

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

**19<sup>th</sup> Meeting of the Fachbeirat  
Berlin, November 28<sup>th</sup> – 30<sup>th</sup>, 2017**



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Max-Planck-Gesellschaft  
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**19<sup>th</sup> Meeting of the Fachbeirat  
Berlin, November 28<sup>th</sup> – 30<sup>th</sup>, 2017**

**Reports**

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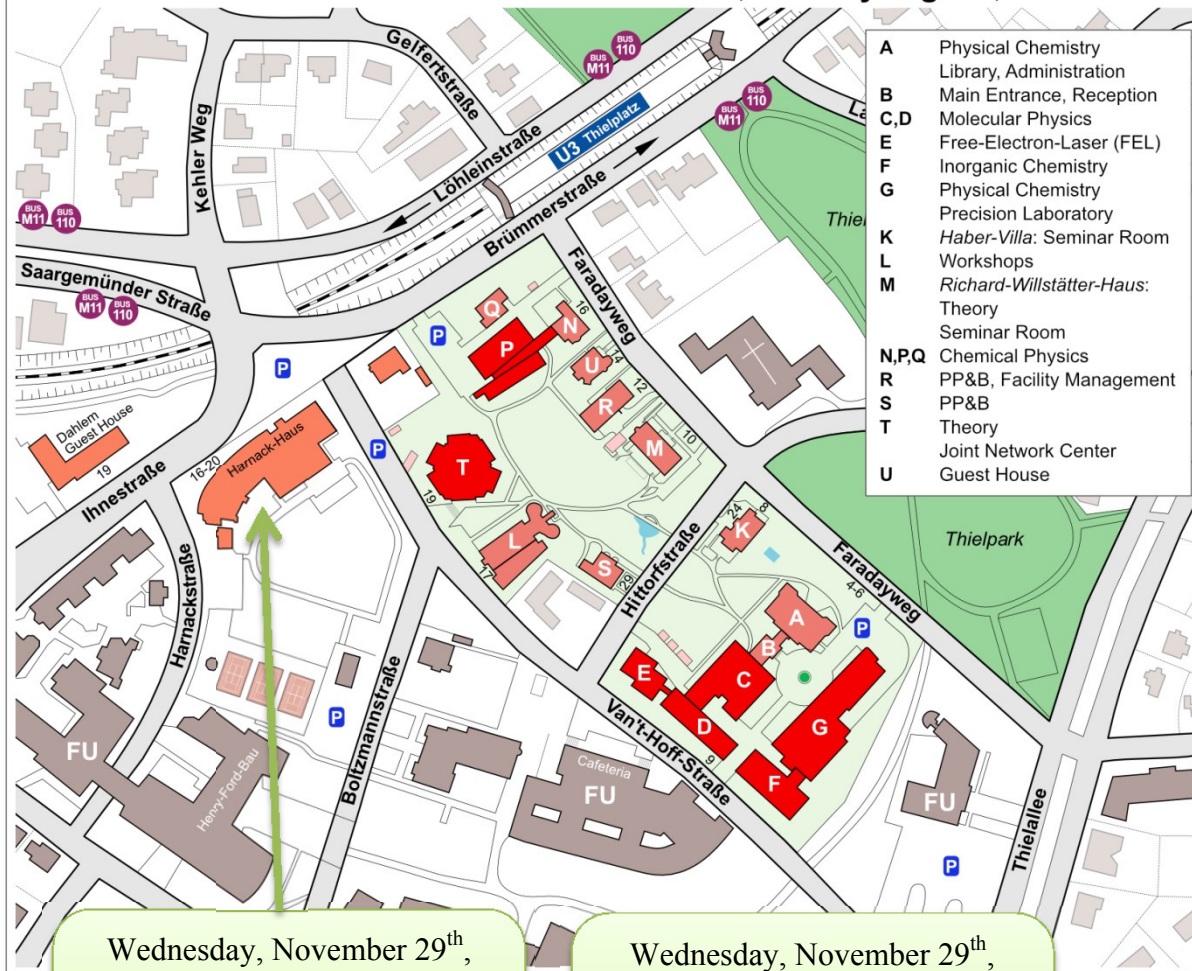
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## Campus Map

### Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

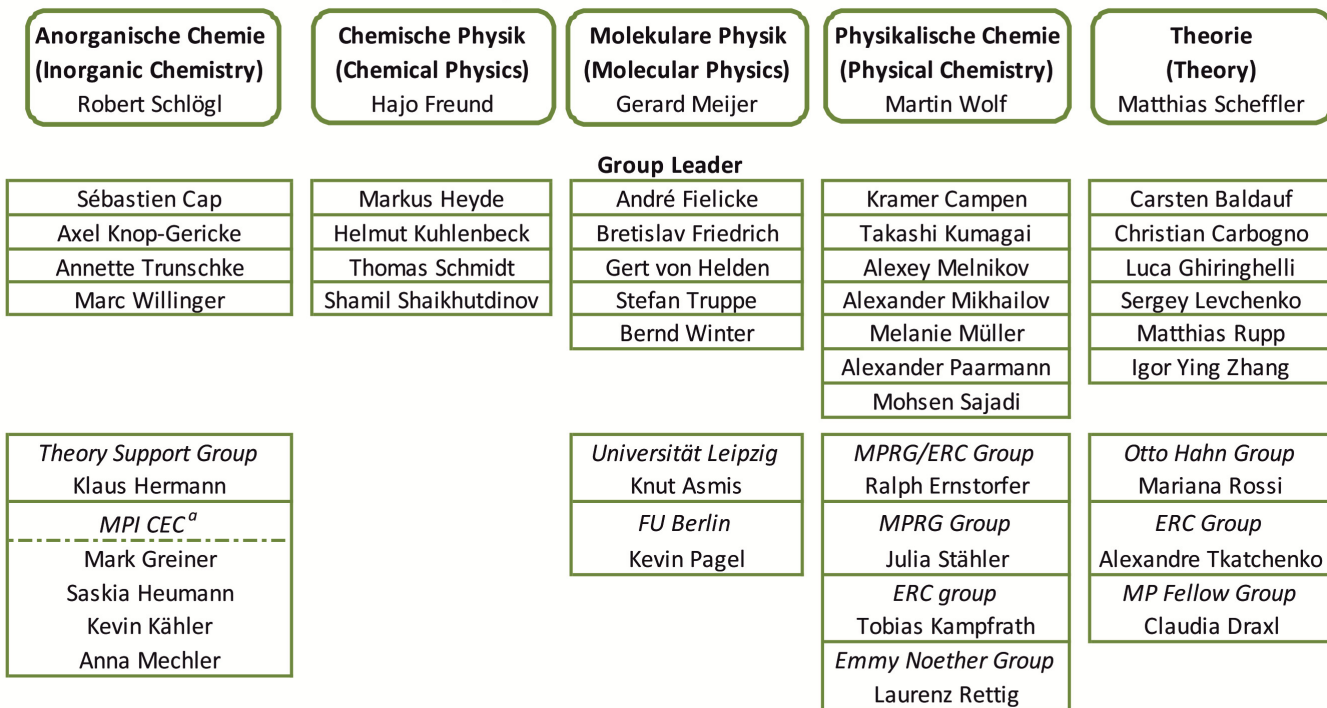


Wednesday, November 29<sup>th</sup>,  
10 – 1.30 p.m.:  
Lectures by the members  
of the Departments  
(Harnack Haus)

Wednesday, November 29<sup>th</sup>,  
2:30 – 5.30 p.m.:  
Poster sessions at the five  
Departments

# Organigramm of the FHI

## Research Departments of the Fritz Haber Institute



<sup>a</sup> MPI for Chemical Energy Conversion, Muehlheim a.d. Ruhr

## Administration, Facilities, and Service Groups



<sup>b</sup> until September 2017

## **Report of the Executive Director**

## **Report of the Executive Director**

Since the last evaluation of the Fritz Haber Institute by the Fachbeirat in November 2015 several important developments have taken place:

- Gerard Meijer has returned as Director of the Department of Molecular Physics effective January 2017. He has modified his research portfolio to include surfaces of liquids and the liquid-gas interface as discussed in the last Fachbeirat-Report.
- The President of the Max Planck Society has called upon Beatriz Roldán Cuenya from Ruhr-Universität Bochum to lead a new Department at the Institute, replacing the Department of Chemical Physics and moving towards the direction Interface Science, discussed and evaluated in the previous Fachbeirat report. She has already accepted the position and has started to organize her move to Berlin. She is part time appointed from June 1<sup>st</sup>, 2017, and will take up her full appointment from October 1<sup>st</sup>, 2017. Hajo Freund will retire end of March 2019, and until this point, Beatriz Roldán's Department will be in a "status nascendi" with respect to the final accommodation of her equipment. Then she moves into the buildings of the Department of Chemical Physics. Space is made available in different buildings, so that there should be a smooth transition.
- Gerhard Ertl's Emeritus position has been renewed effective June, 2017.
- Matthias Scheffler and Hajo Freund have applied in June 2016 for an Emeritus position, including a working group after retirement based on consensus and support by the Kollegium, and have recently received a preliminary notice from the Vice-President that the issue has been settled and the installments may be available at the dates of retirement (H.-J. Freund, March 31<sup>st</sup>, 2019, M. Scheffler, June 30<sup>th</sup>, 2019).
- The 9<sup>th</sup> Gerhard Ertl Lecture was delivered by Jan Peter Toennies in December 2016, and the coming Gerhard Ertl Lecturer has been chosen to be Ben Feringa, Groningen. He will deliver his lecture on December 8<sup>th</sup>, 2017. BASF has agreed to continue to support this event as in the years before.

Research at the Fritz Haber Institute has an enormous breadth ranging from bio-molecules in the gas-phase, via clusters, surfaces and interfaces to materials design and real catalysis.

Originally initiated by the previous Managing Director, Martin Wolf, the institute has held an institutional workshop, in which selected members of all Departments get together to discuss

their latest results and possible avenues for collaborations or research initiatives. The workshops were held from May 26 to 27, 2016 and from May 11 to 12, 2017 in Griebnitzsee, near Berlin.

**Research highlights from the Departments are:**

*1. Department of Inorganic Chemistry:*

“Co-catalysts in ethylene oxidation over Ag”. The intricate interaction of oxygen with silver to yield epoxidation vs. combustion was found to be controlled by co-catalysts like sulfur coming from the feed and/or the bulk of the Ag catalyst.

*2. Department of Chemical Physics:*

„Vibrational spectroscopy of single crystal surfaces using FEL infrared radiation induced neon desorption“: The free electron laser at FHI has been used to report for the first time infrared-laser induced desorption of rare gases from solid surfaces within the framework of an action spectroscopy in order to determine surface vibrational properties at unprecedented surface sensitivity.

*3. Department of Molecular Physics:*

The amino acid serine is known since many years to form unique octameric complexes, having very special properties such as exceptional stability and a strong preference for homochirality. Despite an intense research effort, its structure remained a mystery, which was recently solved by researchers at the MP department using a novel ion mobility/infrared spectroscopy technique in combination with theoretical calculations.

*4. Department of Physical Chemistry:*

The Department has developed time-resolved XUV photoemission spectroscopy at 500 kHz repetition rate providing access to ultrafast structural and excited state dynamics in the full Brillouin zone with unprecedented sensitivity.

*5. Theory Department:*

Discovering and understanding correlations in the practically infinite space of chemical and structural materials, is a major objective of the NOMAD Center of Excellence. New machine-learning and other big-data analytics methods were successfully developed for this goal, and novel insights were obtained, e.g., predicting unexpected topological insulators and classifying metallic/non-metallic behavior.

These results are only examples but representative for the institute research performance, which may also be judged by the overall output and the response of the scientific community via citations.

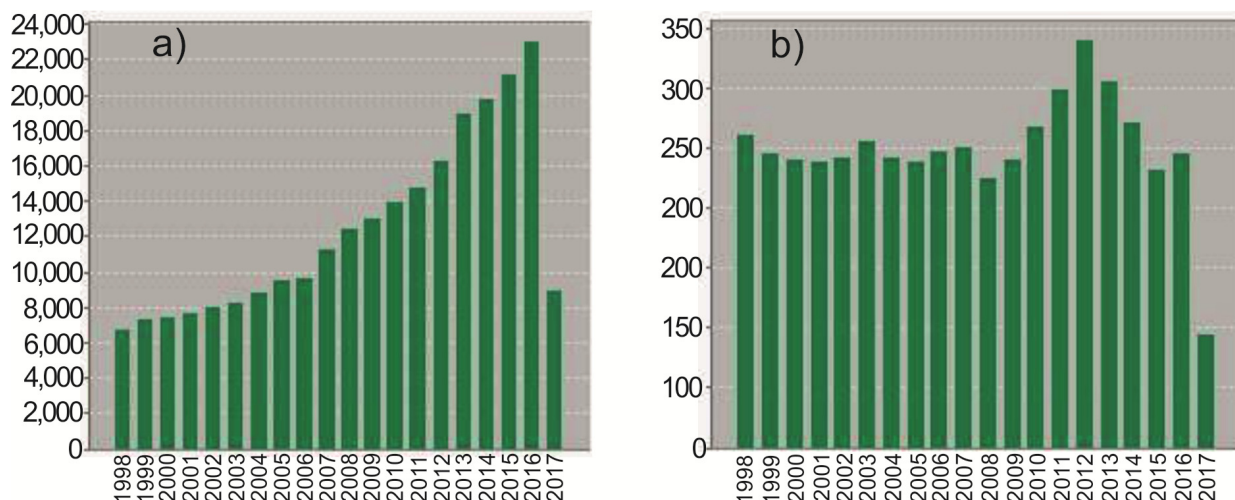


**Table 1:** Citations (a) and Publications (b)

The Fritz Haber Institute has continued to actively support the career of young scientists. The institute has seen 10 habilitations over the last 10 years.

| Name                 | Year | Department          | Currently at                     |
|----------------------|------|---------------------|----------------------------------|
| Christian Frischkorn | 2007 | Physical Chemistry  | Freie Universität Berlin         |
| Christian Hess       | 2007 | Inorganic Chemistry | Technische Universität Darmstadt |
| Thomas Risse         | 2007 | Chemical Physics    | Freie Universität Berlin         |
| Leonhard Grill       | 2009 | Physical Chemistry  | Universität Graz                 |
| Jochen Küpper        | 2009 | Molecular Physics   | DESY                             |
| Niklas Nilius        | 2009 | Chemical Physics    | Universität Oldenburg            |
| Swetlana Schauermann | 2011 | Chemical Physics    | Kiel Universität                 |
| Malte Behrens        | 2013 | Inorganic Chemistry | Universität Duisburg-Essen       |
| Martin Sterrer       | 2013 | Chemical Physics    | Universität Graz                 |
| Carsten Baldauf      | 2016 | Theory              | FHI                              |

Within the same period, 46 scientists (including 9 of the above) have been appointed to high academic positions at universities.

Since the last visit of the Fachbeirat the following scientists from the institute successfully obtained or were offered academic positions:

| Name             | University                              | Since | Department:      |
|------------------|-----------------------------------------|-------|------------------|
| Florencia Calaza | National University of the Littoral, AR | 2015  | Chemical Physics |
| Yi Cui           | Chinese Academy of Science, CN          | 2015  | Chemical Physics |
| Kristen Burson   | Hamilton College, US                    | 2016  | Chemical Physics |



| <b>Name</b>          | <b>University</b>                                       | <b>Since</b> | <b>Department:</b> |
|----------------------|---------------------------------------------------------|--------------|--------------------|
| Tobias Kampfrath     | Freie Universität Berlin, DE                            | 2017         | Physical Chemistry |
| Claude Monney        | Universität Freiburg, DE                                | 2017         | Physical Chemistry |
| Wang Gao             | Jilin University, CN                                    | 2014         | Theory             |
| Saswata Bhattacharya | Indian Institute of Technology, IN                      | 2015         | Theory             |
| Wei Guo              | Beijing University of Technology, CN                    | 2015         | Theory             |
| Wei Liu              | Nanjing University of Science and Technology, CN        | 2015         | Theory             |
| Alexandre Tkatchenko | University of Luxemburg, LU                             | 2015         | Theory             |
| Yong Xu              | Tsinghua University, CN                                 | 2015         | Theory             |
| Guo Xu Zhang         | Harbin Institute of Technology, CN                      | 2015         | Theory             |
| Amrita Bhattacharya  | DST INSPIRE Faculty, National Physical Laboratories, IN | 2016         | Theory             |
| Qimin Yan            | Temple University, US                                   | 2016         | Theory             |
| Bryan Goldsmith      | University of Michigan, US                              | 2017         | Theory             |
| Anthony Reilly       | Dublin City University, IE                              | 2017         | Theory             |

The institute typically supports 80-100 PhD students. Many of them are paid through outside funding.

The institute also hosts 5 apprentices in its various scientific departments and service groups. 2 apprentices already finished their apprenticeships and are employed.

The main research projects of the Fritz Haber Institute continue to be concerned with catalysis, as well as chemical and physical properties of materials and surfaces, interfaces, molecules, clusters, and nanostructures. Currently, the institute has 49 scientific positions out of which 17 are tenured for scientists, in addition to the 5 director positions and 112 positions for technical staff.

As in previous years, we proudly report on awards and honors bestowed on members.

| <b>Name</b>       | <b>Award</b>                                                                 | <b>Year</b> |
|-------------------|------------------------------------------------------------------------------|-------------|
| Christin Büchner  | Feodor Lynen Research Fellowship                                             | 2017        |
|                   | Otto-Hahn Medal                                                              | 2017        |
| Stefano Curtarolo | Friedrich Wilhelm Bessel Research Award                                      | 2016        |
| Hajo Freund       | Elected Foreign Honorary Member, American Academy of Arts and Sciences       | 2016        |
|                   | Dr. Honoris Causa, Karlsruhe Institute of Technology (KIT)                   | 2016        |
|                   | Honorary Senator, Friedrich-Alexander-Universität Erlangen-Nürnberg          | 2016        |
|                   | Dr. Honoris Causa, Friedrich-Alexander-Universität Erlangen-Nürnberg         | 2017        |
|                   | Visiting Einstein Professor at University of Science and Technology of China | 2017        |

| <b>Name</b>           | <b>Award</b>                                                                                               | <b>Year</b>     |
|-----------------------|------------------------------------------------------------------------------------------------------------|-----------------|
| Franz Geiger          | Bessel-Forschungspreis                                                                                     | 2017            |
| Maria Heeneman        | Young Scientist Award at 16 <sup>th</sup> International Congress on Catalysis                              | 2016            |
| Gerd von Helden       | Honorary Professor at the Radboud Universiteit in Nijmegen, The Netherlands                                | 2017            |
| Nadja Heine           | Wolfgang-Paul-Studienpreis                                                                                 | 2016            |
| Travis Jones          | Humboldt-Fellowship                                                                                        | 2016-2017       |
| Maki Kawai            | Humboldt Research Award                                                                                    | 2017            |
| Takashi Kumagai       | PRESTO grant                                                                                               | 2017            |
|                       | G. Ertl Young Investigator Award 2016                                                                      | 2016            |
| Andrew Marshall Rappe | Humboldt Research Award                                                                                    | 2016            |
| Cyriac Massué         | Ernst Haage-Doktorandenpreis                                                                               | 2016            |
| Gerard Meijer         | Knight in the Order of The Netherlands Lion                                                                | 2017            |
| Markus Raschke        | Bessel-Forschungspreis                                                                                     | 2016            |
| Laurenz Rettig        | Emmy Noether-Programm                                                                                      | 2017            |
| Swetlana Schauer mann | Dozentenstipendium des Fonds der Chemischen Industrie (Fellowship of the Association of Chemical Industry) | 05/2012-05/2017 |
| Matthias Scheffler    | Advanced Grant of the European Research Council                                                            | 2017            |
|                       | Member of Leopoldina (German National Academy of Sciences)                                                 | 2017            |
|                       | ‘Visiting Professor’, Institute for Catalysis, Hokkaido University, Japan                                  | Since 2016      |
|                       | Honorary Professor, Humboldt-Universität zu Berlin                                                         | Since 2016      |
| Robert Schlögl        | Innovationspreis des Landes NRW                                                                            | 2016            |
|                       | Ruhr-Preis für Kunst und Wissenschaft                                                                      | 2017            |
|                       | Distinguished Affiliated Professor, Technische Universität München                                         | 2017            |
|                       | ENI Award for Energy Transition                                                                            | 2017            |
| Julia Stähler         | Gaede Award 2016 of the German Vacuum Society                                                              | 2016            |
|                       | Edith Flanigen Award                                                                                       | 2016            |
| Daniel A. Thomas      | Humboldt-Fellowship                                                                                        | 2017            |
| Lutz Waldecker        | Carl-Ramsauer-Preis                                                                                        | 2016            |
|                       | Feodor Lynen Research Fellowship                                                                           | 2016            |

Scientists of the institute were active in serving the scientific community on various levels: refereeing, acting on the boards of scientific journals or conferences, and organizing international workshops and conferences.

