon adsorption and transformation of CO_2 over $Fe_3O_4(111)$ surface. The main motivation of these studies stems from the recent observations that CO_2 can be activated over oxide surfaces and be used for the further transformations to produce valuable chemical compounds. In this ongoing project we were able to find the reaction conditions, at which CO_2 was found to form new surface species, presumably to oxalate species, which is a promising surface intermediate for further chemical transformations towards more complex oxygenates. We are currently applying isotopic labelling of both gas phase CO_2 as well as Fe_3O_4 to spectroscopically identify the nature of the surface species formed. Complementary, co-adsorption studies of CO_2 and H_2O are being carried out, which indicated that water not only strongly affects CO_2 adsorption but also induces new surface chemistry.

2.6.4 ERC Project: Construction of a New UHV Apparatus for Studying Enantio-selective Reactions on Model Chirally Modified Surfaces.

Imparting chirality to non-chiral metal surfaces by adsorption of chiral modifiers is a highly promising route to create effective heterogeneously catalyzed processes for production of enantiopure pharmaceuticals. In this project funded by the European Research Council (ENREMOS) we are aiming at a fundamental level understanding of the structure of chirally modified surfaces, the bonding of the prochiral substrate on the chiral media and the details of the kinetics and dynamics of enantioselective surface reactions. To achieve these atomistic insights, we will apply a combination of ultrahigh vacuum (UHV) based methods for studying reaction kinetics and dynamics (multi-molecular beam techniques) and *in-situ* surface spectroscopic (IRAS) and microscopic (STM) tools on well-defined model surfaces consisting of metal nanoparticles supported on thin single crystalline oxide films. Complementary, the catalytic behaviour of these chirally modified model surfaces will be investigated under ambient pressure conditions with enantiospecific detection of the reaction products that will enable detailed atomistic insights into structure-reactivity relationships. Currently, a new UHV apparatus is being built up and tested and will supposedly go in full operation by the end of 2015.

2.7 Spectro-Microscopy Group (SMART)

Members: A. Fuhrich[d]*, F. Genuzio*[d]*, H.W. Klemm*[d]*, E. Madej*[c]*, H. Marchetto*[c]*, D. Menzel*[e]*, G. Peschel*[d]*, S. Pohl*[b]*, Th. Schmidt*[a]*, M. Springer*[b]*, M. Timm*[b]*, E. Umbach*[e]

The activities of the group have been focused on (1) thin oxide film growth and (2) instrumental development. The chemical and structural properties of iron oxide and silica films have been studied *in situ* and *in real time* with the SMART microscope (SpectroMicroscope with Aberration correction for many Relevant Techniques). The new SMART-II microscope will overcome the space charge limitations of the actual instrument, resulting in an improved lateral resolution of 5 nm in XPEEM (x-ray photoelectron emission microscopy).

2.7.1 Iron Oxide Films

Combining low energy electron microscopy (LEEM) with low energy electron diffraction (LEED) and x-ray photoemission electron microscopy (XPEEM) we studied the phase transformations between Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3, grown as 10 nm thin oxide films on Pt(111) and Ag(111) single crystals. These transformations occur as moving reaction fronts in most cases, the shapes and velocities of which show strong dependences on temperature and oxygen pressure, but also on defects like step bunches of the supporting substrate and domain boundaries in the initial oxide film. We found two regimes for the transformations: while the reaction front of the purely structural transformation from γ-Fe_2O_3 to α-Fe_2O_3 is fast and has a dendritic shape, the conversions involving both, structural and compositional changes (oxidation of Fe_3O_4 to α-Fe_2O_3 and the inverse process) are one to two orders of magnitude slower and have smooth fronts. The rate limiting process, causing the strong difference in the velocity, is the Fe diffusion within the oxide film, either towards the interface to the metal support or to the surface.

Furthermore, we investigated the influence of Fe deposition on the termination of the Fe_3O_4 and α-Fe_2O_3 surfaces. At room temperature deposition, we found a $(2\sqrt{3}x2\sqrt{3})$ reconstruction which is stable upon annealing in UHV up to 450 K. In contrast, deposition in a temperature range 700 K – 820 K yields in the bi-phase reconstruction with the characteristic Moiré pattern in LEED. On the α-Fe_2O_3 surface Fe deposition at RT transforms the initial $(\sqrt{3}x\sqrt{3})$ bi-phase reconstruction to a (1x1) bi-phase reconstruction (i.e. missing $(\sqrt{3}x\sqrt{3})$ spots). This (1x1)-like structure is stable upon annealing up to 700 K and converts back to the known bi-phase termination at higher temperature.

We observed the encapsulation of Pt nanoparticles for the first time on a α-Fe_2O_3 surface. Annealed at T=850 K in UHV the nanoparticles undergo an encapsulation by a layer of FeO, observed in LEED and XPEEM. This process was already found on the Fe_3O_4 surface, but not on O-terminated α-Fe_2O_3. In our case, we used the bi-phase terminated (i.e. Fe terminated) α-Fe_2O_3 surface as support. Hence, the excess of Fe on this surface might be a key factor enabling the encapsulation of the particle.

2.7.2 Silica on Ru(0001)

We followed the preparation and structure of bilayer silica films on Ru(0001) as function of temperature and oxidation conditions. This allowed us to analyse the growth process at different length scales in order to judge on the overall quality and the morphology of the film. It is found that the film growth occurs in a crystalline and a vitreous phase as firstly discovered in our department using STM. However, our combined LEEM/PEEM/LEED/XPS experiments allowed an analysis at the sub-micron level to gain insight into the growth process at a mesoscopic scale. We found that the fully oxidized film can be prepared but that this film contains holes. These are unavoidable and are important to consider, if one wants to use the films for ensemble averaging experiments to investigate migration and reaction of molecules between the silica film and the Ru(0001) substrate.

The phase transition from a crystalline to a vitreous Silica film was observed *in situ* and *in real time* in the LEED mode of our microscope, displaying a continuous transformation from a well ordered (2x2) structure into a diffuse ring. The morphology of the resulting vitreous film was examined with dark field LEEM and was found to be smooth and homogeneous within our instrumental resolution (~20 nm in these experiments).

2.7.3 Iron–silicate on Ru(0001)

Iron-silicate can be seen as a model system for zeolites, which are of great importance for catalysis and widely used in industry as desiccant, detergent or as molecular sieves. Here, the relation between the specific structure and its reactivity is of special interest. In our case, we have studied the growth of one to two atomic layers thin films on a Ru(0001) single crystal support, using two different preparation recipes. In the first recipe, iron and subsequently silicon were deposited at room temperature before annealing in oxygen atmosphere, whereas in the second one, a complete FeO monolayer was prepared first, followed by silicon deposition in oxygen atmosphere at elevated temperature. For the first preparation we found co-existing domains of iron-silicate and silica by LEEM, XPEEM and LEED revealing the local structure and the local chemical composition. The second recipe produced a complete iron-silicate film, which was homogenous in both, structure and chemical composition.

2.7.4 SMART-2

This new aberrations-corrected LEEM-PEEM instrument with a new electrostatic Omega-filter will substitute the SMART-1 instrument, which demonstrated a lateral resolution of 18 nm in energy filtered XPEEM, the worldwide best value for this type of instrument. However, the resolution is limited by space charge effects due to the temporary high electron intensity caused by the pulsed time structure of the synchrotron light. In contrast, without space charge, as shown in LEEM, the electron optics and especially the aberrations correction are sufficient for a resolution of 2.6 nm. Therefore, we are constructing a new beam splitter module with implemented apertures and slits to reduce reasonably the electron beam intensity by cutting away the part not used on the detector. The new Omega filter is optimized for both, a lateral and an energy resolution better than 2 nm and 100 meV, respectively. The final SMART-2 set-up consists of three modules: (1) existing commercial LEEM/PEEM system, (2) central magnetic beamsplitter with aberration correction and space charge reduction and (3) the new electrostatic Omega-filter. The SMART-2 beamsplitter bases on the compact and sophisticated design of the SMART-1 instrument, but with (a) additional field apertures and energy slit for space charge reduction, (b) an aberration corrector adapted to the new LEEM/PEEM system and (c) improved layout of the vacuum components, allowing to implement deflection elements for a full electron optical adjustment (instead of the incomplete and not reliable mechanical adjustment of the old instrument). Because of the compact design and constraint non-magnetic materials, accuracy, vacuum technology and the necessity to connect the module to the existing microscope, it was not easy to fulfill the design goals. However, we found a specific solution in collaboration with the manufacturer of the microscope and the module is now under construction.

The unavoidable aberrations in the electrostatic Omega filter will be corrected by multipoles (hexapoles and quadrupole). By full electron-optical simulations the position and strength of these hexapoles have been optimized. In the final set-up four hexapoles will be implemented: two identical, each in the first and second image plane (i.e. entrance and center) to compensate for the off-axis chromatic aberrations, and an antisymmetric pair of hexapoles placed in the first diffraction plane (between the 1st and 2nd sector of overall four sectors) to compensate for the off-axis geometric aberration. This aberration correction enables a lateral resolution limit better than 2 nm. Furthermore, the magnification of the transfer optics have been optimized to limit the energy resolution down to 75 meV < ΔE < 100 meV for high and medium magnification. For low magnification the energy resolution is determined by the angular spread in the image, corresponding to the size of the entrance slit, which therefore has to be chosen sufficiently small.

3. Publications of the Department of Chemical Physics[1]

2013 (late publications)

Brown, M.A., A.B. Redondo, M. Sterrer, B. Winter, G. Pacchioni, Z. Abbas and J. van Bokhoven: Measure of Surface Potential at the Aqueous-Oxide Nanoparticle Interface by XPS from a Liquid Microjet. Nano Letters **13** (11), 5403-5407 (2013).

Cui, Y., N. Nilius, H.-J. Freund, S. Prada, L. Giordano and G. Pacchioni: Controlling the charge state of single Mo dopants in a CaO film. Physical Review B **88** (20), 205421 (2013).

Demuth, D., R.W. Fischer, H.-J. Freund and M. Baerns: Katalyse - moderne Alchemie? Chemie-Ingenieur-Technik **85** (12), 1807-1814 (2013).

Freund, H.-J., M. Heyde, N. Nilius, S. Schauermann, S.K. Shaikhutdinov and M. Sterrer: Model studies on heterogeneous catalysts at the atomic scale: From supported metal particles to two-dimensional zeolites. Journal of Catalysis **308**, 154-167 (2013).

Junkes, H., W. Erlebach, S. Gewinner, U. Hoppe, A. Liedke, G. Meijer, W. Schöllkopf, M. Wesemann, G. von Helden, H. Bluem, D. Dowell, R. Lange, A.M.M. Todd, L.M. Young and S.B. Webb: Integrating the FHI-FEL into the FHI Research Environment - Design and Implementation Aspects. In: Proceedings of the 35th International Free-Electron Laser Conference. (Eds.) C. Scholl and V. Schaa. JACoW.org, 562-565 (2013). ISBN 978-3-95450-126-7. OPEN ACCESS

Pan, Y., N. Nilius, H.-J. Freund, J. Paier, C. Penschke and J. Sauer: Titration of Ce^{3+} Ions in the CeO_2(111) Surface by Au Adatoms. Physical Review Letters **111** (20), 206101 (2013).

Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, V. Platschkowski, G. von Helden, H. Bluem, M.A. Davidsaver, D. Dowell, K. Jordan, R. Lange, H. Loos, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk: The IR and THz Free-Electron Laser at the Fritz-Haber-Institut. In: Proceedings of the 35th International Free-Electron Laser Conference. (Eds.) C. Scholl and V. Schaa. JACoW.org, 657-660 (2013). ISBN 978-3-95450-126-7. OPEN ACCESS

Stavale, F., N. Nilius and H.-J. Freund: STM Luminescence Spectroscopy of Intrinsic Defects in ZnO(000$\bar{1}$). The Journal of Physical Chemistry Letters **4** (22), 3972-3976 (2013).

Sterrer, M. and H.-J. Freund: Properties of Oxide Surfaces. In: Properties of Composite Surfaces. (Ed.) K. Wandelt. (Surface and Interface Science, Vol. 3). Wiley-VCH, Weinheim, 229-278 (2013). ISBN 978-3-527-41157-3.

Włodarczyk, R., J. Sauer, X. Yu, J.A. Boscoboinik, B. Yang, S.K. Shaikhutdinov and H.-J. Freund: Atomic Structure of an Ultrathin Fe-Silicate Film Grown on a Metal: A Monolayer of Clay? Journal of the American Chemical Society **135** (51), 19222-19228 (2013).

Doctoral Thesis

Peter, M.: Oxygen and CO Adsorption on Supported Pd Nanoparticles and Pd(111). Humboldt-Universität zu Berlin 2013.

---

[1] OPEN ACCESS = Gold open access publication

2014

Aleksandrov, H.A., S.M. Kozlov, S. Schauermann, G.N. Vayssilov and K.M. Neyman: How Absorbed Hydrogen Affects the Catalytic Activity of Transition Metals. Angewandte Chemie International Edition **53** (49), 13371-13375 (2014).

Aleksandrov, H.A., S.M. Kozlov, S. Schauermann, G.N. Vayssilov and K.M. Neyman: How Absorbed Hydrogen Affects the Catalytic Activity of Transition Metals. Angewandte Chemie **126** (49), 13589-13593 (2014).

Asakura, K., H.-J. Freund and K. Fukutani: Special Issue on Surface Science. The Chemical Record **14** (5), 756-758 (2014).

Boscoboinik, A., X. Yu, S.K. Shaikhutdinov and H.-J. Freund: Preparation of an ordered ultra-thin aluminosilicate framework composed of hexagonal prisms forming a percolated network. Microporous and Mesoporous Materials **189**, 91-96 (2014).

Boscoboinik, J.A. and S.K. Shaikhutdinov: Exploring Zeolite Chemistry with the Tools of Surface Science: Challenges, Opportunities, and Limitations. Catalysis Letters **144** (12), 1987-1995 (2014).

Büchner, C., L. Lichtenstein, S. Stuckenholz, M. Heyde, F. Ringleb, M. Sterrer, W. Kaden, L. Giordano, G. Pacchioni and H.-J. Freund: Adsorption of Au and Pd on Ruthenium-Supported Bilayer Silica. The Journal of Physical Chemistry C **118** (36), 20959-20969 (2014).

Büchner, C., L. Lichtenstein, X. Yu, J.A. Boscoboinik, B. Yang, W. Kaden, M. Heyde, S.K. Shaikhutdinov, R. Włodarczyk, M. Sierka, J. Sauer and H.-J. Freund: Ultrathin Silica Films: The Atomic Structure of Two-Dimensional Crystals and Glasses. Chemistry - A European Journal **20** (30), 9176-9183 (2014).

Büchner, C., P. Schlexer, L. Lichtenstein, S. Stuckenholz, M. Heyde and H.-J. Freund: Topological Investigation of Two-Dimensional Amorphous Materials. Zeitschrift für physikalische Chemie **228** (4-5), 587-607 (2014).

Cui, Y., X. Shao, S. Prada, L. Giordano, G. Pacchioni, H.-J. Freund and N. Nilius: Surface defects and their impact on the electronic structure of Mo-doped CaO films: an STM and DFT study. Physical Chemistry Chemical Physics **16** (25), 12764-12772 (2014).

Dostert, K.-H., C. O'Brien, W. Riedel, A.A. Savara, W. Liu, M. Oehzelt, A. Tkatchenko and S. Schauermann: Interaction of Isophorone with Pd(111): A Combination of Infrared Reflection-Absorption Spectroscopy, Near-Edge X-ray Absorption Fine Structure, and Density Functional Theory Studies. The Journal of Physical Chemistry C **118** (48), 27833-27842 (2014).

Duncan, D.A., D. Kreikemeyer-Lorenzo, E. Primorac, O. Karslıoğlu, M. Naschitzki, W. Unterberger, H. Kuhlenbeck and D.P. Woodruff: V-doped TiO_2(110): Quantitative structure determination using energy scanned photoelectron diffraction. Surface Science **630**, 64-70 (2014).

Emmez, E., B. Yang, S.K. Shaikhutdinov and H.-J. Freund: Permeation of a Single-Layer SiO_2 Membrane and Chemistry in Confined Space. The Journal of Physical Chemistry C **118** (50), 29034-29042 (2014).

Freund, H.-J.: Oxygen activation on oxide surfaces: A perspective at the atomic level. Catalysis Today **238**, 2-9 (2014).

Freund, H.-J., N. Nilius, T. Risse and S. Schauermann: A fresh look at an old nanotechnology: catalysis. Physical Chemistry Chemical Physics **16** (18), 8148-8167 (2014). OPEN ACCESS

Freund, H.-J., S.K. Shaikhutdinov and N. Nilius: Model Studies on Heterogeneous Catalysts at the Atomic Scale. Topics in Catalysis **57** (10-13), 822-832 (2014).

Fujimori, Y., W. Kaden, M.A. Brown, B. Roldan-Cuenya, M. Sterrer and H.-J. Freund: Hydrogen Evolution from Metal-Surface Hydroxyl Interaction. The Journal of Physical Chemistry C **118** (31), 17717-17723 (2014).

Genuzio, F., A. Sala, T. Schmidt, D. Menzel and H.-J. Freund: Interconversion of α-Fe_2O_3 and Fe_3O_4 Thin Films: Mechanisms, Morphology, and Evidence for Unexpected Substrate Participation. The Journal of Physical Chemistry C **118** (50), 29068-29076 (2014).

Junkes, H., W. Schöllkopf, M. Wesemann and R. Lange: Design and Implementation Aspects of the Control System at the FHI FEL. In: Proceedings of the 14th International Conference on Accelerator & Large Experimental Physics Control Systems. (Eds.) C. Marshall, J. Fisher and V. Schaa. JACoW.org, 324-327 (2014). ISBN 978-3-95450-139-7. OPEN ACCESS

Kaden, W., C. Büchner, L. Lichtenstein, S. Stuckenholz, F. Ringleb, M. Heyde, M. Sterrer, H.-J. Freund, L. Giordano, G. Pacchioni, C.J. Nelin and P.S. Bagus: Understanding surface core-level shifts using the Auger parameter: A study of Pd atoms adsorbed on ultrathin SiO_2 films. Physical Review B **89** (11), 115436 (2014).

Klingan, K., F. Ringleb, I. Zaharieva, J. Heidkamp, P. Chernev, D. Gonzalez-Flores, M. Risch, A. Fischer and H. Dau: Water Oxidation by Amorphous Cobalt-Based Oxides: Volume Activity and Proton Transfer to Electrolyte Bases. ChemSusChem **7** (5), 1301-1310 (2014).

Liu, B.H., M. McBriarty, M.J. Bedzyk, S.K. Shaikhutdinov and H.-J. Freund: Structural Transformations of Zinc Oxide Layers on Pt(111). The Journal of Physical Chemistry C **118** (49), 28725-28729 (2014).

Nelin, C.J., F. Uhl, V. Staemmler, P.S. Bagus, Y. Fujimori, M. Sterrer, H. Kuhlenbeck and H.-J. Freund: Surface core-level binding energy shifts for MgO(100). Physical Chemistry Chemical Physics **16** (40), 21953-21956 (2014). OPEN ACCESS

Nilius, N., T. Risse, S.K. Shaikhutdinov, M. Sterrer and H.-J. Freund: Model Catalysts Based on Au Clusters and Nanoparticles. In: Gold Clusters, Colloids and Nanoparticles II. (Ed.) D.M.P. Mingos. (Structure and Bonding, Vol. 162). Springer, Berlin, 91-138 (2014). ISBN 978-3-319-07844-1.

Pan, Q., B.H. Liu, M. McBriarty, Y. Martynova, I. Groot, S. Wang, M.J. Bedzyk, S.K. Shaikhutdinov and H.-J. Freund: Reactivity of Ultra-Thin ZnO Films Supported by Ag(111) and Cu(111): A Comparison to ZnO/Pt(111). Catalysis Letters **144** (4), 648-655 (2014).

Pan, Y., N. Nilius, W.-D. Schneider and H.-J. Freund: Adsorption of thioether molecules on an alumina thin film. Surface Science **628**, 111-115 (2014).

Pan, Y., N. Nilius, C. Stiehler, H.-J. Freund, J. Goniakowski and C. Noguera: Ceria Nanocrystals Exposing Wide (100) Facets: Structure and Polarity Compensation. Advanced Materials Interfaces **1** (9), 1400404 (2014).

Pan, Y., L. Zhang, L. Huang, L. Li, L. Meng, M. Gao, Q. Huan, X. Lin, Y. Wang, S. Du, H.-J. Freund and H.-J. Gao: Construction of 2D Atomic Crystals on Transition Metal Surfaces: Graphene, Silicene, and Hafnene. Small **10** (11), 2215-2225 (2014).

Pascua, L., F. Stavale, N. Nilius and H.-J. Freund: Autocatalytic growth of ZnO nanorods from flat Au(111)-supported ZnO films. Physical Chemistry Chemical Physics **16** (48), 26741-26745 (2014).

Ringleb, F., M. Sterrer and H.-J. Freund: Preparation of Pd-MgO model catalysts by deposition of Pd from aqueous precursor solutions onto Ag(0 0 1)-supported MgO(0 0 1) thin films. Applied Catalysis A **474**, 186-193 (2014).

Rocker, J., D. Cornu, E. Kieseritzky, A. Seiler, O. Bondarchuk, W. Hänsel-Ziegler, T. Risse and H.-J. Freund: High field electron paramagnetic resonance spectroscopy under ultrahigh vacuum conditions - A multipurpose machine to study paramagnetic species on well defined single crystal surfaces. Review of Scientific Instruments **85** (8), 083903 (2014).

Schauermann, S., T.L. Silbaugh and C.T. Campbell: Single-Crystal Adsorption Calorimetry on Well-Defined Surfaces: From Single Crystals to Supported Nanoparticles. The Chemical Record **14** (5), 759-774 (2014).

Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, A. Paarmann, G. von Helden, H. Bluem, D. Dowell, R. Lange, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk: The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. In: Proceedings of the 36th International Free Electron Laser Conference. (Eds.) J. Chrin, S. Reiche and V. Schaa. JACoW.org, WEB04 (2014). ISBN 978-3-95450-133-5.

Shiotari, A., B.H. Liu, S. Jaekel, L. Grill, S.K. Shaikhutdinov, H.-J. Freund, M. Wolf and T. Kumagai: Local Characterization of Ultrathin ZnO Layers on Ag(111) by Scanning Tunneling Microscopy and Atomic Force Microscopy. The Journal of Physical Chemistry C **118** (47), 27428-27435 (2014).

Stavale, F., L. Pascua, N. Nilius and H.-J. Freund: Luminescence Properties of Nitrogen-Doped ZnO. The Journal of Physical Chemistry C **118** (25), 13693-13696 (2014).

Uhlrich, J., B. Yang and S.K. Shaikhutdinov: Methanol Reactivity on Silica-Supported Ceria Nanoparticles. Topics in Catalysis **57** (14-16), 1229-1235 (2014).

Willinger, M.G., W. Zhang, O. Bondarchuk, S.K. Shaikhutdinov, H.-J. Freund and R. Schlögl: A Case of Strong Metal-Support Interactions: Combining Advanced Microscopy and Model Systems to Elucidate the Atomic Structure of Interfaces. Angewandte Chemie International Edition **53** (23), 5998-6001 (2014).

Willinger, M.G., W. Zhang, O. Bondarchuk, S.K. Shaikhutdinov, H.-J. Freund and R. Schlögl: Metall-Substrat-Wechselwirkung: Kombination von hochauflösender Mikroskopie und Modellsystemen, um die atomare Struktur von Grenzflächen aufzuklären. Angewandte Chemie **126** (23), 6108-6112 (2014).

Yang, B., S.K. Shaikhutdinov and H.-J. Freund: Tuning Spatial Distribution of Surface Hydroxyls on a Metal-Supported Single-Layer Silica. The Journal of Physical Chemistry Letters **5** (10), 1701-1704 (2014).

Doctoral Thesis

Rocker, J.: Aufbau einer Ultrahochvakuum-Apparatur zur Messung der Elektronenspinresonanz im W-Band. Freie Universität Berlin 2014.

2015

Büchner, C., L. Lichtenstein, M. Heyde and H.-J. Freund: The Atomic Structure of Two-Dimensional Silica. In: Noncontact Atomic Force Microscopy. (Eds.) S. Morita, F.J. Giessibl, E. Meyer and R. Wiesendanger. (NanoScience and Technology, Vol. 3). Springer, Cham, 327-353 (2015). ISBN 978-3-319-15588-3.

Burson, K., P. Schlexer, C. Büchner, L. Lichtenstein, M. Heyde and H.-J. Freund: Characterizing Crystalline-Vitreous Structures: From Atomically Resolved Silica to Macroscopic Bubble Rafts. Journal of Chemical Education, in press. OPEN ACCESS

Calaza, F., C. Stiehler, Y. Fujimori, M. Sterrer, S. Beeg, M. Ruiz Oses, N. Nilius, M. Heyde, T. Parviainen, K. Honkala, H. Häkkinen and H.-J. Freund: Carbon Dioxide Activation and Reaction Induced by Electron Transfer at an Oxide-Metal Interface. Angewandte Chemie International Edition, in press.

Calaza, F., C. Stiehler, Y. Fujimori, M. Sterrer, S. Beeg, M. Ruiz Oses, N. Nilius, M. Heyde, T. Parviainen, K. Honkala, H. Häkkinen and H.-J. Freund: Aktivierung und Elektronentransfer-induzierte Reaktion von Kohlendioxid an einer Oxid-Metall-Grenzfläche. Angewandte Chemie, in press.

Cui, Y., Y. Pan, L. Pascua, H. Qiu, C. Stiehler, H. Kuhlenbeck, N. Nilius and H.-J. Freund: Evolution of the electronic structure of CaO thin films following Mo interdiffusion at high temperature. Physical Review B **91** (3), 035418 (2015).

Cui, Y., S. Tosoni, W.-D. Schneider, G. Pacchioni, N. Nilius and H.-J. Freund: Phonon-Mediated Electron Transport through CaO Thin Films. Physical Review Letters **114** (1), 016804 (2015).

Davis, E., K. Zhang, Y. Cui, H. Kuhlenbeck, S.K. Shaikhutdinov and H.-J. Freund: Growth of Fe_3O_4(001) thin films on Pt(100): Tuning surface termination with an Fe buffer layer. Surface Science **636**, 42-46 (2015).

Dementyev, P., M. Peter, S. Adamovski and S. Schauermann: Chirally-modified metal surfaces: energetics of interaction with chiral molecules. Physical Chemistry Chemical Physics **17** (35), 22726-22735 (2015). OPEN ACCESS

Emmez, E., J.A. Boscoboinik, S. Tenney, P. Sutter, S.K. Shaikhutdinov and H.-J. Freund: Oxidation of the Ru(0001) surface covered by weakly bound, ultrathin silicate films. Surface Science, in press.

Feiten, F.E., J. Seifert, J. Paier, H. Kuhlenbeck, H. Winter, J. Sauer and H.-J. Freund: Surface Structure of V_2O_3(0001) Revisited. Physical Review Letters **114** (21), 216101 (2015).

Fischer, F.D., J. Sauer, X. Yu, J.A. Boscoboinik, S.K. Shaikhutdinov and H.-J. Freund: Ultrathin Ti-Silicate Film on a Ru(0001) Surface. The Journal of Physical Chemistry C **119** (27), 15443-15448 (2015).

Freund, H.-J. and G.A. Somorjai: The Frontiers of Catalysis Science and Future Challenges. Catalysis Letters **145** (1), 1-2 (2015).

Gonchar, A., J.-C. Lian, T. Risse, H.-J. Freund, C. Di Valentin and G. Pacchioni: Characterization of O^--Centers on Single Crystalline MgO(001)-Films. Topics in Catalysis **58 (**12-13), 811-823 (2015).

Klemm, H., G. Peschel, E. Madej, A. Fuhrich, M. Timm, D. Menzel, T. Schmidt and H.-J. Freund: Preparation of silica films on Ru(0001): A LEEM/PEEM study. Surface Science, in press.

Liu, B.H., J.A. Boscoboinik, Y. Cui, S.K. Shaikhutdinov and H.-J. Freund: Stabilization of Ultrathin Zinc Oxide Films on Metals: Reconstruction versus Hydroxylation. The Journal of Physical Chemistry C **119** (14), 7842-7847 (2015).

Neppl, S., R. Ernstorfer, A.L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E.M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J.V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz and R. Kienberger: Direct observation of electron propagation and dielectric screening on the atomic length scale. Nature **517** (7534), 342-346 (2015).

Nilius, N. and H.-J. Freund: Activating Nonreducible Oxides via Doping. Accounts of Chemical Research **48** (5), 1532-1539 (2015).

Nilius, N., M. Sterrer, M. Heyde and H.-J. Freund: Atomic Scale Characterization of Defects on Oxide Surfaces. In: Defects at Oxide Surfaces. (Eds.) J. Jupille and G. Thornton. (Springer Series in Surface Sciences, Vol. 58). Springer, Cham, 29-80 (2015). ISBN 978-3-319-14366-8.

Pan, Q., X. Weng, M.S. Chen, L. Giordano, G. Pacchioni, C. Noguera, J. Goniakowski, S.K. Shaikhutdinov and H.-J. Freund: Enhanced CO Oxidation on Oxide/Metal Interface: From Ultra-High Vacuum to Near-Atmospheric Pressures. ChemCatChem **7** (17), 2620-2627 (2015).

Qiu, H., V. Staemmler, H. Kuhlenbeck, E. Bauer and H.-J. Freund: Weak thermal reduction of biphase Fe_2O_3(0001) films grown on Pt(111): Sub-surface Fe^{2+} formation. Surface Science **641**, 30-36 (2015).

Richter, N., F. Stavale, S.V. Levchenko, N. Nilius, H.-J. Freund and M. Scheffler: Defect complexes in Li-doped MgO. Physical Review B **91** (19), 195305 (2015).

Ringleb, F., Y. Fujimori, M.A. Brown, W. Kaden, F. Calaza, H. Kuhlenbeck, M. Sterrer and H.-J. Freund: The role of exposed silver in CO oxidation over MgO(0 0 1)/Ag(0 0 1) thin films. Catalysis Today **240, Pt. B**, 206-213 (2015).

Sauer, J. and H.-J. Freund: Models in Catalysis. Catalysis Letters **145** (1), 109-125 (2015).

Schauermann, S. and H.-J. Freund: Model Approach In Heterogeneous Catalysis: Kinetics and Thermodynamics of Surface Reactions. Accounts of Chemical Research, in press.

Schöllkopf, W., S. Gewinner, H. Junkes, A. Paarmann, G. von Helden, H. Bluem and A.M.M. Todd: The new IR and THz FEL facility at the Fritz Haber Institute in Berlin. In: Proceedings of Advances in X-ray Free-Electron Lasers Instrumentation III. (Ed.) S.G. Biedron. (Proceedings of the SPIE, Vol. 9512). SPIE, Bellingham, WA, 95121L (2015).

Stacchiola, D., M. Sterrer, S.D. Senanayake and P. Liu: Oxides in Catalysis. Catalysis Today **240, Pt. B**, 183-183 (2015).

Stiehler, C., F. Calaza, W.-D. Schneider, N. Nilius and H.-J. Freund: Molecular Adsorption Changes the Quantum Structure of Oxide-Supported Gold Nanoparticles: Chemisorption versus Physisorption. Physical Review Letters **115** (3), 036804 (2015).

Stuckenholz, S., C. Büchner, M. Heyde and H.-J. Freund: MgO on Mo(001): Local Work Function Measurements above Pristine Terrace and Line Defect Sites. The Journal of Physical Chemistry C **119** (22), 12283-12290 (2015).

Yang, B., S.K. Shaikhutdinov and H.-J. Freund: Ultrathin silicatene/silicon-carbide hybrid film on a metal substrate. Surface Science **632**, 9-13 (2015).

Zhang, K., S.K. Shaikhutdinov and H.-J. Freund: Does the Surface Structure of Oxide Affect the Strong Metal-Support Interaction with Platinum? Platinum on Fe_3O_4(001) vs Fe_3O_4(111). ChemCatChem, in press, DOI: 10.1002/cctc.201500328.

Zhao, H., S.T. Oyama, H.-J. Freund, R. Włodarczyk and M. Sierka: Nature of active sites in Ni_2P hydrotreating catalysts as probed by iron substitution. Applied Catalysis B **164**, 204-216 (2015).

Zhao, X., X. Shao, Y. Fujimori, S. Bhattacharya, L.M. Ghiringhelli, H.-J. Freund, M. Sterrer, N. Nilius and S.V. Levchenko: Formation of Water Chains on CaO(001): What Drives the 1D Growth? The Journal of Physical Chemistry Letters **6** (7), 1204-1208 (2015).

Doctoral Thesis

Emmez, E.: Adsorption on Metal-Supported Silicate Films: Surface and Sub-Surface Chemistry. Freie Universität Berlin 2015.

Fujimori, Y.: Interaction of Surface Hydroxyls with Supported Metal Particles: A Combined Vibrational and Electron Spectroscopic Investigation of Au and Pd on MgO(001) Model Surfaces. Freie Universität Berlin 2015.

Pascua, L.: Exploring the Luminescence Characteristics of Zinc Oxide Thin Films: The Role of Defects, Impurities and Metal Ad-Particles. Freie Universität Berlin 2015.

Stiehler, C.: The Impact of Molecular Adsorption on the Quantized Electronic Structure of Oxide-Supported Nanoparticles: A Model System for Heterogeneous Catalysis. Freie Universität Berlin 2015.

Master's Thesis

Ohle, C.: Systementwurf eines Kfz-Diagnosesystems auf Telematik-Hardware. Beuth Hochschule für Technik Berlin 2015.

4. Invited Talks of the Members of the Department of Chemical Physics

Christin Büchner

Feb 2014	17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany *The Atomic Structure of 2D Glass*
Sep 2014	Seminar, Department of Physics and Technology (AG Bodil Holst), University of Bergen, Bergen, Norway *The Structure of 2D Glass*
Nov 2014	AVS 61st International Symposium and Exhibition, American Vacuum Society, Baltimore, MD, USA *The Structure of 2D Glass*
Jan 2015	Seminar, Department of Chemistry (AG Klaus Rademann), Humboldt-Universität zu Berlin, Berlin, Germany *A Novel 2D Material - Structure and Properties of a Silica Bilayer*

Kristen Burson

Apr 2015	Seminar, Center for Nanoscale Science and Technology (CNST), National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA *Crystalline and Amorphous Silica - A New 2D Material Class*
Sep 2015	EMN Spain Meeting, Energy Materials Nanotechnology, San Sebastian, Spain *Resolving 2D Amorphous Silica Films by Scanning Probe Microscopy*

Florencia Calaza

Dec 2013	Seminar, Institute for the Technical Development of Chemical Industry (INTEC), Universidad Nacional del Litoral (UNL), Santa Fe, Argentina *Interaction of Glycerol on Pd(111) as a Model Metal Catalyst*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Carbon Dioxide Activation and Reaction Induced by Electron-Transfer at an Oxide-Metal Interface*
Aug 2015	Seminar, Institute of Industrial Science, The University of Tokyo, Tokyo, Japan *Surface Science Studies of Model Heterogeneous Catalytic Systems for Energy Conversion from Renewable Sources*

Petr Dementyev

May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Direct Chemisorption Energetics on Monocrystalline Oxides: A D_2O/Fe_3O_4 Case Study*

Emre Emmez

Jun 2014	Interdisciplinary Nanoscience Center, Aarhus University, Aarhus, Denmark *Adsorption on Metal-Supported Sheet-Like Silica Films: Surface and "Sub-Surface" Chemistry*

Hans-Joachim Freund

Nov 2013	Lecture, Institute of Chemistry, University of Szeged, Szeged, Hungary *Model Catalyst Design: A Material Science Perspective at the Atomic Level*

Dec 2013	9th International Symposium on Atomic Level Characterizations for New Materials and Devices ’13 (ALC ’13), Kona, HI, USA *Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-Dimensional Zeolites*
Jan 2014	Cardiff Catalysis Institute’s Annual Conference, Cardiff, UK *Ultra-Thin Oxide Films as Designable Model Catalysts*
Jan 2014	Festkolloquium, 60. Geburtstag von Prof. Dr. Dick, Universität Regensburg, Regensburg, Germany *Thin Oxide Films and the “Physics” of Catalysis: The Expected and the Unexpected*
Jan 2014	Seminar, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, USA *Model Catalyst Studies: From Supports to Supported Nanoparticles*
Mar 2014	47. Jahrestreffen Deutscher Katalytiker, Weimar, Germany *Model Catalyst Design: A Materials Science Perspective at the Atomic Level*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Symposium in Honor of Prof. Ted Oyama, Dallas, TX, USA *From Supported Nanoparticles on Thin Oxide Films to Thin Glass and Thin Zeolites*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Symposium on Clusters in Catalysis, Dallas, TX, USA *Metal and Oxide Nanoparticles on Thin Oxide Film Supports*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Symposium on Surface and Catalytic Reaction for Energy Efficiency, Dallas, TX, USA *Influence of Buried Dopants on Surface Chemistry*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Symposium on Thermodynamics, Reactivity, and Spectroscopy of the Heavy Elements, Dallas, TX, USA *Structure and Spectroscopy of Clean and Modified* $CeO_2(111)$ *Surfaces*
Mar 2014	The Richard B. Bernstein Lectures, Department of Chemistry, University of Wisconsin-Madison, Chicago, IL, USA *Model Systems for Heterogeneous Catalysts at the Atomic Level*
Mar 2014	The Richard B. Bernstein Lectures, Department of Chemistry, University of Wisconsin-Madison, Chicago, IL, USA *Thin Oxide Films and the “Physics” of Catalysis*
Apr 2014	Colloquium, Alberto Luiz Coimbra Institute – Graduate School and Research in Engineering (COPPE), Federal University of Rio de Janeiro (UFRJ), Rio de Janeiro, Brazil *Thin Oxide Films and the “Physics” of Catalysis*
Apr 2014	Colloquium, Brazilian Center for Research in Physics (CBPF), Rio de Janeiro, Brazil *Model Systems in Heterogeneous Catalysis at the Atomic Level*

Apr 2014	Lecture, Brazilian Center for Research in Physics (CBPF), Rio de Janeiro, Brazil *Spectroscopic Techniques in Surface Science*
May 2014	113th General Assembly of the German Bunsen Society for Physical Chemistry, Hamburg, Germany *A Fresh Look at an Old Nano-Technology: Catalysis*
May 2014	Centennial Shell Catalysis Conference 2014, Amsterdam, The Netherlands *Model Catalyst Design: An Approach at the Atomic Level*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Current Topics and Future Directions of CP Department*
May 2014	Symposium “Functional Interfaces in Catalysis and Nanotechnology”, Institut de Science et d’Ingénierie Supramoléculaires (ISIS), Strasbourg, France *Model Systems for Heterogeneous Catalysts at the Atomic Level*
Aug 2014	The 17th International Symposium on Silicon Chemistry (ISOS XVII), Berlin, Germany *Two Dimensional Silica: From Crystal to Glass*
Sep 2014	13th European Vacuum Conference, Aveiro, Portugal *Silica Thin Films: From Crystal to Glass in Two Dimensions*
Sep 2014	30th European Conference on Surface Science (ECOSS-30), Antalya, Turkey *Thin Oxide Films and the “Physics” of Catalysis*
Oct 2014	25th Anniversary of the Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands *Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level*
Oct 2014	CRC-SU Joint International Symposium on Chemical Theory for Complex Systems, Catalysis Research Center, Hokkaido University and Stockholm University, Stockholm, Sweden *Model Catalyst Design: A Material Science Perspective at the Atomic Level*
Oct 2014	Inaugural Lecture, Chemical Section, Hungarian Academy of Sciences, Budapest, Hungary *Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-Dimensional Zeolites*
Nov 2014	Frontiers in Surface and Materials Science: Theory and Practice, Symposium in Honor of the 60th Birthday of Francesc Illas and Gianfranco Pacchioni, Barcelona, Spain *Model Catalysts: Almost 20 Years of Fruitful Exchange between Theory and Experiment*
Nov 2014	Nanoscience Days 2014 (NSDAYS 2014), University of Jyväskylä, Jyväskylä, Finland *Thin Oxide Films and the “Physics” of Catalysis*

Jan 2015	3rd International Symposium on Chemistry for Energy Conversion and Storage (ChemEner2015), Berlin, Germany *Model Systems in Catalysis for Energy Economy*
Feb 2015	10. LeLa-Jahrestagung “MINT in Schülerlaboren”, Berlin, Germany *Modellstudien an Heterogen-Katalysator-Systemen auf atomarem Niveau*
Mar 2015	249th ACS National Meeting and Exposition, American Chemical Society, A Symposium in Honor of Donald Truhlar, Denver, CO, USA *Silica Thin Films: From Crystals to Glass in Two Dimensions*
Mar 2015	249th ACS National Meeting and Exposition, American Chemical Society, Symposium on Surface Chemistry and Catalysis on Oxides, Denver, CO, USA *Model Catalyst Design: A Material Science Perspective at the Atomic Level*
Mar 2015	Interdisciplinary Surface Science Conference (ISSC-20), Birmingham, UK *Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-Dimensional Zeolites*
Apr 2015	CECAM Workshop, Emergent Structural and Electronic Phenomena at Interfaces of Nanoscale Oxides, Lausanne, Switzerland *Model Catalyst Support Design: Oxide Surfaces at the Atomic Level*
May 2015	International SFB FOXSI Symposium, Functional Oxide Surfaces and Interfaces, Vienna, Austria *Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level*
Jun 2015	24th North American Meeting (NAM) of the Catalysis Society, Pittsburgh, PA, USA *Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level*
Jul 2015	Workshop, The Theory and Practice of Catalysis, Telluride Science Research Center, Telluride, CO, USA *Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level*
Aug 2015	250th ACS National Meeting and Exposition, American Chemical Society, Symposium “Advances in Ceria Based Catalysis: Structural, Electronic and Chemical Properties Tailored for Chemical Conversion”, Boston, MA, USA *Structure and Spectroscopy of Clean and Modified Ceria Surfaces*
Aug 2015	250th ACS National Meeting and Exposition, American Chemical Society, Symposium “Catalysis by Mixed Oxides”, Boston, MA, USA *Structure-Reactivity Relationship in Mixed Metal Oxides*
Aug 2015	EuropaCat-XII “Catalysis: Balancing the use of fossil and renewable resources”, Kazan, Russia *Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level*
Aug 2015	UniCat / CCSS Joint Scientific Meeting, Evanston, IL, USA *Metal-Insulator-Metal (MIM) Structures for CO_2 Activation*
Sep 2015	Workshop on Layered Materials, Trest, Czech Republic *Two Dimensional Silica: From Crystal to Glass*

Yuichi Fujimori

Jul 2015	RIKEN Seminar, Wako, Japan *Electrochemistry at Water/Oxide Interfaces*

Francesca Genuzio

Sep 2015	Seminar, DSM/IRAMIS/SPCSI/LCSI (Laboratoire de Chimie des Surfaces et Interfaces), Gif-sur-Yvette, France *Spectro-Microscopic Characterization of Thin Fe-Oxide Films: Interconversion and Effects of Metal (Fe-Pt) Deposition*

Markus Heyde

Jan 2014	GDCh-Kolloquium und GDCh-JungChemikerForum (JCF), Gesellschaft Deutscher Chemiker, Ulm University, Ulm, Germany *Die Struktur von 2D-Glas*
Sep 2014	Workshop, Structure Formation at Interfaces and Surfaces, University of Münster, Münster, Germany *The Structure of Glass*
Sep 2015	PNCS XIV, 14th International Conference on the Physics of Non-Crystalline Solids, Niagara Falls, NY, USA *The Structure of 2D Glass*

Francisco Ivars Barcelo

Sep 2015	Seminar, Universitat de València, Valencia, Spain *Reactions on Model Surfaces Studied by Molecular-Beam/Surface-Spectroscopy Apparatus*

Heinz Junkes

Jun 2014	Sino-German FEL Symposium "FELiChEM visits FHI-FEL", Fritz Haber Institute, Berlin, Germany *The Epics Control System at FHI FEL*
Mar 2015	11. IT-Verantwortlichen-Treffen, Berlin, Germany *Quo Vadis - Wissenschaftliche Datenverarbeitung*
May 2015	EPICS Collaboration Meeting, Experimental Physics and Industrial Control System, Spring 2015, East Lansing, MI, USA *Adding Site-Specific Laser-Shot-Numbers to Timestamp*
May 2015	EPICS Collaboration Meeting, Experimental Physics and Industrial Control System, Spring 2015, East Lansing, MI, USA *Driver/Device Support sis3316/ip*

Hagen Klemm

Oct 2014	RDH Doctoral Seminar, Institut für Energietechnik, Technische Universität Berlin, Berlin, Germany *Spectro-Microscopy Investigation of Silica Thin Films on Ru(0001)*

Helmut Kuhlenbeck

Aug 2015	CRC Summer School, SFB 1109, Erkner, Germany *Ordered Oxide Layers for Model Catalysis Studies - Preparation, Characterization and Examples*

Helder Marchetto

Jul 2014	Seminar, University of Dayton, Dayton, OH, USA *Introduction to Low Energy Electron Microscopy and Surface Science Applications*
Jul 2014	Seminar, Wright-Patterson Air Force Research Laboratory, Fairborn, OH, USA *Introduction to Low Energy Electron Microscopy and Surface Science Applications*
Jul 2015	Seminar, Diamond Light Source Ltd, Didcot, UK *Advances in Photoemission Electron Microscopy*

Dietrich Menzel

Oct 2013	Colloquium, Lawrence Berkeley National Laboratory, Berkeley, CA, USA *Ultrafast Charge Transfer at Graphene Monolayers on Differently Coupled Substrates*
Jun 2014	European Workshop on Epitaxial Graphene and 2D Materials (EWEG/2D), Primosten, Croatia *Ultrafast Charge Transfer to Graphene Monolayers: Substrate Coupling, Local Density of States, Final State Dimensionality and Two-Step Processes*
Oct 2014	Colloquium, Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA, USA *Electronically Induced Surface Processes, from MGR to MNP*
Oct 2014	Dynamics, Interactions and Electronic Transitions at Surfaces (DIET-14), Pacific Grove, CA, USA *From MGR to MNP: My Half Century of DIET*
Sep 2015	Workshop of the Chemical Physics Department of the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Schloss Ringberg, Kreuth, Germany *Highly Stable Intercalation and Encapsulation of Rare Gas Atoms under Monolayers of Graphene and BN*

Leandro Pascua

Apr 2015	Seminar, Department of Physics (AG Katharina J. Franke), Freie Universität Berlin, Berlin, Germany *Exploring the Luminescence Characteristics of ZnO Thin Films with STM: The Role of Defects, Impurities and Metal Ad-Particles*

Gina Peschel

Dec 2014	Seminar, Department of Physics (AG Katharina J. Franke), Freie Universität Berlin, Berlin, Germany *Spectro-Microscopy on Silica and Iron Doped Silica on Ru(0001)*

Thomas Risse

Apr 2014	Workshop, EPR-Solar, Berlin, Germany *Chemical Activation on Well-Defined Oxide Surfaces*

Sep 2014	IXth Conference of European Federation of EPR Societies (EFEPR 2014), Marseilles, France *Paramagnetic Centers at Single Crystalline Oxide Surfaces: An EPR Perspective*
Oct 2014	Annual Meeting, New Frontiers in Sensitivity for EPR Spectroscopy: From Biological Cells to Nano Materials (SPP 1601), Schwerpunktprogramm der DFG, Schwerte, Germany *Site-Directed Spin Labeling of Sulfite Oxidase Using Non-Natural Amino Acids*

Swetlana Schauermann

Mar 2014	DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Dresden, Germany *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
May 2014	Colloquium, Young Faculty Association, Ruhr-Universität Bochum, Bochum, Germany *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
Jun 2014	International Workshop, Reactivity and Catalysis on Metallic Nanoclusters, Helsinki, Finland *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
Jun 2014	Seminar, Nanoscience Center (NSC), University of Jyväskylä, Jyväskylä, Finland *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
Feb 2015	Physikalisch-chemisches Kolloquium, University of Oldenburg, Oldenburg, Germany *Selective Transformations of Multi-Unsaturated Hydrocarbons over Pd: New Mechanistic Insights*
Apr 2015	Meeting, From the witches cauldrons in materials science, Center of Interface Science (CIS), Goslar, Germany *Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics*
Aug 2015	Dynamics at Surfaces, Gordon Research Conference (GRC), Newport, RI, USA *Selective Transformations of Multi-Unsaturated Hydrocarbons over Pd: New Mechanistic Insights*

Thomas Schmidt

Nov 2013	Workshop, X-Ray and Electron Beams for Materials Characterization, DFG-Graduiertenkolleg “Funktionalisierung von Halbleitern”, Philipps-Universität, Marburg, Germany *Leem/Peem Basics*
Nov 2013	Workshop, X-Ray and Electron Beams for Materials Characterization, DFG-Graduiertenkolleg “Funktionalisierung von Halbleitern”, Philipps-Universität, Marburg, Germany *Leem/Peem Studies on Thin Film Growth*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Spectromicroscopic Investigations of Thin Oxide Films*
Feb 2015	Seminar, MAX IV Laboratory, Lund, Sweden *Iron Oxide Film Growth Studied by Aberration-Corrected Spectromicroscopy*

Wolf-Dieter Schneider

Dec 2013	9th International Symposium on Atomic Level Characterizations for New Materials and Devices ’13 (ALC ’13), Kona, HI, USA *Transport Properties and Electronic Structure of Individual Metallic Nanoislands on Dielectric Supports: A Local View*
Jan 2014	Evolution of Surface Systems and Techniques - 30 Years of SAOG, Swiss Working Group of Surface and Interface Science, Fribourg, Switzerland *Spectroscopic Manifestations of Low-Dimensional Physics: A Local View*
Jan 2014	Symposium on Surface and Nano Science 2014 (SSNS’14), Furano, Japan *Coulomb Charge Rings and Quantum-Size Effects in Metal Islands on Dielectric Supports*
Mar 2014	27th Symposium on Surface Science 2014 (3S'14), St. Christoph am Arlberg, Austria *Coulomb Charge Rings and Quantum-Size Effects in Metal Islands on Dielectric Supports*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Symposium on Supramolecular Self-Assembly at Surfaces, Dallas, TX, USA *Chiral Supramolecular Self-Assembly in Two Dimensions*
Jun 2014	International Summer School on Physics at the Nanoscale, Devet Skal, Czech Republic *Spectroscopic Manifestations of Low-Dimensional Physics: A Local View (Two Lectures)*
Jul 2014	International Workshop on Nanomaterials and Nanodevices, Beijing, China *Electron Quantization Effects in Pristine and Isophorone-Modified Gold Nano-Islands on MgO Thin Films*
Jul 2014	International Workshop on Nanomaterials and Nanodevices, Wuhan, China *Luminescence Experiments with the Scanning Tunneling Microscope: The Quest for Molecular Resolution*

Sep 2014	Workshop of the Chemical Physics Department of the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Schloss Ringberg, Kreuth, Germany *Chiral Supramolecular Self-Assembly in Two Dimensions*
Oct 2014	Laureate Lecture, Rudolf-Jaeckel-Prize 2014, 8th Symposium on Vacuum Based Science and Technology, Kaiserslautern, Germany *Spectroscopic Manifestations of Low-Dimensional Physics: A Small World*
Jan 2015	Symposium on Surface and Nano Science 2015 (SSNS'15), Furano, Japan *Phonon-Mediated Electron Transport through CaO Thin Films*
Mar 2015	28th Symposium on Surface Science 2015 (3S'15), Les Arcs, France *Phonon-Mediated Electron Transport through CaO Thin Films*
Apr 2015	Symposium in Honor of Prof. Menzel´s 80th Birthday, Munich, Germany *Phonon-Mediated Electron Transport through CaO Thin Films*
May 2015	Laudatio and Colloquium in honour of Prof. Laubschats´s 60th birthday, Dresden, Germany *Spectroscopic Manifestations of Low-Dimensional Physics: A Small World*
Jun 2015	15th Swiss Discussion Meeting "Molecules on Surfaces" (MOLCH 15), Basel, Switzerland *Chiral Supramolecular Self-Assembly in Two Dimensions*
Sep 2015	Workshop of the Chemical Physics Department of the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Schloss Ringberg, Kreuth, Germany *Surface Phonon-Polariton Mediated Electron Transport through CaO Thin Films*

Shamil Shaikhutdinov

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Structure and Reactivity of Metal-Supported Ultrathin Oxide Films*
Nov 2014	7th International Symposium on Surface Science (ISSS-7), Matsue, Japan *Ultrathin Silicate Films on Metals*
May 2015	Seminar, Department of Materials Science, University of Milano-Bicocca, Milano, Italy *Ultrathin Silicate Films on Metals*

Martin Sterrer

Jan 2014	9th International Workshop on Oxide Surfaces (IWOX-IX), Tahoe City, CA, USA *Towards Realistic Models of Oxide-Supported Metal Catalysts*
Feb 2014	29th Workshop on Novel Materials and Superconductors, Obertraun, Austria *Towards Realistic Surface Science Models of Heterogeneous Catalysts*
Mar 2014	Seminar, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany *Surface Science Models of Heterogeneous Catalysts – Probing Metal-Support Interaction with XPS and Auger Parameter Analysis*
Jun 2014	Catalysis, Gordon Research Conference (GRC), New London, NH, USA *Surface Science and Catalyst Preparation - From Science to Art?*

Nov 2014	2014 IBS Research Conference, Korean Advanced Institute of Science and Technology, Daejeon, South Korea *Effects of Oxide-Support Hydroxylation on the Properties of Metal Nanoparticles*
Nov 2014	International Conference on Electronic Materials and Nanotechnology for Green Environment (ENGE 2014), Jeju, South Korea *Towards Realistic Models of Oxide-Supported Metal Catalysts*
Jan 2015	Seminar, Institute of Physical and Theoretical Chemistry, University of Graz, Graz, Austria *Preparation of Oxide-Supported Metal Catalysts – A Surface Science Approach*
Jan 2015	TOTAL Catalysis Club meeting, Brussels, Belgium *Surface Science and Catalyst Preparation*
Feb 2015	Debye Colloquium, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands *Preparation of Oxide-Supported Metal Catalysts - A Surface Science Approach*
Mar 2015	Nano and Photonics, 6th European Conference on Applications of Femtosecond Lasers in Materials Science and Photonics Austria, Mautendorf/Salzburg, Austria *Models of Oxide-Supported Metal Catalysts*
Mar 2015	Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria *Supported Oxide Thin Films in Fundamental Catalysis Research - Interaction with Water and Catalyst Preparation*
May 2015	Joint SFB FOXSI seminar, Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria *From UHV into the Liquid: Surface Science Model Studies at Increasing Chemical Complexity*
May 2015	Seminar, Department of Materials Science and Physics, University of Salzburg, Salzburg, Austria *Interaction of Water with Thin Film Oxide Surfaces*

Christian Stiehler

Jan 2014	Seminar, Ultrafast Spectroscopy and Surface Dynamics, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *The Impact of Molecular Adsorption on the Quantized Electronic Structure of Planar Au Clusters on MgO Thin Films*
Nov 2014	Seminar, Department of Experimental Physics, Brazilian Center for Research in Physics (CBPF), Rio de Janeiro, Brazil *The Impact of Molecular Adsorption on the Quantized Electronic Structure of Planar Au Clusters on MgO Thin Films*
Nov 2014	Seminar, Surface Science, Department of Applied Physics (AG Abner de Siervo), University of Campinas (UNICAMP), Campinas, Brazil *The Impact of Molecular Adsorption on the Quantized Electronic Structure of Planar Au Clusters on MgO Thin Films*

Apr 2015	Seminar, Ultrafast Spectroscopy and Surface Dynamics, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *The Impact of Molecular Adsorption on the Quantized Electronic Structure of Oxide-Supported Nanoparticles*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *The Impact of Molecular Adsorption on the Quantized Electronic Structure of Oxide-Supported Nanoparticles*

Department of Molecular Physics **Former Director: Gerard Meijer**
Interim Director: Martin Wolf

Staff scientists:

Bretislav Friedrich
Gert von Helden

Guest scientists, staying for at least six months:

Xiaowei Song	*AvH Fellow*
Doo-Sik Ahn	*AvH Fellow*
Jongcheol Seo	

Guest scientists (temporary), paid from external funds:

Ad van der Avoird	*AvH Awardee*	University of Nijmegen, The Netherlands
Mike Bowers	*AvH Awardee*	University of California, Santa Barbara, CA, USA
Phil Bunker		National Research Council of Canada, Ottawa, Canada
Mike Duncan	*AvH Awardee*	University of Georgia, Athens, GA, USA
Mark Johnson	*AvH Awardee*	Yale University, New Haven, USA
Boris Sartakov		Russia Academy of Science, Moscow, Russia
Bum Suk Zhao		Ulsan National Institute of Science and Technology, Ulsan, South Korea

Graduate students:	10	(4 from external funds)
Master students:	5	
Trainees:	4	
Technicians:	7	

Guest group leaders:

Knut Asmis	Universität Leipzig
André Fielicke	Technische Universität Berlin
Kevin Pagel	Freie Universität Berlin
Gabriele Santambrogio *until 4/2015*	University of Florence

Free-Electron Laser Facility:

Head: Wieland Schöllkopf 1 Technician

Recent Developments at the Department of Molecular Physics

Interim director: Martin Wolf

1. General Remarks

Since the last Fachbeirat in February 2014, the Department of Molecular Physics underwent significant restructuring. At present, Martin Wolf takes the role as the acting director and the decision about the new director is not yet finalized. The current status of the search process is described in the report of the executive director.