The institute has increasingly participated in competing for funds from the European Research Council. So far, researchers at the institute have been awarded 3 ERC Starting Grants, 3 ERC Advanced Grants and 2 ERC Consolidator Grants.

| ERC Grant          | Name     | Period     |            | Principle Investigator |
|--------------------|----------|------------|------------|------------------------|
| Starting Grant     | VDM-CMAT | 01.09.2011 | 31.08.2016 | Alexandre Tkatchenko   |
| Starting Grant     | STRUBOLI | 01.12.2011 | 30.11.2016 | Martin Sterrer         |
| Advanced Grant     | MOLCHIP  | 01.02.2010 | 31.01.2015 | Gerard Meijer          |
| Advanced Grant     | CRYVISIL | 01.01.2016 | 31.12.2020 | Hajo Freund            |
| Starting Grant     | ENREMOS  | 01.01.2014 | 31.03.2016 | Swetlana Schauer mann  |
| Consolidator Grant | TERAMAG  | 01.07.2016 | 30.06.2021 | Tobias Kampfrath       |
| Consolidator Grant | FLATLAND | 01.10.2016 | 30.09.2021 | Ralph Ernstorfer       |
| Advanced Grant     | TEC1p    | 01.10.2017 | 31.09.2022 | Matthias Scheffler     |

The Fritz Haber Institute continues to be very attractive for scientists from abroad according to the Alexander von Humboldt Foundation. Our institute is ranked first among the non-university institutions even though some of those centers are an order of magnitude bigger in personnel and budget.

| Absolute rankings | Institution                                                                                   | Number of guest researchers |      |               |      | Total number |
|-------------------|-----------------------------------------------------------------------------------------------|-----------------------------|------|---------------|------|--------------|
|                   |                                                                                               | Fellows                     |      | Award winners |      |              |
|                   |                                                                                               | female                      | male | female        | male |              |
| 1                 | Fritz-Haber-Institut der MPG, Berlin                                                          | 9                           | 28   |               | 17   | 54           |
| 2                 | MPI für Kolloid- und Grenzflächenforschung, Potsdam                                           | 9                           | 19   |               | 8    | 36           |
| 3                 | MPI für Eisenforschung GmbH, Düsseldorf                                                       | 5                           | 19   |               | 6    | 30           |
| 3                 | MPI für Kohlenforschung, Mülheim an der Ruhr                                                  | 3                           | 22   |               | 5    | 30           |
| 5                 | MPI für biophysikalische Chemie, Göttingen                                                    | 7                           | 13   |               | 8    | 28           |
| 5                 | MPI für Polymerforschung, Mainz                                                               | 6                           | 18   |               | 4    | 28           |
| 7                 | Forschungszentrum Jülich (FZJ)                                                                | 8                           | 15   |               | 4    | 27           |
| 7                 | MPI für Gravitationsphysik, Potsdam                                                           | 2                           | 16   |               | 9    | 27           |
| 9                 | Deutsches Archäologisches Institut, Berlin                                                    | 4                           | 18   |               | 1    | 23           |
| 9                 | MPI für Astronomie, Heidelberg                                                                | 4                           | 15   | 1             | 3    | 23           |
| 11                | Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt, Neuherberg | 8                           | 11   |               | 3    | 22           |
| 11                | Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum (GFZ)                              | 6                           | 10   | 1             | 5    | 22           |

**Table 2:** The top 11 non-university research institutes and other institutes in Germany chosen by AvH fellows and AvH award winners. The full list of the “Humboldt Rankings” can be found at <https://www.humboldt-foundation.de/web/humboldt-rankings-2017.html>

| Absolute rankings | Institution                                                      | Number of guest researchers |      |               |      | Total number |
|-------------------|------------------------------------------------------------------|-----------------------------|------|---------------|------|--------------|
|                   |                                                                  | Fellows                     |      | Award winners |      |              |
|                   |                                                                  | female                      | male | female        | male |              |
| 1                 | Fritz-Haber-Institut der MPG, Berlin                             | 9                           | 27   |               | 16   | 52           |
| 2                 | MPI für Kohlenforschung, Mülheim an der Ruhr                     | 3                           | 22   |               | 4    | 29           |
| 3                 | MPI für Gravitationsphysik, Potsdam                              | 2                           | 16   |               | 9    | 27           |
| 4                 | MPI für Astronomie, Heidelberg                                   | 4                           | 15   | 1             | 3    | 23           |
| 5                 | MPI für Kolloid- und Grenzflächenforschung, Potsdam              | 6                           | 11   |               | 5    | 22           |
| 6                 | Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum (GFZ) | 6                           | 9    | 1             | 5    | 21           |
| 7                 | MPI für Festkörperforschung, Stuttgart                           | 1                           | 12   | 1             | 6    | 20           |
| 7                 | MPI für Polymerforschung, Mainz                                  | 4                           | 13   |               | 3    | 20           |
| 9                 | MPI für Kernphysik, Heidelberg                                   | 6                           | 9    |               | 4    | 19           |
| 10                | Deutsches Elektronen-Synchrotron (DESY) Hamburg/Zeuthen          | 2                           | 5    |               | 10   | 17           |
| 11                | Forschungszentrum Jülich (FZJ)                                   | 5                           | 9    |               | 2    | 16           |

**Table 3:** The top 11 non-university research institutes and other institutes in Natural Sciences in Germany chosen by AvH fellows and AvH award winners. The full list of the “Humboldt Rankings” can be found at <https://www.humboldt-foundation.de/web/humboldt-rankings-2017.html>

The institute is involved in the following collaborative research centers (Sonderforschungsbereiche (SFB)) and clusters that strengthen the interaction with the Berlin universities:

- CRC/SFB 658 “Elementary processes of molecular switches at surfaces”,
- CRC/SFB 1109 "Understanding of Metal-Oxide/ Water Systems at the Molecular Scale: Structural Evolution, Interfaces and Dissolution",
- CRC/SFB 910 “Control of Self-Organizing Nonlinear Systems”,
- CRC/SFB 951 “Hybrid Inorganic/Organic Systems for Opto-Electronics”,
- Cluster of Excellence: UniCat “Unifying Concepts in Catalysis”.

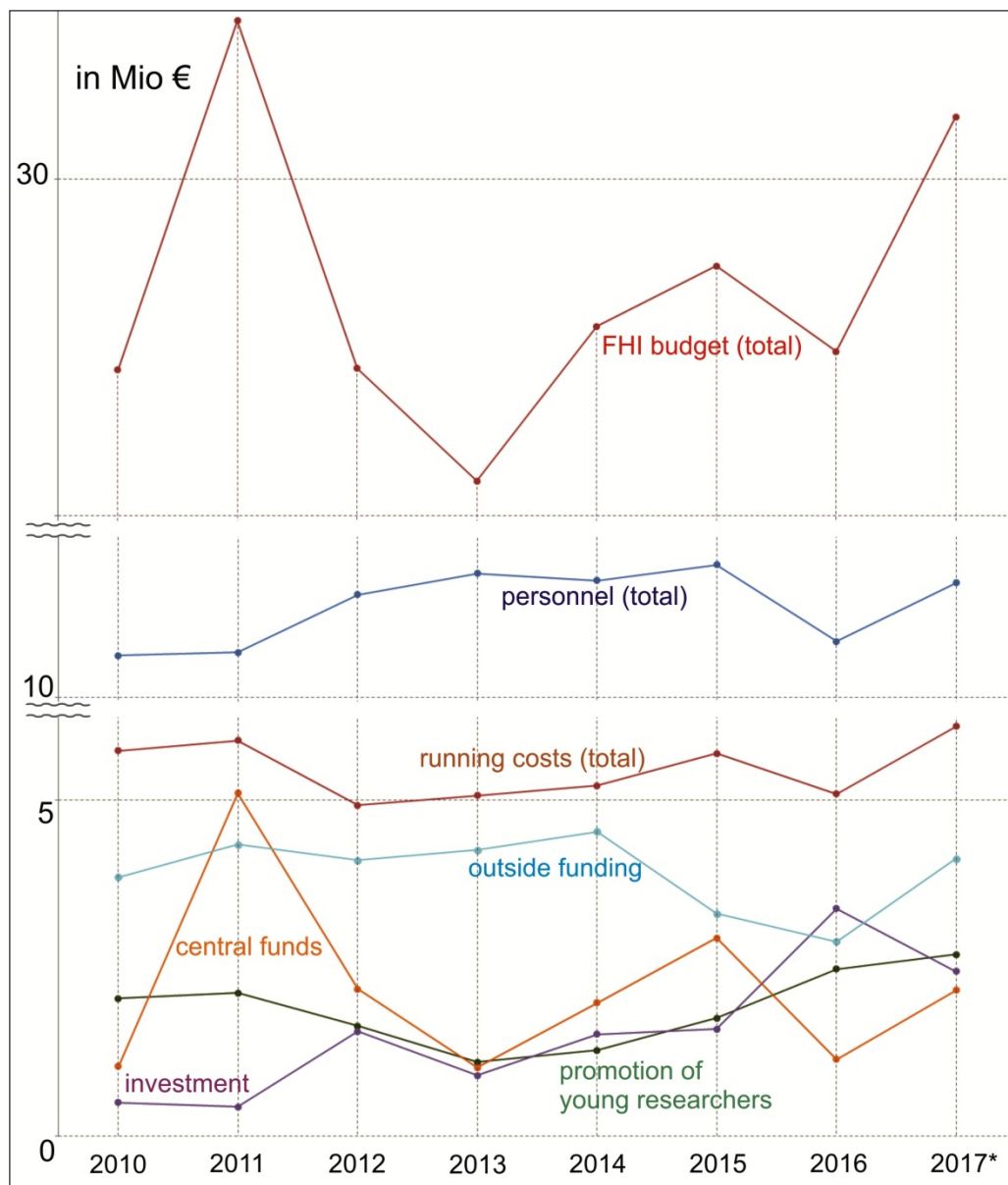
Recently, a letter has been sent by the Presidents of the three Berlin Universities and the Charité to President Stratmann and Matthias Scheffler supporting the idea of a nation-wide Max Planck School on “Quantum Materials” under the condition that their institutions remain the PhD granting bodies and the right to grant PhD is not extended to non-university institutions. The Kollegium fully supports this Letter by the University Presidents.

Many scientists of the institute participate in DFG Priority Programs (Schwerpunktprogramm SPP1538, SPP1666, SPP1543, SPP1613/2) that link institutes all over Germany or in DFG co-funded projects with foreign countries such as DFG-NSFC with China and DFG-FAPERJ

with Brazil. In addition, many projects are financed or co-financed by other agencies, such as DAAD, G.I.F., Japan Science and Technology Agency (JST), BMBF, EU, Leibniz-Gemeinschaft and DOE.

There are also collaborations with industrial labs, e.g. BASF, Volkswagen, Clariant, Thyssen-Krupp, Obrist, Bosch, QuatumWise.

The budget data in the figure reflect the trends described above: Overall stability!



*Development of the Budget of the Fritz Haber Institute over the last 7 years [(\*) scheduled].*

The total personnel is the sum of personnel financed from the core budget and the PhD student- ships of the MPG. Running costs, investment and central funds refer to the budget provided by the MPG. The peak in 2011 is due to the installment for the succession in the Department of Physical Chemistry and to extra funds from the BAR (Beratender Ausschuss

für EDV-Anlagen in der MPG). Outside funding represents all externally awarded funds including studentships, post-doctoral positions, investments and running costs.

The renovation of the institute's buildings, some of which are more than 100 years old, as addressed in the previous report to the Fachbeirat, is going according to plan. During the last years the infrastructure of the institute has been renewed. It concerned the electro-technical and the IT supply of the seventeen buildings on campus.

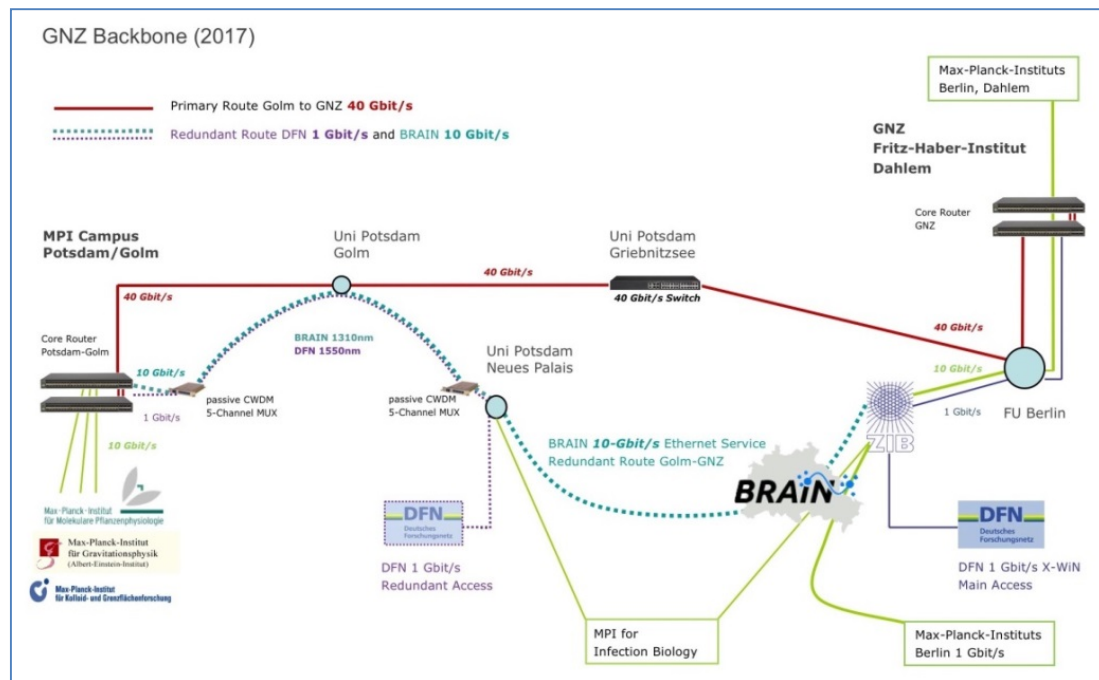
The necessitated civil engineering efforts to sink shafts and manholes and construct tunnels across the entire campus, to connect the newly erected building R on the site of Faradayweg 12 with all buildings on campus have been accomplished. This replacement establishes a sustainable infrastructure that allows for future modifications, should new developments require this. Finally the institute grounds were reworked and reestablished beautifully. On behalf of the Kollegium, Robert Schlögl supervised the entire process and we are grateful for his and the central services outstanding engagement.

In the following, I will briefly report on the activities of the service groups.

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

The Joint Network Center (Gemeinsames Netzwerkzentrum) of the Berlin-Brandenburg Max Planck institutions is a regional **IT competence center**, located and managed at the FHI. This group focusses on networking, backup, virtualization, cloud and security services. In addition, the GNZ provides consulting services and coordinates IT projects from planning via purchase to initial operation. At present, the center supports 13 Max Planck institutions in the Berlin-Brandenburg area including all 8 Max Planck Institutes. The GNZ deals with wide area (DFN X-WiN), metropolitan area (BRAIN to Potsdam) and local area (LAN and WLAN) **networks**. Special emphasis is placed on network security and central manageability.

Until the beginning of 2017 the GNZ operated a DWDM-line (Dense Wavelength Division Multiplexing) including 4x GbE and 2x 4GbFC from Berlin (GNZ) to Golm (MPI Campus).



### GNZ Network Infrastructure Mid 2017

Within a project the GNZ has examined an alternative internal connection of the MPIs (intranet). Different technologies were compared in this examination. One technology was completely convincing in terms of bandwidth as well as costs and easy maintenance. In this case the **40Gb Ethernet** technology will be used. The GNZ has developed and tested the concept in 2016. The BAR-proposal was submitted in September 2016 and was described as a **very exemplary** one. As a result, the procurement of the devices was triggered. After creating a sufficient redundancy route (10GbE via BRAIN) and the move of all services from the main route to the new redundancy route, the main route was reconfigured. After completion and repeated tests, the main route went successfully into productive operation in May 2017.

The group is committed to the newly founded **KNITS** (Competence Network IT Security), which takes care of the reorientation of IT security in the MPS.

**DoS-Protection** (Denial of Service) covers the protection against deliberately generated overload by too many incoming data packages. The GNZ has therefore integrated the DoS-protection of the DFN into its own service.

In the years 2016 and 2017 the GNZ is also represented in the **BAR**-committee (Gerd Schnapka as an appointed member). The committee advises the president, the institutes and the general administration on the fundamental questions of IT deployment in the

MPS and on specific IT procurement projects. The expertise of GNZ is particularly popular in questions of network, infrastructure, security and storage.

In addition to the **firewall** BAR-subcommittee, the GNZ is also involved in the new founded subcommittee for **server room planning**. This permanent subcommittee supports the institutes especially in the initial phase of the planning of structural measures, the technical infrastructure such as air conditioning and power supply and the drafting of the BAR-proposal.

*PP&B (Personal, Computers, Real-time & Image Processing)*

*(Head: Heinz Junkes)*

The activities of PP&B during the period under review were mainly due to the permanent maintenance of the services (Server and desktop systems, storage, compute cluster, mail, web, telephone, building automation, ...) during the major reconstruction projects (2 new buildings, new infrastructure for data and electricity). In 2017 the whole technique has now been concentrated in the new computer room in Geb. R. From there, all the campus buildings are supplied (redundant). The backbone is now powered by 10 Gbit/s lines. All central services are directly linked to the backbone.

The EPICS-based control system at the institute was expanded with new archiving systems. New collaboration tools (Powerfolder, Sandstorm) have been installed. A new electronic lab-book system (labfolder) is in trial operation. If it proves itself it will replace the existing elog system (used for 7 years) lossless.

An IDP (Identity Provider, Shibboleth) was established which is part of the DFN-AAI test federation. We are looking for further tests. Full integration into the pan-european data network GÉANT is planned.

Some software and hardware projects have been implemented to support the administration (Guestapartment reservation, time recording, access control, electronic holiday management).

In order to save on running costs, the telephone provider was changed. We have thus halved the monthly costs for this service. To meet the new network topology, the telephone system has been restructured and new remote units (ACT) have been installed in each building on the campus (including Archiv der MPG and Harnack-Haus). We



thus meet all security requirements that cannot be realized cost-effectively by VoIP. This ensures the future viability of the existing system.

At the end of the year we plan to expand the compute cluster with GPU-nodes to meet the increased demand for parallel computing (BAR application).

#### *Electronics (E-) Lab (Head: Georg Heyne)*

The service group for electronics with about fifteen employees, headed by Georg Heyne, is a central facility that supports the research in the scientific departments. Its primary task is the design, development and construction of complex measuring and control equipment for the experiments, equipment that is not available on the commercial market. An important function of the E-lab is its electro-technical consulting service; advising and supporting the researchers in the configuration and modification, the acquisition and adaptation of electronic equipment and hardware for their experiments. The researchers are also supported in the development and implementation of LabView software for experiment control and measurement. The E-lab has a large stock of spare components and rentable equipment, allowing for fast and inexpensive pilot tests. The rapid-repair service for damaged devices (more than 150 during the last two years) is very important for a smooth continuation of the experiments and is highly appreciated by the researchers.

During the last two years, the E-Lab has developed about 330 different devices, many of which involve high-frequency analogue electronics and complex digital technology. For experiments with the FHI-FEL, for instance, ultrafast ( $> 1$  GHz) amplifiers for pyrodetectors as well as equipment to provide low-jitter trigger signals ( $< 100$  fs) was developed and tested. The latter was essential for the successful synchronization of a 55 MHz femto-second laser system to the FHI-FEL, as described in some more detail in the caption of the block-diagram shown below.



including practical training, entitled "*Introduction to Electrical Metrology*" has been organized by the E-lab for researchers of the FHI in July of 2017. The E-lab has also provided (longer) interships for several refugees, partly in preparation for a (master) study at the TU or FU Berlin.

### *Mechanical Workshops (Head: Petrik Bischoff)*

The mechanical workshop is divided into three departments:

Precision Engineering: 16 technicians, 1 apprentice

Mechanical Technology: 2 technicians

Wood Technology: 1 technician

In general, all departments deal with the following topics and tasks:

1. The construction and development of scientific instruments and apparatuses.
2. The creation of CAD drawings.
3. The processing of different types of materials such as metals, plastics and ceramics of various specifications by means of conventional and computer-aided manufacturing processes including turning, milling, electrical discharge machining (EDM), soldering, welding, grinding and polishing.
4. The production of prototypes by means of 3D printing processes.

The workshop continuously supports the scientific departments of the Fritz-Haber-Institute with high precision and quality of work. Complex assemblies and individual parts are developed and manufactured in close collaborative work with the scientists. The demanding scientific requirements, regarding the accuracy of components and application of new materials, demand a permanent modernization or reorientation of machines and equipment. Modern technologies must be recognized and used if necessary to ensure a high-level service and support. In this regard, all employees must be trained and specialised in new production processes to further improve their skills and maintain the high quality of work.

In 2013 a 5-axis controlled CNC milling machine as well as a start hole EDM machine were installed. In 2015 the workshop was further equipped with a CNC lathing machine which allows manufacturing of parts by applying a combination of turning and milling. The quality in our cutting service has considerably improved due to the installation of both a horizontal and vertical band saw in 2016. Furthermore, an additional 5-axis CNC

milling machine is available since February 2017 offering a spindle speed of up to 18,000 rpm. It is mainly used for aluminum and plastic processing in order to meet the high requirements on surface finish. In addition, mechanical grinding / vibratory grinding is used in the mechanical workshop. Based on this technology extremely highly polished surfaces can be produced. For example, such surface quality is important for high-voltage components used in high vacuum and ultra-high vacuum applications.

Since the beginning of 2017 two new 3D printing processes are available, which greatly complements the existing technologies within the mechanical workshop. Currently, new materials are being tested for a UV-curing 3D printing setup. First components, such as masks, were already successfully produced with a 3D printer provided by the AC department (see Fig.).

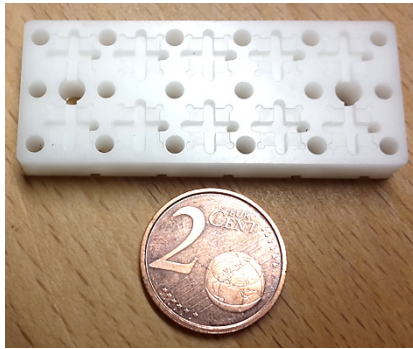


*Figure: Production example of the 3D printer for the department AC*

All above-mentioned machines and processes are operated and controlled by the highly skilled staff of the mechanical workshops. Each employee provides passion and experience to support the researchers in realizing their ideas, and thus, contribute to the success of many scientific projects at the Fritz-Haber-Institute.

#### *Central Services (Head: Sebastian Malotke)*

In 2015/16 a new Infrastructure was installed on the campus of the Fritz-Haber-Institute. Amongst other things it was the infrastructural renewal of the electro-technical services and the data-connection of all 17 buildings of the FHI which was in focus:

Towards this extensive underground engineering construction works was needed in order to sink shafts and conduit lines. Besides new electro-lines the new building R in which the Central Services are now located was also built. The transfer station for the medium-voltage-installation 10KV, a central server room, the central fire alarm system, the workshops and offices of the Central Services are now all located in building R.

Because of this new infrastructural management system the power supply works sustainably, efficiently and very reliable. This reliability is the result of installing 7 new transformers and a medium-voltage-ring-line, which is due to the newly built system easier to maintain. The old low-voltage distribution board has been restored according to recent rules and all 17 buildings received new house connections at low-voltage. All those procedures and activities including more than 40 switching operations were executed during on-going research operations.

The data technology with its new OS2 and OM4 connections between the buildings represents now the latest state of the art. The network will be adjustable to all future scientific demands because of the use of conduits. In order to build a basis for the direct link to the fire brigade a new LWL-ring-line has been installed in parallel. There is a new ground conductor in the incorporated line, which connects all buildings with each other. This led to an enormous improvement regarding earlier potential differences.

Finally all outside facilities had been restored and upgraded to a profitable and proactive factor for the FHI.

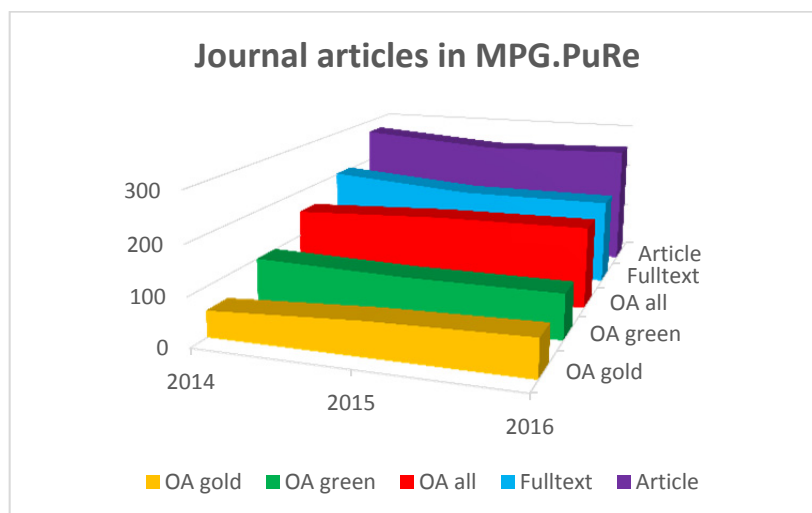
#### *Library (Head: Uta Siebeky)*

The library has focused on publication services over the last two years. The FHI researchers can obtain active support on all matters relating to publication management from the library. The publication output of the institute is displayed and managed via the electronic repository of the Max Planck Society MPG.PuRe ([pubman.mpdl.mpg.de](http://pubman.mpdl.mpg.de)). The Fritz Haber Institute is practicing open access to scientific results as stated in the *Berlin Declaration on Open Access to the Knowledge in the Sciences and Humanities*.

In addition 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 16,200 monographs in a reading room, which is designed as a common room for the whole institute. The library is also in close contact with internal and external collaborators. 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 Fritz Haber Institute is a pioneer within the Max Planck Society in the field of Open Access publishing. The board of directors of the Fritz Haber Institute recommends that researchers deposit a copy of each of their published journal articles on MPG.PuRe according to legal conditions and submit their work to Open Access journals. For the purification of legal issues the library collects the copyright transfer agreements.



The library is actively involved in the deposition of full texts according to the principles of the Berlin Declaration on Open Access. It 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. The library supports scientists financially when publishing articles in original open access journals. Through the library's ongoing commitment to the implementation of open access, a continuous increase of open access publications in MPG.PuRe can be determined. The FHI has published 66% of its journal articles in open access (green and gold) for the publication year 2016.

The library is involved in a project to develop an elaborated and appropriated workflow for publishing management for the Max Planck Institutes of the CPT section. In order to implement the project, the head of the library organizes regular meetings with colleagues from Leipzig and Magdeburg. In June 2017, a two-day workshop was organized for a larger group of colleagues. The next meeting will be held in September 2017 to specify the workflow.

*Administration (Heads: Ralf Nädele\*/Gert von Helden)*

Besides the daily tasks, related to institute finances, safety at work, human resources, purchasing, travel organization, guest housing, reception, cleaning, etc. our administrative service placed its work under the premise of an intensified dialog and a better mutual understanding between services and science. For that purpose, we started the cycle of “Service meets Science”.

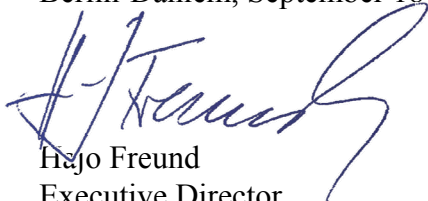
With this program, FHI directors and Group Leaders, invite all services (from the reception desk until the Electronic Lab) and explain what science is done within their specific department. It is usually followed by a visit of the department itself. This allows our non-scientific personnel to actually see where the Laser, purchased through central services, ended up and what it is doing. It also allows mechanics, electronics, etc. to discover their contributions within a running scientific system.

Thanks to Dr. Axel Knop-Gericke, we were also able to visit BESSY II while it was under maintenance and staff members could actually see the electron accelerator and understand how it works.

An intensified contact has been established between scientists in charge of research groups’ administrative staff in charge of supervising the implementation of the legal requirements. This helped to significantly improve documentation of the numerous measures already in place. This yearly “Safety Hour for Group Leaders” creates a platform where questions can be asked and new tendencies been communicated.

We would like to thank the General Administration and in particular the Presidium of the Max Planck Society for a trustful and constructive collaboration. We are all aware of the amount of work the Fachbeirat has to accomplish during its visit. The young students as well as the post-doctoral visitors, the staff scientists, and clearly the directors are most grateful to all members of the Fachbeirat and we are looking forward to interesting scientific discussions.

Berlin-Dahlem, September 18<sup>th</sup>, 2017



Hajo Freund  
Executive Director  
2016-2017

\* until September 2017

**International Max Planck Research School  
‘Functional Interfaces in Physics and Chemistry’**



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

**Spokesperson**

Martin Wolf, FHI

**Coordinator**

Tobias Kampfrath, FHI      until 06/2017      Alex Paarmann      since 07/2017

**Faculty Members**

|                          |               |                         |
|--------------------------|---------------|-------------------------|
| Mario Dähne, TU          |               | Klaus Rademann, HU      |
| Claudia Draxl, HU        |               | Thomas Risse, FU        |
| André Fielicke, TU       | until 03/2017 | Peter Saalfrank, UP     |
| Katharina Franke, FU     |               | Joachim Sauer, HU       |
| Hans-Joachim Freund, FHI |               | Matthias Scheffler, FHI |
| Tobias Kampfrath, FU     | since 07/2017 | Robert Schlögl, FHI     |
| Norbert Koch, HU         |               | Reinhard Schomäcker, TU |
| Gerard Meijer, FHI       | since 01/2017 | Martin Weinelt, FU      |
| Beate Paulus, FU         |               | Martin Wolf, FHI        |

**PhD-Student Members**

|                                       |                    |                                        |                    |
|---------------------------------------|--------------------|----------------------------------------|--------------------|
| Alexandr Alekhin, <i>Russia</i>       | <i>until 02/16</i> | Dominic Lawrenz, <i>Germany</i>        | <i>since 01/17</i> |
| Maristella Alessio, <i>Italy</i>      | <i>since 10/16</i> | Adrián Lewandowski, <i>Argentina</i>   |                    |
| Stephan Appelfeller, <i>Germany</i>   |                    | Xiaoke Li, <i>China</i>                |                    |
| Smadar Attia, <i>Israel</i>           | <i>since 10/16</i> | Bo-Hong Liu, <i>Taiwan</i>             | <i>until 12/15</i> |
| Matthias Baldofski, <i>Germany</i>    |                    | Lukas Marsoner, <i>Italy</i>           | <i>until 06/17</i> |
| Kevin Bethke, <i>Germany</i>          |                    | Giacomo Melani, <i>Italy</i>           | <i>since 10/15</i> |
| Kamil Bobowski, <i>Germany</i>        |                    | Francesca Mirabella, <i>Italy</i>      |                    |
| Earl Davis, <i>Great Britain</i>      |                    | Eike Mucha, <i>Germany</i>             | <i>since 07/17</i> |
| Jan-Christoph Deinert, <i>Germany</i> | <i>until 04/16</i> | Christopher Nicholson, <i>Scotland</i> |                    |
| Petr Dementyev, <i>Russia</i>         | <i>until 06/16</i> | Andrzej Niedziela, <i>Poland</i>       | <i>until 12/15</i> |
| Maria Dragoumi, <i>Greece</i>         | <i>since 01/17</i> | Leandro Pascua, <i>Spain</i>           | <i>until 06/15</i> |
| Emre Emmez, <i>Turkey</i>             | <i>until 12/15</i> | Nikolai Paßler, <i>Germany</i>         | <i>since 01/17</i> |
| Laetitia Farinacci, <i>France</i>     | <i>since 10/16</i> | Agata Plucienik, <i>Poland</i>         | <i>since 01/16</i> |
| Felix Feiten, <i>Germany</i>          | <i>until 04/16</i> | Maryline Ralaarisoa, <i>Madagascar</i> | <i>since 10/17</i> |
| Edoardo Fertitta, <i>Italy</i>        | <i>until 07/16</i> | Nina Richter, <i>Germany</i>           |                    |
| Vinzenz Fleischer, <i>Germany</i>     | <i>until 12/16</i> | Daniela Rolf, <i>Germany</i>           |                    |
| Alexander Fuhrich, <i>Germany</i>     |                    | Reza Rouzegar, <i>Iran</i>             | <i>since 08/17</i> |
| Francesca Genuzio, <i>Italy</i>       | <i>until 02/16</i> | Nora Salas Illanes, <i>Chile</i>       |                    |
| Vivekanand Gobre, <i>India</i>        | <i>until 08/16</i> | Robert Scholz, <i>Germany</i>          |                    |
| Lukas Hammerschmidt, <i>Germany</i>   | <i>until 06/15</i> | Thorsten Schultz, <i>Germany</i>       |                    |

<sup>1</sup> Abbreviations: FU: Freie Universität Berlin; HU: Humboldt-Universität zu Berlin; TU: Technische Universität Berlin; FHI: Fritz-Haber-Institut; UP: Universität Potsdam

|                                      |                    |                                        |                    |
|--------------------------------------|--------------------|----------------------------------------|--------------------|
| Maria Heenemann, <i>Germany</i>      | <i>until 07/17</i> | Jianchao Si, <i>China</i>              | <i>until 03/16</i> |
| Julius Heitz, <i>Germany</i>         | <i>since 07/17</i> | Xin Song, <i>China</i>                 | <i>until 03/17</i> |
| Mallikarjun Karra, <i>India</i>      |                    | Christian Stemmle, <i>Germany</i>      |                    |
| J. Frieder Kettemann, <i>Germany</i> | <i>until 05/17</i> | Stefanie Stuckenholtz, <i>Germany</i>  | <i>until 04/16</i> |
| Sophia Ketterl, <i>Germany</i>       |                    | David Yubero Valdivielso, <i>Spain</i> |                    |
| Tim Küllmey, <i>Germany</i>          | <i>since 02/17</i> | Kristin Werner, <i>Germany</i>         | <i>since 04/16</i> |
| Arpan Kundu, <i>India</i>            |                    | Elisabeth Wolf, <i>Germany</i>         |                    |
| Ka Wei Lau, <i>China</i>             | <i>since 10/16</i> |                                        |                    |

## 1. General Remarks

The International Max Planck Research School (IMPRS) at the Fritz Haber Institute (<http://www.imprs-cs.mpg.de>) was launched in 2002 under the name ‘Complex Surfaces in Materials Sciences’ with Hajo Freund as its spokesperson. After successful evaluation in September 2014 with the new name ‘Functional interfaces in physics and chemistry’ (spokesperson Martin Wolf) the school is now in the middle of its third funding period (10/2014-09/2020). The previous IMPRS coordinator Tobias Kampfrath recently accepted a professorship at the FU Berlin and from July 2017, Alexander Paarmann (PC department) has taken over the coordination of the school.

The IMPRS is a structured PhD program that aims at attracting outstanding students from all over the world. 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 Berlin, the Humboldt-Universität zu Berlin, the Technische Universität Berlin, 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.

The budget of the school comprised of ~400 T€/p.a. provided by the General Administration of the Max Planck Society as requested, complemented by an additional ~200 T€/p.a. that have entered our budget in the form of salaries paid directly by the FHI and the partner universities. Additionally, the Friede Springer Foundation financed one student salary in 2015. The majority of these funds (~ 80 %) was spent for the salaries of IMPRS students. With the remaining budget all school activities including guest speakers, seminars, workshops for the students and secretary office are financed.

We currently look at a total of 117 IMPRS students, counting the present (35) students as well as those 82 students who graduated between 2005 and 2017. About 53 % of the students came from eighteen different foreign countries, for example Italy, Israel, Scotland, Greece, China, South America and India. The total published output amounts to an average of 4-6 papers per student. On average, 4 years were required to obtain a doctoral degree. Most of the students

finished their PhD either with the mark ‘very good’ (‘magna cum laude’: 76%) or ‘with distinction’ (‘summa cum laude’: 18%). Particular highlights 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’, the ‘Edith Flanigen Award’, the Fischer-Nernst Award’ or the ‘Wilhelm-Ostwald-Nachwuchspreis’. With their excellent education, the IMPRS students also had very good career perspectives after obtaining the Ph.D., where many continued to pursue an academic career path. The remainder almost instantaneously found positions in R&D or management units in, often technologically oriented, big German enterprises, such as Siemens or BASF.

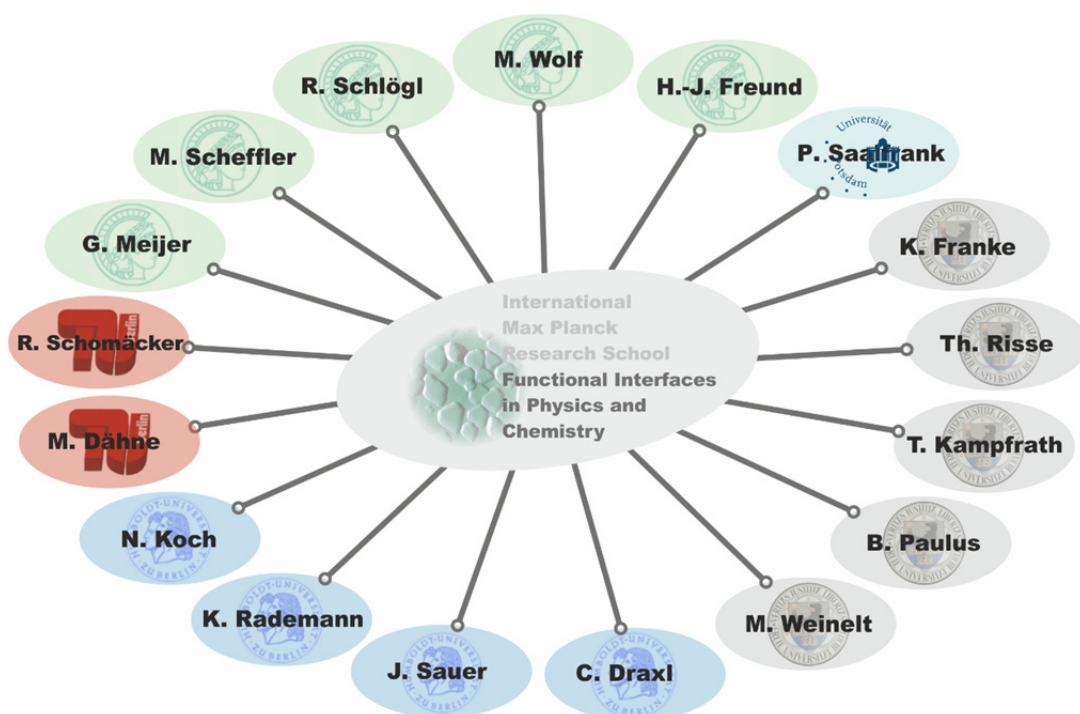


**Figure 1:** Scientific members of the IMPRS ‘Functional Interfaces in Physics and Chemistry’ as of July 2017 (green: FHI, grey: Freie Universität Berlin, blue: Humboldt-Universität Berlin, red: Technische Universität Berlin, light-blue: Universität Potsdam).

## 2. Research achievements

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. All those systems were analyzed with respect to their structural, electronic,

magnetic and optical properties. Adsorption and reactivity studies were performed in order to provide insight into chemical processes taking place at complex surfaces and interfaces. These studies aimed at gaining a better understanding of elementary steps taking place in heterogeneous catalysis and bridge the experiments performed in a laboratory environment to industrial applications. Other experimental achievements were obtained in the fields of ultrafast electron dynamics and surface magnetism, in the characterization of gas-phase molecules and clusters, and in the synthesis of complex materials with yet unrivalled catalytic properties. In the new funding period, new member groups augmented the scientific profile of the school with such topics as interface-specific and ultrafast spectroscopies, charge-transfer across interfaces of organic photovoltaic materials. In addition to experimental work, there is a broad range of theoretical activities being accomplished within the school, and the close connection between theory and experiment is one particular aim of the IMPRS.

### **3. 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’. The respective infrastructure developed during the first two funding periods was found extremely effective and, therefore, continues to ensure high quality of the education provided by the IMPRS. 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 components, (i) two week-long block-courses per year, (ii) bimonthly discussion meetings with the coordinator, and (iii) a number of soft-skill seminars organized by external experts.

The *block courses* 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 and interfaces, with typical topics such as ‘Fundamentals of solids and their interfaces and surfaces’. The advanced courses (held in fall) address more specialized topics associated with surfaces and interfaces, such as ‘Fundamentals of temperature-programmed desorption’ and ‘Application of transition state theory to surface 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, which amounted to a total of 52 lectures given between the fall of 2015 and the spring of 2017. These featured a total of 8 external speakers.