Before the departure of *Gerard Meijer* in the Fall of 2012, the department pursued two main research areas: (i) Investigations of the structure and dynamics of (bio)molecules, clusters, and cluster-adsorbate complexes in the gas phase and (ii) "Cold molecules" aimed at developing experimental techniques to achieve full control of internal as well as translational degrees of freedom of neutral molecules in order to facilitate the investigation of their properties and interactions. As outlined further below, the experimental work on "cold molecules" has been phased out. However, research in the first area (i) continues at a high level, including several highlights which are described in the research section and which also will be presented at the poster session.

At the time of Gerard Meijer's departure, four research group leaders of the molecular physics department (Knut Asmis, Bretislav Friedrich, Gert von Helden and Nicolas Vanhaecke) had permanent contracts with the FHI, while two group leaders (Andre Fielicke and Gabriele Santambrogio) were temporarily employed.

- *André Fielicke* moved already in January 2013 to the Technical University Berlin with a DFG research grant (“Eigene Stelle”). However, part of his research activities, in particular those using the FHI FEL, remain at the FHI.
- *Nicolas Vanhaecke* left the FHI in February 2014 for a position at the European Patent Office in The Hague. The experiment empoying Zeeman-forces to control molecular beams that was under construction in his group moved together with a Postdoc (*Dongdong Zhang*) to the University of Basel. The graduate student under his supervision defended his PhD thesis in the Spring of 2015.
- *Knut Asmis* accepted a call from the University of Leipzig for a W3-Chair in Physical Chemistry and started his new position in March 2014. A part of his group's activity that is funded by the DFG Collaborative Research Center 1109, “Understanding of Metal Oxide/Water Systems at the Molecular Scale”, remains at the FHI (project D1 Asmis).
- *Gabriele Santambrogio* assumed the position of a research group leader (Primo Ricercatore) at the Institute for Optics of the Italian Research Council (CNR) in Florence in January 2014. However, he continued to lead the ERC MolChip project until the end of

its funding period in January 2015. In the meantime, the experimental setup has been transferred to Florence.

With the departure of Nicolas Vanhaecke and Gabriele Santambrogio, the experimental work on cold molecules at the FHI has ended. The transition period was not easy; especially for the individual researchers involved in the "cold molecules" experiments. However, care has been taken to ensure that all those affected could obtain the support needed for the completion of their projects. All postdocs on the corresponding projects have found positions elsewhere. At the time of the last Fachbeirat, two graduate students were active in experiments on cold molecules. One of them very successfully defended his thesis early 2015. The other graduate student who started much later is presently writing up his thesis.

Presently, the department has two active groups that are headed by permanent FHI staff members (Bretislav Friedrich and Gert von Helden). Both groups are highly successful and have overlap with the research in other departments of the FHI and/or at Berlin-area universities. In addition, there are three guest groups affiliated with the FHI FEL. Furthermore, Wieland Schöllkopf, the head of the FHI FEL facility, runs a successful atom-optics experiment in the Molecular Physics department. Below, their research activities, will be briefly described in an overview, followed by detailed reports. In addition, a report on the now finished MolChip project is presented.

2. Research at the Department of Molecular Physics

2.1 Overview

The activities of the FHI based groups are described in section 2.2. The research group of *Bretislav Friedrich* studies interactions of molecules with and in fields, focusing on the manipulation of molecular rotation, quantum computing, and Stark spectroscopy. As a highlight (see Poster MP 2), considerations on how to perform quantum computing with ultracold polar paramagnetic molecules are presented. In addition, Bretislav Friedrich has continued his exploits in the history of science, in particular of quantum mechanics and has co-organized an international symposium on *chemical warfare,* prompted by the centenary of the infamous chlorine cloud attack at Ypres. The research group led by *Gert von Helden* investigates biological molecules in the gas phase. Since summer 2012, Gert von Helden also acts as the "administrative general manager" of the FHI for half of his working time. Despite his significant workload in administration, a large number of successful research projects have been performed by his group, most of them exploiting the FHI FEL. Particularly interesting results are the first observation of beta sheet structures in gas-phase peptide aggregates (see poster MP 5) as well as Coulomb repulsion induced unzipping of helices in the gas phase. *Wieland Schöllkopf* heads experimental research on matter-wave optics with molecular beams and has been able to observe, for instance, quantum reflection and diffraction of weakly bound helium clusters from a reflection grating. Furthermore, Wieland Schöllkopf combined his diffraction method with the COLTRIMS reaction microscope of the group of Reinhard Dörner at Frankfurt University. This combined approach allowed for the first observation of the long-sought Efimov state of the helium trimer (see poster MP 6). *Gabriele Santambrogio* headed the "Molecules on a chip", now based is Florence. A final report on the activities at the FHI is given at the end of section 2.2 and presented in poster MP 8

Section 2.3 reports on the projects of the guest groups. The research focus of the research group of *Knut Asmis* is the structure, reactivity and dynamics of molecular ions and ionic clusters. Of the two cryogenic ion trap instruments of the Asmis group, one has been transferred to Leipzig and the other machine remains at the FHI, coupled to the FHI FEL. Among the most important results are vibrational spectra of microhydrated aluminum and iron oxide clusters (see poster MP 9). The research group of *André Fielicke* investigates strongly-bound metal clusters and their complexes with small chemisorbed molecules. A highlight are the spectroscopic investigations of strongly bound binary clusters (see poster MP 10). *Kevin Pagel* holds a Junior-Professor position at the FU Berlin and there is a formal collaboration between him and the group of Gert von Helden. His main interest is in carbohydrates and their analysis using ion mobility and IR spectroscopy as well as in peptide aggregates. Very recently, Kevin Pagel and his group developed methods for the separation of oligosaccharide and glycopeptide isomers (see poster MP 11).

2.2. Research Groups Based at the FHI

2.2.1 Interactions of Molecules with Fields (Bretislav Friedrich)

Over the reporting period 2013-2015, the research group carried out work on (i) Interactions of polar paramagnetic molecules with combined electric, magnetic and optical fields; (ii) Quantum computing with polar paramagnetic molecules. In addition, the research group embarked on two DFG-funded projects: (iii) Supersymmetry, entanglement, and dynamics of polar paramagnetic molecules subject to combined electric and magnetic fields (jointly with Burkhard Schmidt, Freie Universität Berlin); (iv) Configurations of van der Waals complexes controlled via London dispersion forces as revealed by means of Stark spectroscopy in He nanodroplets (jointly with Alkwin Slenczka, Universität Regensburg).

(i) Interactions with external electric, magnetic or optical fields provide the chief means to manipulate the rotational and translational motion of neutral gas-phase molecules. These interactions create directional states in which the molecular multipole moments become non-vanishing in the laboratory frame so that space-fixed fields can act upon them. Directional states are at the core of numerous applications in molecular physics, such as orientation/alignment of molecules, deflection and focusing of molecular translation, molecular trapping, attaining time-resolved photoelectron angular distributions, diffraction-from-within, separation of photodissociation products, deracemization, high-order harmonic generation and orbital imaging, quantum simulation and quantum computing.

Over the reporting period, we examined the eigenproperties of polar, paramagnetic, and polarizable linear molecules in congruent electric, magnetic, and nonresonant optical fields by numerical diagonalization of the corresponding Hamiltonian matrix. We found that the directionality of the molecular states which can be achieved with the triple-field combination supersedes – in its magnitude as well as controllability – that obtained by the double-field combinations or single fields, as studied previously. The present work expands on what the use of the triple-field combination would entail. The combination of an optical and a magnetic field creates a multitude of degenerate or quasi-degenerate states of opposite parity that can undergo a facile coupling by a superimposed (weak) electric field. This is the essence of the effects of the three congruent fields and the basis for their synergy. That one of the fields – the optical one – can be varied or switched on and off at time scales on the order of the rotational period would lend a manipulation technique based on the triple-field effects a degree of controllability that is needed for such applications as stereo-dynamical collisional studies or quantum computing. In our forthcoming work we will examine the non-adiabatic effects that are expected to arise when the optical field is varied at time scales shorter than the rotational period of the molecule. Also worthy of exploring is the dependence of the triple-field effects on the tilt angles among the three field vectors. Relevant to both is the topology of the eigenenergy surfaces spanned by the three interaction parameters that may result in conical intersections, another subject of our forthcoming study.

(ii) Arrays of trapped ultracold molecules represent a promising platform for implementing a universal quantum computer. In our work, we considered an array of polar paramagnetic molecules (exemplified by polar $^2\Sigma$ molecules) as qubits, entangled by the electric dipole-dipole interaction, and subject to various combinations of concurrent homogeneous and inhomogeneous electric and magnetic fields. We characterized the eigenstates of the array, including their mutually induced directionality, by evaluating their eigenproperties via numerical diagonalization of the appropriate Hamiltonian matrix, whose elements we found analytically. We also evaluated the concurrence of the states as a measure of their entanglement in the presence and absence of fields. A key feature of the system is that in the absence of fields, its states are all Bell states. Applying an inhomogeneous magnetic field disentangles these states and can be used to effect a Bell measurement, which is of consequence for superdense coding and quantum teleportation.

Our findings led us to propose two novel schemes for implementing an optically controlled CNOT gate operation: Scheme I comprises five steps, including an adiabatic switching of the magnetic field, while Scheme II consists of only a single step. The schemes will be further tested by invoking multi-target optimal control theory as a means of optimizing the initial-to-target transition probability via a controlling laser field and of evaluating the fidelity attainable for the schemes. Of key importance is the ability to resolve the transition frequencies involved in the optical control of the gate operations – in the face of broadening due to dipole-dipole coupling and the inhomogeneity in the electric and magnetic fields. We also demonstrate that the former dominates over the latter, thus setting the criteria for the feasibility of the schemes.

(iii) We applied the apparatus of supersymmetric quantum mechanics (SUSY QM) to analyze the problem of the quantum pendulum, i.e., that of a rigid rotor under a cosine potential and/or its variants. It belongs to prototypical problems in quantum mechanics and lurks behind numerous applications in molecular physics. A general solution of the eigenproblem relies on numerical diagonalization of a truncated infinite-dimensional Hamiltonian matrix. The matrix elements are a function of dimensionless parameters η and ζ that characterize, respectively, the strengths of the pendulum's orienting ($\propto \eta \cos\theta$) and aligning ($\propto \zeta \cos^2\theta$) interactions (where θ is a polar angle). For arbitrary non-zero values of the η and ζ parameters, there are no analytic, closed-form solutions to the pendular eigenproblem. We considered a full range of interaction strengths, which convert, jointly or separately, the spherical rotor in a state J into a hindered rotor or a quantum pendulum or a harmonic librator (angular harmonic oscillator) in a state $\tilde{\mathbf{J}}$,m, depending on the values of η and ζ. Following upon our previous studies of both planar and spherical pendula, we were concerned with the topology of the eigenenergy surfaces spanned by the interaction parameters η and ζ for all values of the projection quantum number m as well as with the supersymmetry of the eigenproblem as a means for identifying its analytic solutions – if any.

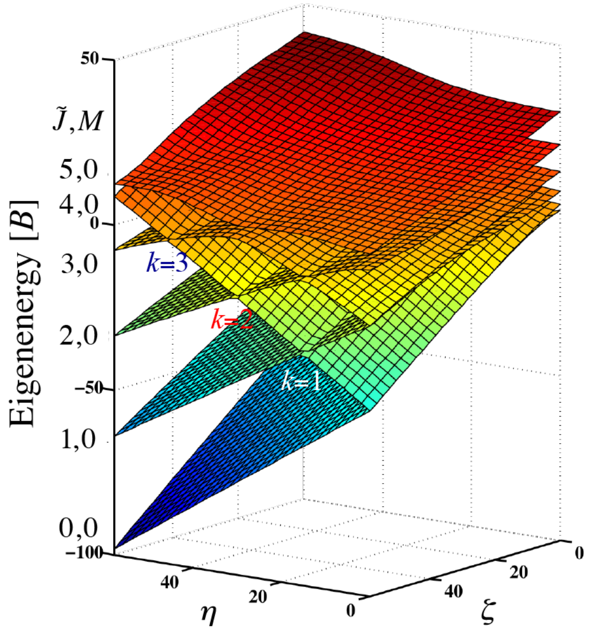


Figure 1: *Quantum pendulum's eigenenergy surfaces spanned by the orienting and aligning interaction parameters* η *and* ζ.

Topology. We found that the loci of all intersections that arise among the eigenenergy surfaces of the quantum pendulum are accurately rendered by a simple formula. Furthermore, since the equation for the loci is independent of the eigenstate, the energy levels exhibit a general pattern that only depends on the values of the topological index $k = \eta/(2\,\zeta^{1/2})$: for each k, there are k single states, followed, in ascending order, by all other states which are nearly doubly degenerate, see Figure 1. This energy-level pattern reflects the fact that above the local minimum of the pendulum potential, states can be bound by both the local and global minima, whereas below the local minimum states can only be bound by the global minimum. Since the energy difference between the global and local minima increases with k, the number of single states bound solely by the global minimum increases with k as well (in fact is equal to k). States bound by both the global and local minima that lie below the maximum of the potential occur as nearly degenerate doublets. All the intersections are avoided, as they only occur between opposite-parity levels coupled by the parity-mixing orienting interaction.

Supersymmetry. We have identified two sets of conditions (termed case 1 and case 2) under which SUSY QM can be applied to the pendular eigenproblem. In particular, these conditions imply a certain ratio of the interaction parameters η and ζ and, thereby, a certain value of the topological index k. This made it possible to identify each case with a particular topology: case 1 with $k = \mp m + 1$; case 2 with $k = 1$ for $m > 0$. In most cases SUSY QM enabled us to obtain analytic expressions for the ground-state wave functions. For one case, we were able to find the excited-state wave function as well. The free rotor has been identified as a subcase of case 1, one which possesses analytic solvability for all states.

We emphasize that the condition for analytic solvability as identified by SUSY coincides with the loci of the avoided eigensurface intersections, which only arise for the combined orienting and aligning interactions whose parameters η and ζ span the eigensurfaces. So far, no SUSY analytic solution has been found for either of these interactions alone. The origin of the connection between eigensurface topology and exact solvability will be the subject of a further investigation.

(iv) We study the structure of van der Waals complexes embedded in He nanodroplets by Stark spectroscopy. The cold environment of a He droplet is conducive to the formation of the complexes and simultaneously befitting for high-resolution spectroscopy. Moreover, the superfluid phase of the He droplet, unlike the solid phase of a matrix, affords a nearly free mobility of the dopant species embedded in the droplet. Since the dopant-to-dopant long-range attractive forces exceed the dopant-to-helium forces, the formation of a molecular complex inside the host system is warranted as soon as its constituents are loaded into the droplet. Compared with complex formation in a seeded supersonic expansion, the helium droplet serves to increase – by orders of magnitude – the effective collision/capture cross section and thus the probability of forming the complex. For each stoichiometry, different complex configurations, termed isomeric variants, can be formed. We identify the isomeric variants for a particular stoichiometry by investigating their dispersed emission spectra.

The configuration of each complex is reflected in its moment of inertia. Stark spectroscopy can render the moment of inertia with high sensitivity – and provide the body-fixed permanent dipole moment of the complex as a bonus.

One of the challenges of this approach is the separation of the field-induced components of the fluorescence signal that pertain to different clusters. This challenge was met recently in Alkwin Slenczka's laboratory at Regensburg for van der Waals complexes of Phthalocyanine (Pc) with a single water molecule, with the following preliminary results: (a) For moderate field strengths, of up to 20 kV/cm, the field effect observed for a Pc-H_2O complex consists of only tiny variations of the inhomogeneous line shape; (b) A preliminary procedure to extract the Stark signal was obtained by normalizing the Stark spectra by the field free spectra. In this way, the field-induced relative change of the signal could be extracted; (c) By making use of this technique, all of the Pc-H_2O clusters identified via the corresponding electronic origin could be measured individually. The theoretical analysis – including simulations – of the spectra is on the way in Bretislav Friedrich's group in Berlin.

2.2.2 Biological Molecules in the Gas Phase (Gert von Helden)

Investigating the structure and dynamics of biological molecules in the absence or controlled presence of solvent molecules can yield important information on their intrinsic structural preferences and can serve as calibration points for theoretical methods. Further, for species that are at home in hydrophobic environments with a low relative permittivity, the solvent-free vacuum can even be closer to its natural environment, compared to a polar (aqueous) solution.

IR spectroscopy has become a frequently used tool to characterize gas-phase peptides and proteins. In many experiments, ions are m/z selected, irradiated by intense and tunable IR light and fragmentation is monitored as a function of IR wavelength. Due to the dynamics of the multiple photon heating process, spectral broadening will occur. Further, the possible presence of different conformers can complicate the interpretation, as the resulting spectra represent the sum of the spectra of the individual components. To address those two complications, two novel setups have been constructed and coupled to the FHI FEL: (i) an ion mobility mass spectrometer combination that allows to separate different conformers and (ii) a helium droplet setup that allows for the measurement of mass/charge selected samples at 0.4 K.

The ion mobility experiments are performed in collaboration with Kevin Pagel (FU Berlin/ FHI) and Mike Bowers (UC Santa Barbara). Over the last two years several systems have been studied. A particular highlight is the ion mobility separation and further IR spectroscopic investigation of protomers (species that have the same atomic composition and structure, differ however on the specific site where protonation occurs) of the small organic molecule benzocaine (*JACS*, **137**, 4236, 2015). In another recent study, the structural changes that occur when peptides aggregate are investigated. Such structural transitions are important in biological processes when peptides or proteins aggregate, form β-sheet rich fibrils and cause diseases such as Parkinson or Alzheimer. While using standard techniques, only ensemble averages can be probed, ion mobility mass spectrometry allows for the investigation of very specific aggregates. Some results for aggregates of the pentapeptide YVEAL (Tyr-Val-Glu-Ala-Leu) are shown in figure 2 below. Shown in b) is a via ion mobility obtained arrival time distribution (ATD) of the triply protonated pentamer $(YVEAL)_5$-$3H^+$ (in short 5/3). Different conformers can have different sizes and more compact species drift faster through the instrument and arrive at an earlier time. Four distinct conformers can be obtained and from the drift time, their collision cross sections can be obtained. A plot of all cross section as a function of aggregate size is shown in a). The dashed line corresponds to spherical, isentropic growth and it can be clearly seen that many species deviate and have more extended structures. Shown in c) are IR spectra for the four 5/3 conformers as well as for one 5/2 conformer. From the shape of the Amide I band, it can be deduced that all conformers have β-sheet contents, which increases with increasing size (collision cross-section). The data shown represents the first spectroscopic identification of β-sheet structures in small peptide aggregates and we soon hope to extend our studies to real biological proteins, such as the Alzheimer Aβ42 protein.

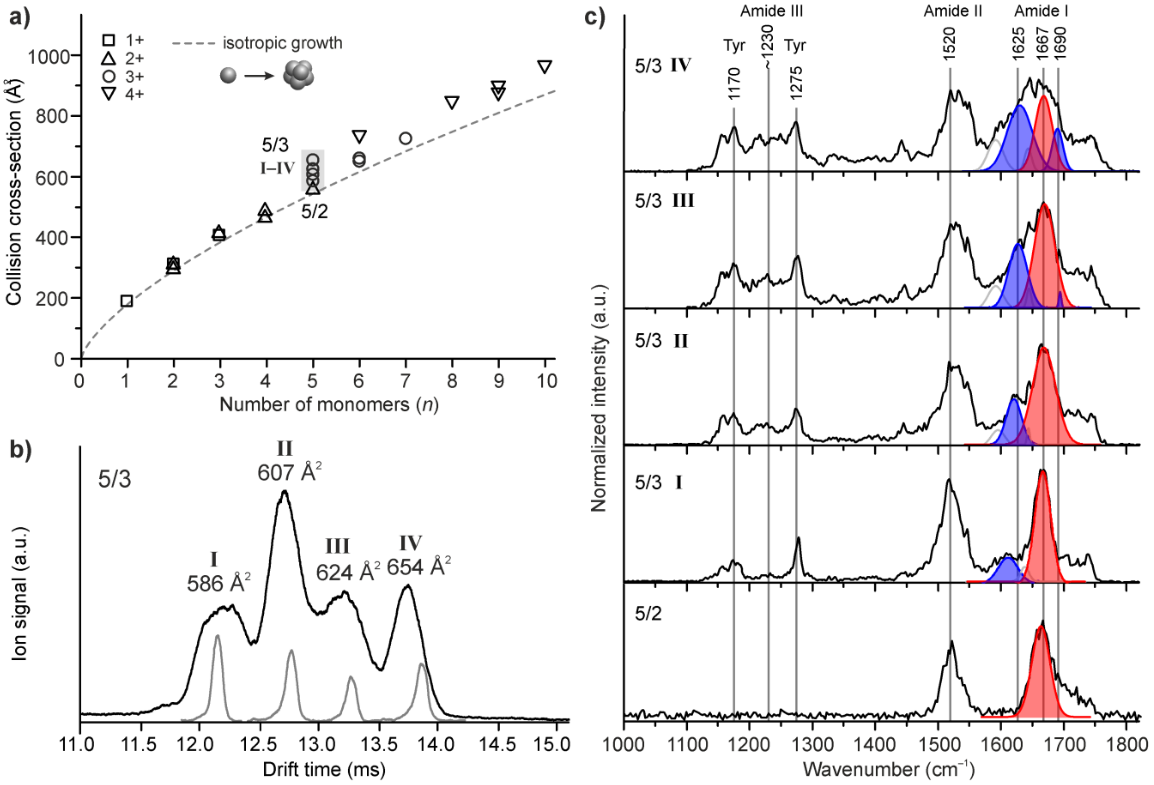


Figure 2: *a) Collision cross sections for oligomers of the peptide YVEAL and the corresponding arrival time distribution for the triply charged pentamer in b). Shown in c) and IR spectra of different conformers of the pentamer. The portion in red corresponds to helical or random structures, while the one in blue is indicative of β-sheet contents.*

In a different experiment, mass/charge selected peptides, proteins or other molecules can be incorporated in liquid helium droplets and investigated via IR spectroscopy at 0.37 K. In the figure 3 below, IR-spectra of Ubiquitin (76 amino acids) and Cytochrome C (104 amino acids) in helium droplets are shown as a function of charge state. With increasing charge state, one can observe the appearance of a new band, labeled Amide-IIa. Its intensity comes at the cost of the "standard" Amide II band (labeled Amide IIb). Their relative intensities are shown in c).

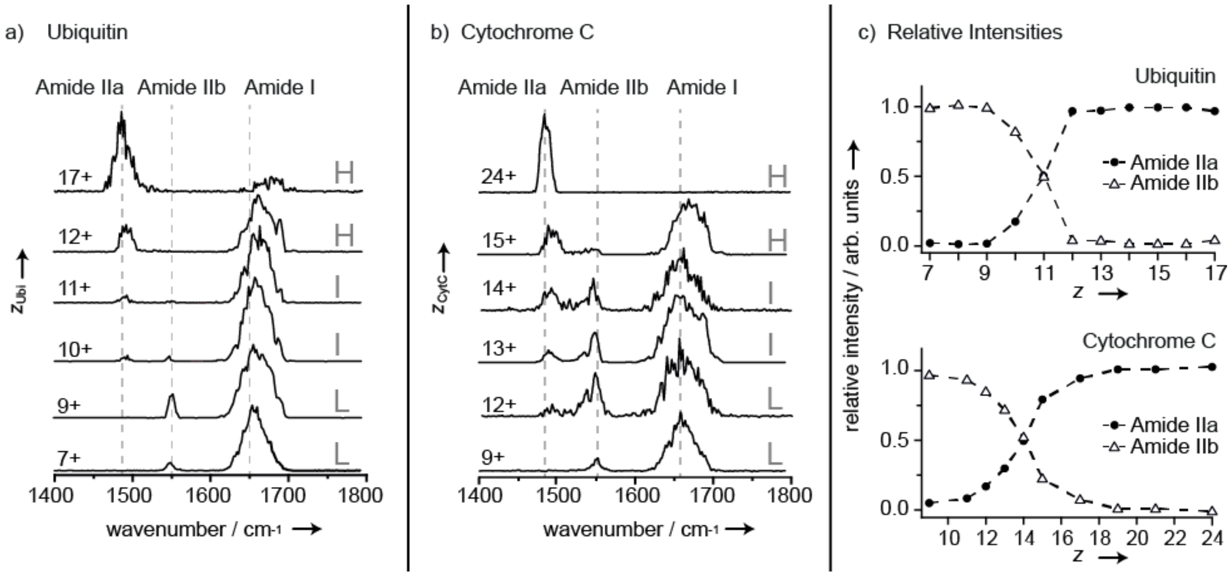


__Figure 3:__ IR spectra of Ubiquitin (a) and Cytochrome C (b) as a function of charge state. The band appearing for higher charge states (labeled Amide IIa) is a marker for the coulomb repulsion induced unzipping of the protein. The relative intensities of helical vs. unzipped conformation is shown in c).

Extensive modeling shows that the two peaks Amide IIa and IIb can be attributed to different structures of the proteins. For proteins in the gas phase, attractive forces such as hydrogen bonding as well as Van der Waals interactions tend to drive a protein into a compact shape. This is counteracted by repulsive coulomb forces, which want to maximize the distances between charges. The here observed changes in spectra correspond to a transition of predominantly helical structures with an strong internal hydrogen bonding network to extended, single strand β-sheet structures which exhibit only little internal hydrogen bonding. Those transitions occur at different charge states, as the coulomb repulsion energy is a function of the size of the molecule.

In a further very promising experiment that is conduced in collaboration with Kevin Pagel (FU Berlin) and Peter H. Seeberger (MPI for Colloids and Interfaces), carbohydrates inside liquid helium droplets are investigated. For six at first glance very similar synthetic trisaccharide-isomers that only differ in a very subtle way in the composition, connectivity or configuration of one building block, highly structured spectra could be recorded. Much to our surprise, those spectra are markedly different from carbohydrate to carbohydrate. Extending the scope to monosaccharides, disaccharides and more complex systems may lead to the identification of characteristic bands or patterns that allow to deduce structural information encoded in their spectra.

2.2.3 Atom Optics and Quantum Reflection of Molecular Beams (Wieland Schöllkopf)

We have continued our experimental investigations based on matter-wave diffraction of molecular beams. The motivation behind our studies is twofold. (i) We aim at the development of new matter-wave optical methods, such as, for instance, diffraction by a quantum reflection grating. (ii) We continue to apply the diffraction technique to further investigate small helium clusters, He_2 and He_3, which represent unusual quantum systems. Especially the helium trimer has recently been in the focus of our interest, because this weakly bound 3-body system has been predicted since 1976 to be, arguably, the only naturally occurring 3-body system having an *Efimov state*. By combining diffraction by a nanoscale transmission grating with the *COLTRIMS* reaction-microscope technique is has now been possible to observe the long-sought Efimov state.

(i) Diffraction of molecular beams from a *quantum reflection* grating

In the first line of experiments we have continued our studies of diffraction of molecular beams quantum reflected from a ruled diffraction grating. These experiments are carried out in collaboration with Prof. Bum Suk Zhao and his group from UNIST (Ulsan National Institute of Science and Technology), South Korea. In 2014 and 2015 a total of five students from this group have been joining our lab, all of them funded by the Korean Government Global Internship Program of the Korean Ministry of Education.

The investigation of quantum reflection of molecular beams of helium and deuterium from a ruled blazed diffraction grating allowed us to observe *universal diffraction*: Different atoms, clusters, and molecules show diffraction patterns of identical relative peak intensity distribution. The relative intensity distribution only depends on the particle's de Broglie wavelength, but it is not affected by the particle specific interaction. This is in contrast to previous matter-wave diffraction experiments where the particle specific interaction with the diffracting element (this could be either a material grating or a light wave) was observed to significantly alter and, possibly, suppress the diffraction peak visibility. By applying a secondary scattering model we were able to trace the universal behaviour back to the peculiar principles governing quantum reflection.

In quantum reflection an atom or molecule approaching a solid surface is scattered back at the attractive particle-surface van der Waals potential. For typical experimental conditions (thermal energies of the atoms or molecules) quantum reflection probabilities are usually totally negligible. Only if the incident velocity of the particle is sufficiently small, the slope of the attractive potential appears to be steep on a length scale set by the incident particle's de

Broglie wavelength. In such a situation the potential slope, effectively, appears as a potential step. According to quantum mechanics, at a potential step, an incident wave-function shows a non-vanishing reflection probability that even approaches unity in the limit of zero incident velocity. In our experiment a sufficiently small velocity component perpendicular to the surface is achieved by grazing incidence of the molecular beam onto the grating (grazing angles on the order of 1 mrad and less). This way we can observe quantum reflection probabilities of up to tens of percent for He atoms and D_2 molecules. We can also observe non-destructive quantum reflection of He_2 and He_3. These van der Waals bound helium clusters are quantum reflected tens of nanometer above the surface, where the surface induced forces are too week to break up the fragile bonds.

(ii) Observation of the *Efimov state* in He_3

In 1970 Vitaly Efimov predicted universal behaviour of a 3-body system (trimer), if the corresponding 2-body system (dimer) is sufficiently close to resonance [see e.g. the review by *E. Braaten and H.-W. Hammer, Phys. Rep.* ***428****, 259 (2006)*]. Close to resonance means that the dimer is either very weakly bound (as is the case for He_2) or just not bound. Either case is characterized by a large magnitude of the scattering length having positive (negative) sign for the weakly bound (just unbound) dimer situation. Efimov's theory predicts an infinite number of 3-body excited states at resonance, *i.e.* in the limit of infinite absolute magnitude of the scattering length corresponding to vanishing 2-body bond strength. Unlike classical excited vibrational states Efimov states are predicted to disappear successively when, as theorists can easily do, the 2-body interaction strength is increased or decreased starting from the resonance point.

Efimov's scenario holds independently of the details of the particle interaction. In fact, Efimov originally considered nuclear systems, such as the 3 nucleon system, as possible candidates for trimers showing this peculiar behaviour. In nuclear systems, however, Efimov trimer states have not yet been observed. First experimental evidence for the Efimov effect was found in 2006 in ultracold dilute atomic gases, where it is possible to artificially tune the effective interaction strength by applying an external magnetic field close to a Feshbach resonance.

For atomic helium it just happens that the binding energy of the only bound state of He_2 (~100 neV) is sufficiently weak to support one Efimov state in He_3. This has been predicted by calculations from many theory groups since 1976 using various models of the He-He pair potential. The experimental method of diffraction by a nanoscale transmission grating, which allowed us to detect He_3 in its ground state, did not reveal evidence for the Efimov state, because it is essentially insensitive to the internal state of the molecule.

As described already in the last Fachbeirat booklet, we have been collaborating with the group of Prof. Reinhard Dörner at the University of Frankfurt combining their *COLTRIMS* reaction microscope with the transmission-grating diffraction method. To this end, part of our diffraction setup was installed at the *COTRLIMS* lab in Frankfurt. This approach permits to first separate He_3 from He and He_2 by grating diffraction, and then to selectively image the wave-function of He_3 by *COLTRIMS*. Here, a powerful ultrashort pulse from a femtosecond laser is used to ionize all three helium atoms of the trimer at the same time. This triggers a Coulomb explosion of the ions in which the repulsive Coulomb potential energy is released as kinetic energy of the 3 ions. From the detected momenta of the fragments the positions of the He atoms at the time of ionization and, hence, the vibrational wave-function of the neutral trimer can be reconstructed. This experimental approach has turned out to be very fruitful and allowed to image the wave-functions of the pure and mixed-isotope trimer systems $^4He_3$ and $^3He^4He_2$, respectively, thereby confirming $^3He^4He_2$ to form a so-called quantum halo state. In addition, it also made it possible to observe, for the first time, the long-sought Efimov state in $^4He_3$. Observation of the wave-function of the Efimov state is not only an experimental confirmation of Efimov's 3-body theory, but it also serves as a sensitive benchmark test for quantum chemistry calculations based on state-of-the-art He-He interaction potentials.

2.2.4 Micro-structured Devices to Manipulate Molecules - ERC Project MolChip

(Gerard Meijer/ Gabriele Santambrogio)

For physics, the atom chip and ion chip have been employed in fields as diverse as quantum computation, many-body non-equilibrium physics, and gravitational sensing. For chemistry, the lab-on-a-chip shrinks the pipettes, beakers and test tubes of a modern lab onto a microchip-sized substrate, with applications from the international space station to antiterrorism. The molecule chip promises a marriage between fundamental quantum physics and the richness of the chemical world. A particular advantage of using molecules instead of atoms on a chip is that they can be coupled to photons over a wider range of frequencies due to their rotational and vibrational degrees of freedom. Moreover, for chemists the molecule chip offers the prospect of extending the control of molecular concentrations and interactions to the level of single molecules with the accuracy in interaction energy reduced to the mK scale and below.

In the last years, it was demonstrated that neutral molecules can be loaded on a microchip directly from a supersonic beam. Once the molecules are trapped, they can be decelerated to a standstill, for instance, or re-ejected at low speed for high resolution spectroscopic measurements. The position of the trapped molecules is controlled with an accuracy of few microns and all molecules are in a single quantum state.

Trapped molecules can be transferred between quantum states with absolute selectivity. First, this was demonstrated for rotational transitions, by coupling the molecule chip to a mm-wave radiation source. Then, this technique was extended into the infrared region using laser light. More recently, time-resolved spatial imaging of molecules on the chip was shown, adding the final fundamental component to the molecule chip. For this, resonant-enhanced multi-photon ionization was used, which is quantum state selective, intrinsically background-free, and of general applicability. Imaging detection allows for the determination of the phase space distribution of the molecules in the microtraps. This was exploited, for instance, for the measurement of the temperature of the trapped molecules.

A completely new 3-dimensional design for the molecule chip is currently being tested. In this 3D chip, the hundreds of ring-shaped micro electrodes consist of two parts; one is lithographically deposited in a trench etched in a silicon wafer, the other is a 20 micron-thick wire that is spanned across the trench. This new design is expected to greatly increase the number of molecules that can be loaded on a chip and thus the palette of experiments that this technology will allow.

By adiabatically expanding the ensemble of molecules trapped on the chip their temperature can be reduced to about 5 mK without any significant losses in the number of molecules. However, this is not cold enough to achieve quantum degeneracy or to match the precision of spectroscopic measurements on atoms. Therefore, sympathetic cooling was identified as the most promising method for a second-cooling stage toward μK temperatures in molecular ensembles. Sympathetic cooling is based on the conceptually simple idea of bringing cold molecules into thermal contact with a bath containing ultracold atoms. Schemes to produce CO molecules in their electronic, vibrational and rotational ground state starting from the decelerated metastable state have been investigated and a particularly convenient path has been identified that allows for the accumulation of ground state molecules by optical pumping in a uni-directional and highly efficient way.

2.3 Guest Groups

2.3.1 Gas Phase Vibrational Spectroscopy of Clusters (Knut Asmis)

Knut Asmis continue to supervise a small research group in the Department of Molecular Physics at the FHI. This involves weekly visits from Leipzig to the FHI. The group currently consists of an A.v.H. postdoctoral student, Dr. Xiaowei Song, and two Ph.D. students, Matias Fagiani and Sreekanta Debnath. This part of the Asmis group's activity is funded by project D1 of the DFG Collaborative Research Center 1109 “Understanding of Metal Oxide/Water Systems at the Molecular Scale” (Apr. 2014 – Dec. 2017).

The Asmis group uses gas phase vibrational spectroscopy to study the structure, reactivity and dynamics of gas phase ions by way of action spectroscopy. Infrared photodissociation (IRPD) spectra of mass-selected, thermalized and messenger-tagged cluster ions are measuring using a custom-designed triple mass spectrometer with an integrated cryogenically cooled radio-frequency ion-trap. The setup allows measuring single- and double-resonance (i.e. isomer-specific) IRPD spectra of ions (<2000 amu) at variable temperature (10-300 K) and across a wide range of the IR spectral range (200-4000 cm^{-1}). As tunable and intense IR light sources we use the radiation from the IR free electron lasers as well as from a table-top OPO/OPA laser system. The instrument is directly coupled to the beam line of the FHI FEL.

As part of the CRC 1109, the project D1 focuses on studying the vibrational spectroscopy of small Al-, Fe- and Si-oxide cluster ions and their complexes with water. The long-term goal is to understand oxide formation and dissolution at a molecular level in order to ultimately design oxides with desirable properties. We started out by measuring IRPD spectra of small aluminum oxide anions (AlO_{1-4}^-, $Al_2O_{3-6}^-$) and iron oxide cations ($(Fe_2O_3)_{1-5}^+$) in the mid-IR range (400-1200 cm^{-1}) in order to understand their IR spectroscopy, determine scaling factors and identify typical binding motifs. This was followed by a systematic study of nominally fully oxized, electronically closed-shell clusters, i.e. $(Al_2O_3)_{1-6}AlO_2^-$ and $(Fe_2O_3)_{1-4}FeO^+$. More recently, we succeeded in successfully implementing a dual valve / dual channel laser vaporization source, optimized for producing larger metal oxide ion / water complexes by formation and stabilization of water complexes subsequent to the formation of the metal oxide ions by laser vaporization. Using this technique first IRPD spectra of $Fe_3O_4(H_2O)_{1-4}^+$ have been measured in the O-H stretching (3000-3800 cm^{-1}) as well as in the mid-IR region (350-1800 cm^{-1}), showing that the water molecules remain intact on the rather unreactive $Fe_3O_4^+$ moiety and that water-water hydrogen bond formation is observed upon addition of the third water molecule. The complete data is currently being evaluated and assigned in collaboration with the theory group of J. Sauer (HU Berlin, project D2).

With the successful defense of Nadja Heine's Ph.D. thesis "Vibrational Spectroscopy of Gaseous Hydrogen-Bonded Clusters: On the Role of Isomer-Specificity and Anharmonicity" in September 2014 at the Freie Universität Berlin with summa cum laude, our work on ion solvation at the FHI has been mainly concluded and transferred to the University of Leipzig. The atmospherically-relevant part in Nadja's thesis has been summarized in a recent review article (*Int. Rev. Phys. Chem.* **34**, 1, 2015). During the present period the work on ion solvation included the completion of the isomer-specific IRPD measurements (IR^2MS^2 technique) on small protonated water clusters. The work on $H^+(H_2O)_n{}^+\cdot H_2$ with n=7-10 (*J. Phys. Chem. Lett.* **6**, 2298, 2015) allowed isolating the IRPD spectra of four isomers of the protonated water heptamer and pinpointing the quasi-planar (2D) to cage (3D) transition in-between n=8 and n=9 at lowest internal temperatures. This structural transition had been previously observed to occur for n>10 in hotter cluster. The work on $H^+(H_2O)_5{}^+\cdot H_2$ involved measuring IRPD spectra over nearly the complete IR spectral range as well as isomer-specific IR^2MS^2 spectra and shows unambiguously that the protonated water pentamer experimentally prefers a single isomeric form in contrast to recent predictions based on ab initio molecular dynamics simulations.

The collaboration with A.v.H. awardee Mark Johnson (Yale University) involved two topics. The work on larger protonated water clusters (*PNAS,* **111**, 18132, 2014) was aimed at characterizing the size dependence of hydrogen bond stretching vibrations involving H_3O^+ ions in protonated water clusters. This involved measuring IRPD spectra of $H^+(H_2O)_n{}^+$ clusters with n=2-28 into the far-IR range (200-1000 cm^{-1}). The IRPD study on the temperature dependence of the water dimer dissociation in the presence of I^- in $I^-(H_2O)_2$ allowed unprecedented insight into thermodynamic quantities of the dissociation reaction (*J. Phys. Chem. A.* **119**, 1859, 2015).

The collaboration with the mass spectrometry group of E. Uggerud (Oslo University) on $[Cl\text{-}Mg\text{-}CO_2]^-$ in the context of CO_2 activation lead to the first published IRPD spectrum using radiation from the FHI FEL (*Angew. Chem. Int. Ed.* **53**, 14407, 2014). In this study a novel binding motif for mononuclear metal-CO_2 complexes was identified, in which the CO_2 moiety is nearly doubly negatively charged, leading to a bent geometry and a dramatic red-shift of the CO_2 antisymmetric stretching mode by more than 1200 cm^{-1}. Our work on CO_2 activation is continued and currently focuses on the interaction with titanium oxide cluster ions with carbon dioxide. This work is part of a longstanding and very fruitful collaboration with the group of D. Neumark (UC Berkeley), in which we measured IRPD spectra of messenger-tagged $(TiO_2)_{3-8}^-$ anions and $(Ti_3O_6)^-(CO_2)_{1,2}$ complexes.

Finally, we extended our work on boron-containing clusters to a survey study of bare boron cluster cations B_n^+ with $n \leq 50$ in collaboration with the Fielicke (TU Berlin) and Heine (Leipzig) groups. The clusters were produced according to a procedure developed by A. Fielicke employing an isotopically enriched boron target for laser vaporization. Currently we are analyzing the results and checking, if these clusters indeed exhibit the unusual structures and properties predicted by recent DFT calculations.

2.3.2 Spectroscopy and Chemistry of Metal Clusters and Cluster Complexes (André Fielicke)

Since the beginning of the year 2013 this group, formerly part of the department MP, is located at the Technical University Berlin. However, still a significant part of their activities make use of the FHI's Infrared Free Electron Laser. These activities focus on the investigation of the structures of clusters and complexes with small molecules in the gas phase using vibrational spectroscopy. For this, the group has installed a molecular beam experiment at one of the beam lines of the FEL that allows the characterization of charged and neutral gas-phase clusters using different types of infrared multiple photon excitation spectroscopy.

The focus of the group is the structural characterisation of strongly bound clusters, mainly composed of metals and semimetals, and their complexes with small molecules. At present, the FHI IR-FEL covers a spectral range of about 200-3000 cm^{-1}, allowing for the spectroscopy of internal and external vibrational modes of cluster-bound ligands giving inside into binding geometries and bond activation, and also the investigation of internal cluster modes for strongly bound clusters composed out of light elements, i.e. Si or B. Due to the inaccessibility of the far-IR below 200 cm^{-1} the investigation of internal vibrational modes of most transition metal clusters is strongly limited yet.

Recently we have implemented in our experiment a dual target laser ablation cluster source that allows the well-controlled preparation of binary clusters. Starting with two separate solid targets of silicon and boron we have synthesized boron doped silicon clusters and obtained the IR spectra for selected neutral clusters using the infrared-UV two color ionization technique. In these cases the boron atoms essentially substitute Si in the cluster structure, although significant distortions occur due to shorter Si-B bond length compared to Si-Si. This work is part of our activities within the DFG funded research group FOR 1282 “Controlling the Electronic Structure of Semiconductor Nanoparticles by Doping and Hybrid Formation” (DFG grant FI 893/4) where we study the effects of doping on the structural and electronic properties of small silicon clusters in collaboration with the group of Otto Dopfer (TU Berlin).

A second research focus is the activation of small molecules by (binary) metal clusters. As an example we have investigated the activation of single CO molecules by cobalt clusters doped with a few manganese atoms, using the frequency of the internal CO stretch as a quantitative measure. Following the concept of d-band shaping one would, with increasing Mn content, expect a gradual decrease in the strength of the C-O bond – in case the resulting d-band structure is just determined by a superposition of Mn and Co orbitals. The experimental results, however, give a more complicated picture and in the size range of 12-14 metal atoms, Co substitution by Mn does not lead to any observable effect at all. Similarly, unexpected shifts indicating a weaker CO activation in the doped clusters has also been found for small Mo doped Pt clusters. The latter study has been performed together with the group of E. Janssens (KU Leuven, Belgium). Within this collaboration we have also started to investigate the activation and binding of molecular hydrogen by aluminum clusters doped by single (or two) atoms of transition metals (Co, Rh, V), a process possible relevant for hydrogen storage applications. While pure cationic Al clusters do not, or very slowly, react with H_2, the transition metal dopant facilitates binding of H_2, its activation, leading finally to dissociation. The resulting different binding motifs of H are probed by infrared multiple photon dissociation spectroscopy.

Related to this problem of H_2 activation by metal clusters we have recently been able to detect for certain complexes between cobalt clusters and D_2 the D-D stretch at ~2400 cm^{-1} proving the presence of molecular hydrogen species in these complexes. This is of particular interest as it may explain the temperature dependent change in the spectra of the corresponding H_2 complexes which could be due to a stabilization of an intermediate molecular adsorbate at low temperature. In the past, however, this has been only indirectly inferred from the intensity change of a band at ~600 cm^{-1} that we tentatively assigned to the Co-(H_2) stretch vibration, whereas at present theoretical studies suggest a prompt dissociation of H_2 and observation of different isomers containing dissociated H (collaboration with J. Jellinek, Argonne National Laboratory, USA).

2.3.3 Ion Mobility-Mass Spectrometry of Complex Carbohydrates (Kevin Pagel)

Our research is focused on the structural analysis of biological macromolecules using gas phase methods. In particular, two classes of molecules are in focus: i) non-covalently associated peptide and protein complexes and ii) complex oligosaccharides. Peptides and protein complexes are typically investigated using a combination of ion mobility-mass spectrometry and gas phase infrared spectroscopy techniques that utilize the free electron laser installed at the Fritz Haber Institute. Most of these experiments are performed in close collaboration with the group of Gert von Helden as discussed in detail above.

The second key topic of our group is the separation and structural analysis of complex oligosaccharides using ion mobility-mass spectrometry. Besides the well-known function of large carbohydrates as energy source, smaller sugars – often referred to as oligosaccharides – are of enormous importance for a variety of biological functions. They can be linked to proteins as post-translational modifications or exist as free oligosaccharides, for example in milk. In comparison to other biopolymers such as DNA and proteins, oligosaccharides are largely under-studied. This is predominantly a result of their structural diversity. While DNA and proteins are exclusively assembled in a linear fashion, oligosaccharides are additionally branched and exhibit a complex stereochemistry. As a result, their in-depth structural analysis represents a significant challenge to date.

Currently, the vast majority of biologically relevant oligosaccharides is characterized using mass spectrometry-based techniques (MS) that are directly descending form those established in proteomics. When measuring the *m/z* of a sugar, however, a fundamental problem immediately unfolds: entire classes of the constituting monosaccharide building blocks exhibit an identical atomic composition and, consequently, an identical mass. Therefore, carbohydrate MS data can be highly ambiguous and often it is not possible to clearly assign a particular molecular structure. Over the last two years we have started to address this issue by implementing an additional gas-phase separation step using ion mobility spectrometry *(IMS).* Here, ions travel through a gas-filled cell aided by an electric field and are separated not only according to their mass and charge as in conventional MS, but also according to their size and shape. As a result, structural isomers, which exhibit an identical m/z but a different structure can be separated. In addition, the drift time measured in IM-MS can be converted into a collision cross section (CCS), which is a molecular property that is independent of instrument parameters and as such highly suitable to be implemented into databases. The long-term goal of this project is to establish an IM-MS based carbohydrate analysis platform that simultaneously uses m/z and CCSs information of oligosaccharides and their gas phase fragments for structural assignments and sequencing.

In the last two years we made significant progress towards this goal. The first problem that we addressed in collaboration with Prof. David J. Harvey (Department of Biochemistry, University of Oxford, Oxford) was the lack of suitable reference compounds that can be used as calibrant to accurately estimate the CCS of oligosaccharides using commercially available IM-MS instruments. To close this gap we first established a calibration protocol using sodiated carbohydrates, which were released from well-characterized, commercially available glycoproteins using an easy to follow procedure. Later, these data were complemented with CCSs of negatively charged carbohydrates, which are known to yield far more informative fragmentation spectra.

In a collaboration with the group of Pauline M. Rudd (National Institute of Bioprocessing Research and Training, Dublin), we next investigated the impact of adduct formation and ion polarity on the separation of carbohydrate isomers. Experiments on a series of isobaric milk sugars revealed, that species, which can be distinguished neither by chromatography nor tandem MS, can be separated with baseline resolution using IM-MS. However, for a successful separation of these species, the ionization mode turned out to be absolutely crucial. Sodiated ions exhibited almost identical and therefore inconclusive CCSs, while deprotonated ions differed significantly in size, which enables baseline separation. These experiments formed the basis for a more extensive study on a small library of synthetic oligosaccharides, which was performed in collaboration with the group of Peter H. Seeberger (Max Planck Institute for Colloids and Interfaces, Potsdam, Germany). Using a series of six synthetic trisaccharide isomers we were for the first time able to systematically assess the abilities of IM-MS for the separation of different types of carbohydrate isomers. Our data reveal that especially linkage- and stereoisomers, which are difficult to distinguish using established techniques, can be separated and unambiguously identified on basis of their CCS. More strikingly, the experiments showed that even minor isomeric components with relative concentrations as low as 0.1% are still clearly detectable when mixtures are analyzed.

More recently, we also extended our investigations from released oligosaccharides to glycosylated peptides. First data show that the position of the sugar within the peptide sequence can be clearly identified using IM-MS when multiple glycosylation sites exist. More importantly, however, our data reveal that also glycopeptides, which merely differ in the regiochemistry of the attached glycan can be distinguished using fragmentation and subsequent IM-MS analysis.

Taken together, the results from the last two years clearly show that IM-MS is an exceptionally effective tool for the structural analysis of both, biological as well as synthetic oligosaccharides. The full benefit of the method will become apparent once CCS data of oligosaccharides and their fragments are deposited in our recently released database glycomob.org.

3. Publications of the Department of Molecular Physics[1]

2013 (late publications)

Junkes, H., W. Erlebach, S. Gewinner, U. Hoppe, A. Liedke, G. Meijer, W. Schöllkopf, M. Wesemann, G. von Helden, H. Bluem, D. Dowell, R. Lange, A.M.M. Todd, L.M. Young and S.B. Webb: Integrating the FHI-FEL into the FHI Research Environment - Design and Implementation Aspects. In: Proceedings of the 35th International Free-Electron Laser Conference. (Eds.) C. Scholl and V. Schaa. JACoW.org, 562-565 (2013). ISBN 978-3-95450-126-7. OPEN ACCESS

Kim, Y.S., S.H. Jeon, A. Bostwick, E. Rotenberg, P.N. Ross, A.L. Walter, Y.J. Chang, V.R. Stamenkovic, N.M. Markovic, T.W. Noh, S. Han and B.S. Mun: Role of preferential weak hybridization between the surface-state of a metal and the oxygen atom in the chemical adsorption mechanism. Physical Chemistry Chemical Physics **15** (43), 19019-19023 (2013). OPEN ACCESS

Marx, S., D. Adu Smith, M. Abel, T. Zehentbauer, G. Meijer and G. Santambrogio: Imaging Cold Molecules on a Chip. Physical Review Letters **111** (24), 243007 (2013).

Schnell, M., P. Bunker, G. von Helden, J.-U. Grabow, G. Meijer and A. van der Avoird: Stark Effect in the Benzene Dimer. The Journal of Physical Chemistry A **117** (50), 13775-13778 (2013).

Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, V. Platschkowski, G. von Helden, H. Bluem, M.A. Davidsaver, D. Dowell, K. Jordan, R. Lange, H. Loos, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk: The IR and THz Free-Electron Laser at the Fritz-Haber-Institut. In: Proceedings of the 35th International Free-Electron Laser Conference. (Eds.) C. Scholl and V. Schaa. JACoW.org, 657-660 (2013). ISBN 978-3-95450-126-7. OPEN ACCESS

Wang, X., M. Kirste, G. Meijer and S.Y.T.v.d. Meerakker: Stark Deceleration of NO Radicals. Zeitschrift für physikalische Chemie **227** (11), 1595-1604 (2013). OPEN ACCESS

Wanko, M., T. Wende, M.M. Saralegui, L. Jiang, A. Rubio and K.R. Asmis: Solvent-mediated folding in dicarboxylate dianions: aliphatic chain length dependence and origin of the IR intensity quenching. Physical Chemistry Chemical Physics **15** (47), 20463-20472 (2013). OPEN ACCESS

Zieger, P.C., C. Eyles, S.Y.T.v.d. Meerakker, A.J.A. van Roij, H.L. Bethlem and G. Meijer: A Forty-Segment Molecular Synchrotron. Zeitschrift für physikalische Chemie **227** (11), 1605-1645 (2013). OPEN ACCESS

---

[1] OPEN ACCESS = Gold open access publication

2014

Boll, R., A. Rouzée, M. Adolph, D. Anielski, A. Aquila, S. Bari, C. Bomme, C. Bostedt, J.D. Bozek, H.N. Chapman, L. Christensen, R. Coffee, N. Coppola, S. De, P. Decleva, S.W. Epp, B. Erk, F. Filsinger, L. Foucar, T. Gorkhover, L. Gumprecht, A. Hömke, L. Holmegaard, P. Johnsson, J.S. Kienitz, T. Kierspel, F. Krasniqi, K.-U. Kühnel, J. Maurer, M. Messerschmidt, R. Moshammer, N.L.M. Müller, B. Rudek, E. Savelyev, I. Schlichting, C. Schmidt, F. Scholz, S. Schorb, J. Schulz, J. Seltmann, M. Stener, S. Stern, S. Techert, J. Thøgersen, S. Trippel, J. Viefhaus, M. Vrakking, H. Stapelfeldt, J. Küpper, J. Ullrich, A. Rudenko and D. Rolles: Imaging molecular structure through femtosecond photoelectron diffraction on aligned and oriented gas-phase molecules. Faraday Discussions **171**, 57-80 (2014).

Bučar, K., M. Žitnik, A. Mihelič, F. Penent, P. Lablanquie, J. Palaudoux, L. Andrić, M. Braune and R. Püttner: Quenching of the 2pnd $^1P^o$ doubly excited states of helium by a dc electric field. Physical Review A **90** (1), 013412 (2014).

Chang, Y.-P., F. Filsinger, B.G. Sartakov and J. Küpper: CMIstark: Python package for the Stark-effect calculation and symmetry classification of linear, symmetric and asymmetric top wavefunctions in dc electric fields. Computer Physics Communications **185** (1), 339-349 (2014).

Dulitz, K., M. Motsch, N. Vanhaecke and T.P. Softley: Getting a grip on the transverse motion in a Zeeman decelerator. The Journal of Chemical Physics **140** (10), 104201 (2014).

Fournier, J.A., C.T. Wolke, C.J. Johnson, M.A. Johnson, N. Heine, S. Gewinner, W. Schöllkopf, T.K. Esser, M.R. Fagiani, H. Knorke and K.R. Asmis: Site-specific vibrational spectral signatures of water molecules in the magic $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ clusters. Proceedings of the National Academy of Sciences of the USA **111** (51), 18132-18137 (2014).

Friedrich, B.: Fritz Haber a „válka chemiků“. Vesmir **06**, 2014/6 (2014).

Friedrich, B.: Křehké vztahy atomů helia. Vesmir **93** (3), 145-147 (2014).

Grätz, F., D.P. Engelhart, R.J.V. Wagner, G. Meijer, A.M. Wodtke and T. Schäfer: CO (a $^3\Pi$) quenching at a metal surface: Evidence of an electron transfer mediated mechanism. The Journal of Chemical Physics **141** (4), 044712 (2014).

Gruene, P., B. Butschke, J.T. Lyon, D.M. Rayner and A. Fielicke: Far-IR Spectra of Small Neutral Gold Clusters in the Gas Phase. Zeitschrift für physikalische Chemie **228** (4-5), 337-350 (2014).

Heine, N., E. Kratz, R. Bergmann, D. Schofield, K.R. Asmis, K.D. Jordan and A.B. McCoy: Vibrational Spectroscopy of the Water-Nitrate Complex in the OH Stretching Region. The Journal of Physical Chemistry A **118** (37), 8188-8197 (2014).

Heine, N., T.I. Yacovitch, F. Schubert, C. Brieger, D.M. Neumark and K.R. Asmis: Infrared Photodissociation Spectroscopy of Microhydrated Nitrate-Nitric Acid Clusters $NO_3^-(HNO_3)_m(H_2O)_n$. The Journal of Physical Chemistry A **118** (35), 7613-7622 (2014).

Hoffmann, W., J. Hofmann and K. Pagel: Energy-Resolved Ion Mobility-Mass Spectrometry - A Concept to Improve the Separation of Isomeric Carbohydrates. Journal of the American Society for Mass Spectrometry **25** (3), 471-479 (2014).

Hofmann, J., W.B. Struwe, C.A. Scarff, J.H. Scrivens, D.J. Harvey and K. Pagel: Estimating Collision Cross Sections of Negatively Charged N-Glycans using Traveling Wave Ion Mobility-Mass Spectrometry. Analytical Chemistry **86** (21), 10789-10795 (2014).

Ilchen, M., L. Glaser, F. Scholz, P. Walter, S. Deinert, A. Rothkirch, J. Seltmann, J. Viefhaus, P. Decleva, B. Langer, A. Knie, A. Ehresmann, O.M. Al-Dossary, M. Braune, G. Hartmann, A. Meißner, L.C. Tribedi, M. AlKhaldi and U. Becker: Angular Momentum Sensitive Two-Center Interference. Physical Review Letters **112** (2), 023001 (2014).

Jiang, L., S.-T. Sun, N. Heine, J.-W. Liu, T.I. Yacovitch, T. Wende, Z.-F. Liu, D.M. Neumark and K.R. Asmis: Large amplitude motion in cold monohydrated dihydrogen phosphate anions $H_2PO_4^-(H_2O)$: infrared photodissociation spectroscopy combined with *ab initio* molecular dynamics simulations. Physical Chemistry Chemical Physics **16** (4), 1314-1318 (2014).

Junkes, H., W. Schöllkopf, M. Wesemann and R. Lange: Design and Implementation Aspects of the Control System at the FHI FEL. In: Proceedings of the 14th International Conference on Accelerator & Large Experimental Physics Control Systems. (Eds.) C. Marshall, J. Fisher and V. Schaa. JACoW.org, 324-327 (2014). ISBN 978-3-95450-139-7.

Kim, J.-Y., D.-S. Ahn, S.-W. Park and S. Lee: Gas phase hydration of amino acids and dipeptides: effects on the relative stability of zwitterion vs. canonical conformers. RSC Advances **4** (31), 16352-16361 (2014).

Küpper, J., S. Stern, L. Holmegaard, F. Filsinger, A. Rouzée, A. Rudenko, P. Johnsson, A.V. Martin, M. Adolph, A. Aquila, S. Bajt, A. Barty, C. Bostedt, J. Bozek, C. Caleman, R. Coffee, N. Coppola, T. Delmas, S. Epp, B. Erk, L. Foucar, T. Gorkhover, L. Gumprecht, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, N. Kimmel, F. Krasniqi, K.-U. Kühnel, J. Maurer, M. Messerschmidt, R. Moshammer, C. Reich, B. Rudek, R. Santra, I. Schlichting, C. Schmidt, S. Schorb, J. Schulz, H. Soltau, J.C.H. Spence, D. Starodub, L. Strüder, J. Thøgersen, M.J.J. Vrakking, G. Weidenspointner, T.A. White, C. Wunderer, G. Meijer, J. Ullrich, H. Stapelfeldt, D. Rolles and H.N. Chapman: X-Ray Diffraction from Isolated and Strongly Aligned Gas-Phase Molecules with a Free-Electron Laser. Physical Review Letters **112** (8), 083002 (2014).

Li, Y., J.T. Lyon, A. Woodham, A. Fielicke and E. Janssens: The Geometric Structure of Silver-Doped Silicon Clusters. ChemPhysChem **15** (2), 328-336 (2014).

Maier, T.M., A.D. Boese, J. Sauer, T. Wende, M.R. Fagiani and K.R. Asmis: The vibrational spectrum of FeO_2^+ isomers - Theoretical benchmark and experiment. The Journal of Chemical Physics **140** (20), 204315 (2014).

Miller, G.B.S., T.K. Esser, H. Knorke, S. Gewinner, W. Schöllkopf, N. Heine, K.R. Asmis and E. Uggerud: Spectroscopic Identification of a Bidentate Binding Motif in the Anionic Magnesium-CO_2 Complex ($[ClMgCO_2]^-$). Angewandte Chemie International Edition **53** (52), 14407-14410 (2014).

Miller, G.B.S., T.K. Esser, H. Knorke, S. Gewinner, W. Schöllkopf, N. Heine, K.R. Asmis and E. Uggerud: Spectroscopic Identification of a Bidentate Binding Motif in the Anionic Magnesium-CO_2 Complex ($[ClMgCO_2]^-$). Angewandte Chemie **126** (52), 14635-14638 (2014).

Rolles, D., R. Boll, M. Adolph, A. Aquila, C. Bostedt, J.D. Bozek, H.N. Chapman, R. Coffee, N. Coppola, P. Decleva, T. Delmas, S.W. Epp, B. Erk, F. Filsinger, L. Foucar, L. Gumprecht, A. Hömke, T. Gorkhover, L. Holmegaard, P. Johnsson, C. Kaiser, F. Krasniqi, K.-U. Kühnel, J. Maurer, M. Messerschmidt, R. Moshammer, W. Quevedo, I. Rajkovic, A. Rouzée, B. Rudek, I. Schlichting, C. Schmidt, S. Schorb, C.D. Schröter, J. Schulz, H. Stapelfeldt, M. Stener, S. Stern, S. Techert, J. Thøgersen, M.J.J. Vrakking, A. Rudenko, J. Küpper and J. Ullrich: Femtosecond x-ray photoelectron diffraction on gas-phase dibromobenzene molecules. Journal of Physics B **47** (12), 124035 (2014).

Santamaria, L., V.D. Sarno, I. Ricciardi, S. Mosca, M.D. Rosa, G. Santambrogio, P. Maddaloni and P.D. Natale: Assessing the time constancy of the proton-to-electron mass ratio by precision ro-vibrational spectroscopy of a cold molecular beam. Journal of Molecular Spectroscopy **300**, 116-123 (2014).

Schmidt, B. and B. Friedrich: Supersymmetry and eigensurface topology of the planar quantum pendulum. Frontiers in Physics **2**, 00037 (2014). OPEN ACCESS

Schmidt, B. and B. Friedrich: Topology of surfaces for molecular Stark energy, alignment, and orientation generated by combined permanent and induced electric dipole interactions. The Journal of Chemical Physics **140** (6), 064317 (2014).

Schöllkopf, W.: Mit Kanonen auf Tröpfchen. Physik Journal **13** (11), 22-23 (2014).

Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, A. Paarmann, G. von Helden, H. Bluem, D. Dowell, R. Lange, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk: The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. In: Proceedings of the 36th International Free Electron Laser Conference. (Eds.) J. Chrin, S. Reiche and V. Schaa. JACoW.org, WEB04 (2014). ISBN 978-3-95450-133-5. OPEN ACCESS

Stanca-Kaposta, E.C., F. Schwaneberg, M.R. Fagiani, T. Wende, F. Hagemann, A. Wünschmann, L. Wöste and K.R. Asmis: Infrared Photodissociation Spectroscopy of $C_{2n+1}N^-$ Anions with n = 1-5. Zeitschrift für physikalische Chemie **228** (4-5), 351-368 (2014).

Stern, S., L. Holmegaard, F. Filsinger, A. Rouzée, A. Rudenko, P. Johnsson, A.V. Martin, A. Barty, C. Bostedt, J.D. Bozek, R.N. Coffee, S. Epp, B. Erk, L. Foucar, R. Hartmann, N. Kimmel, K.-U. Kühnel, J. Maurer, M. Messerschmidt, B. Rudek, D.G. Starodub, J. Thøgersen, G. Weidenspointner, T.A. White, H. Stapelfeldt, D. Rolles, H.N. Chapman and J. Küpper: Toward atomic resolution diffractive imaging of isolated molecules with x-ray free-electron lasers. Faraday Discussions **171**, 393-418 (2014). OPEN ACCESS

Voigtsberger, J., J. Becht, N. Neumann, F. Sturm, M. Kunitski, A. Kalinin, J. Wu, S. Zeller, M. Schöffler, W. Schöllkopf, D. Bressanini, A. Czasch, L.P.H. Schmidt, R. Grisenti, T. Jahnke and R. Dörner: Experimental observation of the vibrational wavefunction of $^4He_2$, $^4He_3$ and $^4He_2{}^3He$ using strong laser-fields. Journal of Physics: Conference Series **488** (13), 132024 (2014). OPEN ACCESS

Voigtsberger, J., S. Zeller, J. Becht, N. Neumann, F. Sturm, H.-K. Kim, M. Waitz, F. Trinter, M. Kunitski, A. Kalinin, J. Wu, W. Schöllkopf, D. Bressanini, A. Czasch, J. Williams, K. Ullmann-Pfleger, L. Schmidt, M. Schöffler, R. Grisenti, T. Jahnke and R. Dörner: Imaging the structure of the trimer systems $^4He_3$ and $^3He^4He_2$. Nature Communications **5** (12), 5765 (2014).

Warnke, S., C. Baldauf, M.T. Bowers, K. Pagel and G. von Helden: Photodissociation of Conformer-Selected Ubiquitin Ions Reveals Site-Specific Cis/Trans Isomerization of Proline Peptide Bonds. Journal of the American Chemical Society **136** (29), 10308-10314 (2014). OPEN ACCESS

Woodham, A. and A. Fielicke: Gold Clusters in the Gas Phase. In: Gold Clusters, Colloids and Nano-Particles I. (Ed.) D.M.P. Mingos. (Structure and Bonding, Vol. 161). Springer, Cham, 243-278 (2014). ISBN 978-3-319-07847-2.

Zhang, X., C. Eyles, C.A. Taatjes, D. Ding and S. Stolte: Quasi-Quantum Treatment of the rotationally inelastic NO-He scattering. Journal of Physics: Conference Series **488** (10), 102026 (2014). OPEN ACCESS

Doctoral Thesis

Grätz, F.: Molecule-Surface-Scattering with Velocity-Controlled Molecular Beams. Freie Universität Berlin 2014.

Heine, N.: Vibrational Spectroscopy of Gaseous Hydrogen-Bonded Clusters: On the Role of Isomer-Specificity and Anharmonicity. Freie Universität Berlin 2014.

Woodham, A.: Binding and activation of oxygen by anionic, neutral and cationic gold clusters. Technische Universität Berlin 2014.

2015

Braune, M., G. Hartmann, M. Ilchen, A. Knie, T. Lischke, A. Reinköster, A. Meißner, S. Deinert, L. Glaser, O. Al-Dossary, A. Ehresmann, A.S. Kheifets and J. Viefhaus: Electron angular distributions of noble gases in sequential two-photon double ionization. Journal of Modern Optics, in press.

Dulitz, K., N. Vanhaecke and T.P. Softley: Model for the overall phase-space acceptance in a Zeeman decelerator. Physical Review A **91** (1), 013409 (2015).

Engelhart, D.P., F. Grätz, R. Wagner, H. Haak, G. Meijer, A. Wodtke and T. Schäfer: A new Stark decelerator based surface scattering instrument for studying energy transfer at the gas-surface interface. Review of Scientific Instruments **86** (4), 043306 (2015).

Fagiani, M.R., L.L. Zeonjuk, T.K. Esser, D. Gabel, T. Heine, K.R. Asmis and J. Warneke: Opening of an icosahedral boron framework: A combined infrared spectroscopic and computational study. Chemical Physics Letters **625**, 48-52 (2015).

Friedrich, B.: Fritz Haber und der „Krieg der Chemiker“: Leben und Werk eines umstrittenen Wissenschaftlers. Physik in unserer Zeit **46** (3), 118-125 (2015).

Gonzalez Florez, A.I., D.-S. Ahn, S. Gewinner, W. Schöllkopf and G. von Helden: IR spectroscopy of protonated leu-enkephalin and its 18-crown-6 complex embedded in helium droplets. Physical Chemistry Chemical Physics **17** (34), 21902-21911 (2015). OPEN ACCESS

Heine, N. and K.R. Asmis: Cryogenic ion trap vibrational spectroscopy of hydrogen-bonded clusters relevant to atmospheric chemistry. International Reviews in Physical Chemistry **34** (1), 1-34 (2015).

Heine, N., M.R. Fagiani and K.R. Asmis: Disentangling the Contribution of Multiple Isomers to the Infrared Spectrum of the Protonated Water Heptamer. The Journal of Physical Chemistry Letters **6** (12), 2298-2304 (2015).

Hofmann, J., H.S. Hahm, P.H. Seeberger and K. Pagel: Identification of Carbohydrate Anomers Using Ion Mobility-Mass Spectrometry. Nature, in press.

Kerpal, C., D.J. Harding, D.M. Rayner, J.T. Lyon and A. Fielicke: Far-IR Spectra and Structures of Small Cationic Ruthenium Clusters: Evidence for Cubic Motifs. The Journal of Physical Chemistry C **119** (20), 10869-10875 (2015).

Kunitski, M., S. Zeller, J. Voigtsberger, A. Kalinin, L.P.H. Schmidt, M. Schöffler, A. Czasch, W. Schöllkopf, R.E. Grisenti, T. Jahnke, D. Blume and R. Dörner: Observation of the Efimov state of the helium trimer. Science **348** (6234), 551-555 (2015).

Li, Y., J.T. Lyon, A. Woodham, P. Lievens, A. Fielicke and E. Janssens: Structural Identification of Gold-Doped Silicon Clusters via Far-Infrared Spectroscopy. The Journal of Physical Chemistry C **119** (20), 10896-10903 (2015).

Santamaria, L., V.D. Sarno, I. Ricciardi, M.D. Rosa, S. Mosca, G. Santambrogio, P. Maddaloni and P.D. Natale: Low-Temperature Spectroscopy of the $^{12}C_2H_2$ ($\upsilon_1 + \upsilon_3$) Band in a Helium Buffer Gas. Astrophysical Journal **801** (1), 50 (2015).

Schewe, H.C., Q. Ma, N. Vanhaecke, X. Wang, J. Kłos, M.H. Alexander, S.Y.T. van de Meerakker, G. Meijer, A. van der Avoird and P.J. Dagdigian: Rotationally inelastic scattering of OH by molecular hydrogen: Theory and experiment. The Journal of Chemical Physics **142** (20), 204310 (2015).

Schmidt, B. and B. Friedrich: Supersymmetry and eigensurface topology of the spherical quantum pendulum. Physical Review A **91** (2), 022111 (2015). OPEN ACCESS

Schöllkopf, W., S. Gewinner, H. Junkes, A. Paarmann, G. von Helden, H. Bluem and A.M.M. Todd: The new IR and THz FEL facility at the Fritz Haber Institute in Berlin. In: Proceedings of Advances in X-ray Free-Electron Lasers Instrumentation III. (Ed.) S.G. Biedron. (Proceedings of the SPIE, Vol. 9512). SPIE, Bellingham, WA, 95121L (2015).

Schubert, F., K. Pagel, M. Rossi, S. Warnke, M. Salwiczek, B. Koksch, G. von Helden, V. Blum, C. Baldauf and M. Scheffler: Native like helices in a specially designed β peptide in the gas phase. Physical Chemistry Chemical Physics **17** (7), 5376-5385 (2015). OPEN ACCESS

Schubert, F., M. Rossi, C. Baldauf, K. Pagel, S. Warnke, G. von Helden, F. Filsinger, P. Kupser, G. Meijer, M. Salwiczek, B. Koksch, M. Scheffler and V. Blum: Exploring the conformational preferences of 20-residue peptides in isolation: Ac-Ala$_{19}$-Lys + H$^+$ vs. Ac-Lys-Ala$_{19}$ + H$^+$ and the current reach of DFT. Physical Chemistry Chemical Physics **17** (11), 7373-7385 (2015). OPEN ACCESS

Sharma, K. and B. Friedrich: Directional properties of polar paramagnetic molecules subject to congruent electric, magnetic and optical fields. New Journal of Physics **17** (4), 045017 (2015). OPEN ACCESS

Struwe, W.B., J.L. Benesch, D.J. Harvey and K. Pagel: Collision cross sections of high-mannose *N*-glycans in commonly observed adduct states – identification of gas-phase conformers unique to [M − H]$^-$ ions. Analyst, in press.

Struwe, W.B., K. Pagel, J.L.P. Benesch, D.J. Harvey and M.P. Campbell: GlycoMob: an ion mobility-mass spectrometry collision cross section database for glycomics. Glycoconjugate Journal, in press.

Sun, S.-T., L. Jiang, J.W. Liu, N. Heine, T.I. Yacovitch, T. Wende, K.R. Asmis, D.M. Neumark and Z.-F. Liu: Microhydrated dihydrogen phosphate clusters probed by gas phase vibrational spectroscopy and first principles calculations. Physical Chemistry Chemical Physics, in press. OPEN ACCESS

Urner, L.H., B.N.S. Thota, O. Nachtigall, S. Warnke, G. von Helden, R. Haag and K. Pagel: Online monitoring the isomerization of an azobenzene-based dendritic bolaamphiphile using ion mobility-mass spectrometry. Chemical Communications **51** (42), 8801-8804 (2015). OPEN ACCESS

Warnke, S., G. von Helden and K. Pagel: Analyzing the higher order structure of proteins with conformer-selective ultraviolet photodissociation. Proteomics, **15** (19), 2804-2812 (2015).

Warnke, S., J. Seo, J. Boschmans, F. Sobott, J.H. Scrivens, C. Bleiholder, M.T. Bowers, S. Gewinner, W. Schöllkopf, K. Pagel and G. von Helden: Protomers of Benzocaine: Solvent and Permittivity Dependence. Journal of the American Chemical Society **137** (12), 4236-4242 (2015). OPEN ACCESS

Wolke, C.T., F.S. Menges, N. Toetsch, O. Gorlova, J.A. Fournier, G.H. Weddle, M.A. Johnson, N. Heine, T.K. Esser, H. Knorke, K.R. Asmis, A.B. McCoy, D.J. Arismendi-Arrieta, R. Prosmiti and F. Paesani: Thermodynamics of Water Dimer Dissociation in the Primary Hydration Shell of the Iodide Ion with Temperature-Dependent Vibrational Predissociation Spectroscopy. The Journal of Physical Chemistry A **119** (10), 1859-1866 (2015).

Doctoral Thesis

Schewe, H.C.: Colliding radicals. High resolution spectroscopy and collision studies with velocity-controlled OH beams. Radboud Universiteit Nijmegen 2015

4. Invited Talks of the Members of the Department of Molecular Physics

David Adu Smith

Dec 2013	QUEST Institute for Experimental Quantum Metrology, Physikalisch-Technische Bundesanstalt, Brunswick, Germany *Non-Equilibrium Many-Body Quantum Systems and Prethermalization*

Knut R. Asmis

Jun 2014	69th International Symposium on Molecular Spectroscopy, University of Illinois, Champaign-Urbana, IL, USA *Isomer-Specific* IR^2MS^2 *Spectroscopy of Protonated Water Clusters*
Jun 2014	Sino-German FEL Symposium “FELiChEM visits FHI-FEL”, Fritz Haber Institute, Berlin, Germany *Vibrational Spectroscopy of Gaseous Ions*
Nov 2014	GDCh Seminar, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Germany *Spektroskopische Untersuchungen an Gasphasenclustern - Auf den Spuren von Ostwald und Arrhenius*
Nov 2014	Seminar, Leipzig Graduate School on Clouds, Aerosols and Radiation, Leipzig, Germany *Vibrational Spectroscopy of Hydrogen-Bonded Clusters Relevant to Atmospheric Chemistry*
Mar 2015	APS March Meeting 2015, American Physical Society, San Antonio, TX, USA *Ion Microsolvation Probed by Cryogenic Ion Trap Vibrational Spectroscopy*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Structural Characterization of Metal-Containing Gas Phase Clusters and their Complexes with* CO_2
Jun 2015	594th WE-Heraeus-Seminar, Spectroscopy and Applications of Cold Molecular Ions, Bad Honnef, Germany *Ion Microsolvation Probed by Cryogenic Ion Trap IR Spectroscopy*
Jul 2015	Colloquium, Physical and Theoretical Chemistry, Technische Universität Kaiserslautern, Kaiserslautern, Germany *Auf den Spuren von Ostwald und Arrhenius: Spektroskopische Untersuchungen an Gasphasenclustern*
Jul 2015	Conference, Defining New Directions in Cold Chemical Physics, Boulder, CO, USA *Probing Solvation with Cryogenic Ion Trap Vibrational Spectroscopy*
Aug 2015	14th National Conference on Chemical Dynamics, Xi’an, Shaanxi, China *Structure and Dynamics of Hydrogen Bonded Networks Probed by Cryogenic Ion Trap Vibrational Spectroscopy*
Sep 2015	Seminar, Department of Chemistry, Fudan University, Shanghai, China *Structure and Dynamics of Hydrogen Bonded Networks Probed by Cryogenic Ion Trap Vibrational Spectroscopy*

Tim K. Esser

Apr 2014	Molecular and Ionic Clusters, Gordon Research Seminar (GRS), Lucca (Barga), Italy *Metal-Ion Selectivity of a Fluorescent Sensor Probed by Gas Phase IR Spectroscopy*

Matias Ruben Fagiani

Oct 2014	SFB 1109, CRC Workshop and Edith Flanigen Award 2014, Berlin, Germany *Structure Characterization of Metal Oxide Clusters in the Gas Phase: Experimental Setup and Technique*
Feb 2015	Gaseous Ions: Structures, Energetics & Reactions, Gordon Research Conference (GRC), Galveston, TX, USA *Resolving the Controversy Regarding the Gas Phase Vibrational Spectrum of the Protonated Water Pentamer*

André Fielicke

Feb 2014	Symposium, Institute of Physical Chemistry, Christian-Albrechts-Universität zu Kiel, Kiel, Germany *Spektroskopie von Metallclusterkomplexen: Oberflächenchemie*
Mar 2014	International Symposium on Clusters, Cluster Assemblies and Nano-scale Materials – ISCANM III, Allahabad, India *Structure and Surface Chemistry of Gold Clusters*
Mar 2014	Seminar, Department of Chemistry, Shiv Nadar University, Delhi, India *Structure and Surface Chemistry of Gold Clusters*
Apr 2014	International Bunsen Discussion Meeting, Gas Phase Model Systems for Catalysis - GPMC 2014, Ulm, Germany *Structure and Surface Chemistry of Gold Clusters*
Apr 2014	UK Metal Cluster Symposium, Oxford, UK *Vibrational Spectroscopy of Metal Cluster Complexes: Investigating the Chemistry on a Small Surface*
May 2014	Molecular and Ionic Clusters, Gordon Research Conference (GRC), Lucca (Barga), Italy *Vibrational Spectroscopy of Metal Cluster Complexes: Investigating the Chemistry on a Small Surface*
Jun 2014	Sino-German FEL Symposium "FELiChEM visits FHI-FEL", Fritz Haber Institute, Berlin, Germany *Vibrational Spectroscopy of Metal Cluster Complexes: Insights into Cluster Chemistry*
Sep 2014	International Workshop on Nanoclusters - Fundamentals to Functionality, Keio University, Yokohama, Japan *Vibrational Spectroscopy of Metal Cluster Complexes: Investigating the Chemistry on a Small Surface*
Nov 2014	Seminar, Physical and Theoretical Chemistry, Technische Universität Kaiserslautern, Kaiserslautern, Germany *Metallclusterkomplexe: Oberflächenchemie en Miniature*

Nov 2014	Seminar, Young Faculty Association, Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Bochum, Germany *Vibrational Spectroscopy of Clusters with a Free Electron Laser: Studying Surface Chemistry en Miniature*
Mar 2015	DPG-Frühjahrstagung, Heidelberg, Germany *Vibrational Spectroscopy of Cluster Complexes with Free Electron Lasers: Surface Science en Miniature*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *The FHI-FEL: Extension to THz Frequencies*
Jul 2015	Clusters & Nanostructures, Gordon Research Conference (GRC), Girona, Spain *Session Chair and Introductory Talk: Electronic Structure, Thermodynamics*
Aug 2015	XXIV International Materials Research Congress 2015, Cancún, Mexico *Structure Determination of Isolated Platinum Group Metal Clusters Using an Infrared Free Electron Laser*

Bretislav Friedrich

Nov 2013	Seminar, CFEL Molecular Physics Seminar, DESY, Hamburg, Germany *Shedding Far-Off Resonant Light on Polar Paramagnetic Molecules*
Mar 2014	Symposium in Honor of Zdenek Herman, J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences, Prague, Czech Republic *Shedding Non-Resonant Light on Molecules*
Nov 2014	Control of London dispersion interactions in molecular chemistry (SPP 1807), Schwerpunktprogramm der DFG, Gießen, Germany *Configurations of van der Waals Complexes Controlled via London Dispersion Forces as Revealed by Means of Stark Spectroscopy in He-Nanodroplets*
May 2015	Symposium, A Garden of Physics, Max Planck Institute for Dynamics and Self-Organization, Göttingen, Germany *A Toast to Jan Peter Toennies*
Sep 2015	51st Symposium on Theoretical Chemistry "Chemistry in Motion", Potsdam, Germany *How Did the Tree of Knowledge Get its Blossom: The Rise of Physical and Theoretical Chemistry (with an Eye on Berlin)*

Henrik Haak

May 2014	Symposium on Dynamics at Surfaces, Schloss Ringberg, Kreuth, Germany *Design of Scientific Instruments for Experiments in Molecular Physics*
Oct 2014	Seminar, European Laboratory for Non-Linear Spectroscopy (Lens), Florence, Italy *Design of Scientific Instruments for Experiments in Molecular Physics*

Nadja Heine

Apr 2014	Molecular and Ionic Clusters, Gordon Research Conference (GRC), Lucca (Barga), Italy *Structure and Microsolvation of Atmospheric Anions:* $NO_3^-(HNO_3)_m(H_2O)_n$

Gert von Helden

Mar 2014	Conference on Molecular Nanostructures, Ascona, Switzerland *Investigating the Structures of Gas-Phase Biomolecules with Optical Spectroscopy and Ion Mobility*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Investigating the Structures of Gas-Phase Biomolecules with Optical Spectroscopy and Ion Mobility Spectrometry*
Jun 2014	Sino-German FEL Symposium “FELiChEM visits FHI-FEL”, Fritz Haber Institute, Berlin, Germany IR spectroscopy of bio-molecules
Feb 2015	2015 Mesilla Chemistry Workshop on Isolated Biomolecules and Biomolecular Interactions: From the Gas Phase and Towards Solution, Mesilla, NM, USA *IR Spectroscopy of Biomolecules in Helium Droplets and after IMS-MS Selection*
Feb 2015	Gaseous Ions: Structures, Energetics & Reactions, Gordon Research Conference (GRC), Galveston, TX, USA *IR Spectroscopy of Peptides and Proteins in Liquid Helium Droplets*
Mar 2015	Seminar, The University of Utah, Salt Lake City, UT, USA *Infrared Spectroscopy of Peptides and Proteins in the Gas Phase*
Mar 2015	Seminar, Wayne State University, Detroit, MI, USA *Infrared Spectroscopy of Peptides and Proteins in the Gas Phase*
Apr 2015	Seminar, Goethe University Frankfurt, Frankfurt, Germany *IR Spectroscopy on Peptides and Proteins after Ion Mobility Selection and in Liquid Helium Droplets*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Action Spectroscopy on Biomolecules: Present and Future*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Bio Inspired Catalysts for the Hydration of Carbon Dioxide to Bicarbonate*
May 2015	Workshop on Modern Topics in Chemical Physics, Schloss Ringberg, Kreuth, Germany *IR Spectroscopy on Peptides and Proteins after Ion Mobility Selection and in Liquid Helium Droplets*
Jun 2015	70th International Symposium on Molecular Spectroscopy, Champaign-Urbana, IL, USA *IR Spectroscopy on Peptides and Proteins after Ion Mobility Selection and in Liquid Helium Droplets*

Heinz Junkes

Jun 2014	Sino-German FEL Symposium “FELiChEM visits FHI-FEL”, Fritz Haber Institute, Berlin, Germany The EPICS control system at FHI FEL

Kevin Pagel

Dec 2013	GlycoBioM Meeting, The National Institute for Bioprocessing Reserach and Training (NIBRT), Dublin, Ireland *Ion Mobility Mass Spectrometry of Carbohydrates – How Polarity and Adduct Formation Affects Separation*
Feb 2014	17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany *Structural Analysis of Biomolecules in the Gas Phase – Combining Ion Mobility Mass Spectrometry and Optical Spectroscopy*
Apr 2014	Seminar, Department of Chemistry, The University of Antwerp, Antwerp, Belgium *Structural Analysis of Biomolecules in the Gas Phase – Combining Ion Mobility Spectrometry and Optical Spectroscopy*
Apr 2014	Strasbourg Workshop on Native Mass Spectrometry and Ion Mobility, Strasbourg, France *Ion Mobility – Mass Spectrometry of Complex Carbohydrates*
Jan 2015	Lecture, School of Analytical Sciences Adlershof (SALSA), Humboldt-Universität zu Berlin, Berlin, Germany *Ion Mobility – Mass Spectrometry of Complex Carbohydrates*
Mar 2015	Proteomic Forum 2015, Berlin, Germany *Ion Mobility – Mass Spectrometry of Complex Carbohydrates*
May 2015	Lise-Meitner-Kolloquium, Institut für Chemie und Biochemie, Organische Chemie, Freie Universität Berlin, Berlin, Germany *Ion Mobility – Mass Spectrometry of Complex Carbohydrates*
Jun 2015	4th Beilstein Glyco-Bioinformatics Symposium, Potsdam, Germany *Separation of Carbohydrate and Glycopeptide Isomers Using Ion Mobility-MS*
Jun 2015	Participants' Camp, GRS Molecular Mechanisms in Regenerative Processes, University of Rostock, Rostock, Germany *Separation of Carbohydrate and Glycopeptide Isomers Using Ion Mobility-MS*
Jun 2015	Tag der Chemie 2015 (29. TDC), Berlin, Germany *Wenn Zucker fliegen lernen: Ionenmobilitäts-Massenspektrometrie von komplexen Kohlenhydraten*
Jul 2015	Meeting and Training Course 2015, Ion Mobility Mass Spectrometry - IM-MS Special Interest Group, British Mass Spectrometry Society, Liverpool, UK *Separation of Carbohydrate and Glycopeptide Isomers Using Ion Mobility-MS*

Jul 2015	Waters Corp. Seminar, Manchester, UK *Separation of Carbohydrate and Glycopeptide Isomers Using Ion Mobility-MS*

Gabriele Santambrogio

Feb 2015	Seminar, Centre for Cold Matter, The Blackett Laboratory, Imperial College London, London, UK *A Molecular Laboratory on a Chip*
Jun 2015	Seminar, VU University Amsterdam, Amsterdam, The Netherlands *Molecule Chip: Toward High Resolution Spectroscopy*
Aug 2015	The 24th Colloquium on High Resolution Molecular Spectroscopy (HRMS), Dijon, France *Molecule Chip: Toward High Resolution Spectroscopy*

Wieland Schöllkopf

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Update on the FHI FEL: User Operation, Projects and Future Development*
Jun 2014	Sino-German FEL Symposium “FELiChEM visits FHI-FEL”, Fritz Haber Institute, Berlin, Germany *Overview of the FHI free-electron laser*
Aug 2014	36th International Free Electron Laser Conference, Basel, Switzerland *The New IR FEL Facility at the Fritz-Haber-Institut in Berlin*
Nov 2014	Workshop on the Scientific Opportunities of a THz-FEL in Sweden, AlbaNova University Center Stockholm, Stockholm, Sweden *The New IR FEL Facility at the Fritz-Haber-Institut in Berlin*
Apr 2015	Conference, SPIE Optics & Optoelectronics: Advances in X-ray Free-Electron Lasers Instrumentation III, Prague, Czech Republic *The New IR FEL Facility at the Fritz-Haber-Institut in Berlin*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *FHI FEL: Results from 1.5 Years of Operation & Future Prospects*
Sep 2015	Seminar, Department of Chemistry, UNIST Campus, Ulsan, South Korea *The Infrared Free-Electron Laser at the Fritz Haber Institute in Berlin: A New Tool for IR Spectroscopy of Molecules, Clusters, and Solids*

Xiaowei Song

Oct 2014	SFB 1109, CRC Workshop and Edith Flanigen Award 2014, Berlin, Germany *Gas Phase Metal Oxide Ion Clusters: Structure and Reactivity*
Apr 2015	Network Meeting of the Alexander von Humboldt Foundation, Bremen, Germany *Gas Phase Ionic Clusters – an Insight to Connect Atoms to Bulk Material*

Stephan Warnke

Mar 2015	1st Ion Mobility-Mass Spectrometry Workshop, FHI, Berlin, Germany *History and Fundamentals: From Home-Built Devices to Commercial Instruments*

Department of Physical Chemistry Director: Martin Wolf

Staff scientists:

Kramer Campen
Markus Eiswirth
Leonhard Grill *until 12/2014*
Karsten Horn
Tobias Kampfrath
Takashi Kumagai
Alexey Melnikov
Alexander Mikhailov
Alexander Paarmann
Julia Stähler

Gerhard Ertl (Emeritus)

Scientists, staying for at least six months, paid by FHI:

Delroy Baugh
Nikita Ilin
Harald Kirsch
Jerry LaRue
Sajadi Hezaveh Mohsen
Ilya Razdolski
Amartya Sarkar
Sesha Vempati
Hendrik Vita

Scientists, staying for at least six month, paid from external funds:

Yunpei Deng *until 3/2015*	*EU*
Holger Flechsig *until 7/2014*	*DFG*
Shigefumi Hata *until 3/2014*	*JSPS*
Marc Herzog	*EU/DFG*
Claude Monney *until 11/2014*	*AvH/SNF*
Fumito Mori	*DFG/VW*
Christophe Nacci *until 1/2015*	*EU*
Melke Nascimiento *until 1/2014*	*DFG*
Francoise Lapointe	*Quebec/MPG*
Amartya Sarkar	*VW/MPG*
Alexander Saywell *until 12/2014*	*EU/DFG*
Akitoshi Shiotari *until 4/2014*	*JSPS*
Vasily Temnov	*AvH*
Yujin Tong	*DFG*
Hamilton Varela *until 7/2014*	*FAPESP*
Lizandra Zimmermann *until 11/2014*	*DAAD*

Graduate students:	24	(10 from external funds)
Master students:	4	
Trainees:	5	
Technicians:	10	

Max Planck Research Group: Structural and Electronic Surface Dynamics

Head: Ralph Ernstorfer

1 post doc
4 graduate students
1 master student

Service Group Electronics Workshop

Head: Georg Heyne

15 staff members 2 apprentices

Service Group Mechanical Workshop

Head: Petrik Bischoff

18 staff members 2 apprentices

Recent Developments in the Department of Physical Chemistry

Director: Martin Wolf

Max Planck Research Group: Structural and Electronic Surface Dynamics

Head: Ralph Ernstorfer

1. General Remarks

Since the last meeting of the Fachbeirat, the Department of Physical Chemistry has continued to develop its research infrastructure in the existing lab space, while the construction of the new building has made significant progress. The research groups and equipment will move into this new building in summer 2016. Several changes have occurred among the group leaders and senior postdocs of the department:

- *Prof. Leonhard Grill* has moved all activities to the University of Graz after the completion of his EU-funded projects at the FHI.
- With the successful completion of PhD thesis work and two DFG projects the part-time appointment of *Prof. Karsten Horn* will terminate at the end of 2015.
- *Dr. Alexey Melnikov* will also leave the institute with the completion of his DFG Project in December 2015. His activities on spin and magnetization dynamics will be continued in part by *Dr. Ilya Razdolski*.
- Since January 2014, *Dr. Alexander Paarmann* has set up a new research group employing the FHI infrared free electron laser (FEL) for time-resolved optical spectroscopy to study ultrafast dynamics in solids, in particular phonon dynamics. His group contributes significantly to the characterization and future development of the FEL.
- *Dr. Alexander Saywell* has moved from a DFG project (“Eigene Stelle”) at the FHI to a position at the University of Nottingham in January 2015.

Two large service groups of the institute, the Electronics and the Mechanical Workshops, are associated with the department. The organization and machine infrastructure of the Mechanical Workshop (headed by *Petrik Bischoff*) has been further improved and the output and support of the workshop for the FHI is well received by the scientists. The Electronics Workshop (headed by *Georg Heyne*) is also well organized and continues to provide excellent service for the institute.

1.1 Research of the Department

The research of the Department of Physical Chemistry focusses on the dynamics of elementary processes at surfaces, interfaces and in solids, aiming at a microscopic understanding of molecular and electronic processes as well as the interactions between various (electronic, spin and lattice) degrees of freedom. Our strategy is to address these problems from several sides using complementary approaches, in particular by the development and application of various time- or spatial-resolved spectroscopic techniques dedicated to the specific physical questions. The research is performed by small teams with specific expertise, and is structured along two main directions: (I) ultrafast dynamics of elementary processes in solids and at interfaces, and (II) molecular processes at interfaces and in complex systems. Although research topics of the individual groups are quite diverse and their selection is primarily curiosity-driven, our complementary approach creates various synergies between the different groups.

The first line of research investigates the dynamics of elementary processes on their relevant time scales, employing ultrafast laser spectroscopy (with, typically, femtosecond time resolution). Both established and newly developed spectroscopic techniques are used to study the electronic structure and low-energy excitations in solids, dynamics of electron transfer processes, vibrational dynamics at interfaces, as well as optically induced phase transitions in solids. The second line of research addresses elementary molecular processes either at the single molecule level, or by employing various schemes of optical excitations including photoinduced surface reactions. Scanning probe microscopy – in part combined with optical excitation or light scattering – is used for imaging, manipulation and spectroscopy as well as inducing and probing chemical processes of individual molecules. Further activities address problems of molecular biophysics and electrochemistry.

The Department of Physical Chemistry currently has the following research groups:

Ultrafast Dynamics in Solids and at Interfaces

- Dynamics of Correlated Materials (*Martin Wolf*)
- Electron Dynamics at Interfaces (*Julia Stähler*)
- Electronic Structure of Surfaces and Interfaces (*Karsten Horn*)
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)
- Time-resolved Second Harmonic Generation Spectroscopy (*Alexey Melnikov*)

Molecular Processes at Interfaces and in Complex Systems

- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Complex Chemical and Biological Systems (*Alexander Mikhailov*)
- Spatiotemporal Self-organization (*Markus Eiswirth*)

Max-Planck-Research Group (MPRG)

- Structural and Electronic Surface Dynamics (*Ralph Ernstorfer)*

A new line of research in the department exploits the potential of the FHI FEL facility for time-resolved optical spectroscopy of solids, in particular of phonons and polaritons. A new research group, headed by *Alexander Paarmann*, has been established, which also develops tools for FEL pulse characterization, sensitive optical detection and non-linear spectroscopy as well as laser synchronization with the FEL.

The MPRG of *Ralph Ernstorfer* is associated with the department and collaborates intensively with regard to the development of high harmonic generation (HHG)-based XUV photoemission. The activity on time-resolved electron diffraction nicely complements the research on ultrafast electronic dynamics of solids in the department.

Promotion and guidance of young scientists in their career development is an important goal of the department, and is implemented by several measures (*e.g.* the IMPRS graduate school, PhD student and department workshops, regular status discussions, nomination for awards and invited talks). In particular, junior group leaders and postdocs are guided to obtain experience in grant applications and to become project leaders in EU or DFG funded projects. Currently, several young group leaders have projects as PIs in three collaborative research centers (Sfb 658, Sfb 951, Sfb 1109), one research unit (FOR 1700) funded by the Deutsche Forschungsgemeinschaft as well as in an EU-funded project (CRONOS). Furthermore, several individual DFG research grants of young scientists exist (see section 3 for a complete list of projects). Very recently, an independent Max Planck Research Group (MPRG) was awarded to *Julia Stähler*, which will start in 2016.

1.2 Selected Research Highlights

The following topics are a selection of research achievements as well as instrument developments in the department, obtained since the last report:

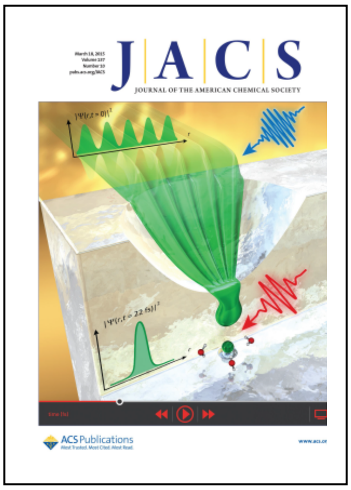
- Femtosecond time-resolved photoemission spectroscopy sheds new light onto the mechanism of the controversial photoinduced phase transition in VO_2: An instantaneous band gap collapse is observed upon photoexcitation, i.e. before the structural phase transition takes place. This transition to metallic monoclinic VO_2 is caused by photohole doping at the top of the valence band and followed by carrier relaxation on a 200 fs timescale. [Phys. Rev. Lett. **113**, 216401 (2014)].
- Critical phenomena in superconductors are typically observed in or close to equilibrium; however, strong indications for universal behavior in the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ have been found for far out-of-equilibrium conditions induced by

femtosecond laser pulses. Strikingly, the dependence of conductivity vs time delay after laser excitation, probed by THz spectroscopy at multiple sample temperatures, are found to fall onto one curve if the time axis is normalized by a suitable scaling factor. These findings can be explained in part by a model based on the dynamic Ginzburg-Landau equation [Phys. Rev. Lett. **114**, 067003 (2015)].

- The charge density wave (CDW) transition in $TiSe_2$ has been elucidated using time-resolved and angle-resolved photoemission spectroscopy (trARPES), suggesting that the momentum- and energy-resolved relaxation times reveal the material's self-energy, and that the excitonic interaction between valence and conduction bands leads to the CDW instability of $TiSe_2$. Furthermore, a detailed study of the ultrafast photoinduced CDW gap dynamics in tri-tellurides revealed a stabilization of the gap due to increased Fermi surface nesting in the excited state [Faraday Discuss. **171**, 299 (2014)].
- A high repetition rate XUV laser source for time- and angle-resolved photoemission spectroscopy has been developed. The light source is based on high-harmonic generation (HHG) driven with a novel optical parametric laser system, and provides spectrally isolated femtosecond pulses with 21.5 eV photon energy at a repetition rate of 500 kHz [Optics Express **23**, 1491 (2015)].
- Hydrogen adsorption on ZnO(10-10) leads to local and site-specific changes of the surface potential, resulting in the formation of a charge accumulation layer and a global work function reduction of up to 600 meV. These sites host sub-surface bound excitons that form within 200 fs after above band gap photoexcitation of ZnO. The exciton formation is suppressed for excitation densities close to the Mott limit. [Phys. Rev. Lett. **113**, 057602 (2014), Phys. Rev. B **91**, 235313 (2015)].
- Functionalization of graphene with fluorine was used to create fluorographene, which exhibits a transformation between a stable as well as a metastable phase, induced by photon irradiation. The latter phase reverts back to the stable phase under blue luminescence [ACS Nano **8**, 7801(2014)].
- A new experimental setup for mid-infrared second harmonic generation (SHG) spectroscopy of solids employing the FHI infrared free electron laser (FHI FEL) has been developed. The high sensitivity of this technique to optical phonon resonances has been demonstrated for silicon carbide in the Reststrahl band [Appl. Phys. Lett. (in press)].
- To fully exploit the potential of the FHI FEL for time-resolved spectroscopy various techniques for optical characterization of the FEL output have been developed focusing on

nonlinear optics and ultrashort pulse operation of the machine. A synchronization system for a femtosecond near-infrared laser oscillator is currently being implemented for mid/near-infrared two-color experiments.

- THz metamaterials allow control of the effective refractive index by tailoring the shape of periodic metal structures. However, this approach usually requires extensive lithography procedures. To generate flexible THz metamaterials in a much easier and even dynamic and contactless manner, a semiconductor substrate is illuminated using fs laser pulses with a spatially shaped beam profile creating transiently metallic regions. Using such femtosecond lithography, a transient wire-grid polarizer and its ultrafast switch-on to manipulate a picosecond electromagnetic THz pulse with subcycle precision has been demonstrated [Light: Science and Applications **3**, e155 (2014)].
- The first measurement of the vertical binding energy (VBE) of the conduction band of the amorphous solid water phase was achieved using fs time-resolved two-photon photoelectron spectroscopy (2PPE). As all elementary processes "during the birth" of a solvated electron have been monitored in real time, the previous inaccessibility of the conduction band VBE could be attributed to the extremely short population lifetime (22 fs) in these excited states. [J. Am. Chem. Soc. **137**, 3520 (2015), see cover].



- Probing short-lived reaction intermediates at surfaces is extremely challenging due to their extremely low concentrations under steady state conditions. However, femtosecond laser excitation can enable temporal gating of such species: For the CO oxidation reaction on Ru(001) initiated by an ultrashort laser pulse new electronic states – attributed to CO_2 reaction intermediates close to the transition state region – have been probed using femtosecond time-resolved x-ray spectroscopy (trRIXS) at the LCLS free electron laser in Stanford. [Science **347**, 978 (2015); Phys. Rev. Lett. **114**, 156101 (2015)].
- The librational mode of interfacial water at the air/liquid water interface has been experimentally probed for the first time and found to be substantially higher in frequency than in bulk liquid water at the same temperature but similar to that in ice. Evidently, from the perspective of water's rotational potential, water at the air/water interface is "ice-like", while viewed from its OH stretch frequency or picosecond structural dynamics water is "liquid-like".

- Tautomerization of individual molecules was studied for porphycene on a Cu(110) surface by using low-temperature scanning tunneling microscopy, revealing a vibrationally mediated excitation mechanism through inelastic electron tunneling. The tautomerization probability can be precisely controlled by placing single adatoms and molecules nearby [Nature Chemistry **6**, 41 (2014)].
- Tip-enhanced Raman spectroscopy (TERS) of graphene nanoribbons grown on Au(111) was applied in an UHV scanning tunneling microscope (STM) setup. The 0.74 nm wide armchair nanoribbons are directly observed by STM and characteristic vibrational modes appear in both the far- and near-field Raman spectra, yielding an enhancement of $4 \cdot 10^5$ in TERS [J. Phys. Chem. C 118, 11806 (2014)].
- Reversible switching of single porphycene molecules on a Cu(111) surface was demonstrated using low-temperature STM. The thermodynamically stable *trans* tautomer can be selectively converted to the metastable *cis* configuration by hot carriers excited by a voltage pulse, whereas *cis* molecules can be switched back to *trans* by thermal activation [ACS Nano **9**, 7287–7295 (2015)].
- A thin-layer electrochemical cell allowing for simultaneously conducting cyclo-voltammetry and interface-specific vibrationally resonant sum frequency generation (SFG) spectroscopy was developed and used to probe the paradigmatic electro-oxidation of formic acid. On Pt(100), weakly adsorbed formic acid was found to play an important role in the so-called *direct* oxidation pathway.
- Hydrodynamic collective effects of active proteins, cyclically changing their shapes, in cytoplasm of a biological cell and in bio-membranes were theoretically investigated. ATP-dependent diffusion enhancement and directed drift-induced by concentration gradients of active proteins were demonstrated, in agreement with experimental data [Proc. Natl. Acad. Sci. (USA) **112**, E3639 -E3644 (2015)].

2. Progress Report

2.1 Ultrafast Dynamics in Solids and at Interfaces

Elementary processes in solids and at interfaces such as electron transfer, vibrational excitation and relaxation, or coupling between electrons, phonons and spins are the underlying microscopic processes of much more complex phenomena, ranging from surface reactions to phase transitions in complex materials. The study of the non-equilibrium, ultrafast dynamics of such fundamental processes provides mechanistic insights into the coupling and energy exchange between various degrees of freedom. To elucidate these processes, several groups in the department perform real-time studies of solids and interfaces on ultrafast time-scales, complemented by studies of the electronic structure and low-energy excitations.

2.1.1 Ultrafast Electron and Lattice Dynamics in Correlated Materials

Strong correlation effects in solid state materials underlie fundamentally important and potentially useful phenomena such as insulator-metal transitions or unconventional superconductivity. In such materials, different degrees of freedom (charge, spin, orbital, and lattice) are often strongly coupled and lead to electronic, magnetic, and structural instabilities. Beyond the investigation of ground state properties, studies of the non-equilibrium properties after optical excitation provide insight into the elementary mechanisms responsible for the formation and destruction of the strongly correlated state. Angle-resolved photoemission spectroscopy (ARPES) is a well-established technique to get access to the spectral function and the single-particle band structure of a solid. We use this method in a pump-probe scheme, where a first laser pulse (pump) drives the sample into non-equilibrium conditions and a second laser pulse (probe) monitors the electronic structure after a certain time delay. The variation of the time difference between pump and probe enables the observation of the transient evolution of the electronic structure on femtosecond timescales.

The group of *Julia Stähler* has investigated vanadium dioxide (VO_2) as a paradigmatic example for strongly correlated materials. VO_2 undergoes an insulator-to-metal transition at 340 K, which is accompanied by a change of the crystal structure from the monoclinic to the rutile phase (see Fig. 1(a)). Despite major scientific efforts over decades, the question whether the monoclinic distortion of the lattice is a sufficient condition for the opening of the gap or if strong electron correlations are responsible to form the insulating state (“Mott gap”) remained unanswered. One approach to tackle this question is to disturb the *electronic* system (i.e. the electron correlation) by optical excitation and to monitor the ultrafast response of the material in the time domain. If the material instantaneously transforms to a metal, the insulating gap originates purely from electron correlation; if lattice reorganization is needed to precede the electronic transition, a finite time for the gap collapse would be expected.

The group recently succeeded to perform the first time-resolved photoemission measurements with sufficient time resolution of the photoinduced phase transition in VO_2. [1] Figure 1(b) shows the photoinduced change of the PES intensity in the band gap of insulating VO_2 in false colors as a function of energy with respect to the Fermi energy (right axis) and pump-probe time delay (bottom axis). Quasi-instantaneously with the photoexcitation at $t = 0$, spectral weight is observed in the band gap, showing that the gap has collapsed. Analysis of the temporal evolution of the photoemission intensity as a function of time shows that the quasi-instantaneous gap collapse occurs faster than the relaxation of hot carriers occurring in approximately 200 fs. In a close collaboration with Angel Rubio (associated with the Theory Department) it could be shown by first-principles many body perturbation theory that the abrupt change of electronic structure can be explained by the photoinduced depopulation of very localized states at the top of the valence band, leading to pronounced changes in the screening of the Coulomb interaction and strong renormalization of the band gap. The combination of theory and experiment thus shows that the insulating gap of VO_2 breaks down instantaneously with the disturbance of electron correlation through photoexcitation, without the necessity of structural rearrangement.

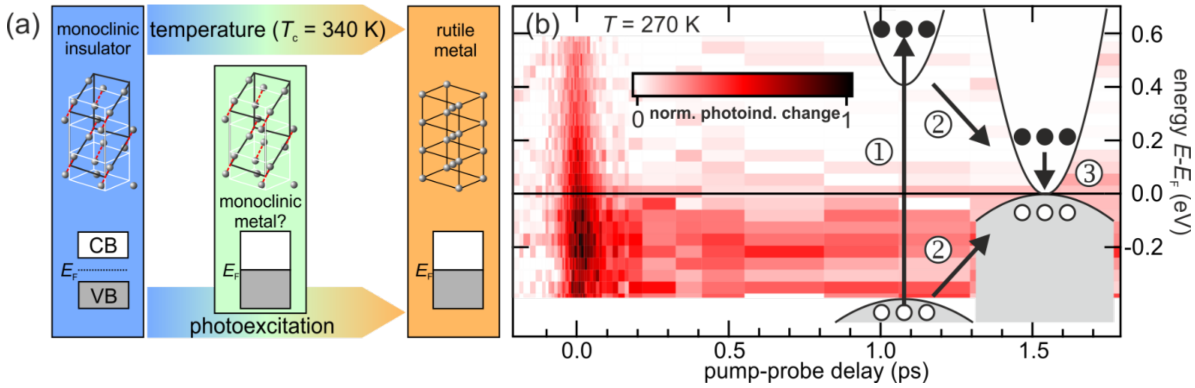


Figure 1: *(a) Thermal and photoinduced transition in* VO_2 *from a monoclinic insulating to a rutile metallic phase. (b) Photoinduced change of the photoemission intensity in the band gap of insulating* VO_2. Inset: *Directly after photoexcitation (1), the gap collapses (2) before carriers relax to the Fermi level (3) within 200 fs.*

Non-equilibrium conditions may lead to novel properties of photoexcited materials which are not accessible in equilibrium. Such excited states are usually characterized by enhanced fluctuations, leading to a reduced or even vanishing order parameter of a broken symmetry ground state, characterized, e.g., by an electronic energy gap. The group of *Martin Wolf* has investigated the charge density wave (CDW) material class of rare-earth tri-tellurides, RTe_3 (RTe_3, R = Te, Ho, Dy) using trARPES and demonstrated direct probing of the transient modulation of the CDW gap as well as vibrational coherent control of the amplitude mode using a three-pulse excitation scheme [2]. Furthermore, the electronic structure reveals a persistent energy gap even in highly excited transient states. This is attributed to a competition between fluctuations in the electronically excited state which tend to reduce order, and transiently enhanced Fermi surface nesting that stabilizes the order.

A key quantity describing the physics of correlated materials is the self-energy, which represents the relevant many-body interactions of a system and determines the lineshape of electronic bands probed by ARPES. The group has investigated the mechanism of the charge density wave instability in $TiSe_2$ – a layered transition metal dichalcogenide – using the time-resolved XUV ARPES setup at the Artemis facility, UK. Analysis of the dynamics in the high-temperature fluctuation regime, which precedes the CDW instability, suggests that the momentum- and energy-resolved relaxation times reveal the imaginary part of the material's self-energy. Comparison with theoretical modelling allows the identification of the Coulomb-mediated electron-hole (excitonic) interaction between the valence and conduction bands as the dominant mechanism leading to the CDW instability of $TiSe_2$.

A related compound, Ta_2NiSe_5, which undergoes an insulator-semiconductor transition at 328 K accompanied by a structural distortion, was investigated by *Julia Stähler*'*s* group. By combining static Raman spectroscopy (in cooperation with the CP department) with femtosecond time-resolved optical spectroscopy as well as time-resolved ARPES, a very strong coupling of the 4 THz mode, which is characteristic for the low-temperature phase, to the photoexcited carrier density was observed. Most remarkably, the ultrafast dynamics of electrons *and* holes in the conduction and valence band indicate that an intrinsic absorption saturation of Ta_2NiSe_5 inhibits a photoinduced phase transition; on the contrary, strong photoexcitation leads to a widening of the band gap, suggesting that photoexcited Ta_2NiSe_5 is *more* insulating than in equilibrium.

To provide access to the full electronic structure in the entire Brillouin zone a high harmonic generation (HHG)-based XUV photoemission setup has been developed in close collaboration with the MPRG of *Ralph Ernstorfer*. Our approach relies on a novel high-average power ultrashort laser system [3] with an optical parametric chirped-pulse amplifier (OPCPA) capable of generating spectrally narrow XUV pulses (21.7 eV with 100 meV bandwidth) at 500 kHz repetition rate for trARPES (see MPRG report for more details). This XUV light source closes a technology gap, which has so far has limited the operation of HHG sources to repetition rates typically below 10 kHz.

[1] D. Wegkamp *et. al*, Phys. Rev. Lett. **113**, 216401 (2014)

[2] L. Rettig *et. al*, Faraday Discuss. **171**, 299 (2014)

[3] M. Puppin *et al.*, Optics Express **23**, 1491 (2015)

2.1.2 Electronic Structure of Metal Oxide Surfaces and Low-dimensional Materials

The group of *Takashi Kumagai* has studied the local electronic structure of ultrathin ZnO films by using low-temperature scanning probe microscopy (STM and AFM). The growth and structure of smooth ZnO films on Ag(111) was investigated in collaboration with the CP department [1]. Fig. 2 (a) shows, as an example, the simultaneously recorded STM image and STS mapping for 2 and 3 ML thick ZnO layers, with a characteristic Moiré pattern resulting from the lattice mismatch between ZnO and Ag(111). The atomic arrangement could be further investigated by noncontact AFM with atomic resolution and DFT calculations in collaboration with the Theory department. Furthermore, the local density of states (empty electronic states) was analyzed by STS, whereby local variations caused by the finite size of the films and defects (highlighted by the dashed circle) could be clearly observed. These results provided microscopic insight into the geometric and electronic structure of this system.

The group of *Julia Stähler* has investigated the impact of hydrogen adsorption on the electronic structure and dynamics at the surface of bulk ZnO single crystals using fs time-resolved photoelectron spectroscopy. In collaboration with Patrick Rinke, Theory Department, it was shown that O-H bond formation, which dominates at low-coverages, leads to distinct a local drop of the potential, significantly reducing the sample work function and leading to downward surface band bending (see Fig. 2b). Due to the *n*-type character of ZnO, this results in a partial filling of the conduction band in the surface region, leading to the formation of a charge accumulation layer (CAL) at the surface. Zn-H bonds, on the contrary, lift the potential upwards, thereby reducing the effect of an O-H precoverage. The complex interplay of both adsorption sites strongly influences the CAL density at the surface and causes a saturation of the work function decrease of 0.6 eV [2].

The hydrogen-induced local potential minima host sub-surface-bound excitons (SX) when ZnO(10-10) is optically excited. After ultrafast ($\tau(E)$ = 20-200 fs) relaxation of photoexcited hot carriers through scattering with optical phonons, electron-hole pairs form that exhibit a temperature-dependent decay and nanosecond lifetimes. The formation probability of SX

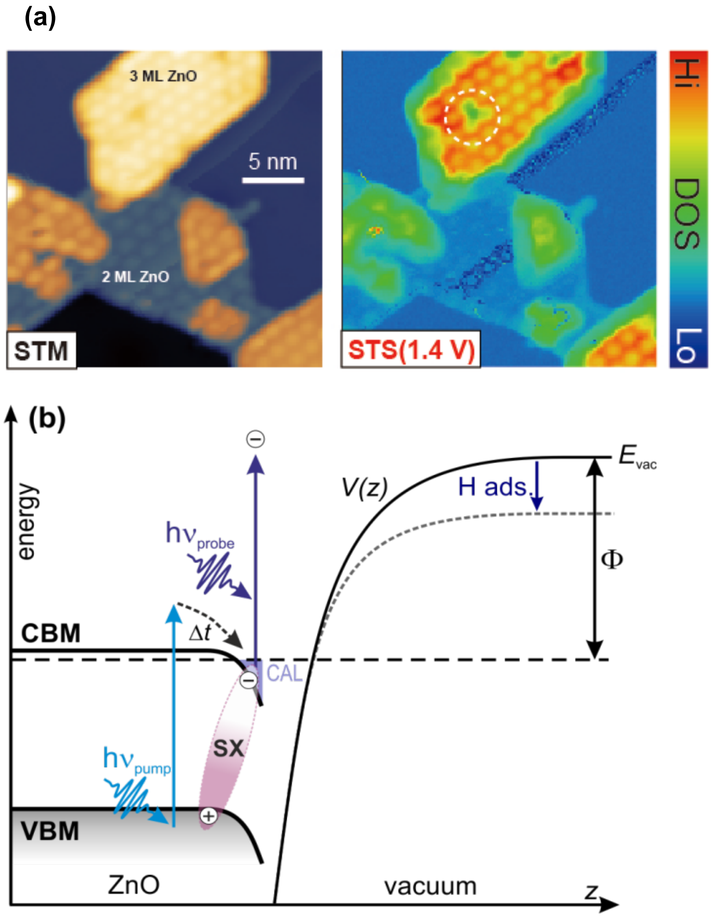


Figure 2 (a) *(Left) STM image of the 2 and 3 ML ZnO films on Ag(111) at 5 K. The characteristic Moiré pattern is observed over the ZnO layers. (Right) STS mapping measured at the resonance state of the 3 ML ZnO layer. (b) Hydrogen adsorption on the ZnO(10-10) surface leads to a reduction of the work function and downward surface band bending. Due to the n-type character of ZnO the conduction band becomes partially filled at the surface, creating a charge accumulation layer (CAL). Above band gap excitation is followed by hot carrier relaxation to the Fermi level and the formation of sub-surface-bound excitons.*

reduces as the excitation density approaches the Mott limit, when the photoexcitation creates an electron-hole plasma that screens the attractive Coulomb interaction [2]. Moreover, hydrogen coverage (and, thus, CAL carrier concentration) dependent experiments unveil that the coupling of excited electrons to the phonons is reduced and thus their lifetime is enhanced. Above a critical density, the screening of the Coulomb attraction even becomes sufficiently large to completely suppress SX formation.

$SrTiO_3$ (STO) is another *n*-type transition metal oxide that exhibits a charge accumulation layer at its surface. Here the CAL is caused by oxygen defects at the surface. The density of the CAL is one order of magnitude larger than the one of hydrogen-terminated ZnO (10-10), thus inhibiting SX formation for this system due to enhanced screening. The response of STO to strong photoexcitation in the near IR was also investigated in *Julia Stähler*'s group: Photons absorbed at in-gap states at the STO surface (at oxygen defects) generate additional charge density in the conduction band. Surprisingly, the highly excited carriers relax on timescales compatible with 2D Fermi liquid theory despite populating energy levels that are degenerate with bulk (3D) conduction band states.

The group of *Karsten Horn* has concentrated on the properties of graphene, both in its pristine form but also modified by adatom functionalization and through contact with metals. A fluorographene modification was found to arise from exposure to fluorine atoms, with a stable as well as metastable phase (induced by photon irradiation), which reverts to the former under emission of blue luminescence. Functionalization of graphene by various adsorbates (NO, SO_2) was found to induce massive changes in its electronic structure, and to promote a reversible transformation into graphene oxide [3].

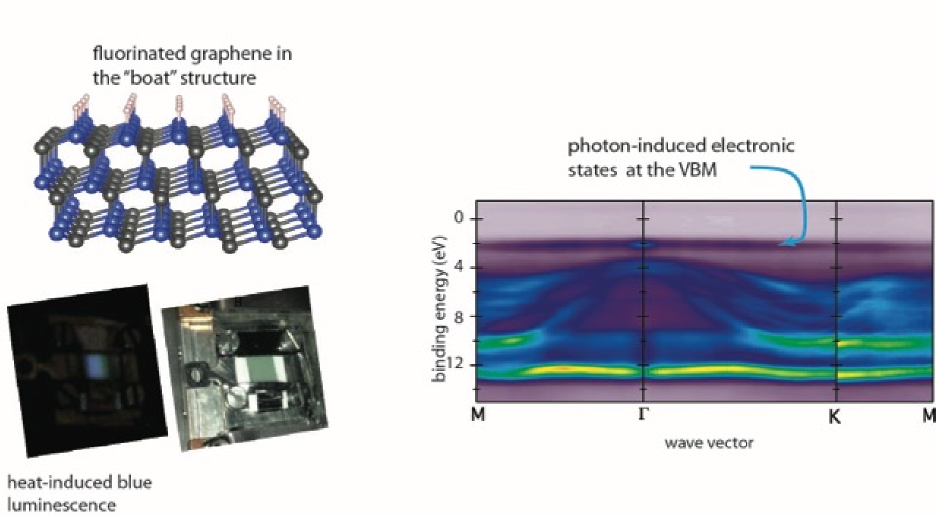


Figure 3: *Single-sided fluorographene exists in the stable „boat“ ground state, but can be converted into a metastable state by UV irradiation, upon which new electronic states appear at the valence band maximum as revealed by ARPES. Annealing reverts the metastable state to the ground state under emission of blue luminescence.*

Graphene interaction with metals may lead to symmetry breaking and band gap opening, a process that was elucidated in detail (for copper as a substrate), through comparison with DFT calculations. Emerging ferromagnetism of thin cobalt films underneath graphene was examined through x-ray magnetic circular dichroism (XMCD), and a transfer of magnetic moment onto the carbon atoms of graphene was found, with a reversal of the out-of-plane ordering of magnetic moment in the metal and graphene.

Self-assembled metal nanowires on semiconducting substrates are an important model system for low-dimensional materials providing a versatile and tuneable environment. The electronic structure of the Ag/Si(557) nanowire system exhibits signatures of a quasi-1D electron gas in electron energy loss spectroscopy, but two-dimensional metallic states at the Fermi level with a super-periodicity were observed by ARPES. These seemingly conflicting views of the dimensionality in this and other nanowire systems can be reconciled by considering the electronic coherence length of excitations probed by ARPES or EELS.

[1] A. Shiotari *et al.*, J. Phys. Chem. C **118**, 27428 (2014).

[2] J.-C. Deinert *et.al.*, Phys. Rev. B **91**, 235313 (2015), *Phys. Rev. Lett.* **113**, 057602 (2014)

[3] A.L. Walter *et al*, ACS Nano **8**, 7801(2014)

2.1.3 Mid-infrared Nonlinear Spectroscopy of Solids

The possibility of transient control of physical properties of a crystal by means of large amplitude lattice vibrations, excited by intense mid-infrared (mid-IR) laser pulses, provides an attractive alternative route to various electronic excitation schemes. The newly established group of *Alexander Paarmann* develops experimental techniques for studying lattice-driven nonlinear phenomena by employing the FHI infrared free-electron laser. These efforts encompass two major components: the development of novel nonlinear mid-IR spectroscopy approaches using the FEL, and the characterization and optimization of the FEL specifically for these experiments.

Despite much progress in the development of intense, broadband THz and mid-IR light sources based on femtosecond table-top lasers, there is still a lack of intense, narrowband lasers in this frequency region. In that regard, the FHI FEL provides a unique opportunity to study sharp phonon resonances in the nonlinear optical response of a solid. The group has developed second harmonic (SH) phonon spectroscopy as a new even-order nonlinear optical technique, see Fig. 4. For the prototype material silicon carbide (SiC), pronounced resonances in the SH spectrum can be related to phonon-induced enhancements of the nonlinear susceptibility and the local fields through the Fresnel transmission, respectively [1]. Furthermore, the high sensitivity of the SH yield to local fields was exploited in studies of field localization of surface phonon polaritons confined to sub-wavelength nanostructures with SH phonon spectroscopy. By improving the sensitivity of mid-IR SH spectroscopy (e.g. by heterodyne detection), the group aims to establish this method for surface- and interface-sensitive vibrational spectroscopy.

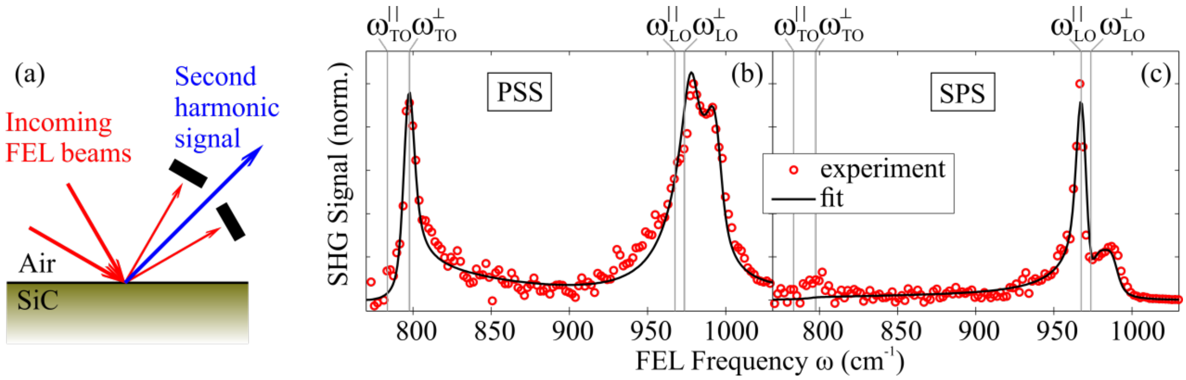


Figure 4: *Second harmonic phonon spectroscopy of SiC. (a) Schematic of the second harmonic experiment employing the FEL in a non-collinear geometry. (b,c) Experimental second harmonic spectra of SiC for two different polarization combinations of incoming and detected beams. For reference, the axial ($\parallel$) and planar ($\perp$) optical phonon frequencies for longitudinal (LO) and transversal (TO) modes in the uniaxial crystal are indicated. From Ref. [1].*

In addition, the group has developed and implemented several experimental approaches to address phonon-driven resonant demagnetization, nonlinear absorption, and second harmonic generation in solids. In part, these frequency-domain studies nicely complement the time-domain experiments in the THz spectroscopy group (*Tobias Kampfrath*): for instance, the role of optical phonon resonances in the ultrafast demagnetization of ferrimagnetic yttrium iron garnet (YIG) has been investigated with both techniques. Similarly, a novel excitation pathway for Raman-active (IR-inactive) phonons by a sum-frequency process at half the phonon frequency was demonstrated with in two complementary approaches: (i) time-domain coherent phonon spectroscopy after excitation with broadband, phase-stable THz pulses and (ii) two-photon absorption spectroscopy employing the tunable FEL radiation.

The characterization of the short pulse and nonlinear operation of the FEL was performed by multiple experimental approaches. The temporal shape of the FEL micropulses was measured using a specifically designed autocorrelator that can operate in the whole tuning range of the FEL [2]. It was demonstrated that the FEL micropulse duration and spectrum, as well as the peak intensities critically depend on the FEL cavity parameters, but also evolve during the FEL macropulse, allowing for precise control of these features for optimal conditions of nonlinear optical experiments. The intrinsic harmonic content of the FEL output (up to the 11th harmonic) has been characterized using a prism-based harmonic separator, and control of the harmonic intensities by variation of the electron beam steering was demonstrated.

A synchronization system for a femtosecond near-infrared (NIR) laser oscillator is currently under construction, and the respective characterization techniques are being developed. The synchronized laser will allow for implementation of time-resolved FEL-pump – NIR-probe experiments, as well as surface specific vibrational sum-frequency spectroscopy.

[1] A. Paarmann *et al.*, Appl. Phys. Lett. **107**, 081101 (2015)

[2] W. Schöllkopf *et al.*, Proc. of SPIE Vol. **9512**, 95121L (2015)

2.1.4 Terahertz Physics: Low-energy Excitations and Control by THz-Fields

The terahertz (THz) frequency range is of key relevance from a fundamental scientific as well as from an applications-related point of view. Many elementary excitations in physical systems have transition energies on the order of 10 meV, for example quasi-free electrons in solids, crystal lattice vibrations, or excitons in semiconductors. As 1 THz corresponds to a photon energy of 4.1 meV, these modes can be probed resonantly and with sub-picosecond time resolution using THz electromagnetic pulses. As today THz pulses with electric-field amplitudes of ~1 MV/cm can be generated in the lab, it has become possible to even drive and control such resonances on sub-picosecond time scales [1]. Furthermore, bit rates in information technology may soon approach the THz range, which requires to manipulate the information carrier (such as the electronic current, spins or light) at THz frequencies, for example with modulators and frequency shifters.

The group of *Tobias Kampfrath* makes use of ultrashort THz and optical laser pulses in order

- To gain insight into the interplay of low-energy excitations in complex materials. Examples are the elusive interaction of lattice and electron spins in magnetically ordered solids or rotational/librational motion of molecules in liquids.
- To gain control over the properties of matter and light at highest frequencies and to explore potential applications. Examples are the ultrafast transport of electron spins and generation of transient metamaterials for THz radiation.
- To develop new and sensitive spectroscopic tools which permit, for example, the detection of ultrafast spin currents (“ultrafast spin amperemeter”) and the measurement of high-frequency Hall effects.

Recent examples for these research activities are described in the following.

Electron dynamics in complex solids: THz pulses are an excellent and ultrafast probe of the conductivity of transient electrons, in particular following excitation with a femtosecond laser pulse. This strategy allows measuring the mobility of conduction electrons of two intrinsic (insulating) polytypes of the semiconductor SiC in a contact-free manner [2]. These measurements are an important characterization of the electrical transport properties of SiC which is considered a key material in high-voltage and high-temperature electronics.

Using a similar approach, a femtosecond laser pulse is applied to suddenly break Cooper pairs in the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSSCO) and a THz probe is used to monitor the subsequent recovery of the superconducting state. Strikingly, the relaxation to equilibrium exhibits a power-law dynamics and scaling behavior. In particular, we found that curves of conductivity vs time at multiple sample temperatures fall onto one curve when the time axis is normalized by a suitable scaling factor. Our findings provide strong indication of universality in systems far from equilibrium [3].

Ultrafast spin transport: Future electronics will potentially not only make use of the electron charge as an information carrier, but also employ the electron spin to encode bits. Successful implementation of such “spintronics” requires the transfer of electron spins through space as well as the manipulation of the spin state. These elementary operations should proceed at a pace exceeding that of today’s computers, that is, at THz frequencies. Currently, we study the high-frequency (THz) behavior of central spintronic effects in metals: the anomalous and spin Hall effect (AHE and SHE). Both phenomena rely on spin-orbit coupling (SOC) that causes a deflection of spin-up and spin-down conduction electrons in opposite directions. We have developed a method that permits measurement of the AHE (i.e. the full conductivity tensor) of standard magnetic metals such as CoFeB over the broad frequency range from 0.5 to 40 THz in a quasioptical, contact-free manner. As the related photon energies (4 meV at 1 THz) coincide with typical SOC band splittings in 3d metals, we hope to gain direct insight into the energetic structure of SOC of conduction electrons.

Ultrafast spin-lattice coupling: The coupling of lattice vibrations and ordered spins in magnetic solids is far from being understood, despite its fundamental and applied relevance for ultrafast spin manipulation (femtomagnetism) and transport of spin angular momentum (spintronics and spin caloritronics). To probe spin-lattice coupling in a direct and highly selective manner and on its natural time scales, we conducted the THz pump-probe experiment shown in Fig. 5(a). As a model ferrimagnetic insulator, yttrium iron garnet (YIG) was chosen because its electronic degrees of freedom are frozen out at room temperature (electronic band gap 2.8 eV). An intense THz pulse exclusively and resonantly excites optical phonons, thereby leaving the electronic subsystem unchanged. Ultrafast demagnetization with a time constant as short as 1 ps is observed [Fig. 5(b)], which is extremely surprising because decoherence of spin precession in YIG is known to occur on much longer time scales of >100 ns. Supported by measurements covering a broad temperature range and time scales from 10^{-13} to 10^{-3} s as well as analytical modeling and *ab initio* calculations, we found evidence for a new microscopic mechanism of phonon-to-magnon conversion.

Surface/interface sensitivity: So far, THz pulses have exclusively addressed the bulk properties of materials (rather than their interfaces). The THz group has recently been able to

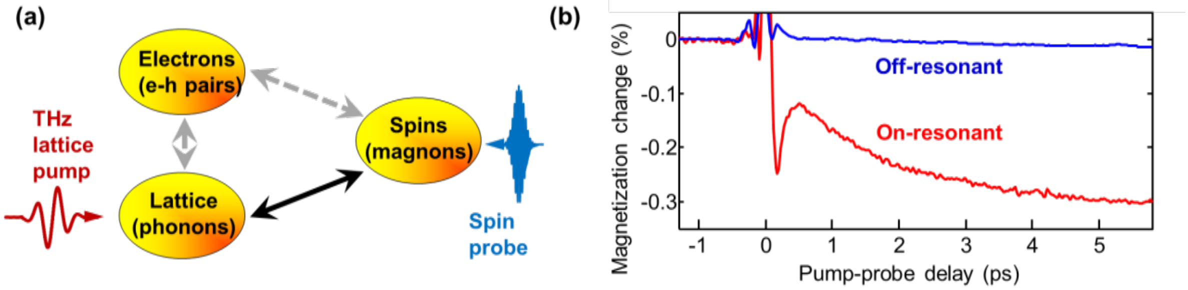


Figure 5*: (a) Pump-probe scheme for probing spin-lattice coupling in a magnetic solid. A THz pump pulse resonantly excites a zone-center optical phonon, and the impact on the spin system is monitored by a delayed pulse probing the transient magnetization. In the case of a magnetic insulator, the orbital electron degrees of freedom are frozen out (dashed arrows). (b) Observation of ultrafast magnetization quenching of yttrium iron garnet (YIG). While off-resonant pumping in the transparency window of YIG results in a negligible signal, resonant phonon excitation leads to a drop of the magnetization with a time constant as short as ~1 ps.*

optically launch and measure THz currents flowing at the surface of the topological insulator Bi_2Se_3. Excitation by a laser pulse (duration 10 fs, photon energy 1.55 eV) shifts electron density from the Se atoms toward the Bi atoms. Our data indicate that this shift current flows predominantly in the first ~2 nm of the surface region. In addition, our results show that previously suggested scenarios based on optically induced changes in the electron group velocity are inoperative or at least result in much less efficient currents than assumed.

Manipulation of THz radiation: The THz group also tested new schemes to manipulate THz radiation using optically induced, time-varying structures. More precisely, a laser beam with a spatially modulated cross-section was directed onto a planar semiconductor slab, in which the optical intensity pattern is translated into a spatial modulation of the refractive index. While dark regions remained dielectric, the illuminated regions became metallic at THz frequencies, owing to the generation of an electron-hole plasma. Compared with standard lithography, such “gray-scale transient lithography” offers improved flexibility. This approach has been used to generate a transient wire-grid polarizer, i.e. a pattern of alternating conducting and dielectric stripes. Ultrafast operation was demonstrated by switching the polarizer on when the leading half of an incident THz pulse had traversed the slab. The trailing edge then encountered a polarizer, resulting in a polarization plane by 45° rotated [4]. This approach is a first step toward more complex operations such as frequency shifting and spectral focusing of THz electromagnetic pulses.

[1] T. Kampfrath, K. Tanaka, K.A. Nelson, Nature Photonics **7**, 680 (2013). (Review article)

[2] A. Rubano, M. Wolf, T. Kampfrath, Appl. Phys. Lett. **105**, 032104 (2014)

[3] L. Perfetti *et al.,* Phys. Rev. Lett. **114**, 067003 (2015)

[4] N. Kamaraju, *et al.*, Light: Science and Applications **3**, e155 (2014)

2.1.5 Ultrafast spin dynamics in epitaxial metallic multilayers

Ultrafast spin dynamics induced by transport of photoexcited spin polarized carriers is of fundamental interest for magnetic applications such as spintronics and data storage. To study the underlying elementary processes on femtosecond time scales, the group of *Alexey Melnikov* has developed a time domain approach that probes the spin dynamics induced by hot carriers in a back pump-front probe scheme (see Fig. 6) with the help of time-resolved second harmonic generation (SHG) [1, 2] and magneto-optical Kerr effect (MOKE) [2]. In the first experiment, the transport of spin polarized hot carriers through an Au/Fe/MgO(001) stack has been demonstrated [1]. One particular focus of the group is the development of generation, control, and monitoring techniques for ultrashort spin current pulses and the study of their spin transfer torque action on a ferromagnet. The latter is an elegant and promising way to excite magnetization dynamics: when spin-polarized hot carriers reach the ferromagnetic layer, the magnetization experiences a torque and starts moving out of the equilibrium.

In metals, spin currents (SC) can be produced by temperature gradients in a bulk FM or across interfaces to a normal metal, which is known as the spin Seebeck effect. Recently, the group has demonstrated the ultrafast spin Seebeck effect, which is based on the spin-dependent interface transmission for non-equilibrium hot carriers (Fig. 6 (a)): large Fe/Au interface transmission for majority electrons provides a spin flux from Fe to Au forming a pulse of superdiffusive spin current. The SC pulse duration is determined by the hot carrier thermalization time on the order of 200 fs: once the HC relax towards the Fermi level the transmission difference vanishes and the HC emission stops. Experimentally, non-equilibrium carriers are excited in the top Fe layer of a Fe/Au/Fe/MgO(001) structure by a 14 fs, 800 nm laser pulse. Generation of about 300 fs-long spin current pulses has been demonstrated by characterization of their shape with SHG after passing the Au layer (Fig. 6 (c)). Upon reflection at the Fe/Au interface of the bottom Fe layer the SC polarized orthogonally to the Fe magnetization M lose the orthogonal component and become polarized anti-parallel to M. Furthermore, subsequent picosecond precessional dynamics of M excited in the second Fe layer by the spin transfer torque has been monitored with MOKE (Fig. 6 (d)). Owing to a spatially non-uniform spin transfer torque, several lowest standing spin wave modes are excited and spectral analysis of these modes allows an estimate of the spin accumulation depth in Fe $\lambda < 4$ nm (Fig. 6 (e)).

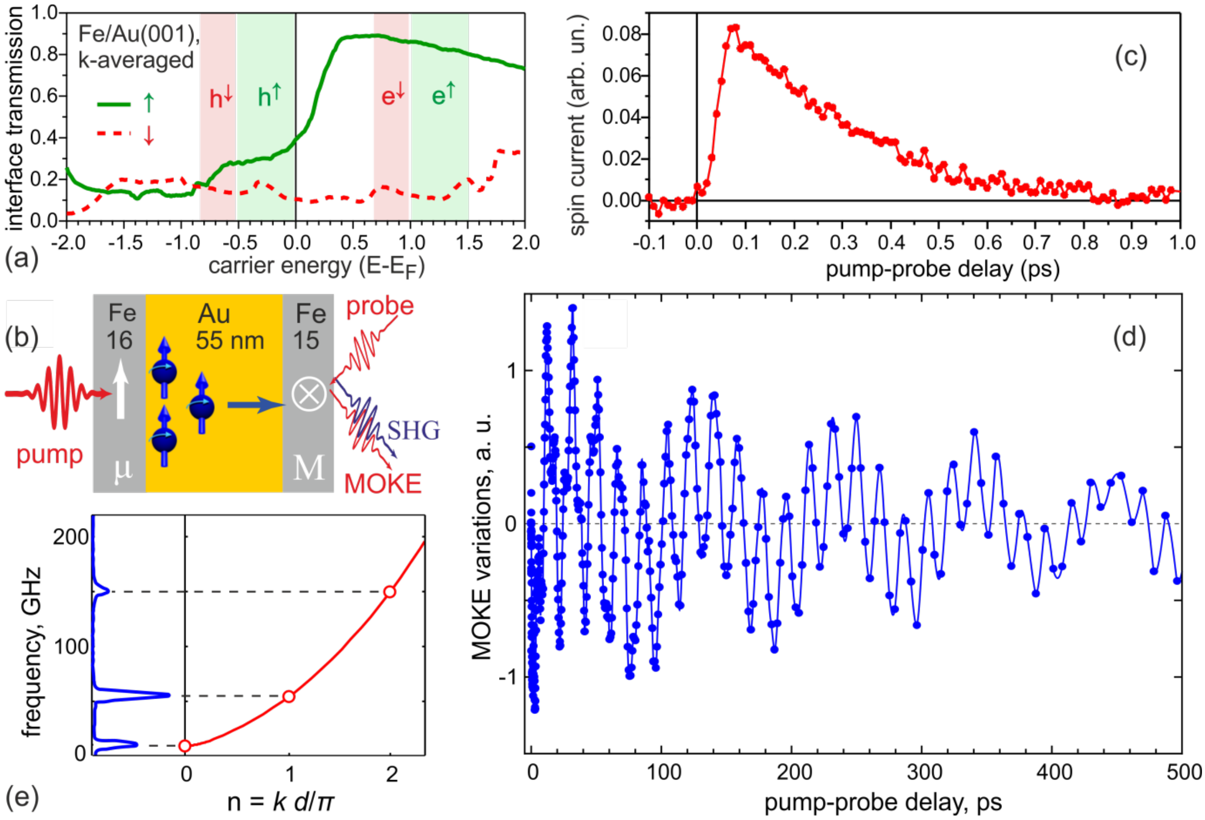


Figure 6: *(a) Ab initio calculated spin-dependent hot carrier transmission of the Fe/Au interface [2]; shadowed areas mark energy ranges where spin-polarized carrier are excited in Fe [1]. (b) Schematic of the experimental geometry. (c) Spin current SC pulse profile given by the SC-induced component of SHG electric field (which is directly proportional to SC in Au in the vicinity of Au/Fe interface) normalized to the magnetization-induced interface contribution. (d) Spin transfer torque -induced MOKE rotation. (e) Fourier spectrum of the MOKE rotation (blue) and the magnon dispersion curve (red solid line) in Fe. Frequencies of the detected modes (open circles) characterized by a wavenumber n are in an excellent agreement with those calculated for the standing waves in a 15-nm-thick Fe film.*

These findings demonstrate the excellent abilities of spin currents for exciting non-uniform spin eigenmodes in thin ferromagnetic films, as compared to other ultrafast mechanisms, such as heat-induced quenching of magnetic anisotropy. Moreover, the obtained results shed light on the properties of ultrafast laser-driven spin currents and its interaction with a non-collinear magnetization.

[1] A. Melnikov *et al.*, Phys. Rev. Lett. **107,** 076601 (2011)

[2] A. Melnikov *et al.*, in Ultrafast Magnetism I, (Eds.) J.-Y. Bigot *et al.*, Springer Proceedings in Physics **159**, p.34 (2015)

2.2 Molecular Processes at Interfaces

Understanding interfacial processes on a molecular level provides insights into fundamental aspects of surface reactions. Studies are performed by several groups in the department with complementary techniques, enabling high spatial resolution using scanning probe microscopy as well as chemical sensitivity using vibrational or x-ray spectroscopy. In these studies, surface molecular dynamics and reactions are stimulated by thermal activation, excitation by light, electric fields or charge transfer. This is complemented by computational studies of biomolecular machines and spatiotemporal pattern formation in electrochemical systems.

2.2.1 Single Molecule Dynamics at Surfaces

Adsorbate dynamics at interfaces is of fundamental importance for understanding catalytic processes as well as for the development of molecular devices. The group of *Takashi Kumagai* studies single molecule processes using various scanning probe techniques including low-temperature scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM), and tip-enhanced Raman spectroscopy (TERS) under UHV conditions. These methods enable imaging and manipulation of single atoms and molecules and to conduct local spectroscopy.

Direct observation of H-bond dynamics: The dynamics hydrogen bonds is relevant for a wide range of chemical and biological processes, but the microscopic understanding often missing. The group has performed detailed studies of H-bond dynamics of molecules on metals surface [1], focusing, in particular, on the intramolecular H-atom transfer reaction (tautomerization) in individual porphycene molecules. Porphycene is a structural isomer of free-base porphyrin and forms a relatively strong H bond in the molecular cavity (in contrast to porphyrin), which offers a unique opportunity to explore H-bond dynamics (see Fig. 7 (a)). It was found that porphycene adsorbs in different tautomeric states depending on surface material and crystal orientation. For example, porphycene exclusively adsorbs as *cis* tautomer on Cu(110) (Fig. 7(b)), while on Cu(111) both *trans* and *cis* tautomers are observed at 5 K (Fig. 7 (c)). The *cis* ↔ *cis* tautomerization can be induced on Cu(110) either by thermal activation, or by excitation in the STM junction. Remarkably, the tautomerization rate can be precisely controlled either by placing a single Cu atom nearby a molecule, or by changing the tautomeric state of neighboring molecules in one-dimensional oligomers [2]. These results highlight the influence of the local environment on the dynamics, which is usually hidden in molecular ensembles probed by spatial averaging spectroscopies. Furthermore, remote control of tautomer-selective switching has been demonstrated on Cu(111) [3] where the thermodynamically stable *trans* molecules are unidirectionally converted to the meta-stable *cis* tautomer through inelastic scattering with hot carriers generated by the STM and traveling along the surface (the *cis* molecules can be switched back to *trans* by thermal activation).

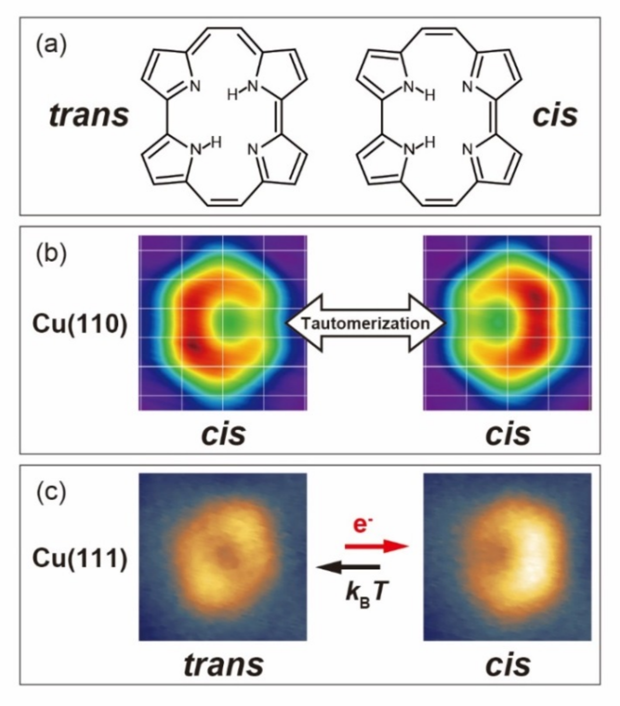


Figure 7: *(a) Chemical structure and tautomers of porphycene. (b) STM image of cis porphycene on Cu(110) at 5 K. The cis ↔ cis tautomerization can be induced either by thermal activation, or by excitation in the STM junction. (c) STM image of trans and cis porphycene on Cu(111) at 5 K. The unidirectional conversion between the tautomers can be controlled by hot carrier injection (STM) or thermal activation.*

Development of tip-enhanced Raman spectroscopy: TERS is a powerful method for imaging and chemical characterization at nanoscale and applicable even at the single-molecule level. Recently, the group reported TERS measurement of graphene nanoribbons (GNRs) on Au(111) at room temperature [4]. The 0.74 nm wide armchair GNRs prepared by on-surface polymerization were imaged by STM, and the characteristic vibration modes were observed in both far- and near-field (tip-enhanced) Raman spectra (whereby the signal was enhanced up to $4\cdot10^5$ in the near-field). However, it was also found that the instability of the STM junction, such as changes of the tip apex and thermal drift of the relative tip position with respect to the surface, makes it extremely difficult to conduct highly reproducible experiments at room temperature. In order to minimize such instabilities and obtain clear-cut data providing detailed physical insights into the molecular process, a new low-temperature optical SPM system is currently being developed.

[1] T. Kumagai, Prog. Surf. Sci. **90**, 239 (2015)

[2] T. Kumagai *et al.,* Nature Chemistry **6**, 41 (2014)

[3] J. N. Ladenthin *et al*., ACS Nano **9**, 7287–7295 (2015)

[4] A. Shiotari, T. Kumagai, M. Wolf, J. Phys. Chem. **118**, 11806 (2014)

2.2.2 Real-time Observation of Photoinduced Surface Reactions

A grand challenge in surface reaction dynamics is the observation of short-lived reaction intermediates and real-time probing of the transition state region. Under steady state conditions, the concentration of such intermediates will be extremely low, in particular if the reaction proceeds at a small number of sites compared to the total surface area. However, if a reaction can be triggered by ultrafast laser excitation temporal gating of such short-lived intermediates may become possible. Such real-time observation of transient species at surfaces requires techniques which are sensitive to the chemical state and simultaneously enable real-time probing of elementary steps with femtosecond time resolution. Using the Stanford x-ray free electron laser, LCLS , the surface science collaboration headed by Anders Nilsson (Stockholm University) has previously applied time-resolved x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) to probe the dynamics of CO desorption from Ru(001) induced by femtosecond laser excitation [1].

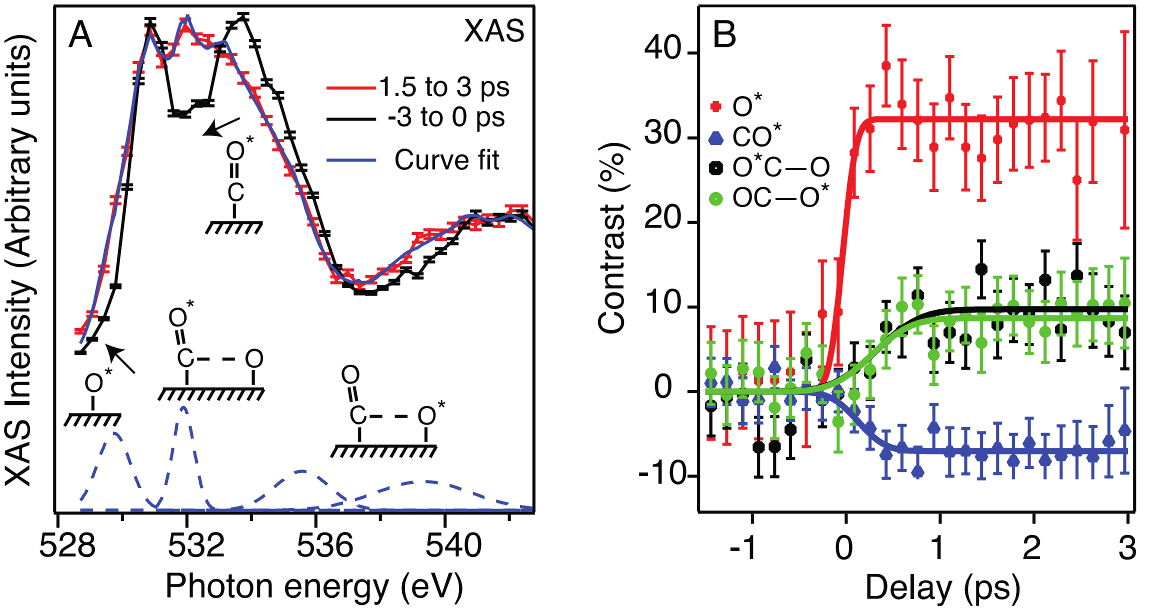


Figure 8: *(A) Pump induced changes of the O 1s x-ray absorption (XAS) spectrum of CO/O/Ru(000). The insets schematically depict the microscopic interpretation of the laser-induced spectral changes as the O and CO species move out from their equilibrium sites (Gaussians plotted with dashed blue lines). (B) Time evolution of the contrast in the four spectral regions (normalized difference between the pumped and unpumped data) [2].*

Recently, this approach has been extended to study chemical bond formation in real time using the example of femtosecond laser induced CO oxidation on Ru(001), a process which has been studied extensively in the past by the group of *Martin Wolf*. In this process non-adiabatic coupling between transiently excited hot metal electrons and adsorbate vibrational degrees of freedom leads to excitation of the reaction coordinate, which mediates CO_2 formation on an ultrafast (picosecond) timescale. Fig. 8 (a) depicts x-ray absorption spectra in the O 1s region of CO and oxygen coadsorbed on Ru(000), before and after excitation with a 400 nm fs laser pulse [2]. Within a few hundred femtoseconds, the laser excitation leads to motions of CO and O on the surface, allowing the reactants to collide, and, with a transient close to a picosecond, new electronic states appear in the O 1s XAS. These transient changes in the electronic structure exhibit a remarkably strong contrast of more than 10% (Fig 8 (b)). Density functional theory calculations indicate that the new electronic states in XAS result from changes in the adsorption sites of CO and O and bond formation between CO and O with a distribution of OC–O bond lengths close to the transition state [2]. After 1 ps, about 10% of the OC–O species populate a region which is close to (but energetically below) the transition state.

These results open the perspective for real time probing of a large number of surface reactions (e.g. water formation or hydrogenation reactions) and to obtain insight into the electronic structure and dynamics of reaction intermediates. However, the extension to other (*e.g.* oxide) surfaces or organic chemistry is still a challenge and requires the development of new photochemical pathways beyond the established femtochemistry at metal surfaces.

[1] M. Dell'Angela *et al.,* Science **339**, 1302 (2013); H.Xin *et al.,* Phys. Rev. Lett. **114**, 156101 (2015)
[2] H. Öström *et al.,* Science **347**, 978 (2015)

2.2.3 Interfacial Molecular Spectroscopy

The group of *Kramer Campen* investigates structure, dynamics and chemical reactivity at solid/gas and solid/liquid interfaces using the laser-based, interface-specific technique vibrational sum frequency (VSF) spectroscopy. In a VSF measurement, pulsed infrared (IR) and visible (VIS) lasers overlap spatially and temporally at an interface, and the light emission at the sum of the frequencies is monitored. This VSF emission is a spectroscopy (as the intensity increases by > 10^4 when the IR frequency is resonant with an interfacial vibration) and it is interface specific by its symmetry selection rules. Because the interfacial specificity is a result of the symmetry of light/matter interaction, it can be straightforwardly applied to any interface: solid/solid, solid/liquid, solid/gas, liquid/gas, and liquid/liquid. In the last two years three systems have been studied: the electrified metal/water, the air/water, and α-Al_2O_3/water interfaces. Depending on the details of the system, conventional, time-averaged VSF spectroscopy has been extended in significant ways.

Electrochemical Interfaces: Molecular level insight into reaction mechanisms in electrochemistry is limited by, at least, two general problems: (i) an inability to experimentally probe species that exist *both* at the solid/liquid interface *and* in much larger concentrations in the adjoining liquid phase and (ii) and inability to observe molecular species which exist for short times (< nanoseconds) during electron transfer. In the last two years the group has developed experiments that address both these limitations: The first problem has been addressed by construction of a thin layer cell that makes it possible to simultaneously conduct both cyclic voltammetry and VSF spectroscopy (and thus correlate oxidation current and interfacial surface speciation). As a proof-of-principle of this idea, the electrooxiation of formic acid on the Pt(100) surface has been characterized. This work shows both the expected CO oxidation (the so-called *indirect pathway*) and allows characterization of a previously unobserved interfacial species, i.e. weakly adsorbed formic acid, and its possible role in the *direct* pathway of electrooxidation [1]. The second limitation has been addressed by constructing an experiment in which electron transfer from gold across the gold/water interface in driven using an intense UV pulse and the resulting transient radical species characterized with VSF spectroscopy.

In the context of electrochemical interfaces and charge transfer across interfaces, hydrated electrons, i.e. excess electrons surrounded by a cavity of water molecules, play a major role. Despite their relevance also in other fields, the vertical binding energy (VBE) of excess electrons in the conduction band of water or ice remained elusive over decades of scientific efforts. The group of *Julia Stähler* recently succeeded in not only the determination of the VBE of the conduction band of amorphous solid water but, furthermore, resolved the femtosecond evolution of the excess electron's VBE during "the birth" of a solvated electron [2]. Using time-resolved two-photon photoelectron (2PPE) spectroscopy, the group could show that conduction band electrons in ice are trapped at preexisting sites already 22 fs after injection. This extraordinarily short lifetime explains the previous inability to determine the binding energy of the conduction band using techniques without a sufficient time resolution or specificity.

Air/Water Interface: Molecular-level insight into the structure of water and solutes at the air/water interface is important because of this interface's environmental ubiquity, because its physics strongly resemble those of hydrophobic solvation more generally, and because it enhances concentrations of many ions relative to bulk. VSF spectroscopy is a natural tool for such work, but prior efforts have largely focused, for technical reasons, on vibrational modes ranging in frequency from 1550-3800 cm^{-1}: C=O, OD (of D_2O), CH, and OH stretch modes. This limitation is important: If we could directly probe the modes that describe water's intermolecular potential, all of which are at IR frequencies < 1500 cm^{-1}, we might gain additional insight into interfacial water structure. Similarly, many solutes of interest, *e.g.* all oxyanions, absorb below 1500 cm^{-1}, and thus directly probing solute structure is only *possible* at lower IR frequencies. In the last two years group of *Kramer Campen* has extended the IR source for VSF to 700 cm^{-1}. This allowed, for the first time, to probe the libration of interfacial water. The resulting resonance is centered at 834 cm^{-1} and is blue-shifted by 160 cm^{-1} from that in liquid water and similar to ice (see Fig. 9).

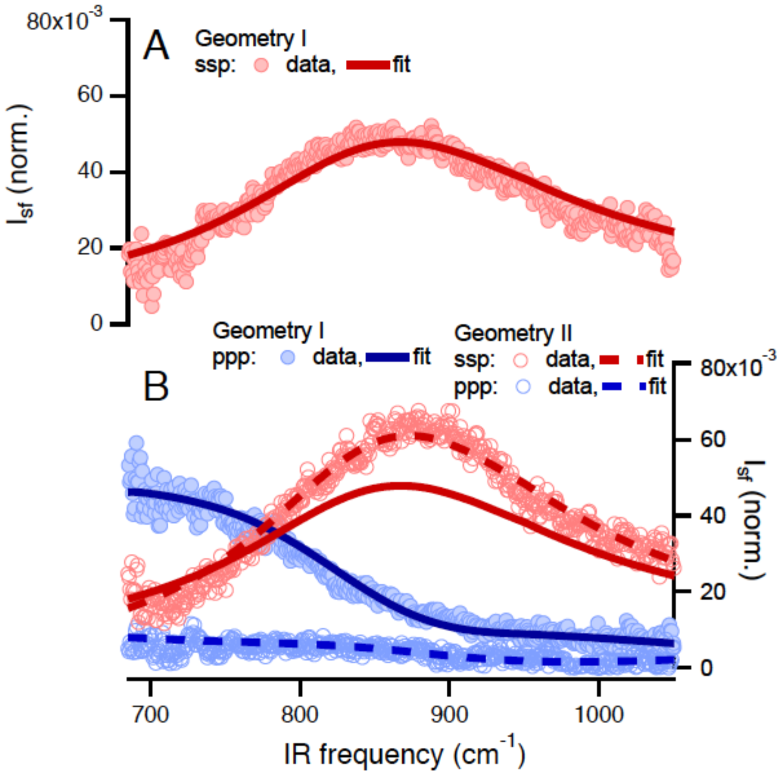


Figure 9: *VSF spectra plotted as a function of incident IR frequency for two different sets of incident angles (i.e. Geometry I and II) and two different polarization conditions (i.e. ssp and ppp). Dashed and solid lines are global fits to the data using a line shape model with a single resonance centered at 834 cm^{-1}. The large difference between data collected under the two polarization conditions is the result of linear optical properties of water (i.e. the Fresnel co-efficients) that are quantitatively accounted for in the data analysis.*

Evidently, while water at the air/water interface appears *liquid-like* when probing the interfacial OH stretch or picosecond time scale structural dynamics [3], viewed from the perspective of the libration (i.e. rotational potential) it is *ice-like*.

In a related set of experiments the interfacial population and structure of the perchlorate anion has been characterized via its Cl-O modes both at the air/water interface of solutions of perchlorate salts and perchloric acid. These results clearly suggest that interface-induced ion pairing in acid solutions occurs at > 10x lower concentrations than in bulk water. Quantification of this and similar phenomena for other solutes see is a prerequisite to a full understanding of such diverse phenomena as the aggregation of hydrophobic solutes in aqueous solution and the reactivity of ionic solutes at the air/water interface.

α-Al_2O_3 / Water Interaction: Understanding α-Al_2O_3/water interaction is important but challenging for a wide variety of industrial and environmental applications. Much of the challenge lies in the multi-scale nature of the problem: while understanding the thermodynamics and kinetics of single water molecule/α-alumina interaction is important, increasing water chemical potential introduces new physics: *e.g.* energetically favorable water adsorption mechanisms may become cooperative, the thermodynamically stable surface termination may change and the surface may donate/accept protons from liquid water. To fully understand water/α-Al_2O_3 interaction it is thus clear that we require methods of probing both interfacial water and the α-Al_2O_3 surface structure and dynamics over more than 10^{10} mbar in water pressure. Additionally, because the surface properties of oxides in general, and of α-Al_2O_3 in particular, depend on the degree of under-coordination of surface atoms, we require insight into the manner in which our results depend on crystal face.

This problem has been addressed over the last two years by probing the three most thermodynamically stable surfaces of α-Al_2O_3 -- the (0001), $(1\bar{1}02)$, and $(11\bar{2}0)$ -- in three types of experiments. (i) We characterize the unimolecular dissociation pathways at sub-monolayer water coverages on single crystal surfaces in UHV via the time-averaged VSF OD (of D_2O) stretch spectral response [4]. We have assigned the resonances we observed based on the dependence of our observed signal on incident beam angles and polarizations, and calculated frequencies and geometries (calculations done in collaboration with group of P. Saalfrank at the University of Potsdam). Given an assignment, the temperature dependent VSF response, and temperature programmed desorption measurements of the same surface, significant experimental constraints on theoretically derived microkinetic models of all surface reactions can be offered. (ii) VSF spectroscopy has been extended to sufficiently low frequency to optically probe surface phonons in ambient air. This capacity allows both quantitative characterization of partially reconstructed surfaces and makes possible probing surface chemistry from the perspective of the solid (via Al-O-H modes) [5]. (iii) We have probed the vibrational relaxation of the OH stretch of surface aluminols via an infrared pump / VSF probe scheme, as a means of probing water structure. Results on the (0001) surface suggest that for this surface, near circumneutral pH, interfacial water is hydrophobic: the first layer of water interacts only weakly with the overlying bulk. Increasing solute concentration (*i.e.* inducing ion adsorption) or changing pH (charging the surface) effectively makes the surface hydrophilic: interfacial water now interacts more strongly with the adjoining bulk liquid.