The 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. Notably, 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 ground of experimental and theoretical methods and concepts for all IMPRS students with their different fields of research (chemistry, physics, material science).

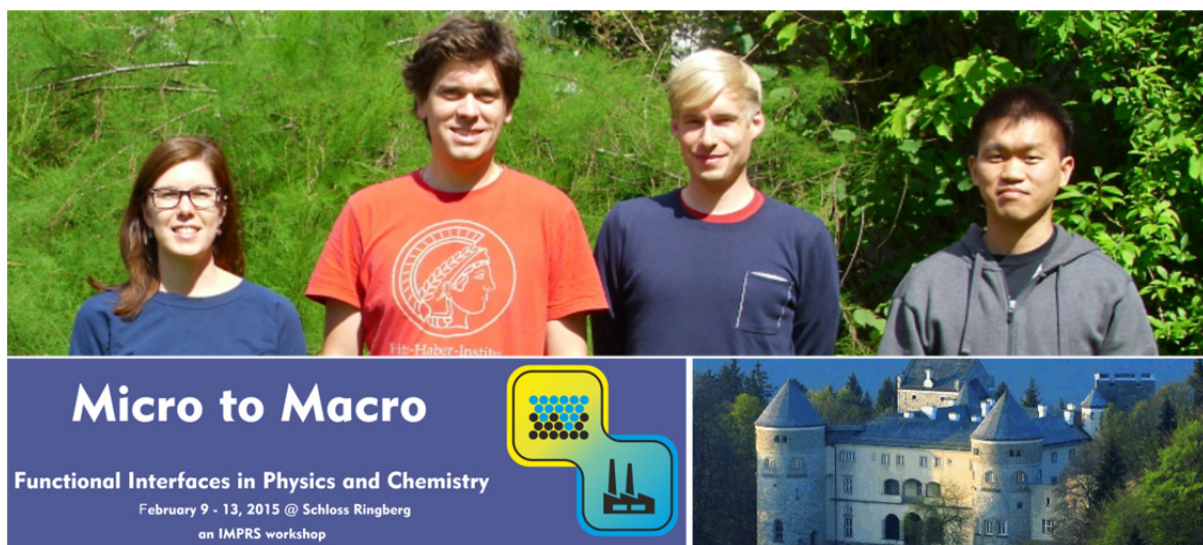


**Figure 2:** IMPRS workshop “Micro to Macro” held in February 2015 at Schloss Ringberg. This special block course was entirely student organized (organization committee from left to right: Stefanie Stuckenholtz, Felix Feiten, Jan-Christoph Deinert, Bo-Hong Liu), featuring 16 well-recognized international speakers.

A particular highlight of the IMPRS *block course* concept is the triyearly student-organized workshop held at Schloß Ringberg in Bavaria, the latest of which held in February 2015 (<http://www.imprs-cs.mpg.de/workshop2015>), see Fig. 2. The IMPRS students 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 was developed by the students providing 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. The next student organized workshop at Schloß Ringberg will be held in February 2018, and the current IMPRS students are eagerly working on the preparations.

The *discussion meetings* (held typically 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, every IMPRS student presents her/his scientific results twice throughout the program, once as a mid-term and once shortly before the Ph.D. defense. These regular talks in front of the school stimulate lively discussions that often provide critical feedback on their scientific work, but also helps the students to improve their presentation skills. The latter is specifically facilitated since each speaker receives written feedback in the form of two templates that two students fill out and that addresses various aspects of the quality of the presentations. In general, the discussion meetings are key to establish and maintain the scientific coherence of the school, as all ongoing research activities are introduced and analyzed. We want to emphasize the open, casual, and informal atmosphere of these meetings that fosters an active participation (especially of young students) and provides an ideal framework 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 2015 to 2017, the following soft-skill seminars have been organized by the School (Table 1). Additionally, the various language classes offered and financed by the FHI are also open to all IMPRS members, who often make use of this opportunity.

| <b>Date</b>           | <b>Topic</b>                                    | <b>Lecturer</b>          |
|-----------------------|-------------------------------------------------|--------------------------|
| 04.-05. June 2015     | Academic Writing                                | Prof. Warren Kretzschmar |
| 15.–16. March<br>2016 | Effective Presentation                          | F. Steven Weir           |
| 05.-06. April 2016    | Effective Presentation                          | F. Steven Weir           |
| 28.-29. June 2016     | Academic Writing:<br>“How to create good texts” | Prof. Warren Kretzschmar |
| 24.-25. Jan. 2017     | “Network and Job Hunting”                       | Rob Thompson             |
| 21.–22. March<br>2017 | Effective Presentations                         | F. Steven Weir           |

| Date                            | Topic                   | Lecturer       |
|---------------------------------|-------------------------|----------------|
| 12.-13. & 19.-20.<br>Sept. 2017 | Effective Presentations | F. Steven Weir |

**Table 1:** *Soft-skill seminars offered to the IMPRS students in the period of 2015-2017.*

### **List of lecture courses organized by the IMPRS**

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.

Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,

Fritz-Haber-Institut der MPG, October 2015 - Febr. 2016.

IMPRS-Block Course: ‘Fundamentals of Molecules, Clusters, Solids and their Interfaces’,

Humboldt-Universität zu Berlin, March 21 - April 01, 2016.

IMPRS-Block Course: ‘Methods of Modern Interface/Surface Science’,

Fritz-Haber-Institut der MPG, October 04 - 14, 2016.

Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,

Fritz-Haber-Institut der MPG, October 2016 - Febr. 2017.

IMPRS-Block Course: ‘Fundamentals of Solids and their Interfaces and Surfaces’,

Fritz-Haber-Institut der MPG, March 27 – April 06, 2017.

IMPRS-Block Course: ‘New Concepts in Experimental and Theoretical Surface Science’

Freie Universität Berlin, September 26 - October 10, 2017.

Lecture Series: ‘Modern Methods in Heterogeneous Catalysis Research’,

Fritz-Haber-Institut der MPG, October 2017 - Febr. 2018



## PhD-Projects within the IMPRS (2015-2017)

*Alekhin, Alexandr*, Russia, Supervisors: Prof. Wolf/Prof. Weinelt (FHI/FU),

“Ultrafast hot carrier driven magnetization dynamics”.

*Alessio, Maristella*, Italy, Supervisors: Prof. Sauer/Prof. Schüt (HU)

“Multi-level hybrid QM: QM methods: Implementation and applications on extended periodic systems”.

*Appelfeller, Stephan*, Germany, Supervisor: Prof. Dähne (TU)

“Atomic structure and electronic properties of rare earth silicide nanowires”.

*Attia, Smadar*, Israel, Supervisors: Prof. Freund/Prof. Risse (FHI/FU)

“Enantioselective reactions on model chirally modified surfaces”.

*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”.

*Davis, Earl*, Great Britain, Supervisor: Prof. Freund (FHI),

“Growth and characterisation of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{S}$  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”.

*Dragoumi, Maria*, Greek, Supervisors: Prof. Scheffler (FHI)

“Electron-phonon coupling in metal-oxides”

*Emmez, Emre*, Turkey, Supervisors: Prof. Rademann/Prof. Freund (HU/FHI),

“The reactivity studies of aluminosilicate (Zeolite) thin films grown on Ru (0001) substrate”.

*Farinacci, Laetitia*, France, Supervisor: Prof. Franke (FU)

“Magnetism of metal-organic networks investigated by scanning tunneling microscopy”

*Feiten, Felix E.*, Germany, Supervisors: Prof. Freund/Prof. Risse (FHI/FU),

“The surface structure of  $\text{V}_2\text{O}_3(0001)$ ”.

*Fertitta, Edoardo, Italy*, Supervisors: Prof. Paulus (FU),  
“Ab-initio investigation of metal-insulator transitions in strongly correlated low dimensional systems”.

*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 Na<sub>2</sub>WO<sub>4</sub>-Mn-SiO<sub>2</sub>-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),  
“Efficient modelling of linear electronic polarization in materials using atomic response functions”.

*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),  
“Charge transfer in catalysis studied by in-situ microwave cavity perturbation techniques”.

*Heitz, Julius, Germany*, Supervisors: Prof. Wolf/Dr. Kampfrath (FHI/FU),  
“Magnetism at terahertz frequencies”.

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

*Kettemann, J. Frieder, Germany*, Supervisors: Prof. Rademann/Prof. Freund (HU/FHI),  
“Electrostatically stabilized noble metal nanoparticles: syntheses and catalytic properties”.

*Ketterl, Sophia, Germany*, Supervisors: Prof. Weinelt/Prof. Rader (FU/HZB),  
“Two-photon photoemission on topological insulators”.

*Küllmey, Tim, Germany*, Supervisor: Prof. Paulus (FU),  
“Theoretical investigations of the electronic structure of interfaces in kesterite thin film solar cells”.

*Kundu, Arpan*, India, Supervisors: Prof. Sauer/Dr. Christen (HU),  
 “*Ab initio* prediction of adsorption isotherms of gases in metal organic framework”.

*Lau, Ka Wei*, China, Supervisor: Prof. Draxl (HU),  
 “Structure and excitations of interfaces between two-dimensional systems”

*Lawrenz, Dominic*, Germany, Supervisor: Prof. Weinelt (FU),  
 “Ultrafast magnetism dynamics by time-resolved photoemission”.

*Lewandowski, Adrián*, Argentina, Supervisor: 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.*, Austria, Supervisor: Prof. Paulus (FU)  
 “Electron correlation effects in layered structures – a theoretical first-principles study”.

*Melani, Giacomo*, Italy, Supervisor: Prof. Saalfrank (Uni Potsdam),  
 “Modelling of non-adiabatic processes at 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”.

*Mucha, Eike*, Germany, Supervisors: Prof. Meijer/Prof. Pagel (FHI/FU),  
 “Carbohydrate ions in helium droplets”.

*Nicholson, Christopher*, Scotland, 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 “.

*Paßler, Nikolai*, Germany, Supervisor: Prof. Wolf (FHI),  
 “Nonlinear interactions of surface phonon polaritons in polar”.

*Plucienik, Agata*, Poland, Supervisor: Prof. Freund (FHI),  
 “Vibrational spectroscopy of deposited clusters with FEL radiation”.

*Ralaizarisoa, Maryline*, Madagaskar, Supervisor: Prof. Koch (HU),  
 “Electronic structure of interfaces with perovskites and Si in hybrid solar cells”.

*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”.

*Rouzegar, Reza*, Iran, Supervisors: Prof. Wolf/Dr. Kampfrath (FHI/FU),  
 “Terahertz emission spectroscopy of magnetic multilayers”.

*Salas Illanes, Nora*, Chile, Supervisors: Prof. Draxl/Prof. Scheffler (HU/FHI)  
 “Quasiparticle selfconsistent GW (QSGW)”.

*Scholz, Robert*, Germany, Supervisor: Prof. Saalfrank (Uni Potsdam),  
 “Laser- and electron driven adsorbate dynamics at metal surfaces: Electronic friction approaches and beyond”.

*Schultz, Thorsten*, Germany, Supervisor: 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),  
 “Vanadium doped TiO<sub>2</sub>(110) thin layers: preparation, structure, and reactivity – methanol partial oxidation “.

*Stemmle, Christian*, Germany, Supervisor: Prof. Paulus (FU),  
 “Big-data in quantum chemistry: analysis of electron correlation in strongly correlated systems (N<sub>2</sub>/N<sub>2</sub><sup>+</sup>)”.

*Stuckenholtz, Stefanie*, Germany, Supervisors: Prof. Freund/Prof. Dähne (FHI/TU),  
 “Combining scanning probe microscopy with temperature programmed desorption on metal supported MgO thin films “.

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

*Werner, Kristin*, Germany, Supervisor: Prof. Freund (FHI),

“Chemistry of CO<sub>2</sub> on metal oxide thin films”.

*Wolf, Elisabeth*, Germany, Supervisors: Prof. Schlögl/Prof. Risse (FHI/FU),

“Charge transport in metal/metal oxide composite catalysts under reaction conditions”.

## **The FHI Free Electron Laser Facility**

# **The FHI Free Electron Laser Facility**

**Head: Wieland Schöllkopf**

## **Summary**

The infrared free electron laser at the Fritz Haber Institute (FHI-FEL) provides intense, tunable infrared radiation to user groups from the experimental departments of the FHI. Since the last meeting of the Fachbeirat in November 2015 a variety of new results have been obtained by applying the FEL radiation to experiments ranging from molecular spectroscopy, spectroscopy of gas-phase clusters and nanoparticles to non-linear spectroscopy of solids and to surface science. In the following, selected user results are summarized and the corresponding links to the user groups' reports in this booklet are provided.

In addition to supplying infrared radiation to our users we have continuously expanded the operating range of the FEL in terms of wavelength, power, and stability. Also, another mode of operation, a reduced repetition rate mode, has been implemented and is available in routine user operation. The reduced repetition rate mode allows for synchronizing femtosecond pulses from a table-top laser to the FEL-pulses with about 100 fs timing jitter. Furthermore, our plans for a system upgrade to a 2-color FEL have been worked out at a detailed technical level. These developments as well as ongoing plans to extend the facility's user lab space will be presented below.

## **1. Introduction**

The wavelength region from 3 to 100  $\mu\text{m}$  is often referred to as the molecular fingerprint region, because fundamental vibrational modes of molecules, clusters or solid materials are to be found in this region. As vibrational modes represent a direct probe of molecular structure, IR spectroscopy is one of the basic methods for molecular structure determination. Moreover, IR radiation can induce reactions and folding dynamics of (bio-) molecules, which can thus be studied as well. In addition, a variety of excitations in solids, including lattice phonons, excitons, or low-energy electronic transitions, lie in the mid- to far-infrared wavelength range.

Several research projects at the FHI take advantage of the possibilities offered by the tunable FHI-FEL radiation. These investigations include: (i) vibrational spectroscopy of metal and metal-oxide clusters in the gas phase; (ii) vibrational spectroscopy of macro-molecules (*e.g.*, peptides and small proteins) in the gas phase or embedded in helium nano-droplets at 0.4 K; (iii) nonlinear spectroscopy based on second-harmonic generation in the Reststrahlen bands of solids such as silicon carbide; and (iv) surface sensitive vibrational spectroscopy of well-

characterized surfaces or of metal clusters adsorbed on such surfaces. The experiments are made possible by the wide tunability, high pulse energy, and narrow spectral width of the FEL radiation. For instance, spectroscopy of optically thin samples in the gas phase exploits the high average photon flux, resonant (vibrational) pumping benefits from the narrow bandwidth of the FEL and nonlinear IR spectroscopy is made possible by the high field strengths that can be achieved when the FEL radiation is focused.

The FHI-FEL generates macro-pulses ( $\leq 10 \mu\text{s}$  long pulse trains at 5 or 10 Hz repetition rate) consisting of several thousand micro-pulses at a repetition rate of 1 GHz. The energy per micro-pulse is close to 10  $\mu\text{J}$  corresponding to 50 - 100 mJ per macro-pulse. The micro-pulse length of just a few ps determines the (Fourier limited) spectral width of typically  $\sim 0.5\%$  FWHM (full width at half maximum) of the central wavelength, which can be reduced to 0.3% at the expense of pulse energy, if needed. The peculiar time structure of the FEL radiation is advantageous, for example, for multiple-photon excitation experiments, when a single photon per micro-pulse can be absorbed many times repeatedly within a macro-pulse, thereby enabling absorption of a large number of photons per macro-pulse. For other studies, such as time-resolved pump-probe experiments in the condensed phase, a pulse structure with a reduced micro-pulse repetition rate is often better suited as this minimizes heating and accumulation effects. As described below, this additional mode of operation is also routinely available at the FHI-FEL.

## **2. Design and specifications of the FHI-FEL**

A detailed description of the FHI-FEL was given at the last meeting of the Fachbeirat; here, we briefly summarize the FEL's main features. The mid-infrared (MIR) FEL, generating wavelengths up to  $\sim 50 \mu\text{m}$ , has been fully operational since November 2013. A possible far-infrared (FIR) FEL has initially been projected as a future upgrade (see Fig. 1). A normal-conducting linear accelerator provides electrons with a beam transport system feeding either of the two FEL branches or the electron diagnostics beamline.

### **2.1 Electron accelerator**

The accelerator system combines a thermionic electron gun, a sub-harmonic buncher cavity and two S-band (2.99 GHz) copper linacs. The first of the two linacs accelerates the electron bunches to a constant energy of 20 MeV. The second one 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 IR radiation pulses essentially inherit this time structure from the electron bunches leading to the above mentioned micro/macro pulse structure. Tab. 1 summarizes the specifications of the electron accelerator system.

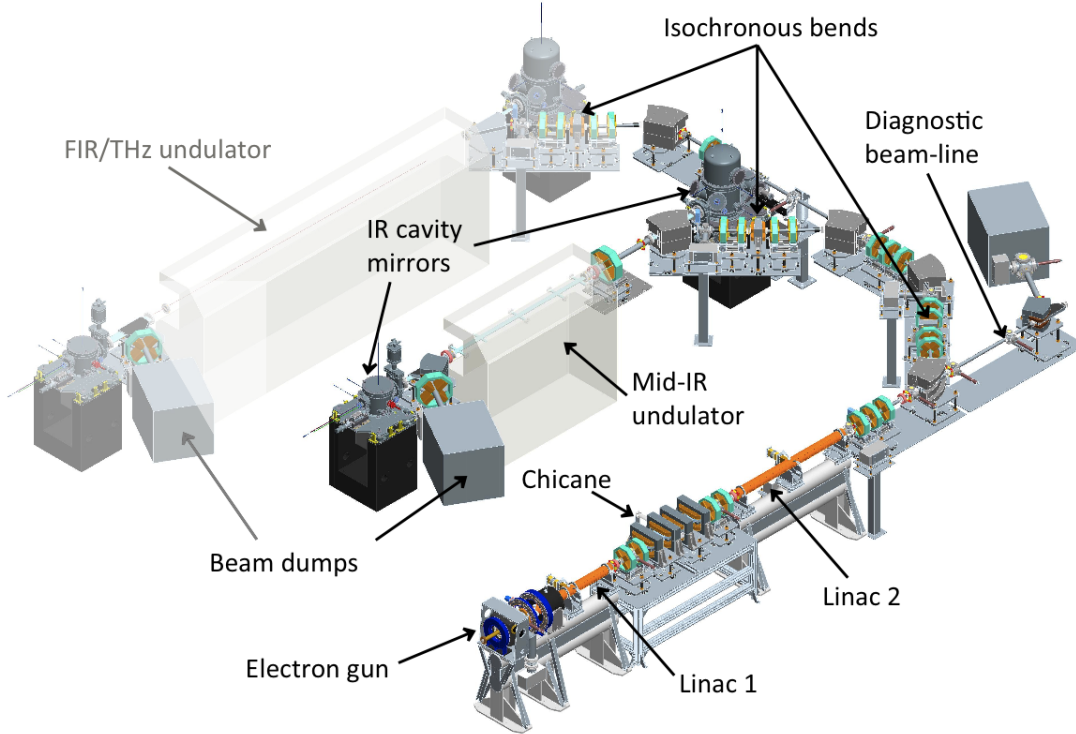


**Figure 1:** Overview of the FHI-FEL installation showing the electron accelerator system, the MIR FEL (operational), as well as the (not yet existing) FIR FEL as it was initially envisaged. A slightly modified FIR FEL design, which allows for 2-color IR/IR pump-probe experiments is outlined at the end of this report.

| Parameter             | Unit    | Typical                   |
|-----------------------|---------|---------------------------|
| Electron energy       | MeV     | 18, 23, 26, 31, 36, or 43 |
| 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    | $\mu$ s | 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 Design and performance of the MIR FEL

In the MIR FEL a planar hybrid-magnet undulator (2 m long, 50 periods) is located within a 5.4 m long IR cavity formed by two concave gold-coated copper mirrors. One of the cavity mirrors is mounted on a precision translation stage allowing for fine adjustment of the cavity length with 1  $\mu\text{m}$  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  $L_0 - q \lambda$ , where  $L_0$  is the nominal cavity length of 5.4 m,  $\lambda$  is the IR wavelength,  $q$  is a user defined factor (usually  $0 < q < 10$ ), and  $\Delta L = q \lambda$  is the cavity detuning. Keeping the cavity detuning at a constant multiple of  $\lambda$  during a wavelength scan significantly increases the wavelength range accessible by an undulator gap scan for a given electron beam energy. In addition, it permits to keep the relative bandwidth of the FEL radiation constant over the scan range.