[1] Y. Tong, K. Cai, M. Wolf, R.K. Campen, Catal. Today (in press)

[2] J. Stähler, J.-C. Deinert, D. Wegkamp, S. Hagen, and M. Wolf, J. Am. Chem. Soc. **137**, 3520 (2015)

[3] M. Sovago, R.K. Campen, H.J. Bakker, M. Bonn, Chem. Phys. Lett., **470**, 7 (2009)

[4] H. Kirsch *et al.*, J. Phys. Chem. C, **118**, 13623 (2014)

[5] Y. Tong *et al.*, J. Chem. Phys., **142**, 054704 (2015)

2.2.5 Computational Dynamics of Protein Machines

The group of *Alexander Mikhailov* has continued theoretical investigations of molecular motors and protein machines, employing coarse-grained spring models to describe the dynamics of such macromolecules on millisecond timescales characteristic for their cycles. Such models are built using experimentally known equilibrium structures of proteins, obtained through x-ray diffraction experiments, and are known to approximately reproduce the processes of slow conformational relaxation in them.

To improve the accuracy of spring models, NMR data were used. In contrast to x-ray diffraction measurements with protein crystals, such data provide information on fluctuations of distances between the atomic amino acid groups (*i.e.*, between the protein residues). Through an iterative optimization procedure based on the NMR data for 1500 different kinds of proteins, a set of elastic spring constants, determining the strength of interactions between various pairs of residues, was computed. Fig. 10 (a) graphically displays computed spring constants for 210 possible residue pairs. It was demonstrated that, by using this common set and by calculating fluctuations of distances between the residues in specific proteins, a

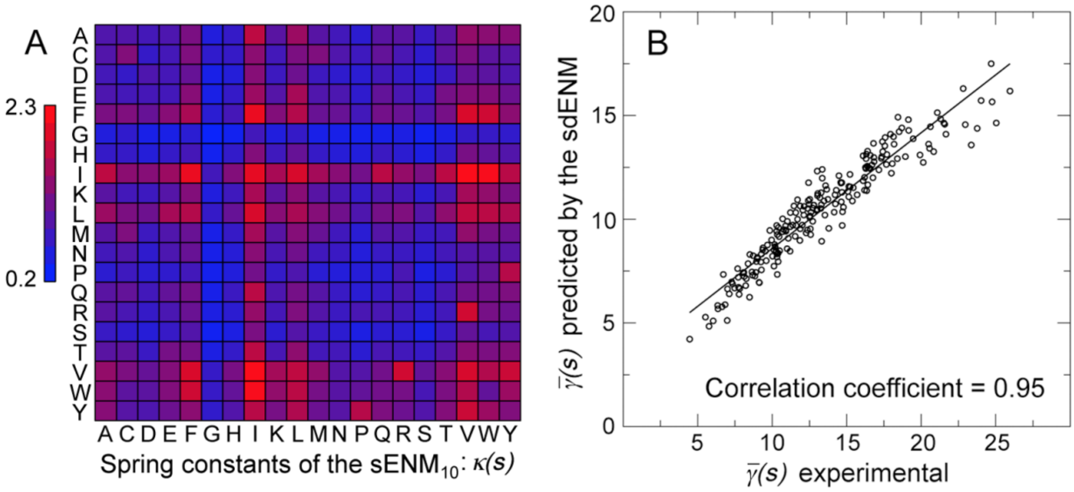


Figure 10: *Improving the accuracy of the spring model for conformational dynamics of proteins. (a) Set of computed spring constants for 210 different pairs of protein residues. (b) Comparison of predictions of the improved spring model with the respective experimental NMR data for 1500 different proteins.*

correlation of 95% with the respective experimental data could be achieved [1]. Fig. 10 (b) illustrates the statistical correlation between theoretical predictions and data extracted from NMR observations for an ensemble of 1500 different proteins, whereby inverse values of predicted and experimental statistical variations of the distance between the residues are displayed.

In this manner accurate and quantitative predictions for protein dynamics can be made. Currently such theoretical descriptions are used in the studies of conformational changes of dynamin, an important membrane protein (cooperation with O. Daumke (MDC for Molecular Medicine, Berlin)). Also hybrid simulation methods for proteins, combining all-atom molecular dynamics (MD) and coarse-grained spring models, are developed together with Y. Togashi and H. Flechsig (Hiroshima University). At the same time, a synthetic molecular motor model is explored in collaboration with J.M. Sancho, University of Barcelona. It intends to reproduce, in a strongly simplified way, the operation of the myosin motor responsible for generation of mechanical forces in muscles. As a model system, a specially designed elastic network with 64 particles connected by elastic springs is used. The system undergoes cyclic conformational changes induced by binding of a ligand, its conversion into a product, and product release. A ratchet mechanism allowing the conversion of cyclic shape changes into steady translational motion of an attached filament is implemented. By varying the temperature, regimes of strong and weak coupling, corresponding to the Brownian ratchet, could be realized, and statistical investigations of the model motor, including estimates of its operation efficiency, have been performed. This approach is seen as providing a road map for subsequent similar investigations of real molecular motors.

Furthermore, collective hydrodynamic effects of active proteins in biological cells are investigated. Diffusion of particles in the interior of biological cells is known to strongly depend on ATP supply. So far, these observations were interpreted as an effect of non-equilibrium fluctuations in active gels formed by actin filaments and myosin motors in the cell. Recent *in vivo* diffusion measurements of microinjected submicron tracers within biological cells in the group of D. Weitz (Harvard University) show however that such explanation is not sufficient. The diffusion coefficient was reduced in these experiments by only about 10% if the activity of myosin motors was chemically inhibited, but ATP supply was maintained. However, the diffusion was dropping down below the measurement limit when ATP supply was stopped. Moreover, substantial diffusion dependence on substrate supply was recently observed *in vitro* in the experiments with water solutions of enzymes, in absence of any molecular motors characteristic for a living cell. As shown in collaboration with R. Kapral (University of Toronto), an alternative explanation of such experimental data is possible [2]. All active proteins in the cell, including molecular motors and protein machines and also most of the enzymes, are repeatedly changing their shapes within each turnover cycle. Therefore, they are mechanically stirring the fluid cytoplasm in which they are immersed. As a result, non-thermal fluctuating flows develop inside the cell. Diffusion enhancement due to advection of particles in such fluctuating flows has been theoretically determined [2]. Numerical estimates reveal that such diffusion enhancement, persistent only as long as the ATP and other substrates are supplied, can indeed account for the experimentally observed effects. Similar phenomena for of active protein inclusions in biological membranes have been analysed.

Additionally, theoretical investigations on the dynamics of complex chemical networks have been performed in the framework of a research project financed by the Volkswagen Foundation.

[1] Y. Dehouck and A.S. Mikhailov, PLOS Comput. Biol. **9**, e1003209 (2013)
[2] A.S. Mikhailov and R. Kapral, Proc. Natl. Acad. Sci. (USA) **112**, E3639 -E3644 (2015)

2.2.6 Spatiotemporal Self-organization

Due to health related issues *Markus Eiswirth* has been on a leave of absence for one year and is now back at the FHI on a part time employment. For that reason no detailed report will be given here.

3. Research Projects Funded from Outside Sources

Kramer Campen and Martin Wolf:

- DFG Collaborative Research Center SFB 658 “Elementary processes of molecular switches at surfaces”, project B9 ***“Molecular switching in self-assembled monolayers at liquid-solid interfaces”*** (selfassembled monolayers, liquid-solid interfaces, static and time-resolved vibrational SFG spectroscopy, from 7/2013)

Kramer Campen:

- DFG Collaborative Research Center SFB 1109 "Understanding of Metal-Oxide/ Water Systems at the Molecular Scale: Structural Evolution, Interfaces and Dissolution", Project B1, **"*Understanding water structure and reactivity at aluminum oxide surfaces using nonlinear vibrational spectroscopy and theory*"** (oxide/ water interfaces, time resolved vibrational SFG spectroscopy, *ab initio* dynamics and thermodynamics, together with P. Saalfrank, Univ. Potsdam, from 4/2014)

Ralph Ernstorfer and Martin Wolf:

- DFG Reseach Unit FOR1700 (Wo 653/8-1) “Metallic nanowires on the atomic scale: Electronic and vibrational coupling in real world systems”, Project E5 “***Time-resolved spectroscopy of photoinduced transitions and electronic excitations in quasi-1D metal wires on semiconductors”*** (electronic structure and dynamics in quasi 1D systems, time-resolved ARPES, from 11/2012)

Takashi Kumagai and Martin Wolf:

- DFG Collaborative Research Center SFB 951 “Hybrid Inorganic/Organic Systems for Opto-Electronics”, project A2 ***“Assembly and local probing of single molecules on ultrathin ZnO films on metals”*** (deposition and imaging of single molecules on utrathin oxide films with STM and AFM, from 7/2015)

Karsten Horn:

- DFG Individual research grant (Ho 797/18-1) "***Graphene-based systems for spintronics: Magnetic interactions at the graphene/3d metal interface (SpinGraph)***” within the program "EuroGRAPHENE" of the European Science Foundation, until 5/2014.
- DFG Priority Program SPP 1459 (De 1679/3-1) “Graphene”, project “***Graphene: electronic structure, transport and functionalization”*** (growth and doping of eptaxial graphene layers, angle-resolved photoemission spectroscopy)

Tobias Kampfrath:

- DFG individual research grant (KA 3305/2-1), "***Femtosecond coherent control of terahertz radiation by transient nanophotonic structures***", (ultrafast optical spectroscopy, THz photonics, from 2/2013).
- DFG priority program SPP 1666 (KA 3305/3-1), "Topological Insulators", project "***Investigation of directional THz spin currents in topological surface states***" (ultrafast spin dynamics in topological insulators, THz emission spectroscopy, together with C. Heiliger, Univ. Gießen and M. Münzenberg, Univ. Rostock, from 6/2013).
- DFG priority program SPP 1538 (KA 3305/4-1), "Spin Caloric Transport", project "***Ultrafast spin-dependent and spin Seebeck effect: beyond diffusive spin transport, toward a spin-caloritronic terahertz emitter***" (ultrafast spin and magnon transport in magnetic metals and insulators, THz emission spectroscopy, ultrafast optical spectroscopy, from 7/2014)

Alexey Melnikov:

- DFG individual research grant (ME 3570/1-3), ***"Ballistic electron-driven magnetization dynamics induced by femtosecond laser excitation"*** (ultrafast spin dynamics and transport, epitaxial metallic multilayer films, non-linear optical SHG spectroscopy, from 10/2013)

Alexander Mikhailov:

- Volkswagen Foundation, international project ***"Self-organizing networks of interacting machines"*** (design and analysis of the networks of molecular machines)
- DFG Collaborative Research Center SFB 910 "Control of Self-Organizing Nonlinear Systems", project A6 ***"Control of self-organization in dynamical networks"*** (control of nonlinear dynamics in chemical and biological networks, until 3/2014)
- DFG Research Training Group GRK 1558 "Nonequilibrium Collective Dynamics in Condensed Matter and Biological Systems", project ***"Active microfluidics based on floating molecular machines"*** (molecular machines at liquid interfaces, until 3/2014)

Alexander Saywell:

- DFG individual research grant ("Eigene Stelle", Sa 2625/1-1), ***"Force induced dissociation of individual molecules"*** (Single molecule spectroscopy and manipulation, low-temperature atomic force microscopy (AFM), until 12/2014)

Julia Stähler:

- Collaborative Research Center SFB 951 “Hybrid Inorganic/Organic Systems for Opto-Electronics”, project B9 ***“Electronic structure and ultrafast carrier dynamics at hybrid inorganic/organic interfaces”*** (time-resolved 2PPE and non-linear optical spectroscopy, organic/inorganic semiconductor interfaces) from 7/2015, from 7/2011 until 6/2015 together with Martin Wolf.

Julia Stähler, Tobias Kampfrath, Ralph Ernstorfer, and Martin Wolf:

- European Research Project (*NMP-2011-SMALL*): ***“Time dynamics and Control in nanostructures for magnetic recording and energy applications (CRONOS)”***, project FHIB, (time-resolved 2PPE and non-linear optical spectroscopy, magneto-optical spectroscopy, THz emission, High-harmonic generation, until 5/2015)

4. Publications of the Department of Physical Chemistry[1]

2013 (late publications)

Atsumi, Y., S. Hata and H. Nakao: Phase ordering in coupled noisy bistable systems on scale-free networks. Physical Review E **88** (5), 052806 (2013).

Bothschafter, E., A. Paarmann, N. Karpowicz, E.S. Zijlstra, M.E. Garcia, F. Krausz, R. Kienberger and R. Ernstorfer: Interband excitation and carrier relaxation as displacive driving force for coherent phonons. The European Physical Journal - Web of Conferences **41**, 04021 (2013). OPEN ACCESS

de Buyl, P., A.S. Mikhailov and R. Kapral: Self-propulsion through symmetry breaking. Europhysics Letters **103** (6), 60009 (2013).

Ertl, G.: A lateral thinker. Nature **502** (7471), S53-S54 (2013).

Ge, A., Q. Peng, H. Wu, H. Liu, Y. Tong, T. Nishida, N. Yoshida, K. Suzuki, T. Sakai, M. Osawa and S. Ye: Effect of Functional Group on the Monolayer Structures of Biodegradable Quaternary Ammonium Surfactants. Langmuir **29** (47), 14411-14420 (2013).

Hsieh, C.-S., R.K. Campen, M. Okuno, E.H.G. Backusa, Y. Nagata and M. Bonn: Mechanism of vibrational energy dissipation of free OH groups at the air-water interface. Proceedings of the National Academy of Sciences of the USA **110** (47), 18780-18785 (2013).

Kumagai, T., F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill: Thermally and Vibrationally Induced Tautomerization of Single Porphycene Molecules on a Cu(110) Surface. Physical Review Letters **111** (24), 246101 (2013).

Lüneburg, S., M. Müller, A. Paarmann and R. Ernstorfer: Microelectrode for energy and current control of nanotip field electron emitters. Applied Physics Letters **103** (21), 213506 (2013).

Neppl, S., R. Ernstorfer, A.L. Cavalieri, J.V. Barth, D. Menzel, F. Krausz, P. Feulner and R. Kienberger: Probing ultrafast electron dynamics in condensed matter with attosecond photoemission. In: Proceedings of Ultrafast Phenomena and Nanophotonics XVII. (Eds.) M. *Betz, A.Y. Elezzabi, J.-J. Song and K.-T. Tsen:* (Proceedings of the SPIE, Vol. 8623). SPIE, Bellingham, WA, 862312 (2013). ISBN 978-0-8194-9392-7.

Paasch-Colberg, T., A. Schiffrin, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J.V. Barth, R. Kienberger, R. Ernstorfer, V.S. Yakovlev, M.I. Stockman and F. Krausz: Optical-field-induced current in dielectrics. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, QTh4D.5 (2013). ISBN 978-1-55752-972-5.

Schubert, O., M. Porer, A. Sell, F. Junginger, B. Mayer, C. Schmidt, S. Maehrlein, A. Pashkin, T. Kampfrath, M. Wolf, K. Kim, A. Leitenstorfer and R. Huber: Multi-THz Nonlinear Optics and Sub-cycle Control of Charge and Spin. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, JF1K.6 (2013). ISBN 978-1-55752-972-5.

Zhang, Z., H. Stark and A.S. Mikhailov: Hydrodynamic ratchet: Controlled motion of a polymer in an alternating microchannel flow. Europhysics Letters **104** (1), 14002 (2013).

---

[1] OPEN ACCESS = Gold open access publication

Master's Thesis

Cataldi, P.: Exciton formation and electron transfer at SP6/oxide interfaces in transient transmission spectroscopy. Università degli Studi di Genova Italy 2013.

2014

Arion, T., O. Takahashi, R. Püttner, V. Ulrich, S. Barth, T. Lischke, A.M. Bradshaw, M. Förstel and U. Hergenhahn: Conformational and nuclear dynamics effects in molecular Auger spectra: fluorine core-hole decay in CF_4. Journal of Physics B **47** (12), 124033 (2014).

Barbiellini, B., J.N. Hancock, C. Monney, Y. Joly, G. Ghiringhelli, L. Braicovich and T. Schmitt: Inelastic x-ray scattering from valence electrons near absorption edges of FeTe and $TiSe_2$. Physical Review B **89** (23), 235138 (2014).

Bi, W., Y. He, M.F. Cabral, H. Varela, J. Yang, R. Jiang and Q. Gao: Oscillatory electro-oxidation of thiosulfate on gold. Electrochimica Acta **133**, 308-315 (2014).

Bisogni, V., S. Kourtis, C. Monney, K. Zhou, R. Kraus, C. Sekar, V. Strocov, B. Büchner, J. Brink, van den, L. Braicovich, T. Schmitt, M. Daghofer and J. Geck: Femtosecond Dynamics of Momentum-Dependent Magnetic Excitations from Resonant Inelastic X-Ray Scattering in $CaCu_2O_3$. Physical Review Letters **112** (14), 147401 (2014).

Böttcher, S., H. Vita and K. Horn: Reversible photon-induced oxidation of graphene by NO_2 adsorption. Surface Science **621**, 117-122 (2014).

Čechal, J., C.S. Kley, T. Kumagai, F. Schramm, M. Ruben, S. Stepanow and K. Kern: Convergent and divergent two-dimensional coordination networks formed through substrate-activated or quenched alkynyl ligation. Chemical Communications **50** (69), 9973-9976 (2014). OPEN ACCESS

Che, M. and G. Ertl: Helmut Knözinger (1935-2014). Angewandte Chemie International Edition **53** (40), 10579-10580 (2014).

Che, M. and G. Ertl: Helmut Knözinger (1935-2014). Angewandte Chemie **126** (40), 10751-10752 (2014).

Deinert, J.-C., D. Wegkamp, M. Meyer, C. Richter, M. Wolf and J. Stähler: Ultrafast Exciton Formation at the $ZnO(10\bar{1}0)$ Surface. Physical Review Letters **113** (5), 057602 (2014).

Delmonde, M.V.F., M.A. Nascimento, R. Nagao, D.A. Cantane, F.H.B. Lima and H. Varela: Production of Volatile Species during the Oscillatory Electro-oxidation of Small Organic Molecules. The Journal of Physical Chemistry C **118** (31), 17699-17709 (2014).

Eschenlohr, A., M. Sultan, A. Melnikov, N. Bergeard, J. Wieczorek, T. Kachel, C. Stamm and U. Bovensiepen: Role of spin-lattice coupling in the ultrafast demagnetization of $Gd_{1-x}Tb_x$ alloys. Physical Review B **89** (21), 214423 (2014).

Flechsig, H.: Computational biology approach to uncover hepatitis C virus helicase operation. World Journal of Gastroenterology **20** (13), 3401-3409 (2014). OPEN ACCESS

Hata, S., H. Nakao and A.S. Mikhailov: Advection of passive particles over flow networks. Physical Review E **89** (2), 020801(R) (2014).

Hata, S., H. Nakao and A.S. Mikhailov: Dispersal-induced destabilization of metapopulations and oscillatory Turing patterns in ecological networks. Scientific Reports **4**, 3585 (2014).

Hata, S., H. Nakao and A.S. Mikhailov: Sufficient conditions for wave instability in three-component reaction-diffusion systems. Progress of Theoretical and Experimental Physics **2014** (1), 013A01 (2014).

Ilchen, M., L. Glaser, F. Scholz, P. Walter, S. Deinert, A. Rothkirch, J. Seltmann, J. Viefhaus, P. Decleva, B. Langer, A. Knie, A. Ehresmann, O.M. Al-Dossary, M. Braune, G. Hartmann, A. Meißner, L.C. Tribedi, M. AlKhaldi and U. Becker: Angular Momentum Sensitive Two-Center Interference. Physical Review Letters **112** (2), 023001 (2014).

Jia, Z., Z. Zeng, R. Li, Z. Xu and Y. Deng: Extremely asymmetric electron localization in H_2^+ controlled with a THz field. Physical Review A **89** (2), 023419 (2014).

Kaluza, P. and A.S. Mikhailov: Autonomous learning by simple dynamical systems with delayed feedback. Physical Review E **90** (3), 090901(R) (2014).

Kamaraju, N., A. Rubano, L. Jian, S. Saha, T. Venkatesan, J. Nötzold, R.K. Campen, M. Wolf and T. Kampfrath: Subcycle control of terahertz waveform polarization using all-optically induced transient metamaterials. Light: Science & Applications **3**, e155 (2014).

Kampfrath, T.: Intense terahertz pulses: probing and controlling fundamental motions of electrons, spins and ions. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SW3F.1 (2014). ISBN 978-1-55752-999-2.

Kampfrath, T., M. Battiato, A. Sell, F. Freimuth, A. Leitenstorfer, M. Wolf, R. Huber, P.M. Oppeneer and M. Münzenberg: Ultrafast spin precession and transport controlled and probed with terahertz radiation. In: Proceedings of the Ultrafast Phenomena and Nanophotonics XVIII. (Eds.) M. Betz, A.Y. Elezzabi, J.-J. Song and K.-T. Tsen. (Proceedings of the SPIE, Vol. 8984). SPIE, Bellingham, WA, 898415 (2014). ISBN 978-0-8194-9897-7.

Kawai, S., M. Koch, E. Gnecco, A. Sadeghi, R. Pawlak, T. Glatzel, J. Schwarz, S. Goedecker, S. Hecht, A. Baratoff, L. Grill and E. Meyer: Quantifying the atomic-level mechanics of single long physisorbed molecular chains. Proceedings of the National Academy of Sciences of the USA **111** (11), 3968-3972 (2014).

Kirsch, H., J. Wirth, Y. Tong, M. Wolf, P. Saalfrank and R.K. Campen: Experimental Characterization of Unimolecular Water Dissociative Adsorption on α-Alumina. The Journal of Physical Chemistry C **118** (25), 13623-13630 (2014).

Kirsch, H., X. Zhao, Z. Ren, S.V. Levchenko, M. Wolf and R.K. Campen: Controlling CH_2 dissociation on Ru(0001) through surface site blocking by adsorbed hydrogen. Journal of Catalysis **320**, 89-96 (2014).

Koch, M., M. Gille, A. Viertel, S. Hecht and L. Grill: Substrate-controlled linking of molecular building blocks: Au(111) vs. Cu(111). Surface Science **627**, 70-74 (2014).

Kouvaris, N.E., T. Isele, A.S. Mikhailov and E. Schöll: Propagation failure of excitation waves on trees and random networks. Europhysics Letters **106** (6), 68001 (2014).

Kübel, M., K. Betsch, N.G. Kling, A.S. Alnaser, J. Schmidt, U. Kleineberg, Y. Deng, I. Ben-Itzhak, G.G. Paulus, T. Pfeifer, J.H. Ullrich, R. Moshammer, M.F. Kling and B. Bergues: Non-sequential double ionization of Ar: from the single- to the many-cycle regime. New Journal of Physics **16** (3), 033008 (2014).

Kumagai, T., F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill: Controlling intramolecular hydrogen transfer in a porphycene molecule with single atoms or molecules located nearby. Nature Chemistry **6** (1), 41-46 (2014).

Lee, J.J., B. Moritz, W.S. Lee, M. Yi, C.J. Jia, A.P. Sorini, K. Kudo, Y. Koike, K.J. Zhou, C. Monney, V. Strocov, L. Patthey, T. Schmitt, T.P. Devereaux and Z.X. Shen: Charge-orbital-lattice coupling effects in the dd excitation profile of one-dimensional cuprates. Physical Review B **89** (4), 041104(R) (2014).

Leicht, P., L. Zielke, S. Bouvron, R. Moroni, E. Voloshina, L. Hammerschmidt, Y. Dedkov and M. Fonin: In Situ Fabrication of Quasi-Free-Standing Epitaxial Graphene Nanoflakes on Gold. ACS Nano **8** (4), 3735-3742 (2014).

Machado, E.G. and H. Varela: Oscillatory Instabilities in the Electrooxidation of Borohydride on Platinum. Journal of the Brazilian Chemical Society **25** (3), 442-447 (2014).

Maniraj, M., A. Rai, S.R. Barman, M. Krajčí, D.L. Schlagel, T.A. Lograsso and K. Horn: Unoccupied electronic states of icosahedral Al-Pd-Mn quasicrystals: Evidence of image potential resonance and pseudogap. Physical Review B **90** (11), 115407 (2014).

Martínez-Blanco, J., B. Walter, A. Mascaraque and K. Horn: Long-Range Order in an Organic Overlayer Induced by Surface Reconstruction: Coronene on Ge(111). The Journal of Physical Chemistry C **118** (22), 11699-11703 (2014).

Mikhailov, A.S. and G. Ertl: Engineering of Chemical Complexity II. (World Scientific Lecture Notes in Complex Systems, Vol. 12). World Scientific, New Jersey (2014). ISBN 978-981-4616-12-6.

Mitrano, M., G. Cotugno, S.R. Clark, R. Singla, S. Kaiser, J. Stähler, R. Beyer, M. Dressel, L. Baldassarre, D. Nicoletti, A. Perucchi, T. Hasegawa, H. Okamoto, D. Jaksch and A. Cavalleri: Pressure-Dependent Relaxation in the Photoexcited Mott Insulator ET-F$_2$TCNQ: Influence of Hopping and Correlations on Quasiparticle Recombination Rates. Physical Review Letters **112** (11), 117801 (2014).

Moreschini, L., P.-H. Lin, C.-H. Lin, W. Ku, D. Innocenti, Y.J. Chang, A.L. Walter, K.S. Kim, V. Brouet, K.-W. Yeh, M.-K. Wu, E. Rotenberg, A. Bostwick and M. Grioni: Consequences of Broken Translational Symmetry in FeSe$_x$Te$_{1-x}$. Physical Review Letters **112** (8), 087602 (2014).

Moser, S., L. Moreschini, H.-Y. Yang, D. Innocenti, F. Fuchs, N.H. Hansen, Y.J. Chang, K.S. Kim, A.L. Walter, A. Bostwick, E. Rotenberg, F. Mila and M. Grioni: Angle-Resolved Photoemission Spectroscopy of Tetragonal CuO: Evidence for Intralayer Coupling Between Cupratelike Sublattices. Physical Review Letters **113** (18), 187001 (2014).

Mota Lima, A.B., E.R. Gonzalez and M. Eiswirth: Complex Electrooxidation of Formic Acid on Palladium. Journal of the Brazilian Chemical Society **25** (7), 1208-1217 (2014).

Müller, M., A. Paarmann and R. Ernstorfer: Femtosecond electrons probing currents and atomic structure in nanomaterials. Nature Communications **5** (10), 5292 (2014).

Nascimento, M., R. Nagao, M. Eiswirth and H. Varela: Coupled slow and fast surface dynamics in an electrocatalytic oscillator: Model and simulations. The Journal of Chemical Physics **141** (23), 234701 (2014).

Nepijko, S.A., A. Chernenkaya, K. Medjanik, S.V. Chernov, D.V. Shapko, I.Y. Protsenko, W. Schulze and G. Schönhense: Investigation of a Ge nanoparticle film by means of electron stimulated photon emission spectroscopy. Journal of Electron Spectroscopy and Related Phenomena **193**, 54-57 (2014).

Nogueira, P.A., B.C. Batista, R.B. Faria and H. Varela: The effect of temperature on the dynamics of a homogeneous oscillatory system operated in batch and under flow. RSC Advances **4** (57), 30412-30421 (2014).

Ostler, M., F. Fromm, R.J. Koch, P. Wehrfritz, F. Speck, H. Vita, S. Böttcher, K. Horn and T. Seyller: Buffer layer free graphene on SiC(0 0 0 1) via interface oxidation in water vapor. Carbon **70**, 258-265 (2014).

Paasch-Colberg, T., A. Schiffrin, N. Karpowicz, S. Kruchinin, Ö. Sağlam, S. Keiber, O. Razskazovskaya, S. Mühlbrandt, A. Alnaser, M. Kübel, V. Apalkov, D. Gerster, J. Reichert, T. Wittmann, J.V. Barth, M.I. Stockman, R. Ernstorfer, V.S. Yakovlev, R. Kienberger and F. Krausz: Solid-state light-phase detector. Nature Photonics **8** (3), 214-218 (2014).

Perini, N., B.C. Batista, A.C.D. Angelo, I.R. Epstein and H. Varela: Long-Lasting Oscillations in the Electro-Oxidation of Formic Acid on PtSn Intermetallic Surfaces. ChemPhysChem **15** (9), 1753-1760 (2014).

Previdello, B.A.F., E.G. Machado and H. Varela: The effect of the alkali metal cation on the electrocatalytic oxidation of formate on platinum. RSC Advances **4** (29), 15271-15275 (2014).

Rettig, L., J.-H. Chu, I.R. Fisher, U. Bovensiepen and M. Wolf: Coherent dynamics of the charge density wave gap in tritellurides. Faraday Discussions **171**, 299-310 (2014).

Rubano, A., M. Wolf and T. Kampfrath: Terahertz conductivity and ultrafast dynamics of photoinduced charge carriers in intrinsic 3C and 6H silicon carbide. Applied Physics Letters **105** (3), 032104 (2014).

Sajadi, M., M. Wolf and T. Kampfrath: Terahertz field enhancement via coherent superposition of the pulse sequences after a single optical-rectification crystal. Applied Physics Letters **104** (9), 091118 (2014).

Saywell, A., W. Greń, G. Franc, A. Gourdon, X. Bouju and L. Grill: Manipulating the Conformation of Single Organometallic Chains on Au(111). The Journal of Physical Chemistry C **118** (3), 1719-1728 (2014).

Schick, D., A. Bojahr, M. Herzog, R. Shayduk, C. von Korff Schmising and M. Bargheer: UDKM1DSIM - A simulation toolkit for 1D ultrafast dynamics in condensed matter. Computer Physics Communications **185** (2), 651-660 (2014).

Schick, D., M. Herzog, A. Bojahr, W. Leitenberger, A. Hertwig, R. Shayduk and M. Bargheer: Ultrafast lattice response of photoexcited thin films studied by X-ray diffraction. Structural Dynamics **1** (6), 064501 (2014).

Schick, D., M. Herzog, H. Wen, P. Chen, C. Adamo, P. Gaal, D.G. Schlom, P.G. Evans, Y. Li and M. Bargheer: Localized Excited Charge Carriers Generate Ultrafast Inhomogeneous Strain in the Multiferroic $BiFeO_3$. Physical Review Letters **112** (9), 097602 (2014).

Schiffrin, A., T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J.V. Barth, R. Kienberger, R. Ernstorfer, V.S. Yakovlev, M.I. Stockman and F. Krausz: Addendum: Optical-field-induced current in dielectrics. Nature **507** (7492), 386-387 (2014).

Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, A. Paarmann, G. von Helden, H. Bluem, D. Dowell, R. Lange, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk: The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. In: Proceedings of the 36th International Free Electron Laser Conference. (Eds.) J. Chrin, S. Reiche and V. Schaa. JACoW.org, WEB04 (2014). ISBN 978-3-95450-133-5.

Shimada, T., N. Kamaraju, C. Frischkorn, M. Wolf and T. Kampfrath: Indication of Te segregation in laser-irradiated ZnTe observed by *in situ* coherent-phonon spectroscopy. Applied Physics Letters **105** (11), 111908 (2014).

Shiotari, A., T. Kumagai and M. Wolf: Tip-Enhanced Raman Spectroscopy of Graphene Nanoribbons on Au(111). The Journal of Physical Chemistry C **118** (22), 11806-11812 (2014).

Shiotari, A., B.H. Liu, S. Jaekel, L. Grill, S.K. Shaikhutdinov, H.-J. Freund, M. Wolf and T. Kumagai: Local Characterization of Ultrathin ZnO Layers on Ag(111) by Scanning Tunneling Microscopy and Atomic Force Microscopy. The Journal of Physical Chemistry C **118** (47), 27428-27435 (2014).

Tang, H., A.S.M. Sutherland, L.M. Osusky, Y. Li, J.F. Holzwarth and C. Bohne: Chiral recognition for the complexation dynamics of β-cyclodextrin with the enantiomers of 2-naphthyl-1-ethanol. Photochemical & Photobiological Sciences **13** (2), 358-369 (2014).

Vita, H., S. Böttcher, K. Horn, E.N. Voloshina, R.E. Ovcharenko, T. Kampen, A. Thissen and Y.S. Dedkov: Understanding the origin of band gap formation in graphene on metals: graphene on Cu/Ir(111). Scientific Reports **4**, 5704 (2014).

Vita, H., S. Böttcher, P. Leicht, K. Horn, A.B. Shick and F. Máca: Electronic structure and magnetic properties of cobalt intercalated in graphene on Ir(111). Physical Review B **90** (16), 164532 (2014).

Walter, A.L., H. Sahin, K.-J. Jeon, A. Bostwick, S. Horzum, R. Koch, F. Speck, M. Ostler, P. Nagel, M. Merz, S. Schupler, L. Moreschini, Y.J. Chang, T. Seyller, F.M. Peeters, K. Horn and E. Rotenberg: Luminescence, Patterned Metallic Regions, and Photon-Mediated Electronic Changes in Single-Sided Fluorinated Graphene Sheets. ACS Nano **8** (8), 7801-7808 (2014).

Wegkamp, D., M. Herzog, L. Xian, M. Gatti, P. Cudazzo, C.L. McGahan, R.E. Marvel, R.F. Haglund, A. Rubio, M. Wolf and J. Stähler: Instantaneous Band Gap Collapse in Photoexcited Monoclinic VO_2 due to Photocarrier Doping. Physical Review Letters **113** (21), 216401 (2014).

Ye, S., Y. Tong, A. Ge, L. Qiao and P.B. Davies: Interfacial Structure of Soft Matter Probed by SFG Spectroscopy. The Chemical Record **14** (5), 791-805 (2014).

Doctoral Thesis

Böttcher, S.: Adsorption und Funktionalisierung von Graphen auf Metalloberflächen. Freie Universität Berlin 2014.

Kirsch, H.: Chemical reactions on surfaces - a SFG study. Freie Universität Berlin 2014.

Master's Thesis

Richter, C.: Electron and Exciton Dynamics at ZnO surfaces. Freie Universität Berlin 2014.

Wlosczyk, S.: Probing α-Al_2O_3 *(1102) Role of Surface Structure. Freie Universität Berlin 2014.*

Bachelor Thesis

Linde, J.: Understanding the oxidation mechanism of formic acid on transition metal electrodes. Freie Universität Berlin 2014.

2015

Alekhin, A., D. Bürstel, A. Melnikov, D. Diesing and U. Bovensiepen: Ultrafast Laser-Excited Spin Transport in Au/Fe/MgO(001): Relevance of the Fe Layer Thickness. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 241-243 (2015).
ISBN 978-3-319-07742-0.

Bisti, F., G. Profeta, H. Vita, M. Donarelli, F. Perrozzi, P.M. Sheverdyaeva, P. Moras, K. Horn and L. Ottaviano: Electronic and geometric structure of graphene/SiC(0001) decoupled by lithium intercalation. Physical Review B **91** (24), 245411 (2015).

Böttcher, S., H. Vita and K. Horn: Photon-Induced Oxidation of Graphene/Ir(111) by SO_2 Adsorption. Surface Science 641, 305-309 (2015).

Braune, M., G. Hartmann, M. Ilchen, A. Knie, T. Lischke, A. Reinköster, A. Meißner, S. Deinert, L. Glaser, O. Al-Dossary, A. Ehresmann, A.S. Kheifets and J. Viefhaus: Electron angular distributions of noble gases in sequential two-photon double ionization. Journal of Modern Optics, in press.

Deinert, J.-C., O.T. Hofmann, M. Meyer, P. Rinke and J. Stähler: Local aspects of hydrogen-induced metallization of the ZnO$(10\bar{1}0)$ surface. Physical Review B **91** (23), 235313 (2015).

Dell'Angela, M., T. Anniyev, M. Beye, R. Coffee, A. Föhlisch, J. Gladh, S. Kaya, T. Katayama, O. Krupin, A. Nilsson, D. Nordlund, W.F. Schlotter, J.A. Sellberg, F. Sorgenfrei, J.J. Turner, H. Öström, H. Ogasawara, M. Wolf and W. Wurth: Vacuum space charge effects in sub-picosecond soft X-ray photoemission on a molecular adsorbate layer. Structural Dynamics **2** (2), 025101 (2015). OPEN ACCESS

Deng, Y. and X. Xie: Real-time probing of the electron dynamics of an atom in a strong infrared laser field. Physical Review A **91** (4), 043414 (2015).

Ernstorfer, R.: Im Fokus ultrakurzer Laser: das Wechselspiel von Elektronen und Kristallstruktur. Jahrbuch 2015, Max-Planck-Gesellschaft, (2015). OPEN ACCESS

Errami, H., M. Eiswirth, D. Grigoriev, W.M. Seiler, T. Sturm and A. Weber: Detection of Hopf bifurcations in chemical reaction networks using convex coordinates. Journal of Computational Physics **291**, 279-302 (2015). OPEN ACCESS

Ertl, G.: Walther Nernst and the Development of Physical Chemistry. Angewandte Chemie International Edition **54** (20), 5828-5835 (2015).

Ertl, G.: Walther Nernst und die Entwicklung der Physikalischen Chemie. Angewandte Chemie **127** (20), 5922-5930 (2015).

Jeon, H., B. Jeong, J. Joo and J. Lee: Electrocatalytic Oxidation of Formic Acid: Closing the Gap Between Fundamental Study and Technical Applications. Electrocatalysis **6** (1), 20-32 (2015).

Jia, Z.-M., Z.-N. Zeng, R.-X. Li, Z.-Z. Xu and Y. Deng: Control of electron localization in the dissociation of H_2^+ and its isotopes with a THz pulse. Chinese Physics B **24** (1), 013204 (2015).

Jin, Z., A. Tkach, F. Casper, V. Spetter, H. Grimm, A. Thomas, T. Kampfrath, M. Bonn, M. Kläui and D. Turchinovich: Accessing the fundamentals of magnetotransport in metals with terahertz probes. Nature Physics **11** (9), 761-766 (2015).

Kampfrath, T., M. Battiato, A. Sell, F. Freimuth, A. Leitenstorfer, M. Wolf, R. Huber, P.M. Oppeneer and M. Münzenberg: Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 324-326 (2015). ISBN 978-3-319-07742-0.

Kim, K.W., M. Porer, A. Pashkin, A. Sell, T. Kampfrath, A. Leitenstorfer and R. Huber: THz Spin Dynamics: Phonon-Induced Spin Order. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 327-330 (2015). ISBN 978-3-319-07742-0.

Kumagai, T.: Direct observation and control of hydrogen-bond dynamics using low-temperature scanning tunneling microscopy. Progress in Surface Science **90** (3), 239-291 (2015).

Ladenthin, J., L. Grill, S. Gawinkowski, S. Liu, J. Waluk and T. Kumagai: Hot Carrier-Induced Tautomerization within a Single Porphycene Molecule on Cu(111). ACS Nano **9** (7), 7287-7295 (2015).

Lemell, C., S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger and J. Burgdörfer: Real-time observation of collective excitations in photoemission. Physical Review B **91** (24), 241101 (2015).

Massimi, L., O. Ourdjini, L. Lafferentz, M. Koch, L. Grill, E. Cavaliere, L. Gavioli, C. Cardoso, D. Prezzi, E. Molinari, A. Ferretti, C. Mariani and M.G. Betti: Surface-Assisted Reactions toward Formation of Graphene Nanoribbons on Au(110) Surface. The Journal of Physical Chemistry C **119** (5), 2427-2437 (2015).

Melnikov, A., A. Alekhin, D. Bürstel, D. Diesing, T.O. Wehling, I. Rungger, M. Stamenova, S. Sanvito and U. Bovensiepen: Ultrafast Non-local Spin Dynamics in Metallic Bi-Layers by Linear and Non-linear Magneto-Optics. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 34-36 (2015). ISBN 978-3-319-07742-0.

Meyer, M., I. Agarwal, M. Wolf and U. Bovensiepen: Ultrafast electron dynamics at water covered alkali adatoms adsorbed on Cu(111). Physical Chemistry Chemical Physics **17** (13), 8441-8448 (2015).

Mielke, J., F. Hanke, M.V. Peters, S. Hecht, M. Persson and L. Grill: Adatoms underneath Single Porphyrin Molecules on Au(111). Journal of the American Chemical Society **137** (5), 1844-1849 (2015).

Mikhailov, A.S. and R. Kapral: Hydrodynamic collective effects of active protein machines in solution and lipid bilayers. Proceedings of the National Academy of Sciences of the USA **112** (28), E3639-E3644 (2015).

Müller, M., A. Paarmann and R. Ernstorfer: Visualization of Photocurrents in Nanoobjects by Ultrafast Low-Energy Electron Point-Projection Imaging. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 667-670 (2015). ISBN 978-3-319-13241-9.

Nacci, C., F. Ample, D. Bleger, S. Hecht, C. Joachim and L. Grill: Conductance of a single flexible molecular wire composed of alternating donor and acceptor units. Nature Communications **9** (7), 7397 (2015).

Nayak, J., M. Maniraj, A. Gloskovskii, M. Krajčí, S. Sebastian, I.R. Fisher, K. Horn and S.R. Barman: Bulk electronic structure of Zn-Mg-Y and Zn-Mg-Dy icosahedral quasicrystals. Physical Review B **91** (23), 235116 (2015).

Neppl, S., R. Ernstorfer, A.L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E.M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J.V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz and R. Kienberger: Direct observation of electron propagation and dielectric screening on the atomic length scale. Nature **517** (7534), 342-346 (2015).

Nicholson, C., C. Monney, U. Krieg, C. Tegenkamp, H. Pfnuer, K. Horn and M. Wolf: Electronic Structure of Self-Assembled Ag Nanowires on Si(557): Spectroscopic Evidence for Dimensionality. New Journal of Physics, in press.

Öberg, H., J. Gladh, M. Dell'Angela, T. Anniyev, M. Beye, R. Coffee, A. Föhlisch, T. Katayama, S. Kaya, J. LaRue, A. Møgelhøj, D. Nordlund, H. Ogasawara, W.F. Schlotter, J.A. Sellberg, F. Sorgenfrei, J.J. Turner, M. Wolf, W. Wurth, H. Öström, A. Nilsson, J.K. Nørskov and L.G.M. Pettersson: Optical laser-induced CO desorption from Ru(0001) monitored with a free-electron X-ray laser: DFT prediction and X-ray confirmation of a precursor state. Surface Science, **640**, 80-88 (2015).

Öström, H., H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell'Angela, J. Gladh, M.L. Ng, J.A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W.F. Schlotter, G.L. Dakovski, J.J. Turner, M.P. Minitti, A. Mitra, S.P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J.K. Nørskov, F. Abild-Pedersen, H. Ogasawara, L.G.M. Pettersson and A. Nilsson: Probing the transition state region in catalytic CO oxidation on Ru. Science **347** (6225), 978-982 (2015).

Paarmann, A., I. Razdolski, A. Melnikov, S. Gewinner, W. Schöllkopf and M. Wolf: Second harmonic generation spectroscopy in the Reststrahl band of SiC using an infrared free-electron laser. Applied Physics Letters **107** (8), 081101 (2015).

Perfetti, L., B. Sciolla, G. Biroli, C.J. van der Beek, C. Piovera, M. Wolf and T. Kampfrath: Ultrafast Dynamics of Fluctuations in High-Temperature Superconductors Far from Equilibrium. Physical Review Letters **114** (6), 067003 (2015).

Punckt, C., P.S. Bodega, P. Kaira and H.H. Rotermund: Wildfires in the Lab: Simple Experiment and Models for the Exploration of Excitable Dynamics. Journal of Chemical Education **92** (8), 1330-1337 (2015).

Puppin, M., Y. Deng, C. Nicholson, C. Monney, M. Krenz, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer: 500 kHz OPCPA-Based UV-XUV Light Source For Time-Resolved Photoemission Spectroscopy. In: Proceedings of Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SF2M.4 (2015).
ISBN 978-1-55752-968-8.

Puppin, M., Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf and R. Ernstorfer: 500 kHz OPCPA delivering tunable sub-20 fs pulses with 15 W average power based on an all-ytterbium laser. Optics Express **23** (2), 1491-1497 (2015).

Puppin, M., Y. Deng, O. Prochnow, J. Matyschok, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer: Fiber-Slab-Pumped OPCPA for XUV-Based Time-Resolved Photoelectron Spectroscopy at 500 kHz Repetition Rate. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 766-769 (2015).
ISBN 978-3-319-13241-9.

Schöllkopf, W., S. Gewinner, H. Junkes, A. Paarmann, G. von Helden, H. Bluem and A.M.M. Todd: The new IR and THz FEL facility at the Fritz Haber Institute in Berlin. In: Proceedings of Advances in X-ray Free-Electron Lasers Instrumentation III. (Ed.) S.G. Biedron. (Proceedings of the SPIE, Vol. 9512). SPIE, Bellingham, WA, 95121L (2015).

Stähler, J., J.-C. Deinert, D. Wegkamp, S. Hagen and M. Wolf: Real-Time Measurement of the Vertical Binding Energy during the Birth of a Solvated Electron. Journal of the American Chemical Society **137** (10), 3520-3524 (2015).

Tong, Y., Q. Peng, T. Ma, T. Nishida and S. Ye: Photocatalytic oxidation of the organic monolayers on TiO_2 surface investigated by *in-situ* sum frequency generation spectroscopy. APL Materials **3** (10), 104402 (2015).

Tong, Y., J. Wirth, H. Kirsch, M. Wolf, P. Saalfrank and R.K. Campen: Optically probing Al—O and O—H vibrations to characterize water adsorption and surface reconstruction on α-alumina: An experimental and theoretical study. The Journal of Chemical Physics **142** (5), 054704 (2015).

Tong, Y., K. Cai, M. Wolf, and R.K. Campen: Probing the Electrooxidation of Weakly Adsorbed Formic Acid on Pt(100). Catalysis Today, in press.

Waldecker, L., R. Bertoni and R. Ernstorfer: Compact femtosecond electron diffractometer with 100 keV electron bunches approaching the single-electron pulse duration limit. Journal of Applied Physics **117** (4), 044903 (2015).

Waldecker, L., T.A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer and S. Wall: Time-domain separation of optical properties from structural transitions in resonantly bonded materials. Nature Materials, in press.

Xin, H., J. LaRue, H. Öberg, M. Beye, M. Dell'Angela, J.J. Turner, J. Gladh, M.L. Ng, J.A. Sellberg, S. Kaya, G. Mercurio, F. Hieke, D. Nordlund, W.F. Schlotter, G.L. Dakovski, M.P. Minitti, A. Föhlisch, M. Wolf, W. Wurth, H. Ogasawara, J.K. Nørskov, H. Öström, L.G.M. Pettersson, A. Nilsson and F. Abild-Pedersen: Strong Influence of Coadsorbate Interaction on CO Desorption Dynamics on Ru(0001) Probed by Ultrafast X-Ray Spectroscopy and Ab Initio Simulations. Physical Review Letters **114** (15), 156101 (2015).

Doctoral Thesis

Vita, H.: Interaction of magnetic and non-magnetic metals with graphene. Humboldt Universität zu Berlin 2015.

Wegkamp, D.: Ultrafast electron dynamics and the role of screening. Freie Universität Berlin 2015.