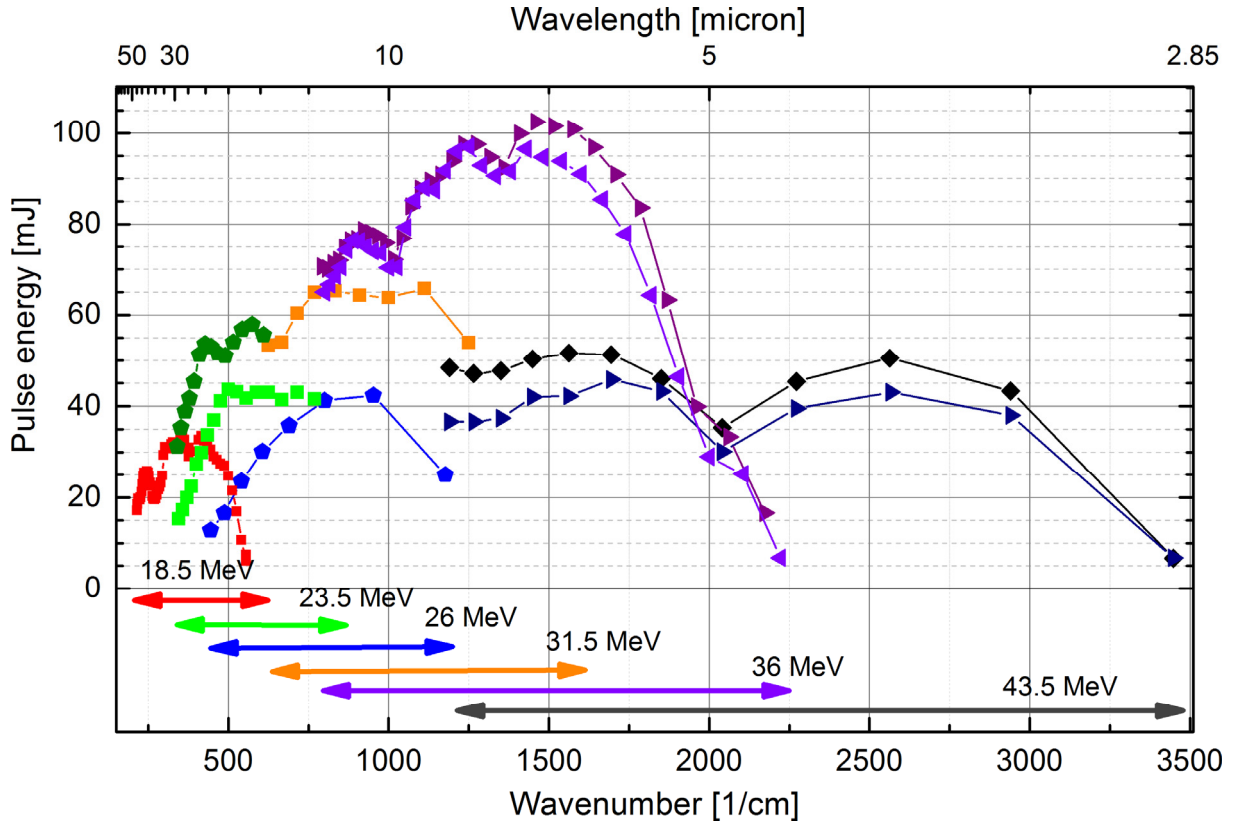


**Figure 2:** Macro-pulse energies measured at narrow bandwidth conditions for six usually used electron energies from 18.5 to 43.5 MeV. Different traces correspond to different electron energies and/or different tunings of the accelerator and/or different settings of the FEL cavity. The arrows at the bottom indicate the wavelength ranges covered by the various electron energies.

The IR pulses coupled out from the FEL cavity pass through an 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.

Measurements of the FEL macro-pulse energy as a function of wavelength are shown in Fig. 2. Lasing has been achieved from 2.9 to 48  $\mu\text{m}$  covering the entire MIR wavelength range. Each trace in Fig. 2 corresponds to an individual machine tune-up, which can slightly vary depending on the spectral width requested by the user. All data shown in Fig. 2, however, correspond to narrow spectral widths between 0.3% and 0.7% (relative FWHM).

### 2.3 Synchronization of an ultrashort pulse table-top laser to the FEL

The group of Alexander Paarmann (PC) embarked on a project to do sum-frequency generation (SFG) spectroscopy and pump-probe experiments by combining the FEL pulses with ultrashort pulses from a table-top laser (see the group's report in the PC section of this booklet). To this end the group operates an Yb-doped fiber laser generating 100 fs long pulses of 45 nJ energy at a central wavelength of 1050 nm with a repetition rate of 55.6 MHz. The latter was chosen because it matches the FHI-FEL's 2-pulse mode. The standard 1 GHz micro-bunch repetition rate 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 simultaneously in the cavity. 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 27.8 MHz. Thus, the 2-pulse mode operates at a pulse repetition frequency of 55.6 MHz. The possible few-pulse modes of the FHI-FEL together with the corresponding repetition rates are listed in Table 2. The modes with rates of less than 200 MHz have been **implemented and are available for user operation.**

| 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 in the 5.4 m long MIR FEL cavity.

To synchronize the fs-laser to the FEL micro-pulses, a commercial clock transfer system (Libera Sync. 3) has been installed. It transfers the 3 GHz reference signal of the FEL's electron accelerator by an optical fiber link over a distance of about 80 m to the user lab, where it is used to generate a feedback signal locking the fs-laser pulses to the 3 GHz reference with a precision specified to  $< 100$  fs. For optical cross-correlation measurements, sum-frequency generation (SFG) in a non-linear crystal (GaSe) is employed. Specifically, a balanced optical cross-correlation (BOC) scheme was implemented, which allows to extract the single-shot timing through two simultaneous, correlated SFG measurements, see Fig. 3a. A very low timing jitter of only  $\sim 100$  fs (rms) was observed (Fig. 3b). Long-term timing drifts of a few ps/hour were found to be clearly correlated to energy drifts of the accelerated electron bunches, accompanied by small shifts in the FEL wavelength. Therefore, it should be possible to further reduce the residual drift and jitter by optimizing the stability of the RF system, for instance by implementing feedback loops to actively stabilize the electron energy.

Finally, this high degree of synchronization allowed the group to study the FEL micro-pulse shape in great detail, which is directly acquired through the SFG signal in each arm of the BOC. This is shown Fig. 3c, for a specific setting of the cavity detuning ( $\Delta L = 1.5 \lambda$ ). The SFG map shows the evolution of the FEL micro-pulse during the macro-pulse. The slightly shortened cavity results in a continuous shift of the pulse timing (sloped lines), gain saturation, and buildup of multiple pulses, resulting in the well-known limit-cycle power oscillations. This direct measurement of the pulse-shape provides unprecedented insight into the dynamics of the lasing process, allowing further optimization and providing crucial information for future time-resolved experiments.

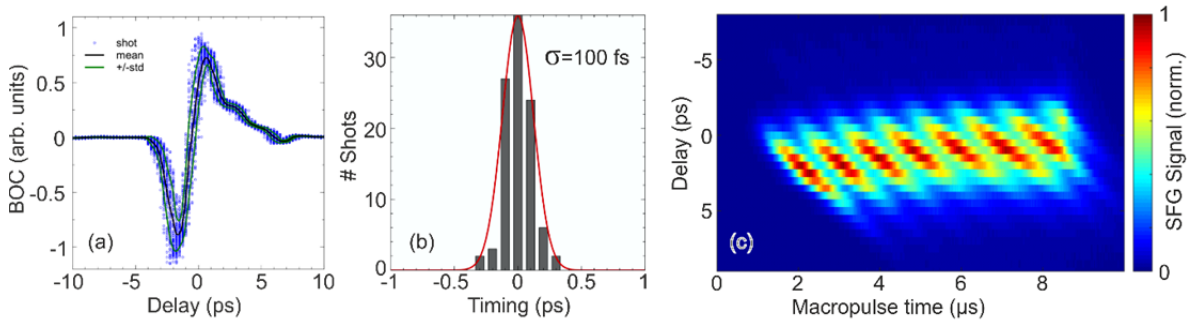


**Figure 3:** Timing and shape of the FEL micro-pulses. (a) Balanced optical cross-correlator signal as the table-top laser timing is scanned with respect to the FEL pulses. In the central, linear region of the curve, the BOC signal directly correlates with the FEL pulse timing, allowing single shot timing measurements. Using this approach, the timing jitter (b) of the FEL is found to be about 100 fs (rms). (c) The macro-pulse time-resolved

*SFG signal directly maps out the FEL micro-pulse shape, here for a cavity detuning of  $1.5 \lambda$ . Well-known limit-cycle oscillations of the FEL power are observed with unprecedented clarity in these signals.*

### **3. FHI-FEL facility and user projects**

The FEL and the user facility are operated by Wieland Schöllkopf (scientist in charge) and Sandy Gewinner (laser engineer). Engineers and scientists from FHI departments provide additional support. For instance, development and administration of the FEL's control system is performed by Heinz Junkes from the computer support group *PP&B*. In addition, Wolfgang Erlebach (engineer) and Andreas Liedke (electrician), both from the MP Department, provide engineering design (*e.g.*, of the IR user beamlines) and installation support, respectively. Also the scientists Gert von Helden (MP) and Alexander Paarmann (PC), whose groups have been using the FHI-FEL radiation most intensively, have been contributing continuously to various aspects of the FEL project including, *e.g.*, the upgrade plans described below. Yuanfang Xu, a visiting PhD-student from the University of Science and Technology China (USTC), Hefei, PR China, whose 18 month Study Abroad Program fellowship from the Chinese Scholarship Council ended, went back to the USTC, where he plans to participate in FELiChEM, a project to build the first Chinese IR FEL facility.

A total of 7 research projects are operational in the basement and ground floor of Building D, adjacent to the FEL-Building (Bldg. E). The experiment of the Kuhlenbeck group (CP) was the most recent to get operational in April 2016. In alphabetical order of the group leaders:

1. Knut Asmis I (Guest-group at MP, Univ. Leipzig):

*Vibrational spectroscopy of gas phase clusters: catalysis, astrochemistry, atmospheric chemistry, and ion solvation*

2. André Fielicke (MP):

*Chemistry of transition metal clusters*

3. Gert von Helden I (MP):

*IR spectroscopy of bio-molecules embedded in helium nano droplets*

4. Gert von Helden II (MP) and Kevin Pagel (Guest-group at MP, FU Berlin):

*IR spectroscopy of bio-molecules combined with ion mobility mass spectrometry*

5. Helmut Kuhlenbeck (CP):

*Vibrational spectroscopy of surfaces and deposited clusters*

6. Alexander Paarmann I (PC):

*Nonlinear Solid State Spectroscopy*

7. Alexander Paarmann II (PC):

*FEL short pulse characterization*

Common to most user experiments at the FHI-FEL is the fact that spectra are not recorded by measuring the transmitted IR intensity as a function of wavelength. Especially for gas phase samples such an absorption signal would be too small to yield a decent signal-to-noise ratio. To circumvent this problem *action spectroscopy* is used instead: 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 the detachment of a weakly attached tag molecule, it can be the ejection of a molecule from a helium nano-droplet or the result of a chemical reaction, or it can be a change of optical or magnetic properties of a solid sample following excitation by the FEL radiation.

The experimental methods of the various FHI-FEL user groups are detailed in the reports of the individual departments, elsewhere in this booklet.

#### **4. Extension plans for the FHI-FEL facility lab space**

Extensive renovation work in Building D is scheduled for 2018. Three user stations in the basement of building D (von Helden (He nano-droplets), Kuhlenbeck, Asmis) can continue operation throughout the renovation period. However, as the lab space in the ground floor will be completely refurbished, the three user experiments there (Paarmann, von Helden (ion mobility), Fielicke) will have to be relocated to the basement to avoid having to stop them for several months. To this end, the FEL beamline system in the basement will be extended. The envisioned beamline extension is shown in Fig. 4. In addition to the 3 existing user stations, 3 more lab fields will be reached on either side of the aisle. Thus, after completion of the renovation work, a total of 9 FEL user stations will be available.

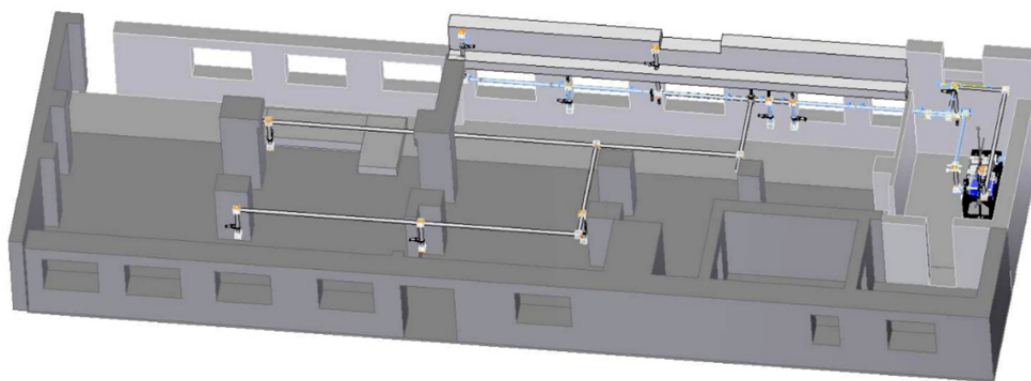


**Figure 4:** View of the extended IR beamline system in the basement and ground floor of Building D. The FEL radiation will be supplied to a total of 9 user stations (6 in the basement, 3 in the ground floor). In this drawing the basement ceiling has been cut out for better visibility.

As with the existing beamline system, some of the beamline mirrors need to be focusing mirrors to re-collimate the beam, that otherwise would diverge due to diffraction effects. We will again carry out detailed optical calculations to identify the required focal lengths of the mirrors. Here, the aim is an optical beamline design that comes closest to a dispersion-free imaging of the FEL's out-coupling hole onto the user stations.

## 5. Plans for a 2-color FEL upgrade

At the last meeting of the Fachbeirat we described our motivation to do pump-probe spectroscopy where two time-delayed optical pulses are applied to the sample. 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 (MIR-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.

The achieved synchronization of the FEL pulses with a femtosecond tabletop laser producing pulses at  $\sim 1 \mu\text{m}$  allows for MIR-NIR 2-color spectroscopy at the FHI-FEL Facility. To implement MIR-MIR two-color spectroscopy we suggested adding a second FEL branch to the FHI-FEL and to upgrade the electron accelerator system such that every second electron

micro-bunch can be sent to the first and every other second bunch to the second FEL. This scheme of a 2-color IR FEL has not been demonstrated before and would be a worldwide unique accelerator based 2-color radiation source.

At the last meeting of the Fachbeirat we outlined a scheme based on generating micro-bunches of alternating energies by a 500 MHz after-burner cavity accelerating every second and decelerating every other second micro-bunch from the existing accelerator system. The scheme included a dispersive dipole magnet downstream of the 500 MHz cavity to separate the low-energy from the high-energy bunches and send them to the two FEL branches.

A technical design and feasibility study by Lloyd Young (formerly Los Alamos National Lab), who designed the existing accelerator and beamline system of the FHI-FEL, indicated the physical feasibility of this approach. Subsequently it turned out, however, that the 500 kW RF amplifier needed to operate the after-burner cavity at 500 MHz is not readily available. While technically feasible, this kind of amplifier would come with a price tag of more than 2 M€. To circumvent the need of hundreds of kW of power at 500 MHz, the new design by Lloyd Young achieves electron bunch separation by a different approach. In this scheme the (longitudinal) electron energy is not changed, but consecutive bunches are deflected in opposite transverse directions by a side-deflecting cavity. Thus, bunch separation is achieved by an angular separation resulting from transverse deflection, alternating at 500 MHz. This approach brings the power requirement down to about 100 kW, thereby reducing the costs of an RF amplifier by a factor of about five. A detailed description of this approach to bunch separation is given on the Poster [FEL 1].

The IR wavelength range that can be covered with the second FEL, for the given range of accessible electron energies, depends on the choice of the 2<sup>nd</sup> undulator's period. In the 2-color scheme the preferable choice would be such that, for any electron energy, one can still operate both FEL's at identical wavelengths. Fig. 5 shows the wavelength ranges calculated for undulator periods of 40, 64, 80, and 110 mm for two near-extreme electron energies of 18 and 46 MeV. Overlap with the scanning range of the existing system (40 mm period) is found for a 2<sup>nd</sup> undulator period of 64 mm. For a period of 80 mm one would just miss overlap. And for 110 mm, the period that had been considered in the initial two-branch single-color design, a significant spectral gap would occur between the 1<sup>st</sup> and 2<sup>nd</sup> FEL at any given electron energy. We conclude from these calculations that the 2<sup>nd</sup> undulator's period should be somewhat smaller than 80 mm to ensure wavelength overlap. This comes with the trade-off of not being able to reach the longest FIR wavelengths close to 1 THz (300 micron) and beyond.



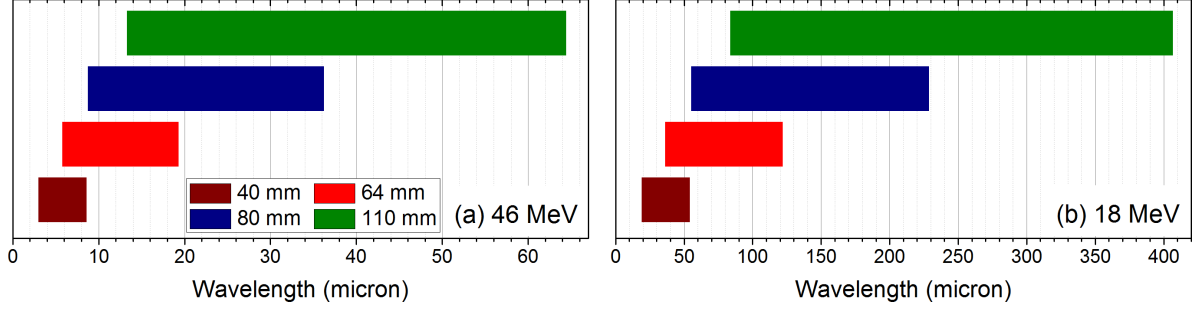


**Figure 5:** Wavelength scan ranges of the 2-color upgrade of the FHI-FEL calculated for undulator periods of 40, 64, 80, and 110 mm and two electron energies of (a) 46 MeV and (b) 18 MeV. For a 2<sup>nd</sup> undulator period of 64 mm one gets significant overlap with the existing undulator (40 mm period). For a 2<sup>nd</sup> undulator period of 80 mm, overlap is just missed. And for 110 mm one would get a significant spectral gap between the 1<sup>st</sup> and 2<sup>nd</sup> FEL.

## 6. Publications from the FHI-FEL facility

2016

*Truong, N.X., M. Haertelt, B.K.A. Jaeger, S. Gewinner, W. Schöllkopf, A. Fielicke, and O. Dopfer.* Characterization of neutral boron-silicon clusters using infrared spectroscopy: The case of Si<sub>6</sub>B. *Int. J. Mass Spectrom.* **395**, 1–6 (2016).

*González Flórez, A.I., E. Mucha, D.-S. Ahn, S. Gewinner, W. Schöllkopf, K. Pagel and G. von Helden.* Charge-Induced Unzipping of Isolated Proteins to a Defined Secondary Structure. *Angew. Chem. Int. Ed.* **55**, 3295–3299 (2016).

*González Flórez, A.I., E. Mucha, D.-S. Ahn, S. Gewinner, W. Schöllkopf, K. Pagel and G. von Helden.* Ladungsinduziertes Entwinden isolierter Proteine zu einer definierten Sekundärstruktur. *Angew. Chem.* **128**, 3356–3360 (2016).

*Weichman, M.L., X. Song, M.R. Fagiani, S. Debnath, S. Gewinner, W. Schöllkopf, D.M. Neumark, and K.R. Asmis.* Gas phase vibrational spectroscopy of cold (TiO<sub>2</sub>)<sub>n</sub><sup>−</sup> (n = 3–8) clusters. *J. Chem. Phys.* **144**, 124308 (2016).

*Song, X., M.R. Fagiani, S. Gewinner, W. Schöllkopf, K.R. Asmis, F.A. Bischoff, F. Berger, and J. Sauer.* Gas phase structures and charge localization in small aluminum oxide anions: Infrared photodissociation spectroscopy and electronic structure calculations. *J. Chem. Phys.* **144**, 244305 (2016).

*Yanagimachi, A., K. Koyasu, D. Yubero Valdivielso, S. Gewinner, W. Schöllkopf, A. Fielicke, and T. Tsukuda.* Size-Specific, Dissociative Activation of Carbon Dioxide by Cobalt Cluster Anions. *J. Phys. Chem. C* **120** (26), 14209–14215 (2016).

*Hoffmann, W., M. Marianski, St. Warnke, J. Seo, C. Baldauf, G. von Helden, and K. Pagel.* Assessing the stability of alanine-based helices by conformer-selective IR spectroscopy. *Phys. Chem. Chem. Phys.* **18**, 19950–19954 (2016).

*Fagiani, M.R., H. Knorke, T.K. Esser, N. Heine, C.T. Wolke, S. Gewinner, W. Schöllkopf, M.-P. Gaijeot, R. Spezia, M.A. Johnson, and K.R. Asmis.* Gas Phase Vibrational Spectroscopy of the Protonated Water Pentamer: The Role of Isomers and Nuclear Quantum Effects. *Phys. Chem. Chem. Phys.* **18**, 26743–26754 (2016).

*Seo, J., St. Warnke, S. Gewinner, W. Schöllkopf, M.T. Bowers, K. Pagel, and G. von Helden.* The impact of environment and resonance effects on the site of protonation of aminobenzoic acid derivatives. *Phys. Chem. Chem. Phys.* **18**, 25474–25482 (2016).

*Seo, J., W. Hoffmann, St. Warnke, M.T. Bowers, K. Pagel, and G. von Helden.* Retention of Native Protein Structures in the Absence of Solvent: A Coupled Ion Mobility and Spectroscopic Study. *Angew. Chem. Int. Ed.* **55**, 14173–14176 (2016).

*von Helden, G., W. Schöllkopf, and K. Pagel.* Structures of peptide aggregates investigated with the new Fritz Haber Institute free electron laser. *Jahrbuch der Max-Planck-Gesellschaft* 2016.

*Paarmann, A., I. Razdolski, S. Gewinner, W. Schöllkopf, and M. Wolf.* Effects of crystal anisotropy on optical phonon resonances in midinfrared second harmonic response of SiC. *Phys. Rev. B* **94**, 134312 (2016).

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Truong, N.X., B.K.A. Jaeger, S. Gewinner, W. Schöllkopf, A. Fielicke, and O. Dopfer. Infrared Spectroscopy and Structures of Boron-Doped Silicon Clusters ( $Si_nB_m$ ,  $n=3-8$ ,  $m=1-2$ ). *J. Phys. Chem. C* **121**, 9560–9571 (2017).

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## **Department of Inorganic Chemistry**

**Staff scientists:**

|                                       |                      |                                          |
|---------------------------------------|----------------------|------------------------------------------|
| Sylvia Becker ( <i>née Reiche</i> )*  | <i>until 11/2016</i> | Axel Knop-Gericke                        |
| Raoul Blume*                          |                      | Anna Mechler*                            |
| Saskia Heumann ( <i>née Buller</i> )* |                      | Detre Teschner*                          |
| Sébastien Cap                         |                      | Olaf Timpe ( <i>FHI Safety Officer</i> ) |
| Michael Hävecker*                     |                      | Annette Trunschke                        |
| Frank Girgsdies                       |                      | Marc G. Willinger**                      |
| Mark Greiner*                         |                      | Sabine Wrabetz                           |
| Kevin Kähler*                         |                      |                                          |

**Guest scientists, staying for at least six months, paid by FHI or CEC:**

|                       |                     |                         |                      |
|-----------------------|---------------------|-------------------------|----------------------|
| Gerardo Algara-Siller |                     | Thomas Lunkenbein       |                      |
| Yuxiao Ding*          |                     | Verena Pfeifer          |                      |
| Maik Eichelbaum       | <i>until 2/2015</i> | Tania Rodenas Torralba* |                      |
| Hua Fan*              |                     | Philipp M. Schleker*    |                      |
| Ramzi Farra*          |                     | Julia Schumann          | <i>until 12/2015</i> |
| Elias Frei            |                     | Katarzyna Skorupska*    |                      |
| Walid Hetaba          |                     | Christoph Sprung        | <i>until 12/2015</i> |
| Fan Hua*              |                     | Dangsheng Su            | <i>(part-time)</i>   |
| Xing Huang*           |                     | Andrey Tarasov          |                      |
| Benjamin Johnson      |                     | Juan Velasco-Vélez*     |                      |
| David Klein*          |                     | Elena Willinger*        |                      |
| Pierre Kube           |                     | Shuchang Wu*            |                      |
| Yang-Ming Lin*        |                     | Qingjun Zhu*            |                      |
| Zigeng Liu*           |                     |                         |                      |

**Guest scientists, staying for at least six months, paid from external funds:**

|                       |                    |                         |                     |
|-----------------------|--------------------|-------------------------|---------------------|
| Emilia Carbonio       | Gregor Koch        | Andreu Ruiz de la Oliva | <i>until 2/2016</i> |
| Maria Dimitrakopoulou | Alexander Klyushin | Holger Ruland*          |                     |
| Qingqing Gu*          | Rik Mom            | Ioannis Spanos*         |                     |
| Jorge Salazar Gómez*  | Milivoy Plodinec*  | Fu Teng                 |                     |
| Travis Jones          | Sven Richter       | Yuanqing Wang           |                     |
| David Klein*          |                    | Zhujun Wang*            |                     |

**Graduate students:** 14 (including 2 from external funds)

1 IMPRS *until 12/2016*

2 joint graduate student TU Berlin/FHI

**Technicians:** 11 (including 4 for Service Group Electron Microscopy)

**Trainees:** 5 (including 2 master students)

**Library Service Group:** Uta Siebeky, Katrin Quetting, Andrea Braaker, Evelyn Prohn *until 1/2017*

\* based at Max Planck Institute for Chemical Energy Conversion (MPI CEC), Mülheim a. d. Ruhr

\*\* Max Planck Institute of Colloids and Interfaces, Potsdam

## **Recent Developments in the Department of Inorganic Chemistry**

**Director: Robert Schlögl**

### **1. General Developments**

#### **1.1 Situation in the Two Locations**

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<sup>[1]</sup> through reaction of hydrogen in the synthesis of methanol and ammonia. Common to all projects is the guidance through the general concept<sup>[2]</sup> of dynamical interfacial processes.

The Department retained its split status into two locations namely in Mülheim (Ruhr) with the activities on carbon synthesis, electrochemistry and energy conversion processes (ammonia synthesis and methanol synthesis) and at FHI Berlin with topics oxidation catalysis, coin metal chemistry and the methodical foci on operando electron spectroscopy and operando microscopy. All other operando methods pursued by the Department are also located at FHI.

The appointment of B. Roldán at the FHI opens several avenues of new collaborations with the AC department. Methodical collaboration will involve liquid phase TEM. B. Roldán will provide the sample holder and a dedicated researcher and we will provide the instrumentation and our expertise in operando gas phase reaction analysis. If the experiments prove to be useful it may be necessary to leave the 300 kV TITAN instrument here in Berlin and purchase new equipment in Mülheim once the EM group moves there. The necessary building operation in Mülheim has practically started and we expect completion in 2020. Collaboration in using operando electron spectroscopy has started between the two departments. Electro-reduction of CO<sub>2</sub> with modified Cu electrodes is the subject of intense investigation. The question about the nature of the Cu species and its oxidation state under operando conditions and possibly in gradients of pH and counter ions is of interest. We find that in analogy to the gas phase activation of CO<sub>2</sub> in methanol synthesis the active form of Cu is not pure metal but merely a partly oxidized form possibly as hydroxide-oxide surface.

In the MPI CEC one new appointment was successfully finished with S. DeBeer whose activities in X-ray spectroscopy and in ammonia synthesis as core projects overlap with the AC activities. Friendly collaboration has started. S. DeBeer will share the EMIL infrastructure

with us (mainly using her beamline PINK that is fed through EMIL with light). In ammonia synthesis we collaborate through a joint library of innovative iron catalysts synthesized by the AC Department and by M. Behrens from Univ. Duisburg-Essen of which S. DeBeer is characterizing the electronic structure of the iron and we are performing catalytic resting and in-depth structural analysis. We find substantial anomalies in the magnetic behaviour of active ammonia iron pointing to an intricate inner structure of the morphological nanoparticles that is correlated with the catalytic performance.

A second appointment at MPI CEC was recently successful. W. Leitner works in activation of CO<sub>2</sub> with homogeneous and heterogenized metal catalysts. This subject leads us in close collaboration on rapid and comprehensive characterization of metal nanostructures for guiding synthetic discovery and optimization. We will develop a dedicated analytical electron microscope allowing the examination of nanostructured immediately after synthesis and without isolation. In addition, our structural analytical facilities will be of substantial use for elucidating the transition from free nanostructures to immobilized nanoparticles. A joint post doc started collaborative experiments by testing Cu-containing molecular systems for CO<sub>2</sub> reduction.

## **1.2 Collaborative Activities of the FHI Branch**

The BASCAT collaborative activity with BASF was renewed in 2017 for another period of 5 years. This includes the collaboration with the TU Berlin at the BASCAT site and the collaboration with BASF central research. The BASCAT activity is the by far largest collaborative activity involving a substantial fraction of the whole Department through the groups of A. Trunschke, A. Knop-Gericke and M. Willinger. The area of activity is functional understanding of selective oxidation of small molecules. Selected issues in C1 chemistry will be studied including the synthesis of higher alcohols.

The oxidation catalysis team led by A. Trunschke carries the main responsibility in the research work of the FHI contribution to BASCAT. This is done through continuous harmonization of research needs at BASCAT with the scientific progress of the FHI group. Methodical developments as well as systemic insight govern this mutual evolution. Following the recommendation of the Fachbeirat at its last meeting we broadened the basis of catalyst materials. As we wish to understand their mode of operation we need homogeneous and phase-pure materials in scalable synthesis procedures. This makes synthesis a time-consuming effort and requires careful synthesis optimization and analytical characterisation.<sup>[3]</sup>



Besides our hydrothermal methodology with autoclaves, staged addition of reactants and microwave synthesis we added methods of high-temperature powder synthesis to arrive at families of perovskite catalysts. Advanced methods of impregnation complement our methodical tools. The rational synthesis of complex oxides requires a deep understanding of the chemistry of the precursor species under synthesis conditions. Here we collaborate with G. Helden (MP Department) in using advanced mass spectrometry and the FHI FEL to identify and characterize the condensation chemistry of Mo and V species in pure and mixed systems. This completes and expands the standard knowledge on poly-oxo-metallates to the conditions relevant for synthesis. We find novel structural details and unexpected dynamics of small isopoly metallates that help explain the processes during synthesis of complex oxides. Exploitation of the results for advanced synthesis protocols can be done in a large autoclave that we installed allowing us to use the spectroscopically relevant dilute solutions and still produce meaningful quantities of material. In the silver epoxidation project we succeeded in generating stable nanoparticles to investigate the unusual inverse particle size effect of EO synthesis. For the alternative EO catalysts Delafossite we found a scalable synthesis of 99.5% phase-pure material. We do not intend to broaden our synthesis efforts beyond such well-defined materials and enter in a discovery mode. Theory has made great progress in predicting observables of active phases in catalytic systems. In an collaboration with F. Neese we developed and tested a generic approach based upon multiple spectroscopic experimentation coupled to model predictions of structures to analyse the geometric and electronic structures of mixtures of potential active sites.  $V_xO_y$  species in various systems were used<sup>[4]</sup> as demanding test case.

The Berlin Cluster of Excellence UniCat is due for renewal. The Department contributes to this initiative through its leading activity in BASCAT and collaborates with the group of R. Schomäcker through a joint student working on the OCM reaction with pure and doped CaO catalysts. This work is inspired by earlier discoveries in the Department of HJ Freund and we try now to convert fundamental insight from there in practical catalysts. In this activity we integrated a study (E. Frei) on Ni-doped MgO for various reactions in CO<sub>2</sub> activation aiming at realizing theoretical predictions made in the Theory Department (S. Levchenko). The new proposal UniSysCat aims at considering catalytic processes as systemic challenges including the concept of dynamical active sites. In order to verify the structure of dynamical catalysts, the Department will contribute its operando capabilities to the project. If we cannot determine the working structure of such catalysts then the claim of following a systemic concept of

catalyst design cannot be verified. The Department considers this a substantial challenge and begins with preparative studies on how to tackle the analytical challenge for selected case studies such as methane activation catalysts. At TU Berlin the Department further collaborates with the group of P. Strasser on functional analysis of electrodes for oxygen activation reactions. Part of this work is covered in a DFG priority program (SPP 1613).

With HZB we were able to finalize the cooperation agreement for a new Joint lab MPG-HZB named BELCAT (Berlin electron spectroscopy facility for catalysis science). Under this cooperation we jointly refurbish the former MPG undulator UE 56 and create a new bending magnet tender X-ray beamline. This will generate two new beamlines for chemical electron spectroscopy using NAP-XPS. In addition, an open port facility for the same experimentation but for users with dedicated own instrumentation is planned. A full range of chemical infrastructures for sample preparation and for reactive chemical environments during experimentation will be installed. A special benefit will be the design of the endstation following our modular concept introduced at the Departmental beamline ISIS that remains under operation also in BELCAT. We have now dedicated modules for powder catalysis, for electrochemistry and for model studies. In order to make these modules available to all users at BESSY, we transferred our design and know-how to the Sample Environment Design Group of HZB who will from now on manufacture and further develop this module concept. We expect that in future only users will be admitted to BELCAT who pre-test their experiments on dedicated module stations without the synchrotron beam. This will greatly boost the scientific productivity of NAP-XPS at BESSY.

The BESSY team around A. Knop-Gericke further invested great efforts to get the EMIL experiment to work. Here the chemical endstation is operational and is being commissioned with the soft-X-ray light. The tender X-ray light is due to arrive in 2018 due to production issues with the cryogenic undulator part that was not operational at the scheduled installation time. In order to be able to perform liquid-phase experiments the team developed and applied<sup>[5]</sup> a sample environment that is based upon an electrochemical flow cell with three electrode set-up and a graphene window through which we can observe the electron spectrum of a working electro-catalyst in contact with a flowing electrolyte and under steady state operation. This currently most advanced experimentation techniques is used for liquid phase studies but was also successfully used for NAP XPS in gas-phase catalysis<sup>[5b]</sup> at flowing conditions and ambient pressure.

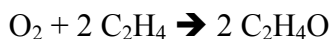
Within the framework of the MAXNET Energy collaboration we support the creation of a competence centre of advanced electron microscopy at the MPI Colloid Science in Golm. Our group leader M. Willinger is transferred for a start-up period of 3 years to this MPI where he supervises the installation and operation of a high-end electron microscope. We use our microscopes at FHI to identify operation procedures and train a person who is intended to take over the role of a group leader there once the operation is stable and some local training creates a user basis.

The cooperation with FEI (now Thermo-Finnigan) on the evolution of operando electron microscopy and chemical routine electron microscopy has practically commenced. We host an application scientist from FEI in our Department (R. Imlau) for developing workflows for chemical electron microscopy including EELS spectroscopy and its theoretical simulation (W. Hetaba) and intensely develop the technology for safe ambient pressure electron microscopy both in the SEM and in the TEM. We envisage that like in the case of TEM where we strive for the evolution of a dedicated chemical electron microscope on the THEMIS platform we also need a dedicated SEM capable of dealing with controlled atmosphere experimentation without impurities and deficiencies of vacuum systems of commercial instruments. A purposely designed sample chamber would further allow to operate much more advanced and multiple detectors to enhance the imaging capabilities of dynamical processes. We presently have started a concept phase dealing with detector testing and sample stage development. We will put forward an application for support of such a development in 2018 to the President of the MPG.

## **2. Scientific Highlight**

### **2.1 The Mode of Operation of Silver as Catalyst in the Epoxidation of Ethylene**

The reaction of ethylene with oxygen gas to ethylene epoxide is a seemingly facile selective oxidation.



The product occurs in two isomers namely ethylene epoxide and acetaldehyde. Only the former is desired, the latter is the intermediate to combustion. The reaction occurs over supported silver catalysts under conditions where silver is metallic despite the presence of oxygen. The phenomenological catalyst development has achieved conversion and selectivity of way above 90% by adding promotor “packages” and by co-feeding small amounts of ethyl

chloride. The relative mild reaction conditions and the seemingly facile catalyst chemistry have provoked numerous surface science studies and a whole lot of theory also in the FHI<sup>[6]</sup> on the mode of operation of this reaction.

The tempting practical target to develop this reaction into the first example of a 100% selective technical process seems well in reach. Industry sells catalyst systems with either near 100% performance at the expense of lifetime of the system or with attractive lifetimes at the expense of catalyst selectivity. Without a real understanding of the structure-function relation involved the combination of the two families seems not possible. The conceptual work is far away from studying technical performance levels and one observes under model reaction conditions selectivity way below 50% and poor conversion. It is thus still not possible to bring the conceptual work in agreement with the performance developments.

Our department studies the reaction of silver with oxygen since almost 2 decades and has developed several in-situ observation techniques. Summarizing this work<sup>[7]</sup> revealed that oxygen reacts to a whole variety of species with different chemical and spectroscopic characteristics. The selection is controlled by kinetic parameters and by the chemical potential of oxygen. This is due to the fact that not only the surface but also the sub-surface volume of silver takes part in the interaction with oxygen. Figure 2.1 summarizes the various forms of atomic and molecular oxygen. In good agreement between theory and experiment one can discriminate low-temperature molecular species from ambient-temperature oxide reconstructions and atomic adsorbates in various local configurations. Oxygen 1s photoemission can well discriminate these latter adsorbate species, giving rise to complex spectra with up to 5 different signals. There is also good experimental and theoretical agreement in the assignment<sup>[8]</sup> that reconstructed oxide systems are active in ethylene activation but merely lead to CO<sub>2</sub> via the intermediate acetaldehyde being an isomer of ethylene epoxide with higher stability and possibly lower activation barrier for its formation. The atomic oxygen species being non-oxides can be discriminated according to their reactivity against probe molecules as nucleophilic or electrophilic. The former activates C-H bonds and can be inserted in activated carbon structures whereas the latter undergoes addition to C=C bonds without C-H activation.

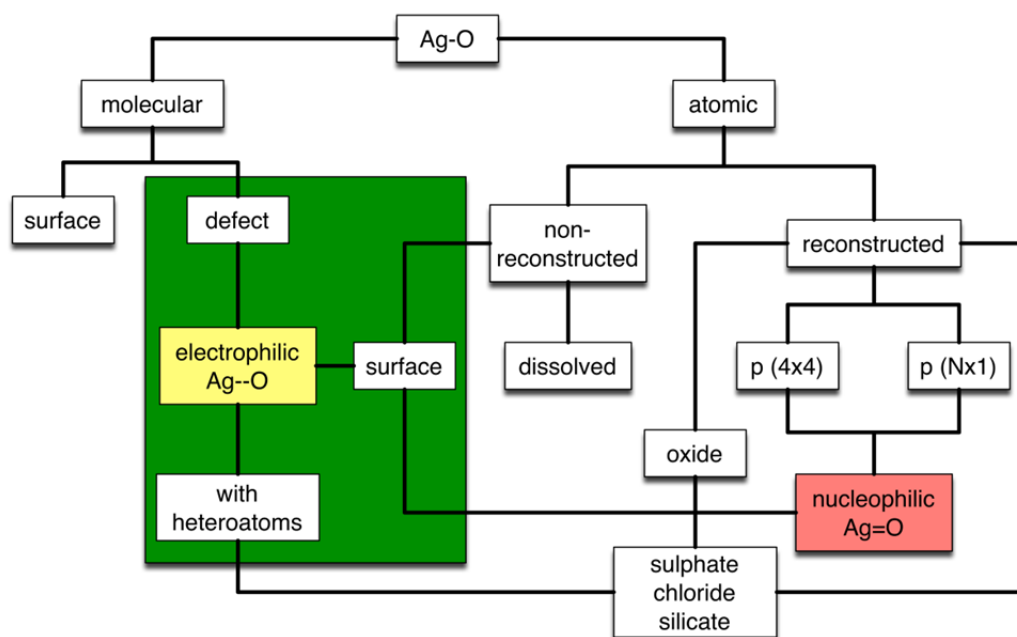


Figure 2.1: Typology of oxygen species at silver. Various conditions of pressure and temperature are needed to generate all of the species. At practical reaction conditions multiple species of non-reconstructed atomic species co-exist. The species in green area are made responsible for the selective epoxidation of ethylene. The “nucleophilic” species fulfills multiple functions in moderating silver metal and activating C-H bonds.

For reaction (1) electrophilic oxygen is required whereas nucleophilic oxygen is detrimental as it leads via C-H activation to combustion. Nucleophilic oxygen is, however essential to open the silver d-band and thus to allow adsorption of ethylene and the formation of electrophilic oxygen. O1s photoemission is a suitable tool<sup>[9]</sup> to determine type and abundance of the respective species. The system Ag-O can further form sub-surface species which slowly occur from adsorbed oxygen<sup>[10]</sup> in almost thermo neutral reaction.