5. Invited Talks of the Members of the Department of Physical Chemistry

Alexandr Alekhin

Nov 2013	Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Ultrafast Non-Local Spin Dynamics in Epitaxial Metallic Multilayers*

Lea Bogner

Jun 2015	Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Dynamics of Exciton Formation and Decay in* $SP6/ZnO(10\bar{1}0)$ *and* $DCV5T\text{-}Me_2/Au(111)$

Lukas Braun

Jul 2014	New Trends in Topological Insulators (NTTI) 2014, Helmholtz-Zentrum Berlin, Berlin, Germany *Ultrafast Photocurrents in the Topological Insulator* Bi_2Se_3 *Probed with Terahertz Emission Spectroscopy*
Jan 2015	Group Seminar, Department of Physics (AG Sergey Ganichev), Universität Regensburg, Regensburg, Germany *Ultrafast Currents at the Surface of the Topological Insulator* Bi_2Se_3
Feb 2015	Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Ultrafast Currents at the Surface of the Topological Insulator* Bi_2Se_3

Kramer Campen

Jun 2014	Workshop, Nonlinear Optics at Interfaces, Telluride Science Research Center, Telluride, CO, USA *Understanding How Water Interacts with* $\alpha\text{-}Al_2O_3$
Aug 2014	Vibrational Spectroscopy, Gordon Research Conference (GRC), Biddeford, ME, USA *Understanding How Water Interacts with* $\alpha\text{-}Al_2O_3(0001)$*: Structure and Dynamics*
Nov 2014	Workshop, Water – the Most Anomalous Liquid, Working Group 4: Quantum Effects, Nordita, Stockholm, Sweden ClO_4^- *at the Air/Water Interface: Population, Desolvation, Aggregation and the Role of* H_3O^+
May 2015	114th General Assembly of the German Bunsen Society for Physical Chemistry, Bochum, Germany *From UHV to the Solid/Liquid Interface: Probing Water Adsorption, Surface Reconstruction and Dynamics on* $\alpha\text{-}Al_2O_3$
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *From UHV to Solid/Liquid Interface: Probing α-Alumina/Water Interaction over 10 Orders of Magnitude in Water Pressure*

Jun 2015 15th International Conference on Vibrations at Surfaces, Donostia-San Sebastian, Spain
From UHV to the Solid/Liquid Interface: Probing Water Adsorption, Surface Reconstruction and Dynamics on α-Al_2O_3

Sep 2015 Workshop, Surface Potentials – Facts, Findings and Fantasies, École polytechnique fédérale de Lausanne, Lausanne, Switzerland
Looking for Solvent Polarization in Nonlinear Optical Signals at Charged Solid/Liquid Interfaces

Yunpei Deng

Oct 2013 The 97th OSA Annual Meeting and Exhibit/Laser Science XXIX, Frontiers in Optics, Orlando, FL, USA
Few Cycle Infrared OPCPA System and Applications

Dec 2013 Conference on High Intensity Laser and Attosecond Science in Israel (CHILI 2013), Tel Aviv, Israel
High Power OPCPA System for XUV Sources at 500 kHz

Ralph Ernstorfer

May 2014 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
Ultrafast Structural and Electronic Dynamics in Low Dimensional Materials

May 2014 Physikalisches-Kolloquium, RWTH Aachen University, Aachen, Germany
Photo-Induced Structural Dynamics in Solids

Aug 2014 SPIE Optics and Photonics, Ultrafast Nonlinear Imaging and Spectroscopy II, San Diego, CA, USA
Femtosecond Low-Energy Electron Diffraction and Imaging

Sep 2014 ELI-ALPS 2nd User Workshop, Extreme Light Infrastructure - Attosecond Light Pulse Source, Szeged, Hungary
Towards Mapping Excited Electronic States in Molecules and Correlated Materials with tr-ARPES

Oct 2014 Workshop, DIET 14, Dynamics, Interactions and Electronic Transitions at Surfaces, Pacific Grove, CA, USA
Femtosecond Low-Energy Electrons Probing Currents and Atomic Structure in Nanomaterials

Feb 2015 4th Banff Meeting on Structural Dynamics: Ultrafast Dynamics with X-Rays and Electrons, Banff, AB, Canada
Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials

Mar 2015 79. Jahrestagung der DPG und DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses, Berlin, Germany
Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials

Mar 2015 Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany
Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents

Apr 2015	Seminar in Solid State Physics, Physik-Institut, University of Zurich, Zurich, Switzerland *Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents*
Gerhard Ertl	
Oct 2013	8th Lorenz Kramer Memorial Lecture, University of Bayreuth, Bayreuth, Germany *Katalyse an Oberflächen*
Nov 2013	100 Years of Ammonia Synthesis, BASF, Ludwigshafen, Germany *The Development of the Haber-Bosch Process*
Nov 2013	Schwarz-Zahradnik Symposium, Berlin-Brandenburg Academy of Sciences and Humanities, Berlin, Germany *From Atoms to Complexity*
Jun 2014	Symposium zum 150. Geburtstag von Walther Nernst, Magnus-Haus Berlin, Berlin, Germany *Walther Nernst und die Entwicklung der Physikalischen Chemie*
Laura Foglia	
Jul 2015	Group Seminar, Department of Physics (AG Fulvio Parmigiani), Università degli Studi di Trieste, Trieste, Italy *Exciton Dynamics in Hybrid Organic-Inorganic Semiconducting Systems*
Jul 2015	Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany *Charge Relaxation Pathways and Exciton Dynamics at an Hybrid Inorganic Organic Interface*
Leonhard Grill	
Dec 2013	Seminar, Institute of Applied Physics, Vienna University of Technology, Vienna, Austria *Controlling Chemical Processes in Single Molecules on Surfaces*
Mar 2014	247th ACS National Meeting and Exposition, American Chemical Society, Dallas, TX, USA *Controlling Chemical Processes at the Level of Single Molecules*
Apr 2014	DPG-Frühjahrstagung, Symposium Molecular Switches and Motors at Surfaces (SYMS), Dresden, Germany *Imaging and Manipulation of Single Functional*
Apr 2014	Sino-German Symposium on π-Conjugated Nanomaterials for Catalysis and Clean Energy Applications, Berlin, Germany *Controlling Chemical Processes at the Level of Single Molecules*
May 2014	Keynote Lecture, International Workshop “On-Surface Synthesis”, Ecole de physique des Houches, Les Houches, France *Covalent Molecular Assembly on Metal Surfaces: Towards Functional Nanostructures*

Sep 2014	64th Annual Meeting of the Austrian Physicsal Society (ÖPG), Pöllau, Austria *Functional Molecules on Surfaces: From Conducting Wires to the Role of Single Atoms*
Sep 2014	Beilstein Nanotechnology Meeting 2014 “Molecular Machines and Devices”, Potsdam, Germany *Manipulating Single Functional Molecules by Scanning Tunnelling Microscopy*
Sep 2014	European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland *Assembly and Manipulation of Single Functional Molecules*
Oct 2014	5th Vacuum Symposium, Institute of Physics, Coventry, UK *Every Atom Counts: Manipulation of Single Functional Molecules on Surfaces*
Nov 2014	Seminar, Institute of Physical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany *Single-Molecule Chemistry: From Fundamental Understanding to Functional Systems*

Karsten Horn

Dec 2013	8th International Conference on Advanced Materials and Devices, Jeju, South Korea *Electronic Structure of Epitaxial Graphene and its Interaction with Semiconductor and Metal Substrates*
Dec 2013	Korea Research Institute of Standards and Science (KRISS), Daejeon, South Korea *Epitaxial Graphene and its Electronic Structure*
Jun 2014	Lecture, Department of Physics, Tohoku University, Sendai, Japan *A Short Walk through the Photoemission Technique and Some of its Applications*
Jun 2014	Seminar, Research Institute of Electrical Communication, Tohoku University, Sendai, Japan *Electronic Structure of Graphene and Related Materials*
Dec 2014	Conference, German Scientists Interactions in Physics with UNamur, Namur, Belgium *Electronic Structure of Graphene and Some of its Interfaces*

Tobias Kampfrath

Nov 2013	Department Seminar, Institute of Solid State Physics, Technische Universität Berlin, Berlin, Germany *Ultrafast Adiabatic Manipulation of Slow Light*
Jan 2014	Center-of-Excellence Colloquium, Fachbereich Physik, University of Marburg, Marburg, Germany *Beyond Body Scanners: How to Use Terahertz Pulses to Observe and Control Spin Dynamics in Solids*

Feb 2014	Department Seminar, Stanford Institute for Materials and Energy Sciences (SIMES), Stanford University, Stanford, CA, USA *How to Use Terahertz Pulses to Probe and Control Spin Dynamics in Solids*
Feb 2014	Photonics West (SPIE OPTO), San Francisco, CA, USA *Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation*
Mar 2014	Joint Symposium, SFB IR-ON and SFB Next-Lite, Vienna University of Technology, Vienna, Austria *Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation*
Apr 2014	Department Seminar, Department of Materials, ETH Zurich, Zurich, Switzerland *Ultrafast Spin Dynamics and Transport Controlled and Probed with Terahertz Radiation*
May 2014	4th EOS Topical Meeting on Terahertz Science and Technology (TST2014), Camogli, Italy *Spintronics with Terahertz Radiation*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Probing and Controlling the Dynamics of Charges and Spins Using THz Radiation*
May 2014	Group Seminar, Institute of Physics (AG Georg Woltersdorf), Martin Luther University Halle-Wittenberg, Halle, Germany *THz Spectroscopy and THz Spintronics*
Jun 2014	Conference, CLEO: 2014 - Laser Science to Photonic Applications, San José, CA, USA *Tutorial: Intense Terahertz Pulses: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions*
Jan 2015	Department Seminar at BESSY, Department of Photovoltaics, Berlin, Germany *THz Spectroscopy and THz Spintronics*
Jan 2015	Workshop, Von Pico zu Femto - Time-Resolved Studies at BESSY II, Helmholtz-Zentrum Berlin, Berlin, Germany *Ultrafast Spin-Lattice Interactions: New Route to Magnetization Control*
Mar 2015	Institute Seminar, Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany *Terahertz Spectroscopy: From Ultrafast Probing toward Control of Electron and Spin Dynamics*
Mar 2015	Optical Terahertz Science & Technology Conference (OTST 2015), San Diego, CA, USA *Tutorial: Material Control with THz Transients*
Apr 2015	Seminar, Department of Inorganic Chemistry, Fritz-Haber-Institut, Berlin, Germany *Terahertz Spectroscopy: From Ultrafast Probing toward Control of the Motion of Electrons, Ions and Spins*

May 2015	Workshop, Ultrafast Dynamics in Condensed Matter, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Terahertz Spectroscopy: From Ultrafast Probing toward Controlling the Motion of Electrons, Phonons and Spins*
Aug 2015	Department Seminar, Institute for Advanced Simulation, Forschungszentrum Jülich, Jülich, Germany *Probing and Controlling Spin Dynamics with Terahertz Pulses*
Sep 2015	CECAM Workshop, Exploration of ultra-fast timescales using time dependent density functional theory and quantum optimal control theory, Lausanne, Switzerland *Probing and Controlling Spin Dynamics with Terahertz Pulses*

Takashi Kumagai

Feb 2014	17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany *Direct Observation of Molecular Dynamics Using Scanning Tunneling Microscopy*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Direct Observation of Molecular Dynamics Using Scanning Probe Microscopy*
Jun 2014	SFB 658 Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany *Control of Intramolecular H Atom Transfer Reaction Using Scanning Tunneling Microscopy*
Apr 2015	Colloquium of the Collaborative Research Centre 951 “Hybrid Inorganic/Organic Systems for Opto-Electronics” (HIOS), Berlin, Germany *Local Characterization of Ultrathin ZnO Layers on Ag(111) by STM and AFM*

Alexey Melnikov

Jan 2014	Department Seminar, Department Molecular Spectroscopy, Max Planck Institute for Polymer Science, Mainz, Germany *Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*
Jul 2014	Group Seminar, Institut für Materialsphysik (AG Cynthia A. Volkert), University of Göttingen, Göttingen, Germany *Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*
Jul 2014	Moscow International Symposium on Magnetism MISM-2014, Moscow, Russia *Non-Locality of Ultrafast Spin Dynamics in Au/Fe/MgO(001) Bi-Layers due to Spin-Dependent Hot Carrier Transport*
Oct 2014	Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany *Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Nov 2014	Seminar, Department of Quantum Electronics, Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia *Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*
Nov 2014	Seminar, P.L. Kapitza Institute for Physical Problems of the Russian Academy of Sciences, Moscow, Russia *Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*
Mar 2015	Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany *Direct Monitoring of Hot Carrier-Formed Spin Currents in Metallic Multi-Layers by Time-Resolved Magneto-Induced Second Harmonic Generation*
Sep 2015	CECAM Workshop, Exploration of ultra-fast timescales using time dependent density functional theory and quantum optimal control theory, Lausanne, Switzerland *Ultrafast Charge- and Spin-Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Alexander S. Mikhailov

Jun 2014	Lecture, Nanoscience Center, University of Barcelona, Barcelona, Spain *Simple Elastic Models of Protein Machines and Elastic Motors*
Sep 2014	Lecture, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan *Simple Elastic Models of Protein Machines*
Sep 2014	Seminar, RIKEN Center for Developmental Biology, Kobe, Japan *Simple Elastic Models of Protein Machines*
Nov 2014	Seminar, Department of Basic Science, The University of Tokyo, Tokyo, Japan *Simple Elastic Models of Protein Machines and Synthetic Motors*
Nov 2014	Seminar, Department of Physics, The University of Tokyo, Tokyo, Japan *Autonomous Learning by Simple Dynamical Systems with Delayed Feedback*
Feb 2015	Lecture, International WE-Heraeus Physics School on "Model systems for understanding biological processes", Bad Honnef, Germany *Hydrodynamic Collective Effects of Active Protein Machines*
Feb 2015	Lecture, International WE-Heraeus Physics School on "Model systems for understanding biological processes", Bad Honnef, Germany *Simple Elastic Models of Protein Machines*
Mar 2015	Lecture, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan *Hydrodynamic Collective Effects of Active Protein Machines*
Mar 2015	Seminar, Department of Biomedical Engineering, Faculty of Life and Medical Sciences, Doshisha University, Kyotanabe, Japan *Hydrodynamic Collective Effects of Active Protein Machines*

Mar 2015 Seminar, Department of Information Sciences, Ochanomizu University, Tokyo, Japan
Simple Elastic Models of Protein Machines

Mar 2015 Seminar, Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto, Japan
Simple Elastic Models of Protein Machines

Jun 2015 Lecture, 8th International Conference, Engineering of Chemical Complexity, Garching, Germany
Hydrodynamic Collective Effects of Active Proteins

Claude Monney

Jan 2014 Artemis User Meeting, Abingdon, UK
Time-Resolved Photoemission Study of an Electronically-Driven Charge Density Wave Phase

Apr 2014 Seminar, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
Time-Resolved Photoemission Study of an Electronically-Driven Charge Density Wave Phase

Sep 2014 SUCCESS-2014: School on UV and X-Ray spectroscopies of correlated electron systems, Les Houches, France
Resonant Inelastic X-Ray Scattering on Correlated Materials

Selene Mor

Apr 2014 Specially Selected Young Scientist Talk, From the witches cauldrons in materials science, Center of Interface Science (CIS), Goslar, Germany
Ultrafast Optical Spectroscopy of Quasi One Dimensional Ta_2NiSe_5

Melanie Müller

Jul 2015 Seminar, Helmholtz-Zentrum Berlin
Femtosecond Low-energy Electrons as Probes for Ultrafast Dynamics on the Nanoscale

Christopher Nicholson

Jul 2014 Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
Ultrafast Photoemission Study of Cr:W(110) Thin Films

Alexander Paarmann

Jul 2014 FHI FEL Symposium, Berlin, Germany
Ultrashort Pulse Operation of the FHI IR-FEL

May 2015 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
Nonlinear Phonon Spectroscopy of Solids Using the FHI IR-FEL

Alexander Saywell

Nov 2013 Seminar, Department of Physical Chemistry, University of Graz, Graz, Austria
Complex Organic Molecules Studied under Ultra-High Vacuum: Electrospray Deposition and On-Surface Synthesis

Julia Stähler

Nov 2013	Seminar, Physics Department (AG Aeschlimann), Technische Universität Kaiserslautern, Kaiserslautern, Germany *Quasiparticle Dynamics at Oxide Surfaces: Electrons, Excitons and Polarons*
Dec 2013	Seminar, Laboratory of Ultrafast Spectroscopy (AG Majed Chergui), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland *Quasiparticle Dynamics at Oxide Surfaces: Electrons, Excitons and Polarons*
Jan 2014	6th International Workshop and School on Time-Dependent Density-Functional Theory: Prospects and Applications, Centro de Ciencias de Benasque Pedro Pascual, Benasque, Spain *Ultrafast Exciton Formation at the ZnO*$(10\bar{1}0)$ *Surface*
Apr 2014	Seminar, Laboratory for Attosecond Physics, (Ferenc Krausz), Max Planck Institute of Quantum Optics, Munich, Germany *Ultrafast Exciton Formation at the ZnO*$(10\bar{1}0)$ *Surface*
May 2014	Institute Colloquium, Institiut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Kiel, Germany *Ultrafast Exciton Formation at the ZnO*$(10\bar{1}0)$ *Surface*
Jul 2014	SFB 767 Colloquium, Fachbereich Physik, Universität Konstanz, Constance, Germany *Instantaneous Band Gap Collapse in Photoexcited Monoclinic* VO_2
Nov 2014	3rd International Ertl Symposium on Surface Analysis and Dynamics, Berlin, Germany *Ultrafast Exciton Formation Dynamics at the ZnO Surface*
Dec 2014	Colloquium Optics and Condensed Matter, Institiut für Angewandte Physik, University of Bonn, Bonn, Germany *Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?*
Dec 2014	Condensed Matter Seminar, Max Planck Institute for the Physics of Complex Systems, Dresden, Germany *Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?*
Feb 2015	Colloquium, Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany *Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?*
Feb 2015	Max Planck Research Group Selection Symposium, Harnack House, Berlin, Germany *Transiently Functional Interfaces: Ultrafast Dynamics of Quasiparticles & Collective Phenomena*
Mar 2015	79. Jahrestagung der DPG und DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Surface Science Division, Berlin, Germany *Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?*

Apr 2015 Department Seminar, The Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands
A Real Time Movie about Ultrafast Phenomena at Hybrid Interfaces

Apr 2015 Meeting, From the witches cauldrons in materials science, Center of Interface Science (CIS), Goslar, Germany
What Happens before Light Emission? A Real Time Movie about Exciton Formation and Decay, the Violation of Kasha's Rule and other Ultrafast Phenomena at Hybrid Interfaces

May 2015 Department Seminar, Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany
Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?

May 2015 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption

Aug 2015 Women in Optics: The Castle Meeting 2015, Marburg, Germany
Exciting! What Happens When Light is Absorbed in a Semiconductor?

Sep 2015 Highlights der Physik, Jena, Germany
Es werde Licht! –Und zwar schnell!!

Lutz Waldecker

Jun 2015 Group Seminar, Faculty of Physics (AG Uwe Bovensiepen), Universität Duisburg-Essen, Essen, Germany
Electron-Lattice Interactions Probed with Femtosecond Electron Diffraction

Martin Wolf

Mar 2014 APS March Meeting 2014, American Physical Society, Denver, CO, USA
Dynamics of Electron Transfer and Exciton Formation at Interfaces

May 2014 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
Current Topics and Developments in the PC Department

May 2014 Seminar, Energy Frontier Research Center, Columbia University, New York, NY, USA
Probing the Transient Electronic Structure During Surface Reactions on Femtosecond Time Scales

Jun 2014 5th International Conference on Photoinduced Phase Transitions and Cooperative Phenomena, PIPT5, Bled, Slovenia
Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved ARPES

Jun 2014 International Workshop, Itinerant Magnetism and Superconductivity - IMS 2014, Dresden, Germany
Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved ARPES

Jun 2014 Physikalisches Kolloquium, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany
Dynamics of Electronic Structure Changes During Surface Reactions and Phase Transitions in Solids

Jul 2014	Faraday Discussion 171, Emerging Photon Technologies for Chemical Dynamics, Sheffield, UK *Coherent Dynamics of the Charge Density Wave Gap in Tritellurides Probed by Time-Resolved ARPES*
Jul 2014	International Workshop on Nanoscale Spectroscopy and Nanotechnology (NSS-8), Chicago, IL, USA *Electronic Structure and Exciton Formation at ZnO Interfaces*
Aug 2014	International School and Workshop on Electronic Crystals ECRYS-2014, Cargèse, France *Time-Resolved Spectroscopy and Ultrafast Dynamics of the Electronic Structure of Photoexcited Solids*
Oct 2014	16th Workshop on Dynamical Phenomena at Surfaces (WDPS-16), Madrid, Spain *Ultrafast Dynamics of Electronic Structure Changes in Photoinduced Processes at Surfaces*
Oct 2014	General Physics Colloquium, Aarhus University, Aarhus, Denmark *Ultrafast Dynamics of Photoinduced Surface Reactions and Phase Transitions in Solids*
Jan 2015	Workshop, Von Pico zu Femto - Time-Resolved Studies at BESSY II, Helmholtz-Zentrum Berlin, Berlin, Germany *Ultrafast Dynamics of Photoinduced Surface Reactions*
Mar 2015	International Workshop on Sum Frequency Generation, Wiesbaden, Germany *Unconventional Approaches to Vibrational Spectroscopy at Interfaces*
Apr 2015	International Workshop: The Future of Gas Phase and Surface Chemistry at FLASH, DESY, Hamburg, Germany *Surface Femtochemistry: From Elementary Steps to Intricacy*
May 2015	International Workshop, Photon Science Roadmap Symposium, DESY, Hamburg, Germany *Surface Chemical Reaction Dynamics Studied with FELs*
May 2015	Physikalisches Kolloquium, Institute of Physics, Universität Kassel, Kassel, Germany *Transient Electronic Structure in Ultrafast Surface Reactions and Phase Transitions in Solids*
Aug 2015	Dynamics at Surfaces, Gordon Research Conference (GRC), Newport, RI, USA *Can we probe the transition state in surface reactions (Hot Topic)*
Aug 2015	RACIRI Summer School 2015, Rügen, Germany *Transient Electronic Structure in Ultrafast Surface Reactions*
Aug 2015	Soft X-Ray in Energy and Time Workshop (SXET), Helmholtz-Zentrum Berlin, Berlin, Germany *Transient Electronic Structure in Ultrafast Surface Chemistry*

Sep 2015	International Conference on Laser Ablation (COLA 2015), Cairns, QLD, Australia *Fundamental Aspects of Laser-Matter Interaction: Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved Photoemission*
Sep 2015	Center for Quantum Computing & Quantum Technology Seminar, University of New South Wales, Sydney, NSW, Australia *Ultrafast Dynamics of Photoexcited Insulators Probed by Time-Resolved Photoemission*

Max Planck Research Group for Structural and Electronic Surface Dynamics

Head: Ralph Ernstorfer

Group members

Scientists:

Roman Bertoni

Doctoral students:

Melanie Müller
Michele Puppin
Thomas Vasileiadis
Lutz Waldecker

Diploma and master's students:

Johannes Feldl

Research projects funded from outside resources

- European Research Project (*NMP-2011-SMALL*): *"Time dynamics and Control in nanostructures for magnetic recording and energy applications (CRONOS)"*, project within work package FHIB (*Optimal control schemes of high-harmonic generation*), together with Martin Wolf.

  Project scientist: Yunpei Deng (until 03/2015).

- DFG Research Unit FOR1700 "*Metallic nanowires on the atomic scale: Electronic and vibrational coupling in real world systems*", Project E5 "*Time-resolved spectroscopy of photoinduced transitions and electronic excitations in quasi-1D metal wires on semiconductors"*, together with Martin Wolf.

  Project graduate student: Christopher Nicholson.

Scientific Scope

Many-body phenomena and the coupling between electron, lattice and spin degrees of freedom are of fundamental importance as they govern the ground state properties of materials as well as relaxation and dissipation effects in non-equilibrium states. Whereas such coupling effects are no physical observables, they can be assessed indirectly through an experimental perturbative approach, as illustrated in Fig. 1: femtosecond light pulses excite a specific subsystem, typically the electrons, and the same or another subsystem's response is observed with various time-resolved probes.

We develop and employ several complementary, ultrafast probes sensitive to the ultrafast response of electrons and crystalline structure: femtosecond electron diffraction (FED) reveals the level of vibrational excitation and the evolution of crystalline long-range order, femtosecond time- and angle-resolved photoelectron spectroscopy (trARPES) shows the temporal evolution of the electronic structure and of excited states, and time resolves optical spectroscopy provides the material's dielectric function. In addition, we established low-energy electrons as an ultrafast probe for transient electric fields and related photocurrents in nanoobjects.

We apply this set of techniques to a range of material systems ranging from bulk crystals, 2D materials, nanowires to clusters. The following section highlights the main research achievements since the last Fachbeirat's evaluation.

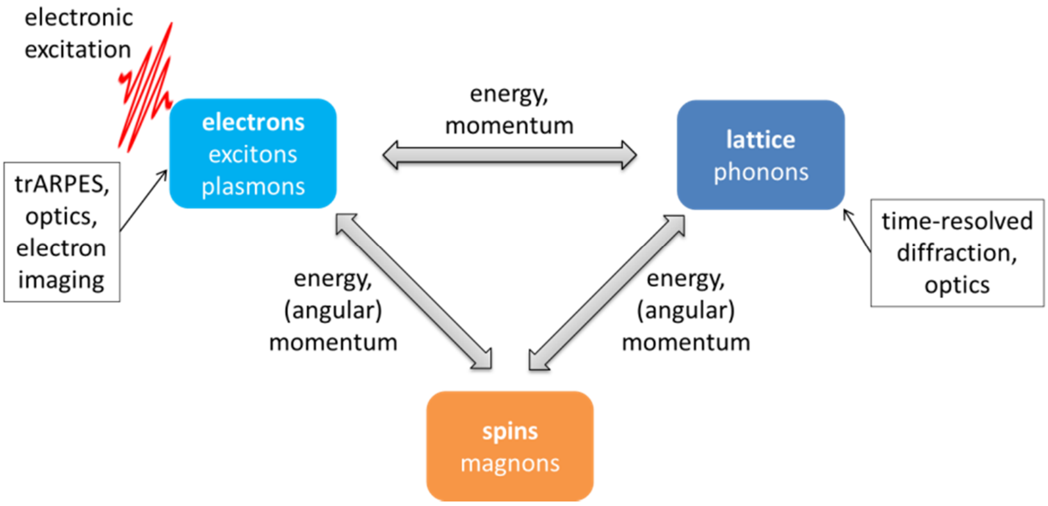


Figure 1: *Illustration of the relation between employed experimental techniques and the accessible physical quantities. The coupling between electronic, phononic and spin degrees of freedom is investigated by different subsystem-specific ultrafast probes through the response of the electronic structure, the crystalline structure and the dielectric function to impulsive excitation of electrons. The research activities comprise the application as well as the development of ultrafast techniques.*

Development of a 500 kHz Femtosecond DUV and XUV Light Source

Time- and angle-resolved photoelectron spectroscopy (trARPES) provides access to electronic structure with time, energy and momentum resolution. The time scale of the relaxation of photo-excited states potentially reveals the relevant coupling mechanisms, which are reflected in the momentum- and energy-dependent self-energy [1]. Current approaches to trARPES are either limited in ***k***-space access due to low probe photon energies or limited in counting statistics due to limited repetition rate. Based on a novel laser system we bridge this technology gap. In collaboration with the *Dynamics of Correlated Materials* group headed by Martin Wolf, an optical parametric chirped pulse amplifier (OPCPA) operating at 500 kHz repetition rate and providing tunable short pulses with a pulse energy exceeding 30 µJ has been developed [2]. The output of this laser system is frequency up-converted to either the deep ultraviolet (DUV) spectral range by means of nonlinear crystals or the extreme ultraviolet (XUV) spectral range by high harmonic generation (HHG) in noble gases, see Fig. 2.

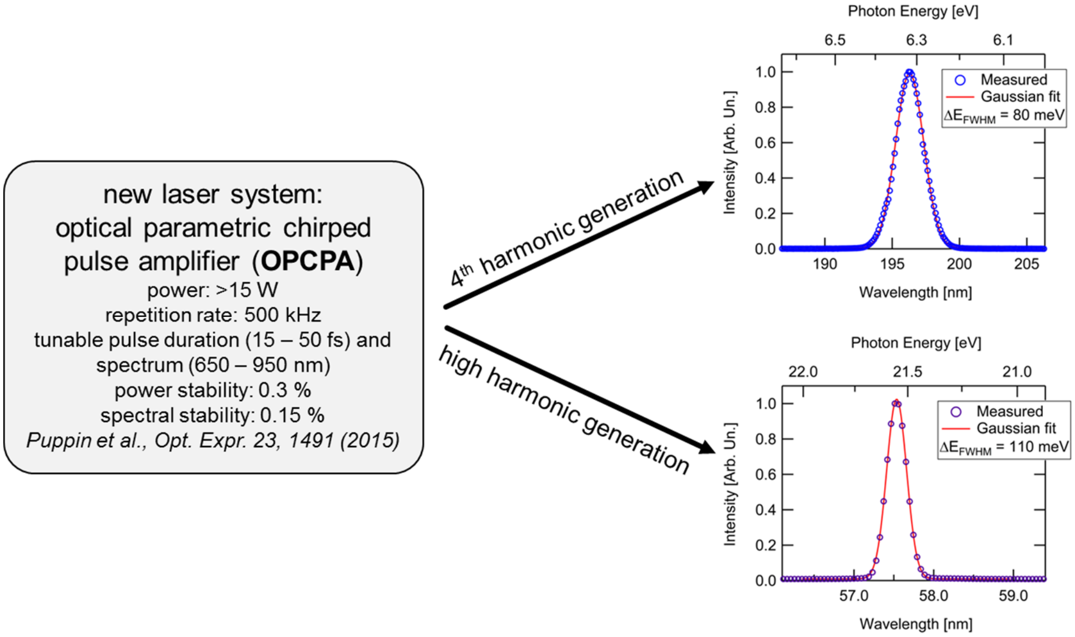


Figure 2: *Generation of high-repetition rate femtosecond DUV and XUV pulses. A novel optical parametric chirped pulse amplifier providing high average power at 500 kHz repetition rate has been developed and is used for generating high-photon energy probes by frequency up-conversion. 4th harmonic generation in nonlinear crystal provides DUV pulses with photon energies up to 6.4 eV and bandwidth supporting sub-30 fs pulse duration (top right panel). Spectrally isolated XUV pulses exceeding 20 eV photon energy with a bandwidth of approximately 100 meV are generated by HHG of the frequency-doubled OPCPA output (bottom right panel). Puppin et al., Optics Express 23, 1491 (2015); poster PC 8.*

Employing a tight-focusing geometry and the 2nd harmonic of the OPCPA output as fundamental of the HHG process, a single isolated harmonic at ~21.5 eV photon energy with a bandwidth of ~100 meV is generated.

Femtosecond Low-energy Electrons as Probes: Visualization of Photocurrents in Nanoobjects

We developed a novel concept for femtosecond point-projection microscopy (fsPPM) and femtosecond low-energy electron diffraction (fsLEED) utilizing laser-triggered electron emission from metal nanotips as pulsed electron source, delivering either divergent or collimated femtosecond single-electron wave packets in the sub-kV energy range. Due to the large scattering cross-section of low-energy electrons and their high sensitivity to electric fields, such electrons represent sensitive probes for the investigation of ultrafast currents and transient electric fields in nanoobjects as well as of atomic structure in low-dimensional materials with femtosecond time resolution [3].

As a proof of concept, we demonstrated the visualization of ultrafast photo-induced currents in III-V semiconductor nanowires, see Fig. 3. Band bending along the radial coordinate of an InP nanowire results in a separation of photo-excited carriers with a flow of electrons from the interior to the surface of the nanowires. The photo-current results in a transient lifting of the band bending, which is reflected in a time-dependent change of the vacuum level in the vicinity of the nanowire. As low-energy electrons are sensitive to small changes of the electrostatic potential on the nanoscale, the fsPPM image of the nanowire reveals the net photocurrent inside the nanowire with approximately 100 fs temporal resolution, see Fig. 3c.

The temporal and spatial resolution of the fsPPM approach is currently limited by the need of keeping the laser pulses exciting the sample and triggering the electron source spatially separated. In order to overcome this limitation, we realized plasmon-driven electron emission from a gold nanotip in collaboration with the group of Markus Raschke, Univ. of Colorado. By means of grating structures engraved in the shaft of nanotips [4], a broadband surface plasmon polariton (SPP) is launched by a femtosecond laser pulse, see Fig. 3d. The continuous focusing of the SPP during the propagation towards the apex leads to fields sufficient for the nonlinear emission of electrons from the tip's apex. Interferometric autocorrelation measurements indicate that the SPP-induced electron emission occurs on the sub-10 femtosecond time scale.

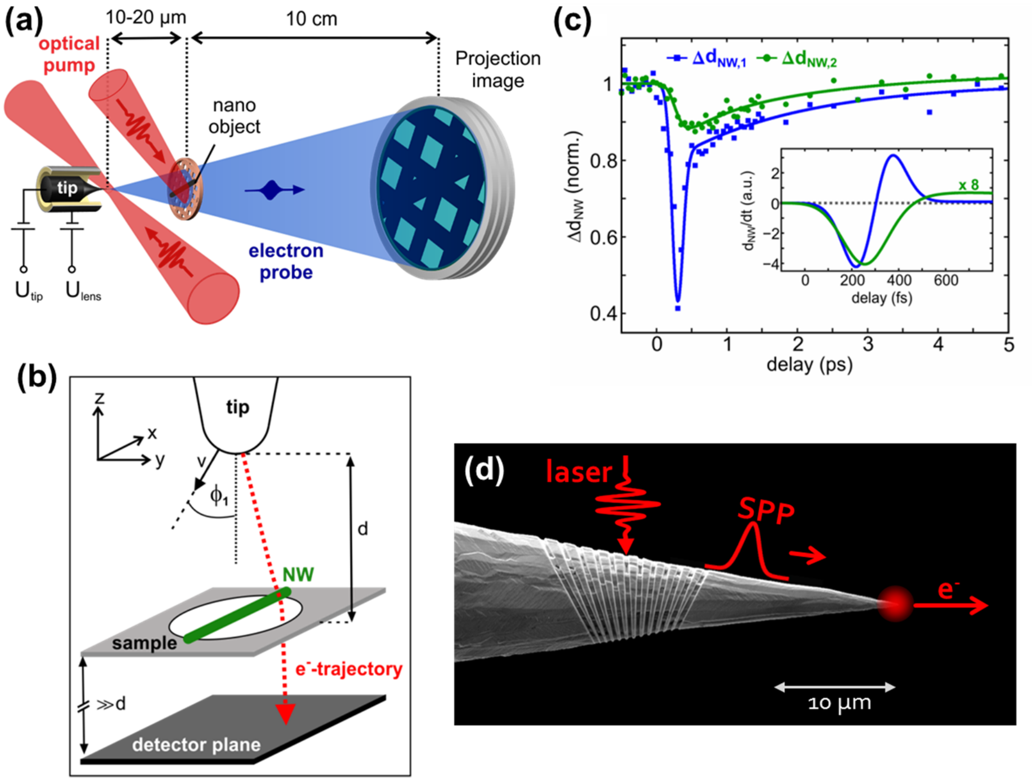


Figure 3: *Visualization of photocurrents in a nanowire with low-energy femtosecond electrons (a-c) and plasmon-induced electron emission from a nanotip (d). Panel (a): Illustration of the experimental setup for fs point-projection microscopy comprising a laser-triggered nanotip as electron source. Panel (b): The trajectory of fs single electrons in the vicinity a nano-sized sample is sensitive to electric fields caused by variations of the electrostatic potential in the vicinity of the nanoobject. Panel (c): The time-dependent change of the projected diameter of a p-i-n-doped InP nanowire after optical excitation with femtosecond laser pulses centered at 800 nm. The photo-induced effect is interpreted as radial current of photo-excited electrons from the interior of the 30 nm thick nanowire to the surface in the p-doped (blue line) and n-doped (green line) segments, respectively. The inset shows the temporal derivative of the measured signal reflecting the time-dependence of the radial photocurrent. Panel (d): SEM image of a gold nanotip with a grating for the efficient coupling of a sub-10 fs laser pulse to a surface plasmon polariton (SPP). While propagating towards the apex, the SPP is focused and reaches intensities sufficient for nonlinear emission of electrons from the tip's apex. Müller et al., Nature Communications 5 (10), 5292 (2014); poster PC9.*

Phase Change Materials: Relating Optical Properties and Crystalline Structure

Phase change materials employed in data storage applications are characterized by their large contrast of opto-electronical properties between their metastable amorphous and crystalline structural states. The ability to reversibly switch the material between those states has found numerous applications in modern data storage technology, where switching is achieved by tailoring temperature profiles in the system after heating with optical or electrical pulses.

Whereas the pathway of thermal phase transformation employed in devices is well established, the existence of non-thermal phase transitions [5], and the microscopic origin of the pronounced optical contrast [6] are still subject to debate. In collaboration with the group of Simon Wall (ICFO, Castelldefels), we investigated the evolution of optical and structural properties of crystalline GST upon excitation with a femtosecond laser pulse by combining two complementary pump-probe techniques. The transient optical properties are investigated by femtosecond optical spectroscopy while the structural response of the lattice is probed with femtosecond electron diffraction, see Fig. 4. Above the threshold for switching, we employed single-shot optical and diffraction measurements to follow the system's response to photoexcitation during the crystalline-to-amorphous phase transition.

Large changes in the dielectric function of up to 30% occur instantaneously after photoexcitation, the amplitude of which increases with fluence, but saturates when crossing the threshold for permanent change. In earlier work on phase change materials, similar observations have been interpreted as non-thermal phase transitions to an amorphous or liquid state [7,8]. In contrast, time-resolved electron diffraction [9] reveals that energy transfer from excited electrons to the lattice occurs only on a few picosecond timescale independent of the excitation level. We interpret the ultrafast dynamics of optical and structural properties in terms of resonant bonding of this material [10]. While electronic excitation depopulates resonantly-bonded states, which dominate the optical properties, the crystalline structure is preserved by the covalently bound backbone until energy transfer due to electron-phonon

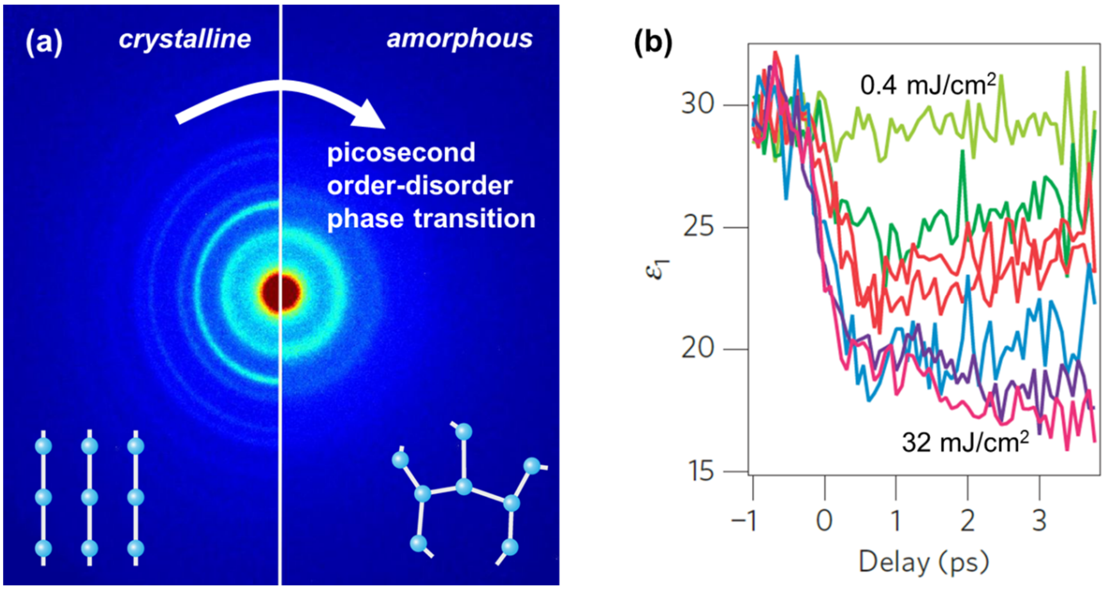


Figure 4: *The response of structural and optical properties of the phase change material GST ($Ge_2Sb_2Te_5$) to electronic excitation is studied with femtosecond electron diffraction (left) and optical spectroscopy. The right panel shows the evolution of the real part of the dielectric function at 800 nm retrieved from simultaneous single-shot measurement of transmission and reflectivity for a range of excitation levels. The light blue curve corresponds to a fluence of 14 mJ/cm^2, which is the threshold fluence for a persistent crystalline-amorphous phase transition. While the dielectric function changes quasi-instantaneously by up to 30%, the loss of crystalline long-range order occurs by thermal melting on the picosecond time scale. Waldecker et al., Nature Materials, aop, doi: 10.1038/nmat4359; poster PC 10.*

coupling leads to melting of the crystal. The large transient change of the optical properties without structural transition may be utilized in optical modulators comprising GST-based heterostructures.

Electron-lattice Interaction in Layered Transition Metal Dichalcogenides, Bulk Crystals and Clusters

In addition to the temporal evolution of crystalline long-range order, femtosecond electron diffraction provides time-resolved information on the excitation level of phonons through the experimentally accessible mean-squared displacement of the atoms. Figure 4a shows the time-dependent atomic mean squared displacement of Al in response to optical excitation with an NIR pulse for three excitation levels. The increase in atomic motion reflects the transfer of energy from the photo-excited electrons to the lattice, which is typically described within a two-temperature model. The assumption, however, that phonon populations follow Bose-Einstein statistics on the femtosecond time scale, is highly questionable. In collaboration with Jan Vorberger (MPIKS Dresden), we introduce a non-thermal lattice model describing the coupling of electrons to individual phonon branches [11].

Besides bulk materials, we investigate the electron-phonon interaction in low-dimensional materials. In collaboration with the group of Richard Palmer (University of Birmingham), size-selected Au clusters on thin graphite are optically excited and studied with femtosecond

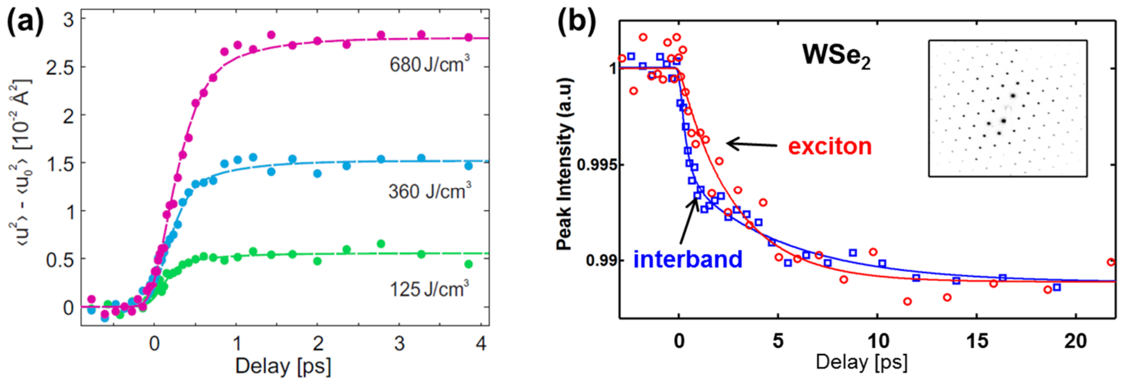


Figure 5: *Investigation of electron-phonon coupling in aluminium and the 2D material* WSe_2*. Left panel: time-resolved electron diffraction reveals the increase in atomic mean squared displacement (dots) in a 30 nm thick film of Al subsequent to excitation of the electrons with three different energy densities. The data is fitted with a non-thermal lattice model (solid lines) describing the energy transfer from electrons to individual phonon branches with coupling constants from first principles calculations. Right panel: dynamics of Bragg peak intensity of multilayer* WSe_2 *in response to optical excitation resonant with the lowest energy excitonic transition (red circles) and with interband transitions at 400 nm (blue squares). Solid lines indicate exponential fits to the data revealing a sequential relaxation process of photo-excited free carriers (blue) due to electron-phonon coupling, in contrast to the mono-exponential relaxation of excitonic states (red). The inset shows a static diffraction of the sample before optical excitation. Waldecker et al., arXiv 1507.03743; poster PC 11.*

electron diffraction. Both, internal coupling between electrons and vibrations as well as coupling between clusters and substrate are investigated. Additionally, we study semiconducting transition metal dichalcogenides (TMDCs), which are a fascinating class of layered materials exhibiting highly anisotropic bonding, pronounced excitonic effects, transitions from indirect to direct bandgaps in the limit of single crystalline layers [12], and spin-valley-layer correlations [13,14]. Currently, we investigate relaxation dynamics subsequent to different kinds of optical excitation in multilayer WSe_2 by probing the evolution of the vibrational excitation of the crystal, see Fig. 5b. The mono-exponential relaxation dynamics subsequent to excitation in resonance with an excitonic band is ascribed to exciton dissociation and carrier relaxation towards the band extrema, whereas relaxation of electrons subsequent to classical interband excitation proceeds through fast intraband relaxation followed by a slower process likely involving intervalley scattering. In perspective, the structural dynamics studies with time-resolved diffraction experiments will be complemented by trARPES experiments providing direct access to momentum-resolved electron relaxation.

Observing the Motion of Electrons on Atomic Length Scales

The propagation of electrons in crystals is described in terms of Bloch wave packets, i.e., coherent superpositions of Bloch states around a central wave vector. Free propagation of

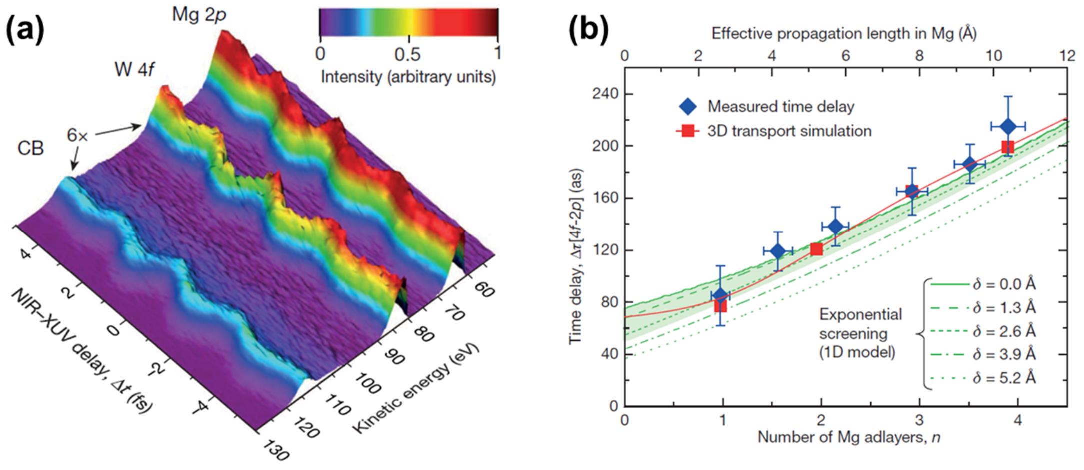


Figure 6: *Investigation of electron propagation and dielectric screening on atomic length scales. Left panel: Attosecond streaking photoelectron spectroscopy from four monolayers of magnesium on a tungsten crystal showing emission from the Mg 2p and W 4f core levels and the sample's conduction band modulated in energy by a sub-2 cycle near-infrared streaking field. Right panel: the time delay between electrons originating from core levels of substrate and adlayer reveals the propagation of electron through the Mg layers and the length scale of dielectric screening of near-infrared light at the surface. Neppl et al., Nature 517 (7534), 342-346 (2015).*

Bloch wave packets in crystals, however, is very limited in space and time as elastic and inelastic scattering processes destroy the wave packet's coherence. In collaboration with the groups of Peter Feulner, Reinhard Kienberger (both TU Munich) and Ferenc Krausz (MPQ, Garching), electron wave packet motion has been investigated on the atomic length and the attosecond time scale [15]. These experiments reveal the electron motion through few layer of magnesium adsorbed on a tungsten crystal and provide information on the length scale of dielectric screening by the metal, see Fig. 6. Additionally, this type of experiments has been employed for investigating collective excitation in photoemission, in particular to discriminate between intrinsic and extrinsic excitation of plasmons [16].

References

[1] M. Sentef, A. Kemper, B. Moritz, J. Freericks, Z.-X. Shen, and T. Devereaux, *Phys. Rev. X* **3**, 041033 (2013).

[2] M. Puppin, Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf, and R. Ernstorfer, *Opt. Express* **23**, 1491 (2015).

[3] M. Müller, A. Paarmann, and R. Ernstorfer, *Nat. Commun.* **5**, 5292 (2014).

[4] S. Berweger, J. M. Atkin, R. L. Olmon, and M. B. Raschke, *J. Phys. Chem. Lett.* **3**, 945 (2012).

[5] A. V Kolobov, M. Krbal, P. Fons, J. Tominaga, and T. Uruga, *Nat. Chem.* **3**, 311 (2011).

[6] K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, and M. Wuttig, *Nat. Mater.* **7**, 653 (2008).

[7] K. Sokolowski-Tinten, J. Solis, J. Bialkowski, J. Siegel, C. Afonso, and D. von der Linde, *Phys. Rev. Lett.* **81**, 3679 (1998).

[8] J. Callan, A. M. Kim, C. Roeser, E. Mazur, J. Solis, J. Siegel, C. Afonso, and J. de Sande, *Phys. Rev. Lett.* **86**, 3650 (2001).

[9] L. Waldecker, R. Bertoni, and R. Ernstorfer, *J. Appl. Phys.* **117**, 044903 (2015).

[10] L. Waldecker, T. A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. E. Simpson, R. Ernstorfer, and S. Wall, *Nat. Mater.*, aop, doi: 10.1038/NMAT4359.

[11] L. Waldecker, R. Bertoni, R. Ernstorfer, and J. Vorberger, *ArXiv* 1507.03743v1 (2015).

[12] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).

[13] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, *Phys. Rev. Lett.* **108**, 196802 (2012).

[14] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, *Nat. Phys.* **10**, 343 (2014).

[15] S. Neppl, R. Ernstorfer, A. L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E. M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J. V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz, and R. Kienberger, *Nature* **517**, 342 (2015).

[16] C. Lemell, S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger, and J. Burgdörfer, *Phys. Rev. B* **91**, 241101(R) (2015).

Publications (2014 - July 2015)

Müller, M., A. Paarmann and R. Ernstorfer: Femtosecond electrons probing currents and atomic structure in nanomaterials. Nature Communications **5 (**10), 5292 (2014).

Paasch-Colberg, T., A. Schiffrin, N. Karpowicz, S. Kruchinin, Ö. Sağlam, S. Keiber, O. Razskazovskaya, S. Mühlbrandt, A. Alnaser, M. Kübel, V. Apalkov, D. Gerster, J. Reichert, T. Wittmann, J.V. Barth, M.I. Stockman, R. Ernstorfer, V.S. Yakovlev, R. Kienberger and F. Krausz: Solid-state light-phase detector. Nature Photonics **8 (**3), 214-218 (2014).

Schiffrin, A., T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J.V. Barth, R. Kienberger, R. Ernstorfer, V.S. Yakovlev, M.I. Stockman and F. Krausz: Addendum: Optical-field-induced current in dielectrics. Nature **507 (**7492), 386-387 (2014).

Ernstorfer, R: Im Fokus ultrakurzer Laser: das Wechselspiel von Elektronen und Kristallstruktur. MPG Jahrbuch 2015.

Lemell, C., S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger and J. Burgdörfer: Real-time observation of collective excitations in photoemission. Physical Review B **91 (**24), 241101 (2015).

Müller, M., A. Paarmann and R. Ernstorfer: Visualization of Photocurrents in Nanoobjects by Ultrafast Low-Energy Electron Point-Projection Imaging. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 667-670 (2015). ISBN 978-3-319-13241-9.

Neppl, S., R. Ernstorfer, A.L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E.M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J.V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz and R. Kienberger: Direct observation of electron propagation and dielectric screening on the atomic length scale. Nature **517 (**7534), 342-346 (2015).

Puppin, M., Y. Deng, C. Nicholson, C. Monney, M. Krenz, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer: 500 kHz OPCPA-based UV-XUV light source for time-resolved photoemission spectroscopy. In: Proceedings of Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SF2M.4 (2015). ISBN 978-1-55752-968-8.

Puppin, M., Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf and R. Ernstorfer: 500 kHz OPCPA delivering tunable sub-20 fs pulses with 15 W average power based on an all-ytterbium laser. Optics Express **23 (**2), 1491-1497 (2015).

Puppin, M., Y. Deng, O. Prochnow, J. Matyschok, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer: Fiber-Slab-Pumped OPCPA for XUV-Based Time-Resolved Photoelectron Spectroscopy at 500 kHz Repetition Rate. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 766-769 (2015). ISBN 978-3-319-13241-9.

Waldecker, L., R. Bertoni and R. Ernstorfer: Compact femtosecond electron diffractometer with 100 keV electron bunches approaching the single-electron pulse duration limit. Journal of Applied Physics **117 (**4), 044903 (2015).

Waldecker, L., T.A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer and S. Wall: Time-domain separation of optical properties from structural transitions in resonantly bonded materials. Nature Materials, advance online publication: doi: 10.1038/nmat4359.

Invited Talks (2014 - July 2015)

Ralph Ernstorfer

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Ultrafast Structural and Electronic Dynamics in Low Dimensional Materials*
May 2014	Physikalisches-Kolloquium, RWTH Aachen University, Aachen, Germany *Photo-Induced Structural Dynamics in Solids*
Aug 2014	SPIE Optics and Photonics, Ultrafast Nonlinear Imaging and Spectroscopy II, San Diego, CA, USA *Femtosecond Low-Energy Electron Diffraction and Imaging*
Sep 2014	ELI-ALPS 2nd User Workshop, Extreme Light Infrastructure - Attosecond Light Pulse Source, Szeged, Hungary *Towards Mapping Excited Electronic States in Molecules and Correlated Materials with tr-ARPES*
Oct 2014	Workshop, DIET 14, Dynamics, Interactions and Electronic Transitions at Surfaces, Pacific Grove, CA, USA *Femtosecond Low-Energy Electrons Probing Currents and Atomic Structure in Nanomaterials*
Feb 2015	4th Banff Meeting on Structural Dynamics Ultrafast Dynamics with X-Rays and Electrons, Banff, AB, Canada *Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials*
Mar 2015	79. Jahrestagung der DPG und DPG-Frühjahrstagung der Sektion Kondensierte Materie (SKM), Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses, Berlin, Germany *Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials*
Mar 2015	Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany *Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents*
Apr 2015	Seminar in Solid State Physics, Physik-Institut, University of Zurich, Zurich, Switzerland *Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents*
Jul 2015	Workshop of the Munich-Centre of Advanced Photonics and IMPRS-APS, Wildbad Kreuth, Germany *Investigating correlation and coupling phenomena in solids: which physical quantities can we access?*

Melanie Müller

Jul 2015	Seminar, Helmholtz-Zentrum Berlin *Femtosecond low-energy electrons as probes for ultrafast dynamics on the nanoscale*

Lutz Waldecker

Jun 2015	Group Seminar, Faculty of Physics (AG Uwe Bovensiepen), Universität Duisburg-Essen, Essen, Germany *Electron-Lattice Interactions Probed with Femtosecond Electron Diffraction*

Theory Department

Director: Matthias Scheffler

Staff scientists:

Carsten Baldauf	Luca M. Ghiringhelli	*external funding*
Sergey V. Levchenko	Patrick Rinke	*until 08/2014*
Matthias Rupp	Alexandre Tkatchenko	*ERC*
Igor Ying Zhang		

Claudia Draxl (Max Planck Fellow)

Angel Rubio (Distinguished Visiting Scientist)

Alexander M. Bradshaw (Emeritus)

Guest scientists, staying for at least six months:

Sebastián Alarcón V.		Heiko Appel	
Viktor Atalla	*until 03/2014*	Susmita Basak	
Saswata Bhattacharya	*until 03/2015*	Marco Casadei	*until 04/2014*
Pablo Garcia Risueno		William P. Huhn	*until 06/2015*
Wei Liu	*until 01/2015*	Mateusz Marianski	
Aliaksei Mazheika		Fawzi R. Mohamed	
Abdullah Özkanlar	*until 05/2015*	Lorenzo Pardini	*until 07/2015*
Karsten Rasim	*until 04/2014*	Norina Richter	*until 06/2015*
Honghui Shang		Tonghao Shen	
Maria E. Stournara		Christopher A. Sutton	
Guo-Xu Zhang	*until 01/2015*		

Scientists (temporary) paid from external funds:

Guillem Albareda P.	*until 05/2014*	*Marie-Curie Fellow, Beatriu de Pinós, Catalonia/ES*
Amrita Bhattacharya		*MP-EPFL Center, CH/DE*
Christian Carbogno		*Einstein Foundation Berlin, DE*
Oliver Hofmann	*until 05/2014*	*Schrödinger Fellowship, FWF, AT*
Chenchen Wang		*UCSB, US*

Graduate students: 19 *(4 from external funds)*

Master students: 8

Joint Network Center (GNZ) of the Berlin-Brandenburg Max Planck Institutions

Head: Gerd Schnapka
Staff members: 8

Recent Developments in the Theory Department

Director: Matthias Scheffler

ERC Group on Organic Functional Materials and Intermolecular Interactions

Head: Alexandre Tkatchenko

1. General Remarks

From the very beginning, research in the Department has been concerned with fundamental aspects of the *ab initio* thermodynamics and statistical mechanics of surfaces, interfaces, clusters, and nanostructures. Since the last meeting of the *Fachbeirat* more emphasis has been put on *big-data driven science*. The associated concepts and methods belong under the headings: statistical learning, machine learning, data mining, and compressed sensing. This research direction of the *Theory Department* started already 15 years ago with our exploratory work on neural networks. However, only in June 2014 together with Claudia Draxl (Max Planck Fellow at the FHI since July 2014), it was decided to expand the groups' *database on computational materials science results* into a worldwide activity: the *NoMaD (Novel Materials Discovery) Repository*. Together with 8 European scientific groups and 4 European high-performance computer centers this will now be advanced even further, namely to the *NoMaD (European) Center of Excellence (CoE)* which will be inaugurated November 1, 2015. The impact and success of both activities (repository and CoE) is already overwhelming. Details are discussed in Section 4.2 below.

A second vital research direction that we are currently reinforcing is electron-vibrational (or electron-phonon: e-ph) coupling. One important example relates to polarons that may be the charge carriers in certain metal oxides and organic systems. Moreover, the thermoelectric effect is obviously controlled by the e-ph interaction. The above effects are described in terms of corrections to the Born-Oppenheimer (BO) approximation. However, for processes where chemical bonds break and new bonds are formed, i.e. at transition states of chemical reactions, it is possible, if not likely, that the BO approximation breaks down, and new concepts need to be developed.

A third successful development in the Department in recent months has been the continuing work on the description of van der Waals interactions in density functional theory (DFT) calculations. The first paper, published in 2009 (*Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data, Phys. Rev. Lett.* ***102***), has already attracted more than 1,000 citations, and the methodological improvements since then are remarkable. They will be discussed in the chapter of the ERC (European Research Council) group of Alexandre Tkatchenko.

Finally, but importantly, we mention the *FHI-aims* code. *FHI-aims* is one of the most accurate and numerically most efficient computer codes for extended materials and large and small clusters. The various improvements and advancements, for example, the development of correlation-consistent basis sets for advanced functionals, *GW* approach, and embedding techniques have been highly significant.

A more complete discussion of the breadth of the work of the Department can be found in Sections 4 and 5, and also in the *Yellow Book,* and on the posters displayed in the Department.

The following Section describes organizational developments, and Section 3 addresses personnel and related matters. Subsequently, Sections 4 and 5 briefly outline some of the scientific work performed in the *Theory Department*: Section 4 describes conceptual, methodological, and technical developments, which enable us to study new types of problems and/or to improve the accuracy of calculations. In Section 5, the main applications studied in the *Theory Department* are sketched and some recent results presented.

The presentation focuses on developments of the last 18 months.

2. Organizational

We summarize various aspects of the present situation in bullet form.