In between the multiple oxygen species we were able to identify spectral features of one form of electrophilic oxygen that clearly performs the epoxidation reaction. It is always a minority species. A clear structure-function analysis<sup>[7]</sup> revealed its desired function. The species is weakly held by the silver surface. We found that the abundance of this species is markedly increased by the action of the ethyl chloride promoter<sup>[11]</sup> explaining thus at least one selectivity enhancing function of its presence.

A serious weakness of this experimentally consistent picture is the fact that theory cannot explain<sup>[9]</sup> the spectral features in photoemission and in XAS of the relevant species. It is excluded that any atomic oxygen species alone can be attributed to the observed spectral features of the epoxidizing species. Having also excluded molecular oxygen as origin of the

relevant species it was finally found that a co-catalyst sulfur is needed to generate an  $\text{SO}_3+\text{O}$  species that exactly matches the observed spectral features.

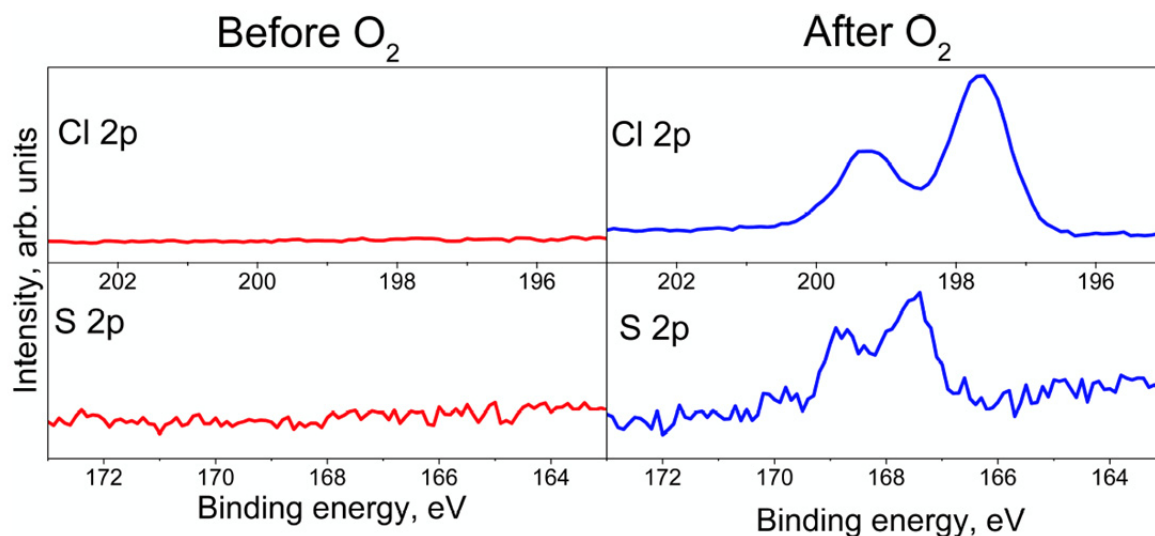


*Figure 2.2: Synchrotron NAP XPS of polycrystalline Ag freshly etched with nitric acid before and after exposure to oxygen penetrating into the sub-surface regime. The Cl species is chloride, the sulfur species is pentavalent with oxygen ligands. This form slowly oxidizes in air to sulfate with hexavalent sulfur.*

The source of the sulfur is the bulk of silver metal from which it segregates to the surface as shown in Figure 2.2 following incorporation of oxygen into the sub-surface regime. The alternative conjecture that a sulfur-containing species is present in the feed ethylene was not verified but cannot be excluded. It is however, not sufficient to form the  $\text{SO}_3+\text{O}$  reconstructed surface but it is essential that the species occurs in unreconstructed form i.e. as molecular adsorbate. The assignment was greatly supported by a collaboration with the group of J. Wintterlin from LMU Munich who described the  $\text{SO}_3+\text{O}$  species first in reconstructed form<sup>[12]</sup> and found their epoxidation activity in model experiments with unreconstructed states of the co-catalyst. The important difference in reactivity between reconstructed and unreconstructed states of oxygen adsorbates was already<sup>[13]</sup> recognized earlier. In retrospect we see that in this early work also the  $\text{SO}_3+\text{O}$  species was formed without however, it being assigned correctly. The species  $\text{SO}_3+\text{O}$  was reported in the literature<sup>[14]</sup> as silver salt synthesized by electro-oxidation. The species was described as strongly oxidizing and is suggested to be a potent selective oxidation catalyst material.

With  $\text{O}_{\text{ads}}$  unable to account for the oxygen species with an O 1s binding energy of  $\sim 530.5$  eV we performed a thorough study. With the structure and function of electrophilic oxygen solved we have begun performing in situ XPS experiments aimed at uncovering both its role

during steady state epoxidation and understanding the mechanism of  $\text{SO}_x$  management during ethylene epoxidation. These experiments have demonstrated that under mbar pressures - and during surface titrations with ethylene - the epoxide selectivity tracks the coverage of  $\text{SO}_3 + \text{O}$ , as expected for the selective species. In Figure 2.3 we show that the  $\text{SO}_3 + \text{O}$  species correlates to the formation of epoxide and inversely to the combustion activity.

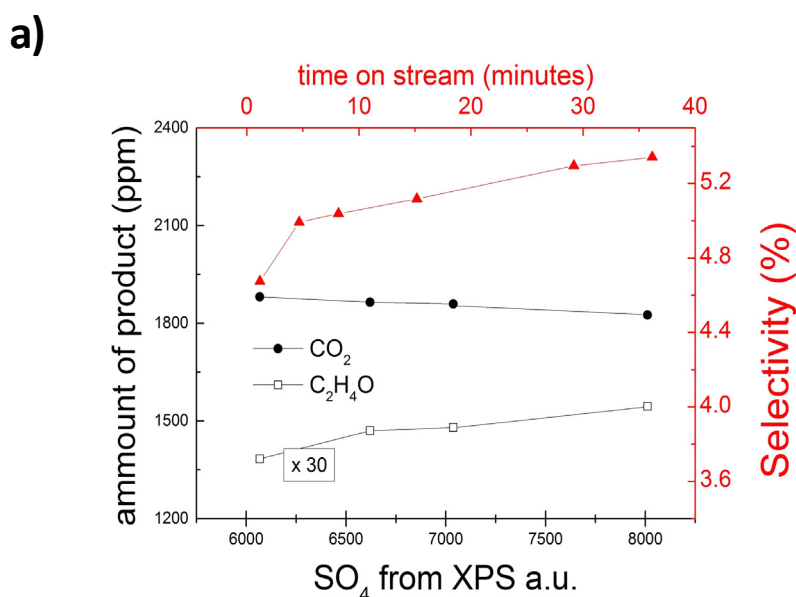


Figure 2.3 Correlation of the  $\text{SO}_3 + \text{O}$  species with catalytic performance measured by gas chromatography at 0.5 mBar pressure during NAP-XPS speciation of the reacting surface.

The speciation measured during the experiment shown in Figure 2.3 reveals that besides the expected  $\text{SO}_3 + \text{O}$  form a lower-valent species coexists with this species. The divalent sulfur species is not present at the surface but represents a sub-surface buffer form for the sulfur. This can be deduced from the S2p spectra taken at various excitation energies given in Figure 2.4. The localization and the valence (as SO) are in line with the anticipated source of sulfur being dissolved zero-valent sulfur in the silver metal. The computed thermodynamic stability diagram shown in Figure 2.4 is in good agreement with the experimental finding.

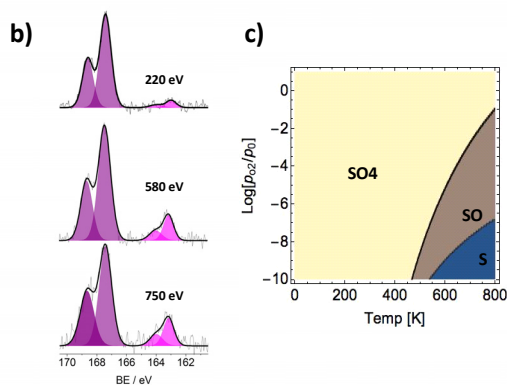


*Figure 2.4 NAP-XPS of sulfur species during epoxidation over polycrystalline silver. Data were taken at increasing excitation energy to increase the bulk-sensitivity of the experiment. The computed phase diagram of the S+O system at relevant conditions are in line with the experimental data being located at the phase boundary between SO and SO<sub>3</sub>+O (here designated SO<sub>4</sub>).*

The system (Ag<sub>n</sub>O) is a prototypical example for a catalytic system in which an intimate entanglement between reactant transformations (ethylene oxidation) and reactions of the catalyst precursor with the reactant oxygen generate an unexpected intricate system with dynamical behavior. Morphological changes through sub-surface migration of oxygen occur at timescales of several 100 h time on stream. This prepares a silver surface with the segregated co-catalyst sulfur and a surface termination maximizing the dynamical restructuring of Ag induced by oxygen adsorption to suppress any surface reconstruction in 2-D phases that are unreactive or detrimental in selectivity. The dynamical reconstruction allows for surface roughening through surface atom displacement and thus creates a continuously disordered (surface liquid) termination at low reaction temperatures. This termination is likely limited to the surface and provides locations to store atomic oxygen that is always generated when an oxygen molecule dissociates at an active site; only one of these atoms should be transferred to the ethylene molecule, the other one should be removed from the reaction site in order to prevent C-H activation and consecutive combustion. The entanglement of the processes is schematically indicated in Figure 2.5 representing a simplified system description of the ethylene oxide synthesis catalysis.



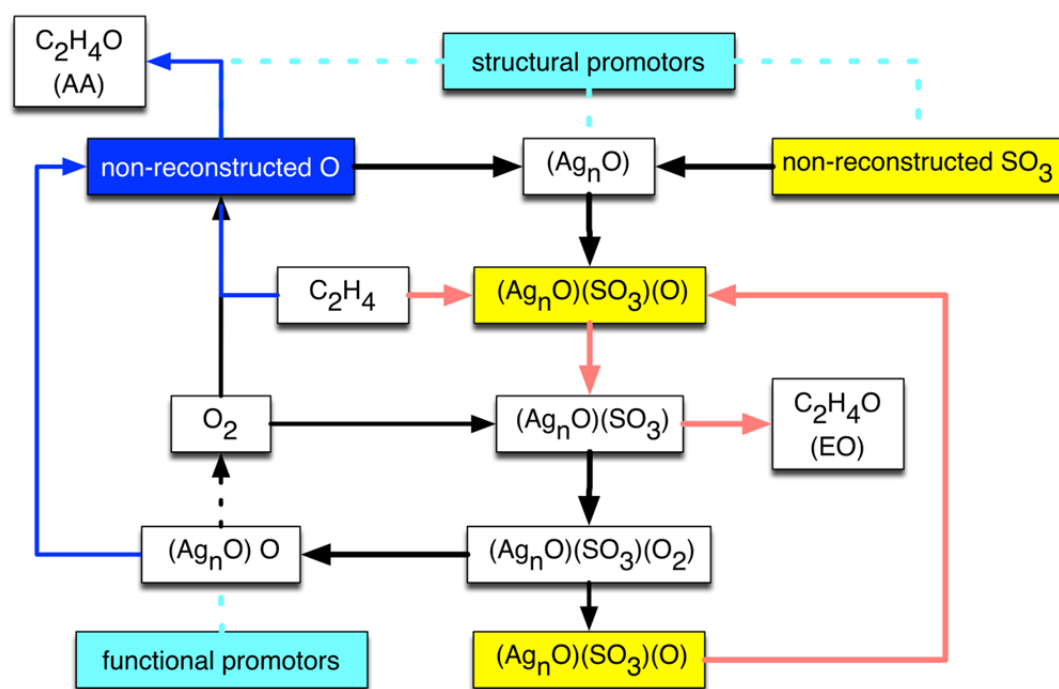


Figure 2.5 System diagram of the catalytic epoxidation of ethylene. The red arrows designate the desired ethylene transformation whereas the blue arrows indicate part of the oxygen management. The sulfur management is omitted for clarity here.

We can verify the existence of the  $SO_3+O$  species in unreconstructed form, the unreconstructed  $(Ag_nO)$  species, nucleophilic oxygen and sub-surface oxygen. The ethylene-containing products cannot be detected under working conditions, only when halting the reaction, we see organic adsorbates as “frozen” species with structures consistent with the expected products. The oxygen management through dissociation of the complex  $(Ag_nO)(SO_3)(O_2)$  to regenerate the active species is presently an assumption. It may also be that ethylene reacts with the complex. As chemically one may expect that the oxygen species in the complex is more a radical than an anion (as it is unlikely to assume high positive charges at the silver being part of a metallic surface with a small opening of the d-band) we consider such a regeneration pathway as one source of finite selectivity that may well inhibit under performance conditions the target of 100% selectivity.

We currently model the whole system by theoretical methods and try to observe the spectral fingerprints of all existing sulfur species during operando conditions. Independent verification by synthetic measures, by operando r-RAMAN experiments by thermal desorption and isotope labeling methods and by changing the reaction feed conditions are also underway. Progress will be shown at the visit of the Fachbeirat.

### 3. Specific Developments

We report here significant achievements in the groups located at the FHI. Comprehensive information can be found at our homepage at the locations of the group leader reports. There is desired overlap of the FHI activities with activities at the MPI CEC. For the purpose of the present evaluation of the Department at the FHI we omitted these activities. The reader may be referred to the CEC homepage for reports of the group leaders located there. We provide to those interested copies of the Fachbeirat Report from MPI CEC where the evaluation occurred in March 2017. The report from this meeting is not available at the time of writing this document. We expect that we can provide the report at the time of the meeting of the Fachbeirat of the FHI.

#### 3.1 Group Reactivity

##### Selective Oxidation Catalysis

Selective activation of C-H bonds in hydrocarbon molecules is a long-term research goal in chemistry in general and heterogeneous catalysis in particular since transformations of hydrocarbon-containing resources into valuable chemicals usually involve C-H activation steps.<sup>[2, 15]</sup> The present project deals with C-H activation and oxygen insertion reactions in partial oxidation of alkanes containing 1-4 carbon atoms over transition metal oxide catalysts. The difficulty in direct oxidation processes of alkanes with heterogeneous catalysts arises from the chemical reactivity of reaction intermediates and/or the desired unsaturated or oxygenated target product towards activated oxygen species concurrently present on the catalyst surface. An efficient oxidation catalyst activates both hydrocarbon substrate and oxygen in an optimal way. Such action requires an intricate active site as the elementary steps of these two essential processes require different electronic and geometric properties. The activation of the two reaction partners proceeds via numerous steps unfolding a complex reaction network of carbon-containing and oxygen intermediates.<sup>[16]</sup> Selectivity, *i.e.*, formation of a single desired product and prevention of ultimately undesired total combustion to the thermodynamically most favourable product CO<sub>2</sub>, poses, therefore, the major challenge. Missing resounding success in the discovery of selective catalysts indicates that utilization of alkanes will require new chemical and technological solutions that imply first of all an improved fundamental understanding of surface chemistry and dynamics of metal oxides in presence of the reactants and the elucidation of the reaction networks.

Our concept relies on controlled synthesis and activation of well-defined metal oxides. In an advancement of our synthetic strategies, which were originally focused on hydrothermal synthesis of Mo-V-based oxides,<sup>[16]</sup> we included molybdates, tungstates,<sup>[3]</sup> doped cerium oxide, and perovskites into our studies assuring in either case phase purity. The aim of the extension is to verify whether structure-function relationships established in case of vanadium oxide-based catalysts exhibit a more general validity. The catalysts are explored in C1-C4 alkane oxidation with focus on propane and selected probe reactions, such as CO or alcohol oxidation, including mechanistic investigations using isotope labelled substrate molecules, and the analysis of solid-state and surface structure under working conditions by *operando* spectroscopy, microscopy, conductivity measurements, and diffraction techniques supported by theory.

### Catalyst Synthesis

Reproducible synthesis of functional materials requires detailed knowledge of the underlying inorganic chemistry. The synthesis of transition metal oxides is particularly intricate since in the course of the condensation process not only the degree of polymerization, but also the valence state of the central atom and the geometry of the coordination polyhedron may change. In a joint project with the department of Molecular Physics we combined ion mobility spectrometry-mass spectrometry (IMS-MS), infrared multiple phonon dissociation (IRMPD) at the Free Electron Laser at the FHI,<sup>[17]</sup> and density functional theory (DFT) techniques to determine the structures of small polyoxomolybdates ( $\text{HMoO}_4^-$  and  $\text{Mo}_n\text{O}_{3n+1}^{2-}$ ,  $n = 2-8$ ) in the gas phase. The results unravel diversity of polyoxomolybdate species present in the sprayed solution that features different topology of clusters of various sizes, ranging from 1-dimensional chains for  $n = 1$  and 3, ring-like structures for  $n = 4$  and 5, to 3-dimensional clusters stemming from Lindqvist-type structure for  $n \geq 6$  (Figure 3.1.1). *Ab-initio* molecular dynamics simulations suggest that the clusters are not rigid but can feature dynamic metal-oxide bond breaking/formation on the picosecond scale. The findings allow a more detailed insight into the structural diversity of polyoxometalate species in solution and in the process of de-solvation that goes along with condensation.

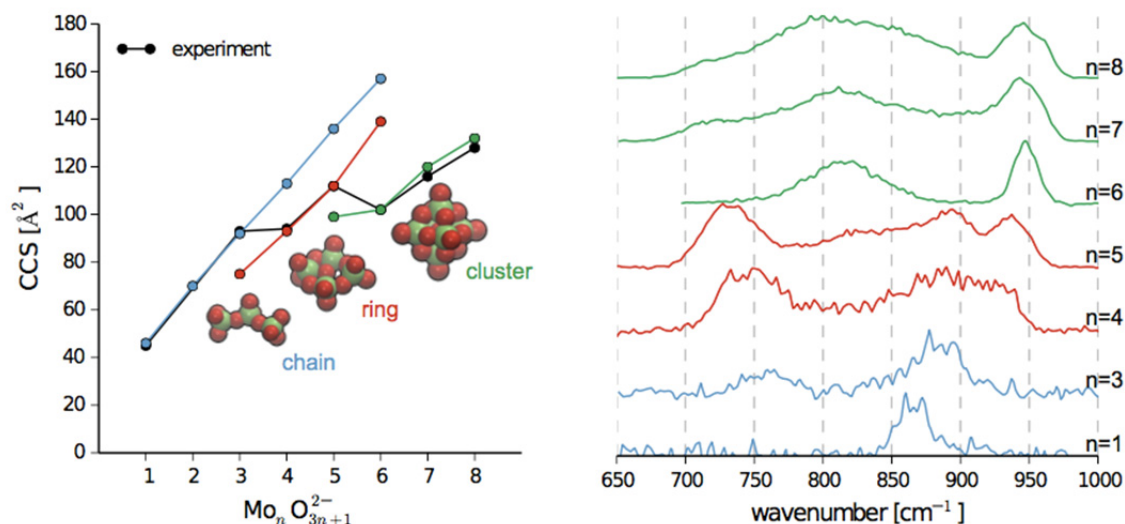


Figure 3.1.1 (Left) The recorded collision cross section (CCS) values as function of ion size  $n$  (black line) and predicted CCS values for model structures that represent different structure types (coloured lines). (Right) Recorded IRMPD spectra for different ion sizes; the colouring corresponds to assignment of different structure types.

Inspection of the vibrational spectra quickly shows that the metal-oxygen bonding situation changes substantially with the structural motifs. In particular the separation between terminal and bridging oxygen species in terms of vibrational energy increases with the dimensionality of the condensation. This is expected to have a marked influence on the hydroxylation and reactivity of the system with respect to restructuring under hydrothermal condensation<sup>[18]</sup> conditions. We expect to use this insight into a rational tuning of the hydrothermal synthesis procedures and have started synthesis experiments making use of the insight into the dynamics of precursor species. Currently we explore reproducibility and stability of such procedures also by synthesizing large amounts of functional identical samples.

### Spotting Active Ensembles in an Embedding Matrix

Recent investigations of silica-supported molybdenum oxide catalysts have shown that only a small number of surface sites might be responsible for the activity of the catalyst in oxidative and non-oxidative activation of C-H bonds in propane and propene, respectively.<sup>[19]</sup> This illustrates the analytical challenge in identifying catalytically relevant surface species (active sites) in the presence of an active phase, which differs chemically and structurally only gradually from the active site, but constitutes the main component of the catalyst. We employed a combination of spectroscopic methods including X-ray absorption, UV-Vis-NIR, infrared and resonance Raman spectroscopy in conjunction with recently developed restricted open shell configuration interaction theory together with time-dependent theory of electronic

spectroscopy performed by D. Maganas in the group of F. Neese at the Max-Planck-Institute of Chemical Energy Conversion (CEC) in Mülheim. The approach was validated to perform equally well with both homogeneous and heterogeneous catalytic cases.<sup>[20]</sup> The protocol was applied to interpret the spectroscopic response of silica-supported vanadium oxide  $\text{VO}_x/\text{SiO}_2$  catalysts and mixed MoV oxides.