- Collaboration with the University of California, Santa Barbara (UCSB, College of Engineering and College of Mathematical, Life, and Physical Sciences) started in 2005. The exchange of postdocs and PhD students between the institutes has turned out to be stimulating and successful. Matthias Scheffler spends about two months per year at the UCSB.
- We are part of an *NSF Partnership for International Research and Education: Electron Chemistry and Catalysis at Interfaces* (PIRE-ECCI). This activity, managed by Susannah Scott at UCSB, helps to intensify collaborations through the exchange of graduate students with chemical-physics institutes in China.
- In 2009 the MPS decided to create *Max Planck Centers* at high-ranking universities outside Germany. The *Theory Department* is part of the *Max Planck - UBC Center for Quantum Materials* which was established in October 2010 at the University of British Columbia (UBC) in Vancouver. The Center is directed by George Sawatzky and Bernhard Keimer who chair a Scientific Board comprised of three Max Planck directors, currently Bernhard Keimer (MPI Stuttgart), Hao Tjeng (MPI Dresden), Matthias Scheffler, and three UBC professors, currently George Sawatzky, Andrea Damascelli, and Ian Affleck.
- At the École Polytechnique Fédérale de Lausanne (EPFL) the *Max Planck - EPFL Center for Molecular Nanoscience and Technology* has been initiated by Klaus Kern (MPI Stuttgart), together with Benoit Deveaud-Plédran (EPFL), Jeffrey Hubbell (EPFL), Thom-

as Rizzo (EPFL), Matthias Scheffler, and Alec Wodtke (MPI Göttingen). The official start was January 1, 2013. Several PhD students jointly work with us and colleagues in Lausanne, receiving their PhDs from EPFL.

- In July 2014 Claudia Draxl was appointed *Max Planck Fellow* at the FHI by the President of the MPS. The initial proposal was supported by the *Fachbeirat*. The *Max Planck Fellows* initiative is designed to strengthen the ties between MPIs and universities. Within this framework a small group headed by Claudia Draxl has been set up at the FHI. The work program includes for example studies on hybrid inorganic/organic systems, electron-phonon coupling, thermoelectric materials, and in particular the *NoMaD (Novel Materials Discovery)* project.
- In March 2015 our proposal of a MP partner group on *Advanced Electronic-Structure Methods* at the University of Science and Technology of China (USTC) was granted. It will be led by Xinguo Ren. The objective of the group is to develop advanced and numerically tractable electronic-structure methods to satisfy the increasing needs for higher accuracy and reliability of first-principles calculations in physics and materials science. The official starting date of the group is September 2015, and an inauguration workshop is planned to take place in Hefei in June 2016.
- Every year, the *Fördernde Mitglieder* (*Supporting Members of the MPS)* contribute to a specific project. In 2015 the *NoMaD (Novel Materials Discovery) Repository* was chosen and supported by their donations (details about the *NoMaD* project are described in Section 4.2).
- In October 2014 the *Berlin Big Data Center (BBDC)* was installed. The *BBDC* is a Competence Center funded by the German Ministry of Education and Research (BMBF) which deals with the development of expressive, declarative, fast, and efficient big-data analytics (enabled by Hadoop and Apache Flink), massive-parallel data handling, and more. Matthias Scheffler is one of the 10 principle investigators (PIs), Volker Markl (TU Berlin) is the director of the center.

As of August 1, 2015, the FHI *Theory Department* is structured into 8 research groups. Nevertheless, most of the work in the Department typically involves more than one of these groups. The groups and their leaders are:

- *Unifying Concepts in Catalysis*, headed by **Sergey V. Levchenko**
- *Ab Initio Statistical Mechanics of Cluster Catalysis and Corrosion*, headed by **Luca M. Ghiringhelli**
- *Heat and Charge Transport*, headed by **Matthias Scheffler**
- *Ab Initio Biomolecular Simulations*, headed by **Carsten Baldauf**
- *Advanced First-Principle Methods for Materials Science and Engineering*, headed by **Igor Ying Zhang**
- *Theoretical Spectroscopy*, headed by **Angel Rubio** (until spring 2016)
- ERC group on *Organic Functional Materials and Molecular Interactions*, headed by **Alexandre Tkatchenko** (see the special chapter for this group)
- *Machine Learning for Materials*, headed by **Matthias Rupp**
- In addition, we host Emeritus **Alexander M. Bradshaw** (since January 2009) who is working on photoionization in molecules and clusters as well as on questions of energy supply and resources in the context of the sustainability debate.

The group headed by Angel Rubio (*Theoretical Spectroscopy*) and the former group of Patrick Rinke (*Many-Body Electronic-Structure Theory*) are gradually moving to the MPI in Hamburg and to the Aalto University in Finland, respectively. However, close collaborations between members of the *Theory Department* and both colleagues will continue in the future. Together with Patrick Rinke, we are working on projects of the Collaborative Research Center (*Sonderforschungsbereich*, SFB) of the German Research Foundation (DFG) on *Hybrid Inorganic/Organic Systems* (HIOS). Angel Rubio is and remains External Scientific Member of the FHI, and he is a PI of the *NoMaD Center of Excellence* (see Section 4.2 b below).

Together with Martin Vingron (director at the MPI for Molecular Genetics) Matthias Scheffler is responsible for the Joint Network Center (*Gemeinsames Netzwerkzentrum*, GNZ) of the Berlin-Brandenburg Max Planck activities. This is a regional IT competence center, serving 8 MPIs and 6 additional institutions. It focuses on networking, backup, virtualization, and security services. The GNZ is headed by Gerd Schnapka, and more information is given on p. 53.

3. Personnel and Related Matters

Since the last visit of the *Fachbeirat* in February 2014 the following noteworthy developments have taken place:

- **Matthias Rupp** joined the *Theory Department* in May 2015 as leader of the new group *Machine Learning for Materials*.
- **Igor Ying Zhang** was promoted to group leader in May 2014. His group is called *Advanced First-Principle Methods for Materials Science and Engineering.*
- In September 2014, **Patrick Rinke** became professor at Aalto University in Finland where he started the *Computational Electronic Structure Theory Group* in the Department of Applied Physics. The *Theory Department* continues to collaborate with him on several projects, e.g. within the HIOS-SFB of the German Research Foundation.
- **Saswata Bhattacharya** accepted a position as assistant professor at the Department of Physics at the Indian Institute of Technology Delhi in April 2015. Collaborations with the FHI, in particular with Luca M. Ghiringhelli, continue on machine-learning methods for metal oxide properties and the development of genetic algorithms for cluster-structure global searches.
- February 2015, **Wei Liu** took on a post as professor in the Department of Materials Science and Engineering at Nanjing University of Science and Technology (China).
- **Guo-Xu Zhang** left the FHI in February 2015 to join the Harbin Institute of Technology (China) as lecturer.
- **Alexandre Tkatchenko** recently accepted the offer for the Chair of Theoretical Condensed Matter Physics at the University of Luxemburg. He is planning to move there in November 2015, but will still participate in several ongoing projects at the FHI.

We are also proud to report that three renowned scientists have received prestigious Humboldt Research Awards which support extended research stays at the FHI. In November 2014 **Krishna Rajan** (Iowa State University, USA) received the award for his pioneering work in the emerging field of Materials Informatics. At the same time, **John Perdew** (Temple University, USA) was granted the award for his ground-breaking research on the analysis and development of new XC-functionals for density-functional theory. Both scientists have paid the institute extensive visits this year and are planning to return several times during coming years to collaborate with scientists of the Department. In April 2015 **Gustavo Scuseria** (Rice University, USA) was awarded the prize for his development, implementation, and application of computational quantum chemistry tools to practical problems.

Mariana Rossi was successfully nominated as Minerva-Fast-Track-Fellow. The program is designed to allow excellent young female scientists a better long-time planning of their career with the aim to increase female scientists in top positions.

Members of the *Theory Department* take part in various national, European (EU and ESF), and international programs. The list of these activities is as follows (sorted alphabetically):

- BMBF – Federal Ministry of Education and Research (Germany), *Berlin Big Data Center (BBDC)*, coordinator: V. Markl; M. Scheffler - since October 2014.
- DFG – German Research Foundation, Cluster of Excellence 314: *Unifying Concepts in Catalysis (UniCat)*, coordinator: M. Driess; M. Scheffler - first funding period: November 2007 - October 2012, new funding period November 2012 - October 2017.
- DFG – German Research Foundation, SFB 951: *Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS)*, coordinator: N. Koch; project B4: P. Rinke, M. Scheffler; project B10: A. Tkatchenko, M. Scheffler, new funding period: July 2015 - June 2019.
- DFG – German Research Foundation, FOR 1543: *Shear-flow Regulation of Hemostasis (SHENC)*, spokesman: R. Schneppenheim; subgroup C1: F. Gräter, C. Baldauf - first funding period June 2011 - August 2014, new funding period: September 2014 - August 2017.
- Einstein Foundation Berlin – Einstein Research Project *ETERNAL: Exploring Thermoelectric Properties of Novel Materials*, K.-R. Müller, C. Draxl, M. Scheffler - since April 2013.
- EU – European Commission, E-Infrastructures: *NoMaD (Novel Materials Discovery) Center of Excellence*, coordinator: M. Scheffler - starting November 2015.
- Max Planck Society and École Polytechnique Fédérale de Lausanne – *MP-EPFL Center for Molecular Nanoscience and Technology*, directors: K. Kern, T. Rizzo; board members: B. Deveaud-Plédran, J. Hubbel, A. Wodtke, M. Scheffler - since 2013.

  The *Theory Department* is currently involved in three projects of the center: *Biomolecules on Their Way to Solvation*, G. von Helden, C. Baldauf, T. R. Rizzo (EPFL); *First-*

Principles High-throughput Design and Discovery of Novel Materials, and Its Application to Thermoelectrics, M. Scheffler, N. Marzari (EPFL); *Peptides at Surfaces: Simulating Organic-Inorganic Interface Systems*, M. Ceriotti (EPFL), C. Baldauf, M. Rossi (Oxford University).

- Max Planck Society and University of British Columbia – *MPS-UBC Center for Quantum Materials*, directors: B. Keimer, G. A. Sawatzky; board members: A. Damascelli, L. H. Tjeng, I. Affleck, M. Scheffler - since 2010.
- NSF – The National Science Foundation, Partnership for International Research and Education (PIRE): *Electron Chemistry and Catalysis*, director: S. Scott; M. Scheffler - since 2005.
- UCSB – University of California, Santa Barbara, College of Engineering and College of Mathematical, Life & Physical Sciences; M. Scheffler (distinguished visiting professor for materials science and engineering) - since 2005.
- Vetenskapsrådet – Swedish Research Council: *Catalysis on the Atomic Scale*, organizer: E. Lundgren; S. V. Levchenko, M. Scheffler - since 2011.

We continue our strong involvement and support of CECAM and Psi-k, e.g. by organizing workshops, tutorials, and schools and working in the *CECAM Council* and the *Psi-k Board of Trustees* (the governances of these two organizations).

CECAM is a high-level European organization devoted to the promotion of fundamental research on advanced computational methods and their application to important problems in frontier areas of science and engineering. It is supported by various European research organizations including MPS and DFG. The CECAM headquarters is at the EPFL Lausanne, and *CECAM* nodes have been established in several member states. We are part of the joint node, *cecam-MM1P.de* which focusses on multi-scale modeling from first principles (MM1P) with emphasis on methods and applications to materials and biophysics. The board of directors of the *MM1P.de* node consists of Thomas Frauenheim (University of Bremen), Eberhard K. U. Gross (MPI Halle), Matthias Scheffler, and Björn Winkler (Goethe University Frankfurt). The node will continue to exist at least until 2018.

Psi-k is a Europe-based worldwide network of researchers working on the advancement of first-principles computational materials science. Its mission is to develop fundamental theory, algorithms, and codes in order to understand, predict, and design materials properties and functions. Theoretical condensed matter physics, quantum chemistry, thermodynamics, and statistical mechanics form the scientific core. Applications encompass inorganic, organic, and bio-materials and cover a whole range of diverse scientific, engineering, and industrial endeavors. Key activities of Psi-k are the organization of conferences, workshops, tutorials, and training schools and the dissemination of scientific thinking in society.

Scientists of the *Theory Department* were involved in various services and activities supporting the surface-science and electronic-structure communities worldwide. For example, they lecture at the *Free University Berlin,* the *Technical University Berlin,* and the *Humboldt-Universität zu Berlin* as well as at the *International Max Planck Research School*. They organized or co-organized conferences, workshops, tutorials, and summer schools on topics in electronic-structure theory, multi-scale modeling, surface science, and biophysics, which have impacted upon the careers of very many students of theoretical materials science. The list of activities in the last 18 months includes:

- Symposium on "Frontiers of Electronic Structure Theory: Non-equilibrium Phenomena at the Nano-scale", March 30 - April 4, 2014 at DPG Spring Meeting, Dresden, Germany; organizers: R. Car (Princeton University, USA), K. Sommer Thygesen (Technical University Denmark, Denmark), and M. Scheffler
- Workshop on "White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back", June 16 - 20, 2014, Saint Petersburg, Russia; organizers: E. Blokhin (HU Berlin, Germany), L. M. Ghiringhelli, S. V. Levchenko, and M. Scheffler
- Workshop on "What About *U*? -- Strong Correlations from First Principles", June 17 - 20, 2014, CECAM-HQ-EPFL, Lausanne, Switzerland; organizers: M. Cococcioni (EPFL, Switzerland), S. Biermann (École Polytechnique, Palaiseau Cedex, France), S. de Gironcoli (SISSA and CNR-DEMOCRITOS IOM, Trieste, Italy), and P. Rinke
- An international symposium on "Inorganic Insights into Catalysis" on the occasion of the 60th birthday of Robert Schlögl, July 3 - 4, 2014, Berlin, Germany; organizers: M. Scheffler, A. Trunschke, and J. Pach
- Hands-on summer school on "Density Functional Theory and Beyond: Computational Materials Science for Real Materials", July 21 - August 1, 2014, Los Angeles, USA; organizers: V. Blum (Duke University, USA), C. Carbogno, M. Scheffler, and C. Ratsch (IPAM, USA)

- FHI-aims developers' and users' meeting on “Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals”, August 19 - 22, 2014, Berlin, Germany; organizers: V. Blum (Duke University, USA), C. Baldauf, C. Carbogno, and M. Scheffler
- Colloquium on the occasion of the 70th birthday of Alexander M. Bradshaw “Oberflächen, Fusion und mehr”, January 30, 2015, Berlin, Germany; organizers: D. Bimberg (TU Berlin, Germany), K. Horn, and M. Scheffler
- CECAM/Psi-k Research Conference on “Frontiers of First-Principles Simulations: Materials Design and Discovery”, February 1 - 5, 2015, Berlin, Germany; organizers: G. Ceder (MIT, USA), N. Marzari (EPFL, Switzerland), and M. Scheffler
- Workshop on “Machine Learning for Many-Particle Systems”, February 23 - 27, 2015, Los Angeles, California, USA; organizers: A. Aspuru-Guzik (Harvard University, USA), G. Csanyi (University of Cambridge, UK), K.-R. Müller (TU Berlin, Germany), and A. Tkatchenko
- Symposium on “Frontiers of Electronic Structure Theory: Many-body Effects on the Nanoscale”, March 15 - 20, 2015 at DPG Spring Meeting, Berlin, Germany; organizers: S. G. Louie (UC Berkeley, USA), E. Runge (TU Ilmenau, Germany), and M. Scheffler
- Workshop on “From Many-Body Hamiltonians to Machine Learning and Back”, May 11 - 13, 2015, Berlin, Germany; organizers: A. Tkatchenko and M. Rupp
- Workshop on “Modeling Many-Body Interactions 2015”, May 26 - 29, 2015, Castelletto di Brenzone, Italy; organizers: R. A. DiStasio Jr. (Princeton University, USA), A. Ambrosetti (University of Padova, Italy), P. L. Silvestrelli (University of Padova, Italy), and A. Tkatchenko
- Workshop on “Methods and Algorithms in Electronic-Structure Theory”, June 3 - 6, 2015, Ringberg Castle, Germany; organizers: M. Kaupp (TU Berlin, Germany), P. Rinke (Aalto University, Finland), P. Saalfrank (University of Potsdam, Germany), and M. Scheffler
- Hands-on workshop on “Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials”, July 13 - 23, 2015, Berlin, Germany; organizers: V. Blum (Duke University, USA), C. Baldauf, and M. Scheffler
- Summer School of the Max-Planck-EPFL Center for Molecular Nanoscience & Technology, July 27 - 31, 2015, Ringberg Castle, Germany; organizers: C. Baldauf, C. Carbogno, and M. Scheffler

Alex Bradshaw has served on several committees of the National Academy of Sciences (Leopoldina), National Academy of Engineering (acatech), and the Royal Society in the UK. He is also a member of an inter-academy study group accompanying the German energy transformation (*Energiewende*) and of the energy steering committee of the European Academies Science Advisory Council (EASAC).

4. New Concepts, Methods, and Techniques

There are two activities which affect, or which are beginning to affect, most of the work in the Department, namely, the continued development of the *FHI-aims code* and the *NoMaD (Novel Materials Discovery)* project. They will be discussed first, followed by more specific issues. The work of the ERC group of Alexandre Tkatchenko will not be described here, but rather in a separate chapter.

4.1 *FHI-aims* Code

The development of the *FHI-aims* code started from an analysis of various electronic-structure theory concepts, in particular the KKR, LMTO, LAPW, and pseudopotential methods. Matthias Scheffler contributed to all of these over the last 40 years or so. In a nutshell, the *FHI-aims* code is as accurate as the best LAPW codes and as fast as *ab initio* pseudopotential codes. At the same time, it is easy to use and designed for massive parallel computers. The code is still “young”, but is gaining increasingly in popularity. All developments are coordinated by Volker Blum (Duke University) and Matthias Scheffler. During the last year several advanced functionals have been implemented and significant speed-ups have been achieved for *GW* and RPA (random-phase approximation) calculations. (Xinguo Ren[1], Volker Blum[2], Hermann Lederer[3], Markus Rampp[3], Florian Merz[3], Andreas Marek[3], Christian Carbogno)

Advanced density functionals as well as second order Møller-Plesset perturbation theory (MP2) and coupled-cluster theory (CCSD and CCSD(T)) require particularly sophisticated basis sets. While the development of CCSD(T) for periodic systems is still ongoing, the progress is significant. (Igor Y. Zhang, Tonghao Shen)

---

[1] University of Science and Technology of China, Hefei, China

[2] Duke University, Durham, USA

[3] Max Planck Computing and Data Facility, Garching, Germany

4.2 *NoMaD (Novel Materials Discovery)* Project

The *NoMaD* project started in 2012 as a joint group activity of Claudia Draxl and Matthias Scheffler funded by the Einstein Foundation. In June 2014 it was decided, to extend it into *i)* a world-wide operating repository for input and output files of *ab initio* electronic structure codes and to seek funding within HORIZON 2020 for *ii)* a Center of Excellence (together with 12 other European partners). Having been recently granted, a code-independent data base will soon be developed that in turn will be complemented by an extensive *Materials Encyclopedia*, graphics, and a big-data analytics environment.

4.2.1 *NoMaD Open Access Repository*

The *NoMaD open access repository* was established to host, organize, and share materials data. It enables the confirmatory analysis of computational materials data, their re-use, and re-purposing for applications not corresponding to the intention of the original calculations and publications. Uploading of data is possible without any barriers, i.e. results are accepted in their raw format as produced by the underlying code. The only conditions are that the list of authors is provided, and that code and code versions can be retrieved from the uploaded files. For a period up to three years, access to these data can be restricted to the owner or made available to other people (selected by the owner). The "open access" data can be downloaded by any user without even registering.

A summary of the concept and a basic tutorial can be found on YouTube:

concept: https://www.youtube.com/watch?v=L-nmRSH4NQM
tutorial: https://www.youtube.com/watch?v=5Xfzj-degqc

Since February 2015 already several hundred thousand files have been uploaded. Presently 10 different electronic-structure codes are supported. (Luca M. Ghiringhelli, Fawzi R. Mohamed, Lorenzo Pardini[4], Christian Carbogno, Claudia Draxl[4])

4.2.2 *NoMaD European Center of Excellence (CoE)*

The *NoMaD CoE* is funded by the European Commission in its E-Infrastructures program. It is a joint activity of 8 scientific groups and 4 high-performance computer centers in Europe. The PIs are: A. Bode (Leibniz-Rechenzentrum, Garching), C. Draxl (HU Berlin), D. Frenkel (University Cambridge), S. Heinzel (MPS Data and Computing Facility), F. Illas (University of Barcelona), K. Koski (CSC-IT Center for Scientific Computing, Helsinki), J. M. Cela

---

[4] Humboldt-Universität zu Berlin, Germany

(Barcelona Supercomputing Center), R. Nieminen (Aalto University), A. Rubio (MPI MPSD, Hamburg), M. Scheffler, K. Thygesen (Technical University Denmark, Lyngby), A. De Vita (King's College London). The starting date is November 1, 2015.

The main goals are to build a materials encyclopedia and to develop new tools for big-data analytics. However, for the next 12 months the first big challenge will be to build a code-independent data base, accepting the results from about 40 different electronic-structure codes, with the *NoMaD Repository* as a starting point. Force-field studies will be included as well. (Luca M. Ghiringhelli, Fawzi R. Mohamed, Christian Carbogno, Claudia Draxl[4])

4.3 Validation and Verification of Codes, Basis Sets, and XC-Functionals

Validation and verification of codes, basis sets, XC-functionals, treatment of relativity, and pseudopotentials (if used) have been very much neglected in computational materials science. The same holds for the question about the accuracy and error bars of the various approximate functionals that describe the many-electron exchange and correlation (XC). Recently, we have begun to address this weakness; the corresponding activities are briefly summarized below.

4.3.1 Equation of State for Elemental Solids and PBE XC

The *ab initio* materials science community is dealing with many different codes. K. Lejaeghere and S. Cottenier from Gent University, Belgium, initiated a community effort addressing the question: "do two different DFT codes or pseudopotentials really yield identical predictions?". For this, 15 different codes were compared with respect to the calculated equations of state for 71 elemental crystals. The *FHI-aims* code was part of this study. The best three codes, WIEN2k, exciting, and *FHI-aims* have the same quality. CPU-time requirements and user-friendliness were not part of the analysis, but in these issues the *FHI-aims* code shows the best performance. (Volker Blum[2], Alexandre Tkatchenko, Guo-Xu Zhang)

4.3.2 Test Set for Materials Science and Engineering

A test set for materials science and engineering (MSE) is at present being established with well-converged theoretical reference values for a hierarchy of methods, from (semi-)local density-functional approximations (DFAs) to the state-of-the-art MP2 and RPA, thus setting the standard for the implementation and applicability of electronic-structure methods for solids. At this point, the MSE test set contains results for first and second row elements and their binary compounds with various cubic crystal structures and bonding characters, allowing for systematic benchmarking of manifold chemical interactions. (Igor Y. Zhang, Norina Richter, Xiangyue Liu, Sergey V. Levchenko, Luca M. Ghiringhelli)

4.3.3 *GW*100: Benchmarking G_0W_0 for Molecular Systems

We established a benchmark set of 100 molecules that comprises well-converged ionization potentials and electron affinities computed at the G_0W_0@PBE level. Experimental values are included for reference. While benchmarking electronic-structure methods and implementations have become standard practice in quantum chemistry, we have for the first time benchmarked three *GW* codes. We found unprecedented agreement between the local-orbital codes TURBOMOLE and *FHI-aims* and good agreement with the plane-wave code BerkeleyGW. We expect that the *GW*100 test set will be a cornerstone in future methods development for excited states. (Patrick Rinke[5], Xinguo Ren[1])

4.4 Electron-Phonon Coupling and Heat Transport

Electron-phonon (e-ph) coupling causes a noticeable renormalization of bandgaps in semiconductors and of charge carriers (formation of polarons). We analyzed the strong sensitivity of e-ph matrix elements on the choice of the approximate XC functionals in DFT. Indeed, the use of hybrid functionals is mandatory, and the parameter α that determines the amount of exact exchange, may be chosen to minimize the localization/delocalization error. The latter is also called the “piecewise linear condition” and represents a property of exact DFT. (Sebastian Kokott, Honghui Shang, Christian Carbogno, Sergey V. Levchenko, and Patrick Rinke[5])

The accurate assessment of heat transport in materials with large thermal conductivity is computationally extremely challenging with *ab initio* molecular dynamics, since the strong harmonic character of the interatomic interactions typically leads to long phonon lifetimes and mean free paths. To overcome this hurdle, we have implemented a transformation formalism that translates between real space trajectories and occupations in reciprocal phonon space, which enables to apply reliable inter- and extrapolation techniques. In turn, this reduces the required computational effort by four orders of magnitude, as we demonstrate for silicon both for semi-empirical potentials and within an *ab initio* framework. (Christian Carbogno)

---

[5] FHI and Aalto University, Finland

4.5 Towards a Density-Functional Theory for Quantum Electrodynamics (QEDFT)

In order to construct a QEDFT we employ the Sham-Schlüter equation as this provides a direct way to connect the nonlocal self-energy of many-body perturbation theory with the local effective Kohn-Sham potential of QEDFT. In this way, the static as well as the time-dependent optimized effective potential (OEP) integral equations are derived for QED that takes the coupling of quantized electrons and photons into account. (Johannes Flick, Christian Schäfer[6], Camilla Pellegrini[7], Heiko Appel, Michael Ruggenthaler[6], Ilya V. Tokatly[8], Angel Rubio[9])

4.6 Density Functionals Applied to Molecular Dissociation

Starting from the Bethe-Goldstone equation (BGE) which provides the exact solution of one- and two-electron systems, we propose a non-empirical screened second-order BGE (sBGE2) correlation functional with a simplicity comparable to standard second-order perturbation theory. In conjunction with the exact exchange, the sBGE2 approximation provides an accurate description of both H_2^+ and H_2 dissociations, which so far was a big challenge in DFAs. We also extend sBGE2 to a general-purpose orbital-dependent functional, which provides a satisfactory description of N_2 and C_2 dissociations, which is a challenge for DFT as well as for wave-function theory. More importantly, this difficult challenge is conquered together with a consistent improvement over (semi)-local density functionals for various chemical situations, including atomization energies, reaction barriers, and weak interaction. (Igor Y. Zhang, Patrick Rinke[5])

5. Applications – Some Highlights

This Section briefly sketches some application highlights and certain results and insights obtained during the last one and a half years. Not all of this work has been published or submitted for publication. Work predominantly done in Alexandre Tkatchenko's ERC group is discussed in his chapter.

---

[6] MPI for the Structure and Dynamics of Matter, Hamburg, Germany

[7] Universidad del Pais Vasco UPV/EHU, San Sebastian, Spain

[8] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

[9] FHI and MPI for the Structure and Dynamics of Matter, Hamburg, Germany

5.1 Surfaces, Adsorption, and Heterogeneous Catalysis

5.1.1 Graphene on 3C-SiC and H Intercalation

Graphene can be grown on various substrates, among which silicon carbide (SiC) supports some of the highest-quality films. Using the *ab initio* atomistic thermodynamics approach, we had previously studied graphene films at the Si-terminated side of 3C-SiC(111). In recent months we extended this work to the C-terminated 3C-SiC(111) surface, considering many possible structures and Si and C reservoirs at any reasonable temperature and pressure. We identified a hitherto unknown lowest-energy (3×3) graphene precursor structure in excellent agreement with experimental STM images. In general, we find that graphene will only be stable when the SiC substrate is becoming unstable which makes monolayer graphene growth on the C-side of SiC very difficult. (Lydia Nemec, Patrick Rinke[5], Jan Kloppenburg[10], Björn Lange[2], Volker Blum[2])

5.1.2 *Ab initio* Atomistic Thermodynamics for Various Adsorbate Systems: Adsorbate Phases, Clustering, and Coverage-Dependent Chemistry

Two different classes of systems were considered: *a)* H_2O at MO (001), with M = Ca, Mg, Sr and *b)* H and CH_x at Ru (0001) with $x = 0$-4. For the XC treatment, we used the PBE and HSE06 hybrid functional combined with the self-consistent many-body dispersion approach. The structure search was performed using a first-principles genetic algorithm.

For *a)*, the results predict ordered one-dimensional (1D) adsorbed water structures on CaO(001), which is in agreement with scanning tunneling microscopy and infrared spectroscopy studies performed in the CP Department. On MgO(001) and SrO(001) such water structures are not found to be stable. CaO(001) is special and only here the proper balance between adsorbate-adsorbate and adsorbate-surface interactions is reached, which is largely ruled by the substrate lattice constant.

Part *b)* of this work is a collaboration with the PC Department. Here, the influence of hydrogen adsorption on the adsorption and reactions of CH_x ($x = 0$-4) on Ru(0001) is studied at realistic temperatures and hydrogen pressures. Adsorbed hydrogen changes the preferred site and the stability of CH_2 species, which is crucial for understanding the Fischer-Tropsch synthesis. Moreover, adsorbed hydrogen is found to have a profound influence on the C-C coupling reactions: While it generally reduces all the coupling reaction barriers, some reaction pathways become more favorable. (Xunhua Zhao, Sergey V. Levchenko)

---

[10] FHI and Duke University, Durham, USA

5.1.3 Effects of Surface-Site Coordination on the Thermodynamic Stability of Point Defects

We analyzed the thermodynamic stability of O-vacancy and O/O_2-ad-species at steps and corners at MgO surface. The defects are modelled using MgO clusters, described at the hybrid-functional level and embedded into a field of norm-conserving non-local pseudopotentials and point charges. The low-energy defect structures are found using an *ab initio* genetic algorithm. The long-range response of the oxide to the charge carriers trapped at the defects is taken into account using a polarizable force field. Unexpectedly, we found that O-ad-species rather than O-vacancies are the dominant defects at realistic conditions. This is explained by an interplay between bond-breaking, bond-making, and charge-carrier trapping. (Saswata Bhattacharya[11], Daniel Berger[12], Karsten Reuter[12], Sergey V. Levchenko, Luca M. Ghiringhelli)

5.2 Organic Materials and Interfaces

5.2.1 Length Dependence of Ionization Potentials of Trans-Acetylenes Studied by an Internally Consistent DFT/*GW* Approach

The Ionization Potential (IP) was calculated for the paradigmatic quasi-one-dimensional trans-acetylene family of conjugated molecules, from short to long oligomers and to the infinite polymer trans-polyacetylene (TPA). Our IP predictions are based on an "internally-consistent" scheme: We adjust the exchange mixing parameter α of the PBEh hybrid density functional, so that the highest-occupied Kohn-Sham level of DFT-PBEh(α^*) agrees with the IP calculated from *GW*@PBEh(α^*). We find that α^* is system-dependent and converges with increasing oligomer length. Also the IP varies with oligomer length, and it converges to the value for TPA with a smooth, inverse-length-exponential behavior. (Maximilian Pinheiro Jr.[13], Marilia J. Caldas[13], Patrick Rinke[5], Volker Blum[2])

5.2.2 Integer versus Fractional Charge Transfer at Metal(/Insulator)/Organic Interfaes: Cu/TCNE and Cu/NaCl/TCNE

Semilocal and hybrid density-functional theory was used to study the charge transfer and the energy-level alignment at a representative interface between an extended metal substrate and an organic adsorbate layer. Upon suppressing electronic coupling between the adsorbate and the substrate by inserting thin, insulating layers of NaCl, the hybrid functional localizes elec-

---

[11] Indian Institute of Technology Delhi, New Delhi, India
[12] Technische Universität München, Germany
[13] Universidade de São Paulo, Brasil

tronic charge. The laterally inhomogeneous charge distribution resulting from this spontaneous breaking of translational symmetry is reflected in observables such as the molecular geometry, the valence and core-level spectroscopy, and the evolution of the work function with molecular coverage.

The studies were extended to the adsorption of organic molecules on the wide-bandgap, *n*-doped ZnO. Here, the molecules exhibit a combination of charge transfer and backtransfer, reminiscent of the Blyholder model of CO adsorption. (Oliver T. Hofmann[14], Patrick Rinke[5], Georg Heimel[4])

5.2.3 Pressure Dependence of Band Parameters of Organic Semiconductors

Band gaps, effective masses, and electric conductivities of semiconductors noticeably depend on strain that may be imposed by fabrication conditions of practical devices. Previously, we had studied these issues for inorganic semiconductors. Now we have investigated two prototypical organic systems, namely trans-polyacetylene and anthracene. For these materials, the state-of-the-art density-functional approximations do not provide a reliable description.

The calculations reveal that the electronic band structure and gap of crystalline trans-polyacetylene are not only determined by the dimerization, but are also influenced by interchain interactions, which lead to a splitting of valence and conduction band. Corresponding results are found for crystalline anthracene. We also computed the pressure-dependent electronic transport coefficients for both organic semiconductors using the Boltzmann transport equation in the constant relaxation time approximation. (Franz Knuth, Christian Carbogno, Volker Blum[2])

5.2.4 Insight into Organic Reactions from the Random-Phase Approximation and its Corrections

The performance of the random-phase approximation (RPA) and beyond-RPA approximations for the treatment of electron correlation are benchmarked on three different molecular test sets. The test sets are chosen to represent three typical sources of error which can contribute to the failure of most density-functional approximations in chemical reactions. The first test set (atomization and n-homodesmotic reactions) offers a gradually increasing balance of error from the chemical environment. The second test set (Diels-Alder reactions cycloaddition = DARC) reflects more the effect of weak dispersion interactions in chemical reactions. Final-

---

[14] Graz University, Austria

ly, the third test set (self-interaction error 11 = SIE11) represents reactions which are exposed to noticeable self-interaction errors. This work seeks to answer whether a universal many-body approximation exists to address all these challenges. (Adrienn Ruzsinszky[15], Igor Y. Zhang)

5.3 Biophysics

5.3.1 Improving the Theoretical Description of Peptide-Cation Interactions

Metal cations trigger the three-dimensional structure of peptides and proteins, but can also cause misfolding as it is discussed, for example, in Alzheimer's disease. The understanding of the atomistic basis of the effect of metal cations requires a reliable description of the energetics. Based on representative amino acid-cation complexes, we assessed the accuracy of energy functions in comparison to coupled-cluster theory. Empirical force fields (FF) severely fail to reproduce the reference data, mainly due to the static assignment of partial charges in conventional FF. Density-functional approximations offer higher accuracy, but the often-stressed "chemical accuracy" is only reached with hybrid functionals augmented by a dispersion correction. (Markus Schneider[16], Volker Blum[2], Carsten Baldauf)

5.3.2 Sampling and Representing the Potential-Energy Surface of Molecules from First Principles

The frequent inadequacy of empirical FF to correctly describe the structures and energetics of bio-organic molecules motivated us to develop the software *Fafoom* that performs structure searches using the all-electron code *FHI-aims*. The result of such search is an ensemble of low-energy minima. The relative location of these minima to each other is described by means of their distance in torsion-angle space. Applying a sensible cut-off to long distances allows for drawing a network with nodes being the minima and edges being the distance between them. This identifies a set of likely direct transitions on which we employ transition state searches with the *aimsChain* routine (by Luca M. Ghiringhelli and Yingyu Yao[17]). The collected information, i.e. energies of minima and transition states, represents a reduced potential-energy surface that can be illustrated as barrier tree or disconnectivity graph. (Adriana Supady, Volker Blum[2], Carsten Baldauf)

---

[15] Temple University, Philadelphia, USA

[16] FHI and MP – EPFL Center, Lausanne, Switzerland

[17] FHI and UBC-MPS Center, Vancouver, Canada

5.3.3 Protein-Ligand Interactions from Semi-Empirical Quantum Mechanics

The current standard in describing the interaction between small molecular ligands and large biological macromolecules (proteins) are empirical energy functions that are trained to reproduce static crystal-structure data. However the complicatedness of the involved interactions (e.g. charge transfer, van der Waals, H bonding) is not described reliably by commonly used simplified functional forms. We demonstrate that a combination of the semi-empirical PM6 method (augmented with corrections for H bonding, dispersion, and halogen bonds) in conjunction with the implicit solvent model COSMO performs superior to the standard methods in describing structure and energetics of the binding-energy landscape of protein-ligand interactions. (Adam Pecina[18], René Meier[19], Pavel Hobza[18], Carsten Baldauf)

5.4 And more…

5.4.1 Thermoelectric Materials

In order to convert some of the significant amount of waste heat into electricity, a better understanding of electron-phonon coupling and heat transport is required (see Section 4.4). Clathrates and skutterudites have been identified as particularly promising materials for thermoelectric applications and both materials classes are presently studied in the Department in collaboration with Claudia Draxl[4] and the experimental group of Juri Grin[20]. In collaboration with them we discuss the implications of our theoretical findings for the synthesis of novel thermoelectric materials with improved heat-transport properties.

For Si_{46} and Ge_{46} clathrates, we find fundamentally different distortions and stabilities of the vacancy, in spite of the isoelectronicity of these two materials. Consequently, these two materials also behave differently upon filling their cages with K or Ba. For Ge-based clathrates, K or Ba guest atoms favor the formation of 2 or 3 vacancies, $\square$, and the lowest free-energy structures (including vibrational and configurational entropies) are $K_8Ge_{44}\square_2$ and $Ba_8Ge_{43}\square_3$. Conversely vacancy formation is energetically unfavorable in filled Si_{46} clathrates. These results resolve some experimental dubieties.

Using a cluster-expansion of DFT total energies, we have extended these investigations to ternary clathrates such as $(Sr, Ba)_8Al_xSi_{46-x}$.

---

[18] IOCB Prague, Czech Republic

[19] Universität Leipzig, Germany

[20] MPI for Chemical Physics of Solids, Dresden, Germany

For $CoSb_3$ and $CoAs_3$ skutterudites, we are presently performing a systematic analysis of the vibrational properties as function of the filling with guests (Ga, In, Sn, etc.). It is found that different guests exhibit very different vibrational dynamics ranging from coherent phonon modes to the formation of localized polarons. (Amrita Bhattacharya, Susmita Basak, Maria Troppenz[4], Santiago Rigamonti[4], Christian Carbogno, Claudia Draxl[4])

5.4.2 Quantum Electrodynamics

For the case of density-functional theory for quantum electrodynamics, we have so far considered prototypical model systems that are commonly used in quantum optics, as well as one-dimensional real-space models. Our results for these systems are very promising and we are currently working on an implementation of our approach for real systems. (Johannes Flick, Christian Schäfer[6], Camilla Pellegrini[7], Heiko Appel, Michael Ruggenthaler[6], Ilya V. Tokatly[8], Angel Rubio[9])

5.4.3 Big-Data Driven Materials Science; Importance of Causal Descriptors

Machine learning is able to identify structure in big data that may be invisible to humans. We have emphasized and demonstrated that successful learning should be based on a set of descriptive, physically meaningful parameters (termed descriptors) that are related to the property of interest. Employing compressed sensing strategies that had been originally developed and used in the field of signal processing, we are able to identify the optimum descriptors. Applications to quantitative structure identification of crystals and to bandgaps of semiconductors demonstrate the importance of causal descriptors. For example, even when carbon containing materials are not included in the learning process, the approach predicts the existence and extraordinary high stability of C-diamond. (Luca M. Ghiringhelli, Sergey V. Levchenko, Claudia Draxl[4])

5.4.4 Machine Learning of Quantum Mechanical Properties of MgO Clusters

Electronic-structure calculations of similar systems contain redundant information. Machine learning (ML) models exploit this to interpolate between a computationally feasible number of *ab initio* reference calculations possibly enabling computational savings of several orders of magnitude. For a diverse set of 9,000 small organic molecules Matthias Rupp has developed a ML model to predict proton and carbon nuclear magnetic resonance chemical shifts, core level excitations, and forces on atoms, reaching accuracies close to the underlying DFT reference data. Metal-oxide clusters are more challenging due to their larger flexibility of bonding. First results indicate that these ML models can be trained on such systems as well, estimating Mulliken and Hirshfeld partial charges in a dataset of 3,000 MgO clusters with a relative root mean squared error of 2.1-3.1%. (Matthias Rupp, Saswata Bhattacharya[11], Luca M. Ghiringhelli)

5.4.5 Risks, Resources, and Resilience

Several times in the last few decades the possibility of raw material scarcity, even of raw material exhaustion, has given rise to concern. Prominent catchwords in this debate have been, for example, “oil crisis”, “geo-political factors”, “resource security”, “rare earth elements” and “mineral depletion”. It transpires that immediate concern is largely unwarranted, although our society does well to think about the sustainable stewardship of natural resources, as well as the search for resilient solutions. In any case, it is legitimate to ask whether supply risk can be assessed and put on a semi-quantitative, comparative basis – not an easy task in an area containing so many socio-economic concepts. Using appropriate indicators we present here a comparative study of the supply risks associated with the constituent elements in two types of thin film photovoltaic module, CdTe, and CIGS. On the basis of the indicators used (geochemical parameters, market data, political assessment indices, etc.) and their weighting using an analytical hierarchy process, CdTe modules are found to be marginally more secure from a supply risk perspective. (Alexander M. Bradshaw, Christoph Helbig[21], Christoph Kolotzek[21], Andrea Thorenz[21], Axel Tuma[21])

---

[21] University Augsburg, Germany

6. Publications of the Theory Department[22]

2013 (late publications)

Carbogno, C., A. Groß, J. Meyer and K. Reuter: O_2 Adsorption Dynamics at Metal Surfaces: Non-adiabatic Effects, Dissociation and Dissipation. In: Dynamics of Gas-Surface Interactions: Atomic-level Understanding of Scattering Processes at Surfaces. (Eds.) R. Díez Muiño and H.F. Busnengo. (Springer Series in Surface Sciences, Vol. 50). Springer, Berlin, 389-419 (2013). ISBN 978-3-642-32954-8.

Cudazzo, P., M. Gatti and A. Rubio: Local-field effects on the plasmon dispersion of two-dimensional transition metal dichalcogenides. New Journal of Physics **15** (12), 125005 (2013). OPEN ACCESS

Cudazzo, P., M. Gatti, A. Rubio and F. Sottile: Frenkel versus charge-transfer exciton dispersion in molecular crystals. Physical Review B **88** (19), 195152 (2013).

Fuks, J.I., M. Farzanehpour, I.V. Tokatly, H. Appel, S. Kurth and A. Rubio: Time-dependent exchange-correlation functional for a Hubbard dimer: Quantifying nonadiabatic effects. Physical Review A **88** (6), 062512 (2013).

Hofmann, O.T., V. Atalla, N. Moll, P. Rinke and M. Scheffler: Interface dipoles of organic molecules on Ag(111) in hybrid density-functional theory. New Journal of Physics **15** (12), 123028 (2013). OPEN ACCESS

Hofmann-Mees, D., H. Appel, M. Di Ventra and S. Kümmel: Determining Excitation-Energy Transfer Times and Mechanisms from Stochastic Time-Dependent Density Functional Theory. The Journal of Physical Chemistry B **117** (46), 14408-14419 (2013).

Roth, F., P. Cudazzo, B. Mahns, M. Gatti, J. Bauer, S. Hampel, M. Nohr, H. Berger, M. Knupfer and A. Rubio: Loss spectroscopy of molecular solids: combining experiment and theory. New Journal of Physics **15** (12), 125024 (2013). OPEN ACCESS

Schumann, T., M. Dubslaff, M.H. Oliveira, M. Hanke, F. Fromm, T. Seyller, L. Nemec, V. Blum, M. Scheffler, J.M.J. Lopes and H. Riechert: Structural investigation of nanocrystalline graphene grown on $(6\sqrt{3}\times6\sqrt{3})$ R30°-reconstructed SiC surfaces by molecular beam epitaxy. New Journal of Physics **15** (12), 123034 (2013). OPEN ACCESS

Snyder, J.C., M. Rupp, K. Hansen, L. Blooston, K.-R. Müller and K. Burke: Orbital-free bond breaking via machine learning. The Journal of Chemical Physics **139** (22), 224104 (2013).

Wanko, M., T. Wende, M.M. Saralegui, L. Jiang, A. Rubio and K.R. Asmis: Solvent-mediated folding in dicarboxylate dianions: aliphatic chain length dependence and origin of the IR intensity quenching. Physical Chemistry Chemical Physics **15** (47), 20463-20472 (2013). OPEN ACCESS

Zhang, I.Y., X. Ren, P. Rinke, V. Blum and M. Scheffler: Numeric atom-centered-orbital basis sets with valence-correlation consistency from H to Ar. New Journal of Physics **15** (12), 123033 (2013). OPEN ACCESS

---

[22] OPEN ACCESS = Gold open access publication

2014

Albareda Piquer, G., H. Appel, I. Franco, A. Abedi and A. Rubio: Correlated Electron-Nuclear Dynamics with Conditional Wave Functions. Physical Review Letters **113** (8), 083003 (2014).

Alberdi-Rodriguez, J., M.J.T. Oliveira, P. García-Risueño, F. Nogueira, J. Muguerza, A. Arruabarrena and A. Rubio: Recent Memory and Performance Improvements in OCTOPUS Code. In: Computational Science and Its Applications - ICCSA 2014. (Eds.) B. Murgante, S. Misra, A.M.A.C. Rocha, C. Torre, J.G. Rocha, M.I. Falcão, D. Taniar, B.O. Apduhan and O. Gervasi. (Lecture Notes in Computer Science, Vol. 8582). Springer, Berlin, 607-622 (2014). ISBN 978-3-319-09146-4.

Ambrosetti, A., A. Dario, R.A. DiStasio and A. Tkatchenko: Hard Numbers for Large Molecules: Toward Exact Energetics for Supramolecular Systems. The Journal of Physical Chemistry Letters **5** (5), 849-855 (2014).

Ambrosetti, A., A. Reilly, R.A. DiStasio and A. Tkatchenko: Long-range correlation energy calculated from coupled atomic response functions. The Journal of Chemical Physics **140** (18), 18A508 (2014).

Arion, T., O. Takahashi, R. Püttner, V. Ulrich, S. Barth, T. Lischke, A.M. Bradshaw, M. Förstel and U. Hergenhahn: Conformational and nuclear dynamics effects in molecular Auger spectra: fluorine core-hole decay in CF_4. Journal of Physics B **47** (12), 124033 (2014).

Baldauf, C., M. Ropo, V. Blum and M. Scheffler: How mono-valent cations bend peptide turns and a first-principles database of amino acids and dipeptides. In: Proceedings of the International Conference of Computational Methods in Sciences and Engineering 2014 (ICCMSE 2014). (Eds.) T.E. Simos, Z. Kalogiratou and T. Monovasilis. (AIP Conference Proceedings, Vol. 1618). AIP, New York, 119-120 (2014). ISBN 978-0-7354-1255-2.

Beret, E.C., M.v. Wijk and L.M. Ghiringhelli: Reaction cycles and poisoning in catalysis by gold clusters: A thermodynamics approach. International Journal of Quantum Chemistry **114** (1), 57-65 (2014).

Bhattacharya, S., S.V. Levchenko, L.M. Ghiringhelli and M. Scheffler: Efficient *ab initio* schemes for finding thermodynamically stable and metastable atomic structures: benchmark of cascade genetic algorithms. New Journal of Physics **16** (12), 123016 (2014). OPEN ACCESS

Brehm, M.A., V. Huck, C. Aponte-Santamaría, T. Obser, S. Grässle, F. Oyen, U. Budde, S. Schneppenheim, C. Baldauf, F. Gräter, S.W. Schneider and R. Schneppenheim: von Willebrand disease type 2A phenotypes IIC, IID and IIE: A day in the life of shear-stressed mutant von Willebrand factor. Thrombosis and Haemostasis **112** (1), 96-108 (2014).

Carbogno, C., C.G. Levi, C.G.V. de Walle and M. Scheffler: Ferroelastic switching of doped zirconia: Modeling and understanding from first principles. Physical Review B **90** (14), 144109 (2014). OPEN ACCESS

Carrasco, J., W. Liu, A. Michaelides and A. Tkatchenko: Insight into the description of van der Waals forces for benzene adsorption on transition metal (111) surfaces. The Journal of Chemical Physics **140** (8), 084704 (2014).

Caruso, F., V. Atalla, X. Ren, A. Rubio, M. Scheffler and P. Rinke: First-principles description of charge transfer in donor-acceptor compounds from self-consistent many-body perturbation theory. Physical Review B **90** (8), 085141 (2014).

Chen, H., Y. Xie, G.-X. Zhang and H.-T. Yu: A first-principles investigation of the stabilities and electronic properties of $SrZrO_3$(1 1 0) (1 × 1) polar terminations. Journal of Physics: Condensed Matter **26** (39), 395002 (2014).

Cudazzo, P., M. Gatti and A. Rubio: Interplay between structure and electronic properties of layered transition-metal dichalcogenides: Comparing the loss function of 1T and 2H polymorphs. Physical Review B **90** (20), 205128 (2014).

Dávila, M.E., L. Xian, S. Cahangirov, A. Rubio and G. Le Lay: Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. New Journal of Physics **16** (9), 095002 (2014).

DiStasio, R.A., V. Gobre and A. Tkatchenko: Many-body van der Waals interactions in molecules and condensed matter. Journal of Physics: Condensed Matter **26** (21), 213202 (2014).

Dostert, K.-H., C. O'Brien, W. Riedel, A.A. Savara, W. Liu, M. Oehzelt, A. Tkatchenko and S. Schauermann: Interaction of Isophorone with Pd(111): A Combination of Infrared Reflection-Absorption Spectroscopy, Near-Edge X-ray Absorption Fine Structure, and Density Functional Theory Studies. The Journal of Physical Chemistry C **118** (48), 27833-27842 (2014).

Falke, S.M., C.A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A.D. Sio, A. Rubio, G. Cerullo, E. Molinari and C. Lienau: Coherent ultrafast charge transfer in an organic photovoltaic blend. Science **344** (6187), 1001-1005 (2014).

Flick, J., H. Appel and A. Rubio: Nonadiabatic and Time-Resolved Photoelectron Spectroscopy for Molecular Systems. Journal of Chemical Theory and Computation **10** (4), 1665-1676 (2014).

Ghiringhelli, L.M.: Application of (Kohn-Sham) Density-Functional Theory to Real Materials. In: Many-Electron Approaches in Physics, Chemistry and Mathematics. (Eds.) V. Bach and L. Delle Site. (Mathematical Physics Studies, Vol. 2). Springer, Cham, 191-206 (2014). ISBN 978-3-319-06378-2.

Grässle, S., V. Huck, K.I. Pappelbaum, C. Gorzelanny, C. Aponte-Santamaría, C. Baldauf, F. Gräter, R. Schneppenheim, T. Obser and S.W. Schneider: von Willebrand Factor Directly Interacts With DNA From Neutrophil Extracellular Traps. Arteriosclerosis, Thrombosis, and Vascular Biology **34** (7), 1382-1389 (2014).

Heine, N., T.I. Yacovitch, F. Schubert, C. Brieger, D.M. Neumark and K.R. Asmis: Infrared Photodissociation Spectroscopy of Microhydrated Nitrate-Nitric Acid Clusters $NO_3^-(HNO_3)_m(H_2O)_n$. The Journal of Physical Chemistry A **118** (35), 7613-7622 (2014).

Kirsch, H., X. Zhao, Z. Ren, S.V. Levchenko, M. Wolf and K. Campen: Controlling CH_2 dissociation on Ru(0001) through surface site blocking by adsorbed hydrogen. Journal of Catalysis **320**, 89-96 (2014).

Kronik, L. and A. Tkatchenko: Understanding Molecular Crystals with Dispersion-Inclusive Density Functional Theory: Pairwise Corrections and Beyond. Accounts of Chemical Research **47** (11), 3208-3216 (2014).

Liu, W., A. Tkatchenko and M. Scheffler: Modeling Adsorption and Reactions of Organic Molecules at Metal Surfaces. Accounts of Chemical Research **47** (11), 3369-3377 (2014).

Malic, E., H. Appel, O.T. Hofmann and A. Rubio: Energy transfer in porphyrin-functionalized graphene. Physica Status Solidi B **251** (12), 2495-2498 (2014).

Malic, E., H. Appel, O.T. Hofmann and A. Rubio: Förster-Induced Energy Transfer in Functionalized Graphene. The Journal of Physical Chemistry C **118** (17), 9283-9289 (2014). OPEN ACCESS

Marek, A., V. Blum, R. Johanni, V. Havu, B. Lang, T. Auckenthaler, A. Heinecke, H.-J. Bungartz and H. Lederer: The ELPA library: scalable parallel eigenvalue solutions for electronic structure theory and computational science. Journal of Physics: Condensed Matter **26** (21), 213201 (2014).

Marom, N., T. Körzdörfer, X. Ren, A. Tkatchenko and J.R. Chelikowsky: Size Effects in the Interface Level Alignment of Dye-Sensitized TiO_2 Clusters. The Journal of Physical Chemistry Letters **5** (12), 2395-2401 (2014).

Nyakatura, E.K., R.R. Araghi, J. Mortier, S. Wieczorek, C. Baldauf, G. Wolber and B. Koksch: An Unusual Interstrand H-Bond Stabilizes the Heteroassembly of Helical αβγ-Chimeras with Natural Peptides. ACS Chemical Biology **9** (3), 613-616 (2014).

Nyakatura, E.K., J. Mortier, V.S. Radtke, S. Wieczorek, R.R. Araghi, C. Baldauf, G. Wolber and B. Koksch: β- and γ-Amino Acids at α-Helical Interfaces: Toward the Formation of Highly Stable Foldameric Coiled Coils. ACS Medicinal Chemistry Letters **5** (12), 1300-1303 (2014).

Palma, C.-A., K. Diller, R. Berger, A. Welle, J. Björk, J.L. Cabellos, D.J. Mowbray, A.C. Papageorgiou, N.P. Ivleva, S. Matich, E. Margapoti, R. Niessner, B. Menges, J. Reichert, X. Feng, H.J. Räder, F. Klappenberger, A. Rubio, K. Müllen and J.V. Barth: Photoinduced C-C Reactions on Insulators toward Photolithography of Graphene Nanoarchitectures. Journal of the American Chemical Society **136** (12), 4651-4658 (2014).

Peköz, R., S. Wörner, L.M. Ghiringhelli and D. Donadio: Trends in the Adsorption and Dissociation of Water Clusters on Flat and Stepped Metallic Surfaces. The Journal of Physical Chemistry C **118** (51), 29990-29998 (2014).

Peng, Y., L.M. Ghiringhelli and H. Appel: A quantum reactive scattering perspective on electronic nonadiabaticity. The European Physical Journal B **87** (7), 155 (2014).

Raja, I.A., V. Gobre, R.V. Pinjari and S.P. Gejji: Encapsulation of alkyl and aryl derivatives of quaternary ammonium cations within cucurbit[n]uril ($n = 6,7$) and their inverted diastereomers: density functional investigations. Journal of Molecular Modeling **20** (3), 2138 (2014).

Reilly, A. and A. Tkatchenko: Role of Dispersion Interactions in the Polymorphism and Entropic Stabilization of the Aspirin Crystal. Physical Review Letters **113** (5), 055701 (2014). OPEN ACCESS

Rodriguez-Reyes, J.C.F., C.G.F. Siler, W. Liu, A. Tkatchenko, C.M. Friend and R.J. Madix: van der Waals Interactions Determine Selectivity in Catalysis by Metallic Gold. Journal of the American Chemical Society **136** (38), 13333-13340 (2014).

Rossi, M., S. Chutia, M. Scheffler and V. Blum: Validation Challenge of Density-Functional Theory for Peptides - Example of $\text{Ac-Phe-Ala}_5\text{-LysH}^+$. The Journal of Physical Chemistry A **118** (35), 7349-7359 (2014).

Ruggenthaler, M., J. Flick, C. Pellegrini, H. Appel, I.V. Tokatly and A. Rubio: Quantum-electrodynamical density-functional theory: Bridging quantum optics and electronic-structure theory. Physical Review A **90** (1), 012508 (2014).

Sarmiento-Pérez, R., S. Botti, C.S. Schnohr, I. Lauermann, A. Rubio and B. Johnson: Local versus global electronic properties of chalcopyrite alloys: X-ray absorption spectroscopy and *ab initio* calculations. Journal of Applied Physics **116** (9), 093703 (2014).

Schatschneider, B., S. Monaco, J.-J. Liang and A. Tkatchenko: High-Throughput Investigation of the Geometry and Electronic Structures of Gas-Phase and Crystalline Polycyclic Aromatic Hydrocarbons. The Journal of Physical Chemistry C **118** (34), 19964-19974 (2014).

Schuler, B., W. Liu, A. Tkatchenko, N. Moll, G. Meyer, A. Mistry, D. Fox and L. Gross: Publisher's Note: Adsorption Geometry Determination of Single Molecules by Atomic Force Microscopy [Phys. Rev. Lett. 111, 106103 (2013)]. Physical Review Letters **112** (12), 129902 (2014).

Squire, R.H., N.H. March and A. Rubio: Are there really cooper pairs and persistent currents in aromatic molecules? International Journal of Quantum Chemistry **114** (7), 437-440 (2014).

Verdenhalven, E., A. Knorr, M. Richter, B. Bieniek and P. Rinke: Theory of optical excitations in dipole-coupled hybrid molecule-semiconductor layers: Coupling of a molecular resonance to semiconductor continuum states. Physical Review B **89** (23), 235314 (2014).

Wagner, C., N. Fournier, V.G. Ruiz, C. Li, K. Muellen, M. Rohlfing, A. Tkatchenko, R. Temirov and F.S. Tautz: Non-additivity of molecule-surface van der Waals potentials from force measurements. Nature Communications **5** (11), 5568 (2014).

Warnke, S., C. Baldauf, M.T. Bowers, K. Pagel and G. von Helden: Photodissociation of Conformer-Selected Ubiquitin Ions Reveals Site-Specific Cis/Trans Isomerization of Proline Peptide Bonds. Journal of the American Chemical Society **136** (29), 10308-10314 (2014).

Wegkamp, D., M. Herzog, L. Xian, M. Gatti, P. Cudazzo, C.L. McGahan, R.E. Marvel, R.F. Haglund, A. Rubio, M. Wolf and J. Stähler: Instantaneous Band Gap Collapse in Photoexcited Monoclinic VO_2 due to Photocarrier Doping. Physical Review Letters **113** (21), 216401 (2014).

Yan, Q., A. Janotti, M. Scheffler and C.G.V. de Walle: Origins of optical absorption and emission lines in AlN. Applied Physics Letters **105** (11), 111104 (2014).

Yan, Q., P. Rinke, A. Janotti, M. Scheffler and C.G.V. de Walle: Effects of strain on the band structure of group-III nitrides. Physical Review B **90** (12), 125118 (2014).

Doctoral Thesis

Schubert, F.: Conformational equilibria and spectroscopy of gas-phase homologous peptides from first principles. Freie Universität Berlin 2014.

Zhang, G.-X.: Understanding the role of van der Waals forces in solids from first principles. Freie Universität Berlin 2014.

2015

Aponte-Santamaría, C., V. Huck, S. Posch, A.K. Bronowska, S. Grässle, M.A. Brehm, T. Obser, R. Schneppenheim, P. Hinterdorfer, S.W. Schneider, C. Baldauf and F. Gräter: Force-Sensitive Autoinhibition of the von Willebrand Factor Is Mediated by Interdomain Interactions. Biophysical Journal **108** (9), 2312-2321 (2015).

Argondizzo, A., X. Cui, C. Wang, H. Sun, H. Shang, J. Zhao and H. Petek: Ultrafast multiphoton pump-probe photoemission excitation pathways in rutile $TiO_2(110)$. Physical Review B **91** (15), 155429 (2015).

Bhattacharya, S., B.H. Sonin, C.J. Jumonville, L.M. Ghiringhelli and N. Marom: Computational design of nanoclusters by property-based genetic algorithms: Tuning the electronic properties of $(TiO_2)_n$ clusters. Physical Review B **91** (24), 241115(R) (2015).

Bieniek, B., O.T. Hofmann and P. Rinke: Influence of hydrogen on the structure and stability of ultra-thin ZnO on metal substrates. Applied Physics Letters **106** (13), 131602 (2015).

Bradshaw, A.M., B. Reuter and T. Hamacher: Could the extensive use of rare elements in renewable energy technologies become a cause for concern? EPJ Web of Conferences **98**, 04007 (2015).

Bradshaw, A.M. and D.P. Woodruff: Molecular orbital tomography for adsorbed molecules: is a correct description of the final state really unimportant? New Journal of Physics **17** (1), 013033 (2015).

Cisnéros, J.C., W. Liu and A. Tkatchenko: Steps or Terraces? Dynamics of Aromatic Hydrocarbons Adsorbed at Vicinal Metal Surfaces. Physical Review Letters **115 (**8), 086101 (2015).

De Sio, A., S.M. Falke, C.A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A. Rubio, G. Cerullo, C.A. Rozzi and C. Lienau: Coherent Ultrafast Charge Transfer in an Organic Photovoltaic Blend. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R. de Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 557-560 (2015). ISBN 978-3-319-13241-9.

Deinert, J.-C., O.T. Hofmann, M. Meyer, P. Rinke and J. Stähler: Local aspects of hydrogen-induced metallization of the ZnO$(10\bar{1}0)$ surface. Physical Review B **91** (23), 235313 (2015).

Ferri, N., R.A. DiStasio, A. Ambrosetti, R. Car and A. Tkatchenko: Electronic Properties of Molecules and Surfaces with a Self-Consistent Interatomic van der Waals Density Functional. Physical Review Letters **114** (17), 176802 (2015).

Gao, W. and A. Tkatchenko: Sliding Mechanisms in Multilayered Hexagonal Boron Nitride and Graphene: The Effects of Directionality, Thickness, and Sliding Constraints. Physical Review Letters **114** (09), 096101 (2015).

Ghiringhelli, L.M. and S.V. Levchenko: Strengthening gold-gold bonds by complexing gold clusters with noble gases. Inorganic Chemistry Communications **55**, 153-156 (2015).

Ghiringhelli, L.M., J. Vybiral, S.V. Levchenko, C. Draxl and M. Scheffler: Big Data of Materials Science: Critical Role of the Descriptor. Physical Review Letters **114** (10), 105503 (2015).

Hansen, K., F. Biegler, R. Ramakrishnan, W. Pronobis, O.A.v. Lilienfeld, K.-R. Müller and A. Tkatchenko: Machine Learning Predictions of Molecular Properties: Accurate Many-Body Potentials and Nonlocality in Chemical Space. The Journal of Physical Chemistry Letters **6** (11), 2326-2331 (2015).

Hellgren, M., F. Caruso, D.R. Rohr, X. Ren, A. Rubio, M. Scheffler and P. Rinke: Static correlation and electron localization in molecular dimers from the self-consistent RPA and GW approximation. Physical Review B **91** (16), 165110 (2015).

Hoffmann, M.J., M. Scheffler and K. Reuter: Multi-lattice Kinetic Monte Carlo Simulations from First Principles: Reduction of the Pd(100) Surface Oxide by CO. ACS Catalysis **5** (2), 1199-1209 (2015).

Hofmann, O.T., P. Rinke, M. Scheffler and G. Heimel: Integer versus Fractional Charge Transfer at Metal(/Insulator)/Organic Interfaces: Cu(/NaCl)/TCNE. ACS Nano **9** (5), 5391-5404 (2015).

Knuth, F., C. Carbogno, V. Atalla, V. Blum and M. Scheffler: All-electron formalism for total energy strain derivatives and stress tensor components for numeric atom-centered rbitals. Computer Physics Communications **190**, 33-50 (2015).

Levchenko, S.V., X. Ren, J. Wieferink, P. Rinke, V. Blum, M. Scheffler and R. Johanni: Hybrid functionals for large periodic systems in an all-electron, numeric atom-centered basis framework. Computer Physics Communications **192**, 60-69 (2015).

Liu, W., F. Maaß, M. Willenbockel, C. Bronner, M. Schulze, S. Soubatch, F.S. Tautz, P. Tegeder and A. Tkatchenko: Quantitative Prediction of Molecular Adsorption: Structure and Binding of Benzene on Coinage Metals. Physical Review Letters **115** (3), 036104 (2015).

Maurer, R.J., V.G. Ruiz Lopez and A. Tkatchenko: Many-body dispersion effects in the binding of adsorbates on metal surfaces. The Journal of Chemical Physics **143** (10), 102808 (2015).

Mortier, J., E.K. Nyakatura, O. Reimann, S. Huhmann, J.O. Daldrop, C. Baldauf, G. Wolber, M.S. Miettinen and B. Koksch: Coiled-Coils in Phage Display Screening: Insight into Exceptional Selectivity Provided by Molecular Dynamics. Journal of Chemical Information and Modeling **55** (3), 495-500 (2015).

Nemec, L., F. Lazarevic, P. Rinke, M. Scheffler and V. Blum: Why graphene growth is very different on the C face than on the Si face of SiC: Insights from surface equilibria and the (3×3)−3C−SiC($\bar{1}\bar{1}\bar{1}$) reconstruction. Physical Review B **91** (16), 161408(R) (2015).

Reilly, A. and A. Tkatchenko: van der Waals dispersion interactions in molecular materials: beyond pairwise additivity. Chemical Science (6), 3289-3301 (2015).

Ren, X., N. Marom, F. Caruso, M. Scheffler and P. Rinke: Beyond the *GW* approximation: A second-order screened exchange correction. Physical Review B **92** (8), 081104(R) (2015)

Richter, N., F. Stavale, S.V. Levchenko, N. Nilius, H.-J. Freund and M. Scheffler: Defect complexes in Li-doped MgO. Physical Review B **91** (19), 195305 (2015).

Rupp, M.: Special issue on machine learning and quantum mechanics. International Journal of Quantum Chemistry **115** (16), 1003-1004 (2015).

Schubert, F., K. Pagel, M. Rossi, S. Warnke, M. Salwiczek, B. Koksch, G.von Helden, V. Blum, C. Baldauf and M. Scheffler: Native like helices in a specially designed β peptide in the gas phase. Physical Chemistry Chemical Physics **17** (7), 5376-5385 (2015).

Schubert, F., M. Rossi, C. Baldauf, K. Pagel, S. Warnke, G. von Helden, F. Filsinger, P. Kupser, G. Meijer, M. Salwiczek, B. Koksch, M. Scheffler and V. Blum: Exploring the conformational preferences of 20-residue peptides in isolation: Ac-Ala_{19}-Lys + H^+ vs. Ac-Lys-Ala_{19} + H^+ and the current reach of DFT. Physical Chemistry Chemical Physics **17** (11), 7373-7385 (2015).

Sezen, H., H. Shang, F. Bebensee, C. Yang, M. Buchholz, A. Nefedov, S. Heissler, C. Carbogno, M. Scheffler, P. Rinke and C. Wöll: Evidence for photogenerated intermediate hole polarons in ZnO. Nature Communications **6** (4), 6901 (2015).

Sforzini, J., L. Nemec, T. Denig, B. Stadtmüller, T.-L. Lee, C. Kumpf, S. Soubatch, U. Starke, P. Rinke, V. Blum, F.C. Bocquet and F.S. Tautz: Approaching Truly Freestanding Graphene: The Structure of Hydrogen-Intercalated Graphene on 6H-SiC(0001). Physical Review Letters **114** (10), 106804 (2015).

Sinai, O., O.T. Hofmann, P. Rinke, M. Scheffler, G. Heimel and L. Kronik: Multiscale approach to the electronic structure of doped semiconductor surfaces. Physical Review B **91** (7), 075311 (2015).

Tkatchenko, A.: Current Understanding of Van der Waals Effects in Realistic Materials. Advanced Functional Materials **25** (13), 2054-2061 (2015).

Zhao, X., X. Shao, Y. Fujimori, S. Bhattacharya, L.M. Ghiringhelli, H.-J. Freund, M. Sterrer, N. Nilius and S.V. Levchenko: Formation of Water Chains on CaO(001): What Drives the 1D Growth? The Journal of Physical Chemistry Letters **6** (7), 1204-1208 (2015).

Doctoral Thesis

Nemec, L.: Graphene Engineering: An *ab initio* Study of the Thermodynamic Stability of Epitaxial Graphene and the Surface Reconstructions of Silicon Carbide. Humboldt-Universität zu Berlin 2015.

7. Invited Talks of the Members of the Theory Department

Guillem Albareda Piquer

Jan 2014	6th International Workshop and School on Time-Dependent Density-Functional Theory: Prospects and Applications, Centro de Ciencias de Benasque Pedro Pascual, Benasque, Spain *Non-Adiabatic Dynamics with the Conditional Wave Functions*
May 2014	CECAM Workshop, Recent progress in adiabatic and non-adiabatic methods in quantum dynamics, Lausanne, Switzerland *A Correlated Electron-Nuclear Dynamics with Conditional Wave Functions*

Heiko Appel

Jan 2014	6th International Workshop and School on Time-Dependent Density-Functional Theory: Prospects and Applications, Centro de Ciencias de Benasque Pedro Pascual, Benasque, Spain *Real-Time Evolution of Correlated Photon-Electron Wavefunctions in Quantum Electrodynamics*
Apr 2014	Block Course, International Max Planck Research School Functional Interfaces in Physics and Chemistry, Berlin, Germany *Introduction to Static and Time-Dependent Density-Functional Theory*
Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *Rieman-Silberstein Vector and Photon Wavefunctions in Quantum Electrodynamics*
Jun 2014	Seminar, Faculty of Physics, Bielefeld University, Bielefeld, Germany *Density Functional Theory for Quantum Electrodynamics: Bridging Quantum Optics and Electronic Structure Theory*
Dec 2014	Seminar, Institute of Physics, University of Rostock, Rostock, Germany *Fock Space Evolution and Electron-Photon Correlations in Quantum Electrodynamics*

Carsten Baldauf

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Peptide Secondary Structure Formation in the Gas Phase from First Principles*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Structure and Dynamics of Peptide Foldamers from First Principles*
Oct 2014	Seminar, Institute of Pharmacy, Freie Universität Berlin, Berlin, Germany *Mechano-Reception in the A Domains Regulates VWF Structure and Function*
Nov 2014	Dagstuhl Seminar, Algorithmic Cheminformatics, Dagstuhl, Germany *Conformational Search and Landscape Representation for Peptide Foldamers*

Feb 2015	XVII. Annual Linz Winter Workshop, Advances in Single-Molecule Research for Biology & Nanoscience, Linz, Austria *Structure and Dynamics of Peptide Foldamers from First Principles*
Mar 2015	1st Ion Mobility-Mass Spectrometry Workshop, FHI, Berlin, Germany *Calculating Theoretical CCSs*
Jul 2015	Summer School of the Max Planck-EPFL Center for Molecular Nanoscience and Technology, Schloss Ringberg, Kreuth, Germany *MD, Vibrational Spectroscopy*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *Methods to Study and Represent the Potential-Energy Surface (PES) of Biomolecules in Isolation*

Björn Bieniek

Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *Ultra-Thin ZnO on Metal Substrates: Electronic Structure and Thermodynamic Stability*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *HDF5 and ESP-Charges in FHI-aims*

Volker Blum

Dec 2013	2013 Fall MRS Meeting and Exhibit, Materials Research Society, Boston, MA, USA *An Integrated All-Electron Path to Theory-Driven Materials Development*

Christian Carbogno

Nov 2013	IPAM Program, Materials for a Sustainable Energy Future, Workshop IV: Energy Conservation and Waste Heat Recovery, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *High Temperature Thermal Conductivity from First Principles*
Apr 2014	Team Meeting on ETSF Electron-Phonon Coupling, Zeuthen, Germany *High Temperature Thermal Conductivity from First Principles*
Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *High Temperature Thermal Conductivity from First Principles*
Jul 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Thermal Transport in Solids from First Principles*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Thermal Conductivity Simulations: Achieving Time and Size Convergence*

Aug 2014	Hands-on Workshop on Excitations in Solids 2014, HoW exciting! Humboldt-Universität zu Berlin, Berlin, Germany *Thermal Conductivity*
Sep 2014	EUPHONON Workshop, Building a European NanoPhononics Community, Le Mans, France *Thermal Conductivities at High Temperatures from First Principles*
Oct 2014	3rd Science Day of the Max Planck-EPFL Center for Molecular Nanoscience and Technology, Berlin, Germany *Towards the First-Principles Discovery of (Novel) Thermoelectric Materials*
Dec 2014	Gruppenseminar, Institute of Theoretical Chemistry, Ulm University, Ulm, Germany *Towards the First-Principles Discovery of (Novel) Thermoelectric Materials*
Jan 2015	Team Meeting on ETSF Electron-Phonon Coupling, Rome, Italy *Thermal Conductivity Simulations: Achieving Time and Size Convergence*
Jan 2015	Winter Workshop, Frontiers of Multiscale Modelling - Current Obstacles and New Horizons for Energy, Materials, and Catalysis, Stubachtal, Austria *Thermal Conductivity Simulations: Reaching the Meso- and Macroscale*
Mar 2015	APS March Meeting 2015, American Physical Society, San Antonio, TX, USA *Accurate Thermal Conductivities from First Principles*
Apr 2015	Kolloquium des Graduiertenkollegs, University of Rostock, Rostock, Germany *Accurate Thermal Conductivities from First Principles*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Heat Transport from First Principles*
Jun 2015	CECAM Workshop, Future Technologies in Automated Atomistic Simulations, Lausanne, Switzerland *Challenges in Novel Materials Discovery (NoMaD) Using Big Data Paradigms*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Phonons, Electron-Phonon Coupling and Transport in Solids*
Jul 2015	Summer School of the Max Planck-EPFL Center for Molecular Nanoscience and Technology, Schloss Ringberg, Kreuth, Germany *Thermal Conductivities from First Principles Molecular Dynamics*

Luca M. Ghiringhelli

Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *Big Data of Materials Science: Critical Role of the Descriptor*
Aug 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Search for Minimum Energy Paths: Nudged Elastic Band and Beyond*

Aug 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Statistical Mechanics and Molecular Dynamics*
Aug 2014	XXVI IUPAP Conference on Computational Physics, CCP2014, Boston, MA, USA *Big Data of Materials Science – Critical Role of the Descriptor*
Oct 2014	Hands-on Course, International Max Planck Research School (IMPRS), Berlin, Germany *Ab initio Statistical Mechanics of Surfaces, Defects and Clusters*
Dec 2014	AScI Workshop, Machine Learning for Materials Science, Aalto University, Helsinki, Finland *Big Data of Materials Science: Critical Role of the Descriptor*
Dec 2014	Workshop on Simulation and Modeling of Emerging Electronics 2014, University of Hong Kong, Hong Kong, China *Big Data of Materials Science: Critical Role of the Descriptor*
Feb 2015	CECAM Conference, Frontiers of first-principles simulations: materials design and discovery, Berlin, Germany *(Statistical) Learning from (Big) Data in Materials Science: The Critical Role of the Descriptor*
Apr 2015	CECAM Workshop, Emergent structural and electronic phenomena at interfaces of nanoscale oxides, Lausanne, Switzerland *Theoretical Evidence of Unexpected O-Rich Phases in MgO Clusters and at Corners of Extended MgO Surfaces*
May 2015	CECAM/Psi-k Workshop, From Many-Body Hamiltonians to Machine Learning and Back, Berlin, Germany *Design of the Feature Space for Feature-Selection Algorithms Yielding Physically Interpretable Descriptors*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Learning Physically Meaningful Descriptors from Data in Materials Science*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Ab initio Molecular Dynamics and Nuclear Quantum Effect*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Big-Data Analytics in Materials Science*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *Big Data of Materials Science: Critical Next Steps*

Arvid Ihrig

Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Localized Resolution of Identity: Accurate and Efficient Evaluation of the Coulomb Operator for Advanced Electronic Structure Methods*

Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Local RI, Correlation and Low-Scaling Hybrids*

Sergey V. Levchenko

May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Effects of Temperature, Pressure and Doping on Stoichiometry and Atomic Structure of Materials: Bulk, Surfaces and Clusters*
Oct 2014	CRC Symposium, FHI, Berlin, Germany *Adsorbate-Adsorbate Interactions on Surfaces at Realistic Conditions: A First-Principles Study*
May 2015	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Activation of Small Molecules at Ni-Doped MgO Surfaces: An ab initio Study*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Periodic Systems*
Jul 2015	Summer School of the Max Planck-EPFL Center for Molecular Nanoscience and Technology, Schloss Ringberg, Kreuth, Germany *Defects in Solids*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *Defect-Defect Interaction at Surfaces and Interfaces at Realistic Conditions: Global Versus Local Effects of Doping*

Norina Richter

Jan 2014	Seminar, Theoretische Chemie, Technische Universität München, Munich, Germany *Importance of Space-Charge Effects for Concentration and Charge State of Defects at Metal-Oxide Surfaces*
Feb 2014	17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany *Space-Charge Transfer at Intrinsic Defects and at (Organic) Adsorbates at Metal-Oxide Surfaces*
May 2014	Workshop on Catalysis from First Principles 2014, Institute of Theoretical Chemistry, Ulm University, Ulm, Germany *Charge-Carrier Doping Effects on Concentrations of Defects at Metal-Oxide Surfaces*

Patrick Rinke

Oct 2013	Colloquium of the Collaborative Research Centre “Hybrid Inorganic/Organic Systems for Opto-Electronics” (SFB 951- HIOS), Berlin, Germany *ZnO-Based Inorganic/Organic Systems from First Principles*
Nov 2013	Seminar, Aalto University, Helsinki, Finland *Hybrid Inorganic/Organic Interfaces from First Principles*

Jan 2014	International Workshop on Computational Physics and Materials Science, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland *Space-Charge Transfer in Hybrid Inorganic-Organic Systems*
Jun 2014	Seminar, University of Luxembourg, Luxembourg *Space-Charge Transfer in Hybrid Inorganic-Organic Systems*
Jul 2014	ICMR Workshop on Ab-Initio Description of Charged Systems and Solid/Liquid Interfaces for Semiconductors and Electrochemistry, University of California, Santa Barbara, CA, USA *Space-Charge Transfer in Hybrid Inorganic-Organic Systems*
Jul 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Excited-State Properties*
Aug 2014	International Conference, Condensed Matter in Paris 2014, Paris, France *Charge Transfer in Organic and Hybrid Organic/Inorganic Systems from First Principles*
Nov 2014	Autumn School on Basics of Electronic Structure Calculations, Tampere University of Technology, Tampere, Finland *Many-Body Theory and the GW Approximation*
Feb 2015	Symposium on Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS Symposium 2015), Berlin, Germany *Space-Charge Transfer in Hybrid Inorganic-Organic Systems*
Feb 2015	Workshop, Towards Reality in Nanoscale Materials VIII, Levi, Finland *Tackling the Charge-Transfer Problem with First Principles*
Mar 2015	APS March Meeting 2015, American Physical Society, San Antonio, TX, USA *Towards a Unified Description of Ground and Excited State Properties: GW vs RPA and Beyond*
May 2015	Physics Colloquium, University of Jyväskylä, Jyväskylä, Finland *Quantum Perspective of Novel Hybrid Materials*
Jul 2015	28th International Conference on Defects in Semiconductors, Helsinki, Finland *Space-Charge Transfer and Charged Defects at Surfaces*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Prediction of Electronic Spectra from First Principles*
Aug 2015	CECAM Summer school, Electronic structure at the cutting edge with the Elk code, Lausanne, Switzerland *Hedin Equations and GW Method*
Aug 2015	XXIV International Materials Research Congress 2015, Cancún, Mexico *Tackling the Charge Transfer Problem in Organic Systems and at Organic/Inorganic Interfaces from First Principles*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *To GW and Beyond: What We Can Learn from Molecular Calculations*

Angel Rubio

Oct 2013	Workshop on Modeling Single-Molecule Junctions: Novel Spectroscopies and Control, Berlin, Germany *Light-Induced Dynamical Processes in Finite and Extended Systems from TDDFT*
Nov 2013	Science Dissemination Talk, Nanotecnología, Fundación Valenciana de Estudios Avanzados, Valencia, Spain *Impacto de La Teoría En Nanociencia: Nuevos Materiales Y Dispositivos*
Nov 2013	The "March" Meeting, A Symposium in Honor of Norman H. March, Namur, Belgium *Non Linear Processes in Low Dimensional Systems within Time-Dependent Density Functional Theory*
Jan 2014	6th International Workshop and School on Time-Dependent Density-Functional Theory: Prospects and Applications, Centro de Ciencias de Benasque Pedro Pascual, Benasque, Spain *Open Session about Challenges and Standing Problems*
Jan 2014	VI International Conference BIFI-2014: Exploring the Role of Computation in Science: From Biology to Physics, Zaragoza, Spain *Light-Induced Processes in Finite and Extended Systems from TDDFT*
Feb 2014	Colloquium of the Institute of Physical and Theoretical Chemistry, University of Würzburg, Würzburg, Germany *Non Equilibrium Dynamical Processes in Low Dimensional Systems from Time-Dependent Density Functional Theory*
Feb 2014	Colloquium of the Instituto de Ciencia de Materiales de Madrid (ICMM), Madrid, Spain *Multi-Scale Modeling in Chemistry and Materials Science: Combining Classical and Quantum Mechanics*
Mar 2014	APS March Meeting 2014, American Physical Society, Denver, CO, USA *Extensions of Density Functional Theory Approaches to Treating Quantum Phenomena and Quantum Entanglement*
Mar 2014	Colloquium, Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain *Modeling Energy Materials from First Principles Simulations: Optoelectronic and Hybrid-Photovoltaic Devices*
May 2014	Workshop on Materials Challenges in Devices for Fuel Solar Production and Employment, International Centre for Theoretical Physics, Trieste, Italy *Understanding Light-Induced Processes in Energy Materials from First Principles TDDFT Simulations*
Jun 2014	2nd Workshop on Surfaces, Interfaces and Functionalization Processes in Organic Compounds and Applications, (SINFO), Trieste, Italy *Non Equilibrium Light-Induced Dynamical Processes in Energy Materials*
Jun 2014	Colloquium Physikalische Chemie, Department Chemie, Ludwig-Maximilians-Universität München, Munich, Germany *Modeling Optoelectronic and Hybrid-Photovoltaic Devices within TDDFT*

Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back St. Petersburg, Russia *Hybrid-Organic Photovoltaic Devices from First Principles Simulations*
Jun 2014	Seminar, Physical Chemistry Department (ISIC), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland *Optoelectronic and Hybrid-Photovoltaic Devices from First Principles Simulations*
Aug 2014	Colloquium, Department of Physics, Stanford University, Stanford, CA, USA *Ab Initio Modelling of Light-Induced Non Equilibrium Dynamical Processes in Organic Materials*
Sep 2014	Applied Mathematics Seminar, Department of Mathematics, University of California, Berkeley, CA, USA *Efficient Implementation of Time-Dependent Density-Functional Theory to Treat Non-Linear Dynamical Processes in Molecular Nanostructures and Solid*
Sep 2014	Colloquium Molecular Foundry, Lawrence Berkeley Laboratory, Berkeley, CA, USA *Non Equilibrium Dynamical Processes in Organic Photovoltaic Applications*
Sep 2014	Colloquium, Department of Chemistry, University of California, Berkeley, CA, USA *First Principles Modeling of Photovoltaic and Optoelectronic Devices: Fundamentals and Applications*
Sep 2014	Physical Seminar, University of Rochester, Rochester, NY, USA *Modeling Non Equilibrium Dynamical Processes in TDDFT: Optoelectronic and Photovoltaic Applications*
Oct 2014	7th European School on Molecular Nanoscience (ESMolNa 2014), Gandia, Spain *Theoretical Spectroscopy: TDDFT*
Dec 2014	2014 Fall MRS Meeting and Exhibit, Materials Research Society, Boston, MA, USA *Novel Electronic and Structural Properties of Two-Dimensional Materials: Silicene, Germenene and Stanene*
Feb 2015	5th Symposium/Workshop of Computational Sciences (SWOCS-5), Pohang, South Korea *Simulation of Photon-Matter Interactions within QED-TDDFT*
Feb 2015	Colloquia, Center for Multidimensional Carbon Materials, Institute of Basic Sciences (IBS), UNIST Campus, Ulsan, South Korea *Non Equilibrium Dynamical Processes in TDDFT: Optoelectronic and Photovoltaic Applications*
Feb 2015	Colloquia, Center for Multidimensional Carbon Materials, Institute of Basic Sciences (IBS), UNIST Campus, Ulsan, South Korea *Novel Electronic and Structural Properties of Two Dimensional Materials: From Carbon-Nanostructures to Silicene*

Jul 2015	Theory Group Meeting, European XFEL, Hamburg, Germany *Ab-initio Simulations of Light-Matter Interactions*
Aug 2015	International Conference on High Pressure Science and Technology, Joint AIRAPT-25 & EHPRG-53, Madrid, Spain *Pressure Induced Phase Transition in Correlated Oxides and Simple Metals: Mott and Charge-Transfer Insulators*
Sep 2015	3rd International Conference on Correlation Effects in Radiation Fields CERF2015, Rostock, Germany *Quantum Electrodynamical Time-Dependent Density Functional Theory (QEDFT): An Ab-initio Framework for the Simulation of Photon-Matter Interactions*
Sep 2015	Chemistry, Materials & Light (CM&L 2015), International Year of Light, Bologna, Italy *Simulating Light-Induced Dynamical Processes in Light Harvesting Complexes*

Matthias Rupp

May 2015	CECAM/Psi-k Workshop, From Many-Body Hamiltonians to Machine Learning and Back, Berlin, Germany *Representing Atoms in Molecules*
Jun 2015	IPAM Workshop on Materials for a Sustainable Energy Future, Reunion Meeting, Institute for Pure and Applied Mathematics, Lake Arrowhead, CA, USA *Machine Learning for Materials Science*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Quantum Mechanics / Machine Learning Models*
Jul 2015	Seminar, Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany *Machine Learning for Quantum Chemistry*

Matthias Scheffler

Nov 2013	IPAM Program, Materials for a Sustainable Energy Future, Workshop IV: Energy Conservation and Waste Heat Recovery, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Lecture, Fuels from Sunlight - Potential and Challenges*
Jan 2014	Conference, Electronic Materials and Applications, The American Ceramic Society, Orlando, FL, USA *Big Data of Materials Science from First Principles - Critical Next Steps*
Jan 2014	Symposium on Surface and Nano Science 2014 (SSNS'14), Furano, Japan *Space-Charge Transfer at Defects and (Organic) Adsorbates at Metal-Oxide Surfaces*
Feb 2014	International Workshop on Advanced Materials 2014, Ras al Khaimah, UAE *Big Data of Materials Science from First Principles - Critical Next Steps*

Mar 2014	APS March Meeting 2014, American Physical Society, Denver, CO, USA *Hybrid Density Functionals Tuned Towards Fulfillment of Fundamental DFT Conditions*
Apr 2014	Shanghai Conference on Theoretical & Computational Chemistry, Shanghai, China *Big Data of Materials Science from First Principles - Critical Next Steps*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Big Data of Materials Science from First Principles - Critical Next Steps*
May 2014	Wiener Physikalisches Kolloquium, Fakultät für Physik, University of Vienna, Vienna, Austria *Big Data of Materials Science from First Principles - Critical Next Steps*
Jun 2014	Interface Chemistry of Materials, PIRE-ECCI, Summer School, Shanghai, China *Big Data of Materials Science from First Principles - Critical Next Steps*
Jun 2014	Seminar, University of Science and Technology of China, Hefei, China *Big Data of Materials Science from First Principles - Critical Next Steps*
Jul 2014	Exciting Workshop Big Data of Materials Science from First Principles, Berlin, Germany *Electronic Structure Theory: Status and Outlook*
Jul 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Electronic Structure Theory: Status and Outlook*
Jul 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *IPAM Overview: Electronic Structure Theory for the Ground State*
Jul 2014	KOSMOS Summer University, Humboldt-Universität zu Berlin, Berlin, Germany *Electronic Structure Theory: Status and Outlook*
Aug 2014	248th ACS National Meeting and Exposition, American Chemical Society, San Francisco, CA, USA *Space-Charge Transfer at Intrinsic Defects and at (Organic) Adsorbates at Metal-Oxide Surfaces*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Big Data of Materials Science from First Principles - Critical Next Steps*
Sep 2014	Seminar, University of Connecticut, Storrs, CT, USA *Big Data of Materials Science from First Principles - Critical Next Steps*
Oct 2014	The 4th International Workshop on Quantum Energy, Chengdu, China *Big Data of Materials Science from First Principles - Critical Next Steps*
Nov 2014	The 17th Asian Workshop on First-Principles Electronic Structure Calculations, Seoul, South Korea *Big Data of Materials Science from First Principles - Critical Next Steps*

Dec 2014	2014 Fall MRS Meeting and Exhibit, Materials Research Society, Boston, MA, USA *Big Data of Materials Science from First Principles - Critical Next Steps*
Jan 2015	CPTS Data Driven Sciences Round Table, Tübingen, Germany *Big Data Analytics in CPT Science*
Feb 2015	IPAM Workshop, Machine Learning for Many-Particle Systems, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Big Data of Materials Science - Critical Role of the Descriptor*
Apr 2015	Symposium on the Occasion of the Retirement of Prof. Dr. Oleg Pankratov, Quantum Theory of Materials, Erlangen, Germany *Big Data of Materials Science - Critical Next Steps*
May 2015	Kolloquium, SFB 840 “Von Partikulären Nanosystemen zur Mesotechnologie”, Bayreuth, Germany *Big Data of Materials Science -- Critical Role Next Steps*
May 2015	Workshop, Computer Simulations for Condensed Phase Systems: From Correlated Electrons to Novel Materials, Rome, Italy *Big Data of Materials Science - Critical Role of the Descriptor*
Jun 2015	IPAM Workshop on Materials for a Sustainable Energy Future, Institute for Pure and Applied Mathematics, Lake Arrowhead, CA, USA *Metal Oxides with Defects and Interfaces: Materials for Energy Conservation, Conversion, and Storage*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Electronic Structure Overview*
Jul 2015	Summer School of the Max Planck-EPFL Center for Molecular Nanoscience and Technology, Schloss Ringberg, Kreuth, Germany *Big Data Analytics, Novel Materials Discovery*
Sep 2015	6th International Conference on Nanoscience and Technology (ChinaNANO 2015), Beijing, China *Big-Data Analytics for Materials Science: Concepts, Challenges and Hype*
Sep 2015	CeNS Workshop 2015 “Channels and Bridges to the Nanoworld”, Venice, Italy *Big Data and Data Analytics for Materials Science*

Honghui Shang

Apr 2014	Team Meeting on ETSF Electron-Phonon Coupling, Zeuthen, Germany *Density-Functional Perturbation Theory for Lattice Dynamics with Numeric Atom-Centered Orbitals*
Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *Density-Functional Perturbation Theory for Lattice Dynamics with Numeric Atom-Centered Orbitals*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Density-Functional Perturbation Theory for Lattice Dynamics in FHI-aims*

Jan 2015	Team Meeting on ETSF Electron-Phonon Coupling, Rome, Italy *First-Principles Evidence for Intermediate Hole Polaron in ZnO*

Alexandre Tkatchenko

Nov 2013	International Symposium on Computational Sciences (ISCS2013), Shanghai, China *Collective van der Waals Interactions in Molecules and Solids*
Nov 2013	Retreat, Intelligent Data Analysis Group, Technische Universität Berlin, Berlin, Germany *First-Principles Atomistic Modeling: Pushing the Limits of Accuracy and Efficiency*
Nov 2013	Seminar, Jilin University, Changchun, Jilin, China *First-Principles Atomistic Modeling: Pushing the Limits of Accuracy and Efficiency*
Dec 2013	CECAM Workshop, Quantum Dynamics in Molecular and Nano-Materials: Mechanisms and Functionality, Tel Aviv University, Tel Aviv, Israel *Collective Phenomena in Organic Materials Described with Coupled Quantum Harmonic Oscillators*
Jan 2014	CECAM Workshop, Two-dimensional inorganic materials (2DIM): property simulations from band structure to devices, Lausanne, Switzerland *van der Waals Interactions in Nanostructures: Breaking Preconceived Notions*
Jan 2014	Colloquium, University of Bonn, Bonn, Germany *van der Waals Interactions in Nanostructures: Breaking Preconceived Notions*
Mar 2014	Hauptvortrag, DPG-Frühjahrstagung, Dresden, Germany *The Many-Body Path Towards Quantitative Modeling of Complex Adsorption Systems*
May 2014	Colloquium, Max Planck Institute for Polymer Research, Mainz, Germany *The Many-Body Path Towards Predictive Modeling of Complex Materials*
May 2014	Colloquium, University of Luxembourg, Luxembourg *The Many-Body Path Towards Predictive Modeling of Complex Materials*
May 2014	E-MRS Spring Meeting, Lille, France *van der Waals Interactions in Molecular Materials: Breaking Preconceived Notions*
May 2014	FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany *Collective van der Waals Interactions in Materials*
Jun 2014	Colloquium, University of Groningen, Groningen, The Netherlands *The Many-Body Path Towards Predictive Modeling of Complex Materials*
Jun 2014	Physics Boat Workshop 2014, Helsinki, Finland/Stockholm, Sweden *van der Waals Interactions in Molecular Materials: Breaking Preconceived Notions*

Jun 2014	Workshop, Many-Body Interactions: From Quantum Mechanics to Force Fields, Telluride Science Research Center, Telluride, CO, USA *Many-Body van der Waals Dispersion: Strong Correlations in Weak Interactions?*
Jul 2014	IPAM Workshop, Density Functional Theory and Beyond: Computational Materials Science for Real Materials, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *van der Waals Interactions in DFT*
Aug 2014	CAMD Summer School on Electronic Structure Theory and Materials Design, DTU Department of Physics, Lyngby, Denmark *Many-Body van der Waals Dispersion: Strong Correlations in Weak Interactions?*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *From Dispersion Interactions to Farsighted Electron Correlation - A Unified Approach Based on Atomic Response Functions*
Sep 2014	16th European Seminar on Computational Methods in Quantum Chemistry (ESCMQC), Houffalize, Belgium *From Dispersion Interactions to Farsighted Electron Correlations – A Unified Approach Based on Atomic Response Functions*
Sep 2014	SMARTER4 Conference, Durham, UK *Structure, Stability, and Vibrations of Molecular Materials: The Role of (Many-Body) Dispersion Interactions*
Oct 2014	Colloquium, Department of Chemistry, UNIST Campus, Ulsan, South Korea *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Oct 2014	Physical Seminar, Department of Chemistry, University of Rochester, Rochester, NY, USA *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Oct 2014	Woodward Lecture, Harvard University, Cambridge, MA, USA *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Oct 2014	Workshop of the SFB 658-Integrated Research Training Group, Lübbenau, Germany *The Many-Body Path Towards Quantitative Modeling of Complex Adsorption Systems*
Nov 2014	Colloquium, University of Bristol, Bristol, UK *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Nov 2014	Seminar, Forschungszentrum Jülich, Jülich, Germany *Non-Additive Effects in Molecular Adsorption*

Dec 2014	Colloquium of the Collaborative Research Centre “Hybrid Inorganic/Organic Systems for Opto-Electronics” (SFB 951- HIOS), Berlin, Germany *The Many-Body Path Towards Quantitative Modeling of Complex Adsorption Systems*
Jan 2015	Colloquium, University of Rostock, Rostock, Germany *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Jan 2015	Winter Workshop, Frontiers of Multiscale Modelling - Current Obstacles and New Horizons for Energy, Materials, and Catalysis, Stubachtal, Austria *van der Waals Correlations in Materials: Current Obstacles and New Horizons*
Feb 2015	IPAM Workshop, Machine Learning for Many-Particle Systems, Institute for Pure and Applied Mathematics, Los Angeles, CA, USA *Many Particles, Collective Variables and Machine Learning*
Apr 2015	Colloquium, Universitat de Barcelona, Barcelona, Spain *Non-Covalent van der Waals Interactions in Molecules and Materials*
Apr 2015	Seminar, Institute of Basic Science, Seoul, South Korea *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Jul 2015	Colloquium, University of Luxembourg, Luxembourg *The Many-Body Path Towards Quantitative Modeling of Complex Molecules and Materials*
Jul 2015	Congress of Theoretical Chemists of Latin Expression, Torino, Italy *Quantum Fluctuation in Molecules*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Practical Approaches to van der Waals Interactions*
Aug 2015	Colloquium, The Rowland Institute at Harvard, Cambridge, MA, USA *van der Waals Interactions for Molecules on Surfaces: Weak or Strong?*
Aug 2015	Dynamics at Surfaces, Gordon Research Conference (GRC), Newport, RI, USA *van der Waals Interactions for Molecules at Surfaces*
Aug 2015	XXIV International Materials Research Congress 2015, Cancún, Mexico *Quantum Fluctuations in Molecules and Materials*
Sep 2015	EUROMAT 2015, European Congress and Exhibition on Advanced Materials and Processes, Warsaw, Poland *Quantum Fluctuations in Molecular Materials*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *Non-Covalent Interactions in Density-Functional Theory*

Igor Ying Zhang

Jun 2014	International Workshop, White Nights of Materials Science: From Physics and Chemistry to Data Analysis, and Back, St. Petersburg, Russia *Toward Simple Orbital-Dependent Density Functionals for Molecular Dissociation*
Aug 2014	FHI-aims Developers' and Users' Meeting, Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals, Berlin, Germany *Assessment of Density Functionals in FHI-aims: Searching for the Next-Generation Density Functional with a Broader Application*
Jun 2015	Workshop, Methods and Algorithms in Electronic-Structure Theory, Schloß Ringberg, Kreuth, Germany *Explore Efficient Orbital-Dependent Density Functionals for a Broader Application*
Jul 2015	Hands-on Workshop Density-Functional Theory and Beyond: First-Principles Simulations of Molecules and Materials, Berlin, Germany *Test Sets and Benchmark Techniques for Materials Science*
Sep 2015	Psi-k 2015 Conference, San Sebastian, Spain *Test Set for Materials Science and Engineering*

ERC Group on Organic Functional Materials and Intermolecular Interactions

Head: Alexandre Tkatchenko

Guest scientists, staying for at least six months:

Wei Liu	*until 01/02/2015*	*ERC*
Wang Gao	*until 31/07/2014*	*ERC*
Mausumi Chattopadhyaya		*AvH*
Fairoja Cheenicode Kabeer		*Harvard EFRC*
Gionni Marchetti		*DFG*
Igor Poltavsky		*ERC*
Limin Zheng		*China Scholarhsip Council (CSC)*

Graduate students: 6 (2 from external funds, CSC and Harvard EFRC)

General Remarks

The ERC (European Research Council) Research Group *Organic Functional Materials and Intermolecular Interactions*, lead by Alexandre Tkatchenko, was established in May 2010 and is hosted by the Theory Department. This group performs fundamental developments of efficient first-principles methods for an accurate modeling of non-covalent interactions in molecules, solids, and interfaces. The developed methods are applied to a wide range of fundamental complex materials, aiming at understanding their qualitative and quantitative structural, cohesive, and electronic properties at the atomic scale. The group currently consists of 5 post-doctoral researchers, and 5 PhD students, together with the PI.

Since the group was established, several postdoctoral researchers and one PhD students have left for academic and industry positions elsewhere. Dr. Wei Liu accepted an offer for full professor in the University of Science and Technology in Nanjing, China (2014). Dr. Wang Gao took an associate professor position in Jilin University, China (2014). Dr. Guo-Xu Zhang took a position as lecturer at Harbin Institute of Technology in China (2015). Dr. Anthony Reilly became a Senior Design Centre Scientist at Cambridge Crystallographic Database Centre (CCDC), UK (2014). Dr. Katja Hansen took a Scientist position at 3M, Duesseldorf (2014). Currently, 3 PhD students (Vivekanand V. Gobre, Victor G. Ruiz, and Nicola Ferri) are in process of submitting their theses. These successful career developments of former and current ERC group members highlight the high quality of the research and scientific training in the group.

Scientific Scope

Non-covalent van der Waals (vdW) interactions are ubiquitous in nature, making the existence of molecular liquids and solids possible; controlling protein-protein and drug-protein binding inside our cells; and giving geckos the ability to "defy gravity" and climb on walls and ceilings. An accurate description of vdW interactions is extremely challenging, since the vdW dispersion energy arises from collective motion of electrons and must be described by many-electron quantum mechanical methods. The lack of accurate and efficient methods for capturing vdW interactions in large and complex systems hinders truly quantitative predictions of properties and functions of technologically relevant materials. The ERC group has successfully addressed this challenging age-old problem, by developing a hierarchy of efficient and advanced quantum-mechanical methods with accuracy and capacity to predict new phenomena in complex materials of fundamental and technological interest. These developments are based on a combination of techniques developed in different fields, such as many-body physics, statistical mechanics, chemistry, and computer science. The methods developed by the group are now widely used worldwide to enable molecular simulations with predictive power for large and complex materials, chemicals, and biological systems.

Research Highlights

Wavelike Nature of van der Waals Interactions at the Nanoscale

With the increasing focus on supramolecular chemistry and nanostructured materials, vdW interactions are being employed and probed at increasingly larger scales and decreasing dimensionality. However, our current understanding of these interactions is largely based on small model systems and idealized pairwise London dispersion picture. As a result of this inconsistency, predictions of both static and dynamic properties of nanoscale structures may fail in quantitative and sometimes even qualitative manner.

We demonstrated that in supramolecular complexes and low-dimensional nanostructures, vdW correlations are more naturally described in terms of coupling between fluctuating dipole waves. This leads to several nontrivial effects in vdW interactions that cannot be explained by dispersion corrections and non-local functionals based on electron density, but that are correctly captured by our developed many-body dispersion (MBD) model. In linear chain structures and layered 2D materials, the interaction energy shows complex power laws that can be systematically tuned from insulating to metallic behavior. The associated wave fluctuations are largely delocalized over the whole system, continuously changing the interaction power law as a function of the separation between nanostructures. For molecules interacting through nanostructures, we observe a regime in which their interaction energy *increases*, instead of decreasing as naively expected from dielectric screening. Further application to carbon-based supramolecular complexes demonstrates that omitting wavelike vdW fluctuations leads to differences in association constants of up to five orders of magnitude where there should be degeneracy according to high-level quantum Monte Carlo calculations.

Taken together, our findings indicate that the wavelike nature of vdW interactions provides a hitherto unexplored avenue that could be used for tailoring the assembly of complex polarizable systems at the nanoscale.

Modeling Quantum Nuclei with Perturbed Path Integral Molecular Dynamics

The quantum nature of nuclear motions plays a vital role in the structure, stability, and thermodynamics of molecules and materials. Whenever interatomic forces are strong, nuclear quantum fluctuations (NQF) can be fairly pronounced at room temperature and even above it. The standard approach to model NQF in chemical and biological systems is path-integral molecular dynamics (PIMD). Unfortunately, conventional PIMD simulations can have exceedingly large computational cost due to the need of employing an excessive number of coupled classical subsystems (beads) for quantitative accuracy. Hence, the development of a non-empirical method for NQF, which is both accurate and efficient, would be desirable.

To achieve this challenging goal we combined perturbation theory with Feynman-Kac imaginary-time path integral approach to quantum mechanics and derive improved non-empirical partition function and estimators to calculate converged quantum observables. Our *perturbed path-integral* (PPI) method requires the same ingredients as conventional approaches, but increases the accuracy and efficiency of path integral simulations by an order of magnitude. Any kind of phase sampling technique, and any thermostat or barostat can be utilized. The converged observables can be obtained either *on-the-fly* or *a posteriori* conventional PIMD simulations, which are utilized as a base of the developed PPI approach.

Applications were carried out for thermodynamics of a quantum harmonic oscillator and double-wall potential, empirical water model containing 256 water molecules within periodic boundary conditions, *ab initio* simulations of nitrogen and benzene molecules, and graphene. For all of these examples, our PPI approach with 4 to 8 classical beads recovers the nuclear quantum contribution to the total energy and heat capacity at room temperature within 3%

accuracy, paving the way toward seamless modelling of nuclear quantum fluctuations in realistic molecules and materials.

Electronic Properties of Molecules, Surfaces, and Interfaces with a Self-Consistent Interatomic van der Waals Density Functional

How strong is the effect of long-range vdW interactions on the electronic properties of molecules and extended systems? It is often argued that the vdW energy has a small, or even negligible, influence on the electron density and derived electronic properties, since the vdW energy represents only a tiny fraction (0.001%) of the total electronic energy.

To answer the question posed above, we derived a fully self-consistent (SC) implementation of the density-dependent interatomic vdW functional of Tkatchenko and Scheffler and its extension to surfaces. Not surprisingly, vdW self-consistency leads to tiny modifications of the structure, stability, and electronic properties of molecular dimers and crystals. However, unexpectedly large effects were found in the binding energies, distances and electrostatic moments of highly polarizable alkali metal dimers. Most importantly, vdW interactions produced complex and sizable electronic charge redistribution in the vicinity of metallic surfaces and at organic/metal interfaces. As a result, for several coinage metal (111) surfaces, self-consistency induces modifications in the surface dipole, leading to an increase of up to 0.30 eV in the computed workfunctions. Furthermore, in the case of HIOS, SC vdW entails modifications of up to 0.22 eV in the shift of the interface workfunction, a property induced by molecular adsorption. The underlying mechanism responsible for the workfunction modifications stems from an interplay between two effects driven by SC vdW interactions: (i) the modification of the interface dipole, and (ii) a reduction in the charge transfer between the molecule and the surface.

The analysis of SC vdW effects demonstrated the important effect of vdW interactions on the electronic properties of different classes of systems, with self-consistency systematically improving the agreement between the theoretical predictions and the experimental measurements. Our work revealed a nontrivial connection between electrostatics and long-range electron correlation effects.

Essential Role of van der Waals Interactions in the Structure, Stability, and Catalytic Processes for Molecules at Surfaces

Hybrid inorganic/organic systems (HIOS) often possess collective electronic, optical, vibrational, and catalytic properties that the separate components forming the interface do not exhibit. These novel interface properties stem from a subtle interplay between a range of covalent and non-covalent interactions. In particular, van der Waals (vdW) dispersion interactions play an essential role in many properties of HIOS, including their structure and stability, and sometimes even their electronic properties and reactivity.

We made systematic efforts in developing efficient first-principles methods that enable quantitative modeling and new qualitative insights into the structure and stability of HIOS. Our DFT+vdW$^{\mathrm{surf}}$ method synergistically combines Lifshitz-Zaremba-Kohn theory with intermolecular perturbation techniques, demonstrating that the collective response of the substrate electrons can modify vdW coefficients in HIOS by up to an order of magnitude. Calculations using this method have shown that the inclusion of collective vdW effects is essential to cover a wide range of interactions in the adsorption of molecules on surfaces. The critical role of screened vdW interactions in the structure and stability of HIOS has implications in catalysis, as demonstrated by the relative stability of reactive intermediates in oxygen-assisted reactions in catalytic systems such as amides, isopropoxys, thiolates, and acetylides on the Au(111) surface.

Further gain in accuracy and conceptual understanding of HIOS is possible by applying the recently developed many-body dispersion (MBD) method. This method allows us to capture anisotropic polarization effects in HIOS and demonstrate strong non-additivity in vdW interactions for atoms, molecular assemblies, and nanostructures adsorbed on metal surfaces. The application of the MBD method enables us to go beyond single molecules on surfaces and efficiently address many-body interactions in dense adsorbed molecular layers, which is necessary to understand the assembly of complex nanostructures on surfaces.

Third-Party Funded Projects

- ERC – European Research Council, Starting Grant: Van der Waals Interactions in Complex Materials; A. Tkatchenko – since 2011.

- DFG – German Research Foundation, SPP 1807 Control of London dispersion interactions in molecular chemistry, spokesperson: Peter R. Schreiner; A. Tkatchenko – since 2015.

- DFG – German Research Foundation, Basis module, project: Exploring Chemical Compound Space with Machine Learning; A. Tkatchenko, K.-R. Müller – since 2014.

- DOE – US Department of Energy, EFRC (Energy Frontier Research Centers): Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC), coordinator: C. Friend; A. Tkatchenko – since August 2014.

- DFG – German Research Foundation, SFB 951, Hybrid Inorganic/Organic Systems (HIOS), spokesperson: Norbert Koch; A. Tkatchenko, M. Scheffler – since 2015.

- INCITE computer time allocation for 300 million CPU hours // Argonne National Laboratory and Oak Ridge National Laboratory (with D. Alfe, A. Michaelides, K. Jordan, M. Gillan), 2013-2015.

Organization of workshops and conferences

- Organizer of the focused session "Van der Waals Interactions in Complex Materials: Bridging Theory and Experiment" at the APS March Meeting 2014, Denver, USA (with R. A. DiStasio Jr.).

- Organizer of a CECAM workshop "Addressing Challenges in First-Principles Based Modeling of Molecular Materials" (with A. Reilly and M. Ceriotti).

- Organizer of IPAM workshop "Machine Learning for Many-Particle Systems", Institute for Pure and Applied Mathematics, UCLA, USA, 2015 (with A. Aspuru, G. Csanyi, and K. R. Mueller).

- Organizer of CECAM workshop "From Many-Body Hamiltonians to Machine Learning and Back", Berlin, Germany, May 2015 (with M. Rupp).

- Organizer of the workshop "Modeling Many-Body Interactions (MMBI 2015)", Lake Garda, Italy, May 2015 (with R. A. DiStasio Jr., A. Ambrosetti, and P. Silvestrelli).

- Proponent and main organizer of a semester program "Understanding Many-Particle Systems with Machine Learning", Institute for Pure and Applied Mathematics, UCLA, USA (approved for Fall 2016). Co-organizers: Klaus-Robert Mueller (TU-Berlin), Gabor Csanyi (Cambridge), Alan Aspuru-Guzik (Harvard), Marina Meila (U. Washington).

Notes