A series of vanadia catalysts supported on mesoporous silica SBA-15 has been prepared with loadings in the range of 2–14 wt-% V and characterized by UV-Vis and Raman spectroscopy in the dehydrated state, and under oxygen and propane oxidative dehydrogenation reaction conditions at elevated temperature up to 550 °C by *in situ* XPS and *in situ* Near Edge X-ray Absorption Spectroscopy (NEXAFS).<sup>[21]</sup> The surface vanadium oxide species undergo significant structural surface reconstructions under reaction conditions resulting in highly dispersed species containing vanadium exclusively in the highest oxidation state under steady-state conditions. It has been shown that *in situ* NEXAFS in the soft energy range and *in situ* XPS are valuable tools for the structural characterization of supported metal oxide clusters complementary assisting other methods. Simulation of measured Raman, UV-vis, and NEXAFS spectra by theory revealed that under limited vanadium loadings on the surface of silica molecular species with predominant trimeric structures provide the best agreement between theory and experiment for all the available spectra.<sup>[20]</sup>

Furthermore, optical absorption as well as multi-wavelength resonance Raman spectroscopy revealed frequency dependencies that are directly related to the topological motifs of a semi-crystalline MoV oxide catalyst (Figure 3.1.2).<sup>[22]</sup> In order to interpret the experimental findings, we constructed a representative library of mono-, di- and multimetallic cluster models extracted directly from the crystallographic super-shell (“M1” structure; ICSD 55097). The construction of model structures was based on a thorough bonding analysis, which involved conventional DFT and local coupled cluster (DLPNO-CCSD(T)) methods. It was shown that due to the local nature of the involved electronic transitions, band assignment protocols developed for molecular systems could be applied to describe the calculated spectral features of the cluster models as well. Quantitative band-fitting analyses of the calculated spectra implied that the monolayer  $\text{Mo}_3\text{V}_4\text{O}_{28}$  (1-D model of a heptagonal ring) as well as the bilayer  $\text{Mo}_4\text{V}_2\text{O}_{24}$  (2-D model of the connecting unit between two heptagonal and hexagonal channels) motifs of the M1 structure contribute to the observed spectral features in a roughly 1:2 ratio.

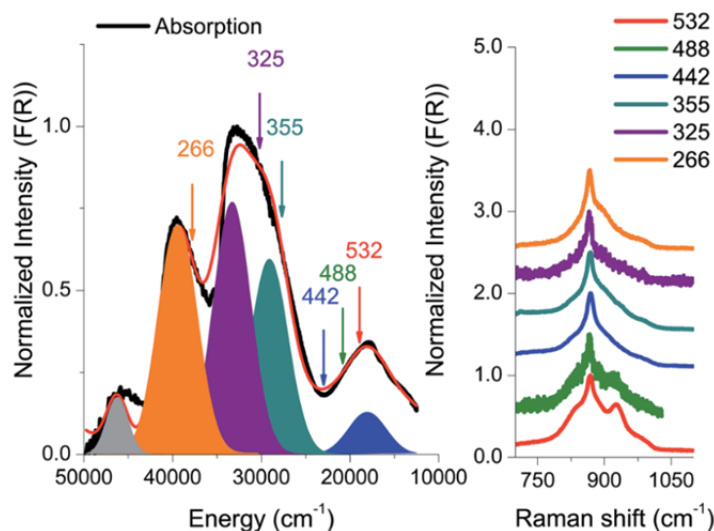


Figure 3.1.2 Experimental absorption spectrum (black) together with the respective rRaman spectra recorded at the pointed excitations (266, 325, 355, 442, 488 and 532 nm). All spectra are presented in normalized Kubelka–Munk ( $F(R)$ ) units. The red absorption spectrum represents a Gaussian fit to the experimental spectrum with a minimum of five individual bands (represented by filled Gaussians).

Although the identification of a catalytic centre in a heterogeneous catalyst is a much more complicated task, we demonstrated that having a theoretical tool with predictive power forms an excellent basis for the design of dedicated spectroscopic experiments in heterogeneous catalysis. With the objective to find guidelines for the design of cluster models representing the surface of the orthorhombic M1 structure as a basis of future studies by theory, high resolution Scanning Transmission Electron Microscopy (STEM) was applied. Tiling the structural regions simplifies the identification of local modifications in the microstructure. Up to 19 different structures were observed in orthorhombic MoV M1 oxide that can be listed and classified into different structural motifs, intergrowth, channels, interstitial regions, and inclinations. The observed defects can be composed of Mo or V enriched metal sites and are expressed by the rearrangement of the  $[(\text{Mo})\text{Mo}_5\text{O}_{27}]$  building blocks. The local structures exhibit different sizes and can form structurally decoupled surface regions that partially cover the crystallographic bulk. Furthermore, the evaluation of 31 orthorhombic MoV oxide crystals yields an average defect concentration of 3.3% and indicates the absence of identical particles. In addition, we have observed 54 of these rearranged structural motifs close to the surface of one MoV oxide particle ( $100 \times 50 \text{ nm}^2$ ). A detailed analysis of the atomic arrangement at the surface of this particle in combination with the site occupancies obtained from refined X-ray diffraction measurements, suggests a surface composition of  $(\text{Mo}_{610}\text{V}_{230}\text{M}_{70})\text{O}_x$  ( $\text{M} = \text{Mo}$  and/or  $\text{V}$ ). The resulting catalog of motifs reproduces individual fragments of the real

structure of a catalyst and can reveal detailed defect-activity correlations that will contribute to a better understanding of heterogeneous catalysis. We currently extend this analysis to specimen that were activated in our operando TEM grid reactor in order to compare the working state of the structural dynamics to the thoroughly analysed defect catalogue for as-synthesized samples. We note that ultimate resolution of the TEM data is required for such type of geometric molecular structure analysis. Care is also necessary to discriminate stimulus-induced dynamics from the reaction-induced surface termination structure. This renders such studies time consuming and requires many observations with suitable specimen, which are not facile to prepare from a needle morphology.

The catalytic properties of MoV oxide in propane oxidation were explored in a conventional fixed bed reactor.<sup>[16]</sup> In contrast to previous reports the desirable oxidation product acrylic acid is formed also over the Te-free M1 structure in significant amounts, implying that Te is not necessarily required as a component of the active ensemble responsible for selective oxygen insertion. The MoV M1 oxide is, however, less selective compared to that of the M1 structure composed of the four metals Mo, V, Te, and Nb. The reason was found by applying a combination of synchrotron-based single crystal structure analysis and NAP-XPS. Determination of the crystal structure of MoV M1 oxide reveals partial occupation of sites in the hexagonal channels of the M1 structure by V, which are occupied by Te in MoVTeNb M1 oxide. Hydrolysis of the M-O bonds (M = V, Te) under reaction conditions allows for migration of the metal in the hexagonal channels to the surface. Accumulation of more than 50 at % V on the surface of the MoV M1 oxide most likely causes post-combustion of formed acrylic acid, whereas enrichment of Te at the surface of MoVTeNb M1 oxide results in dilution of surface  $V^{5+}$  species and, consequently, high selectivity (Figure 3.1.3). The results demonstrate again that the analysis of the surface structure of a heterogeneous catalyst is only meaningful under operation. Further operando studies, in particular by quasi-in situ STEM, are currently in progress.

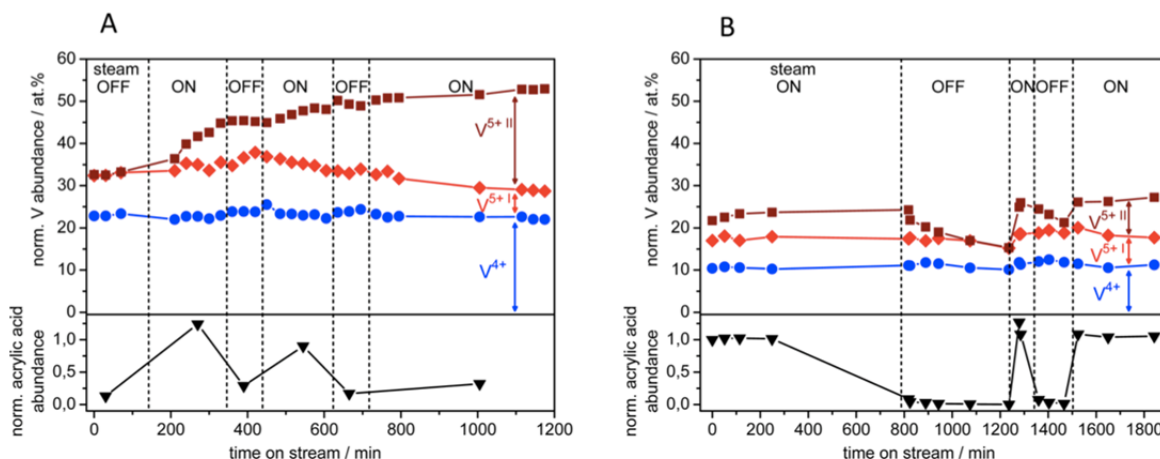


Figure 3.1.3 Normalized abundance of different V species at the surface (0.6 nm information depth) of  $(\text{Mo},\text{V})\text{O}_x$  (A) and  $(\text{Mo},\text{V},\text{Te},\text{Nb})\text{O}_x$  (B) as measured by XPS in the presence of flowing mixtures of  $\text{O}_2/\text{C}_3\text{H}_8/\text{He}$  (steam OFF) and  $\text{O}_2/\text{C}_3\text{H}_8/\text{H}_2\text{O}(\text{g})$  (steam ON), respectively (volume flows of 2/0.5/1.7 sccm), at  $T = 270\text{ }^\circ\text{C}$  (A) and  $400\text{ }^\circ\text{C}$  (B), respectively, and a total pressure of 25 Pa. The V content is given in at % with respect to the sum of metals at the surface. The values are represented in an accumulative way: The blue curve corresponds to the surface concentration of  $\text{V}^{4+}$ ; the red curve corresponds to the sum of the surface concentrations of  $\text{V}^{4+}$  and  $\text{V}^{5+}(\text{I})$ , and the brown curve accounts for the overall surface concentration of V composed of the sum of  $\text{V}^{4+}$ ,  $\text{V}^{5+}(\text{I})$ , and  $\text{V}^{5+}(\text{II})$  (for assignment, see text). The black curve shows the acrylic acid abundance.

### Activation of the Reacting Molecules and Reaction Network

In conjunction with an analysis of surface and bulk structure of vanadium oxide-based catalysts, the reaction network of the substrate molecules, products and intermediates in oxidation of ethane and particularly propane was studied. The catalytic performance of 1) crystalline MoVTenb oxide (M1 structure) that exhibits the electronic properties of a n-type semiconductor, 2) submonolayer vanadium oxide supported on meso-structured silica (SBA-15) as an insulating support, and 3) surface-functionalized carbon nanotubes that contain neither a redox active metal nor bulk oxygen, but only surface oxygen species have been compared in the oxidative dehydrogenation of ethane and propane under equal reaction conditions.<sup>[16]</sup> The catalytic results indicate similarities in the reaction network (Figure 3.1.4) over all three catalysts within the range of the studied reaction conditions implying that differences in selectivity are a consequence of differences in the rate constants. Higher activity and selectivity to acrylic acid over MoVTenb oxide as compared to the other two catalysts are attributed to the higher density of potential alkane adsorption sites on M1 and the specific electronic structure of the semiconducting bulk catalyst. Microcalorimetry has been used to determine and quantify different adsorption sites revealing a low  $\text{V}_{\text{surface}}/\text{C}_3\text{H}_{8\text{ads}}$  ratio of 4 on M1 and a much higher ratio of 150 on silica-supported vanadium oxide. On the latter



catalyst less than one per cent of the vanadium atoms adsorb propane. Barriers of propane activation increase in the order P/oCNT ( $139 \text{ kJ mol}^{-1}$ ) M1 ( $143 \text{ kJ mol}^{-1}$ ) < 6V/SBA-15 ( $162 \text{ kJ mol}^{-1}$ ), which is in agreement with trends predicted by theory.

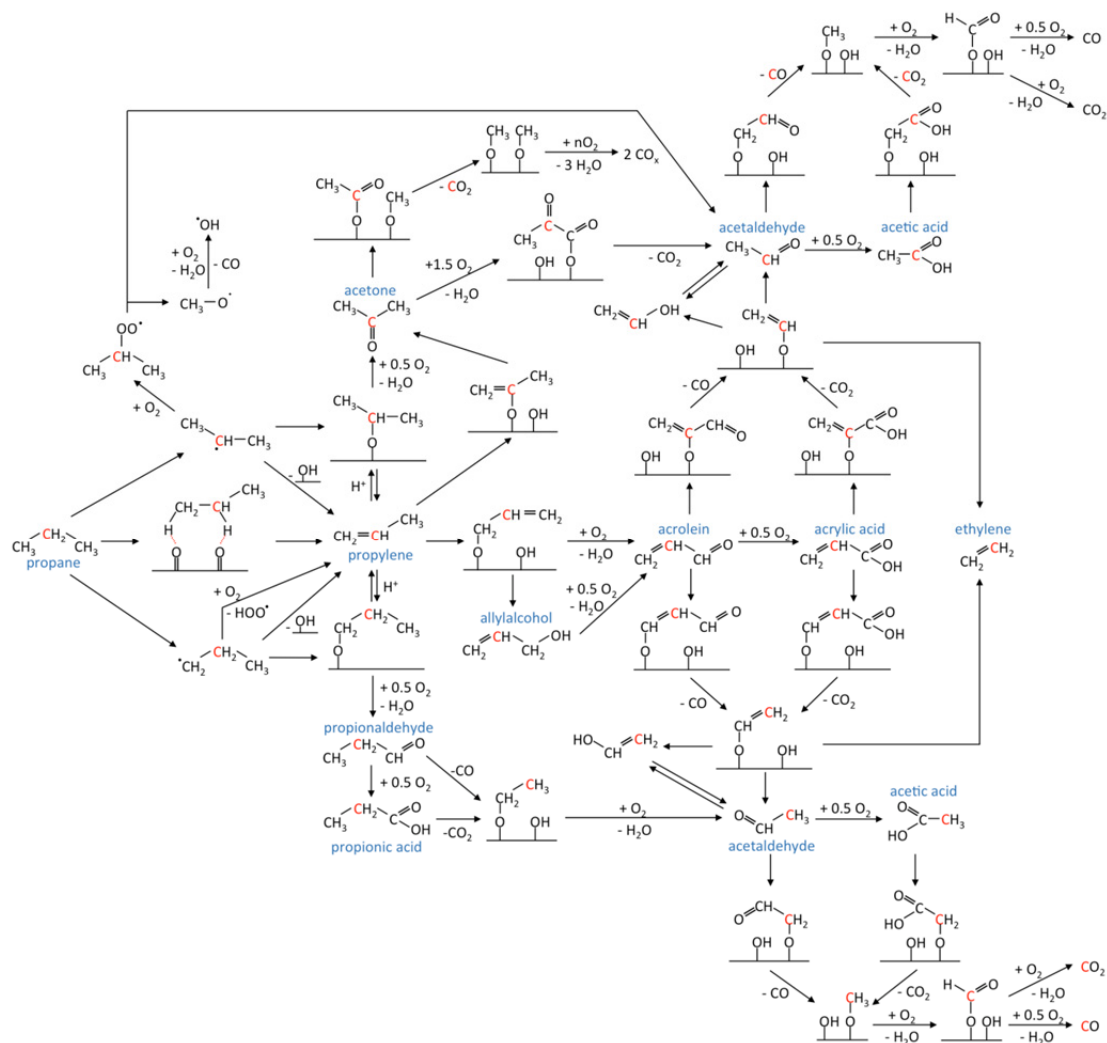


Figure 3.1.4. Proposed reaction network in propane oxidation outlined based on intermediate products detected in the gas phase (blue) over M1 and silica-supported vanadium oxide in dry feed ( $\text{C}_3\text{H}_8/\text{O}_2/\text{He} = 10/5/85$ ) in the temperature range  $100\text{--}450^\circ\text{C}$  during temperature-programmed propane oxidation considering results of the experiments with D- and  $^{13}\text{C}$ -labelled propane (the red colour indicates the  $^{13}\text{C}$ -labelled carbon atom).

Temperature-programmed reaction experiments confirmed the similarities in the network over the two V-containing catalysts (Figure 3.1.4).<sup>[16]</sup> Differences in selectivity were attributed to differences in the rate constants of the individual steps. The most important steps are the abstraction of the first two hydrogen atoms under formation of propylene and the consecutive reactions of acrolein and acrylic acid. The measurement of kinetic isotope effects revealed

fundamental differences in the activation of propane over the two catalysts. Quasi-simultaneous H-abstraction on neighbouring M=O sites (M=V, Mo) might be taken into consideration as an explanation for the KIEs measured over M1. The high density of propane adsorption sites on the surface of M1 as measured by adsorption micro-calorimetry might render such a mechanism possible. In contrast, step-wise abstraction of the two hydrogen atoms including the formation of a propyl species was observed over silica-supported vanadium oxide. The formation pathways of carbon oxides during propane oxidation were studied by means of pulse experiments with  $^{13}\text{C}$ -labelled/unlabelled propane/oxygen mixtures. The final product of the allylic oxidation over M1 is acrylic acid, while the reaction essentially terminates with acrolein formation over silica-supported vanadium oxide. The high concentration of acrylic acid in the product mixture and the preferential formation of unlabelled  $\text{CO}_2$  suggested that over M1 oxidation of acrolein to acrylic acid via oxygen insertion into the C-H bond of the CHO group is faster than oxidation of the vinyl group followed by decarbonylation of the resulting surface species and acetaldehyde formation. In contrast, decarbonylation of acrolein is preferred over silica-supported vanadium oxide as indicated by an increased fraction of unlabelled CO.<sup>[16]</sup>

Our results confirm that control over occurrence and distribution of the various oxygen species on the surface of vanadium oxide catalysts is a key issue to achieve selectivity. We emphasize that the conjecture that oxygen activation is not relevant for controlling selectivity in oxidation as its reaction order is close to zero and thus its elementary steps are fully equilibrated is not a suitable approach when optimizing catalysts. Selective oxidative dehydrogenation of propane to propylene requires the suppression of any electrophilic oxygen species on the catalyst surface, which might be solved by pulsed operation under alternate oxidizing and reducing conditions. The implementation of selective acrolein formation is more challenging, because it requires electrophilic oxygen species and faces the competitive oxidation of propylene in 2-position under formation of acetone and the consecutive oxidation to acetaldehyde that occur in the same temperature range. A more detailed analysis of the impact of reaction parameters on the rates within the network is required to find solutions. We envisage that geometric control of the shape of active sites may become essential to guide the reaction network into one desired reaction. The formation of acrylic acid may be controlled via appropriate design of the solid-state chemistry of the catalysts in terms of oxygen species that selectively insert into the C-H bond of a terminal CHO group. Currently the analysis of

oxygen exchange reaction and surface intermediates in the reduction of oxygen on the surface of V-based catalysts by Raman spectroscopy and complementary techniques is in progress.

We expect that the traditional concentration of research activity on compositional variation of a metal-oxo cluster of unknown size and shape may not provide the ultimate solution. Using only translational structural motifs as development descriptors is inadequate. A more detailed control over geometric access to the active site as well as over the cooperative electronic structure (semiconductor properties) in addition to the local electronic structure will be required. Such multi-parameter optimizations are not likely successful with empirical strategies. The understanding that is slowly evolving from the combination of our studies will be pre-requisite for the envisaged construction of a molecular picture of the properties of a target active site complex.

### **3.2 Electronic Structure Group**

#### **The Silver Oxygen System**

This section reports on model experiments supporting the description of the scientific highlight (section 2 of this report). The bulk of the experiments, theory and collaborations required to arrive at the results shown in section 2 arises from the work of the Electronic Structure Group.

A major challenge in studying the silver oxygen system is the understanding of epoxide selectivity in the reaction with ethylene. The first plausible models dealing with it appeared in the 1940s, postulating that a special form of oxygen is involved in epoxidation. Subsequent studies of the silver oxygen system aimed at identifying the types of oxygen present on and in the silver surface at the oxygen chemical potentials relevant for ethylene epoxidation. Experimentally<sup>[7]</sup> it has been found that two classes of oxygen species are present under such conditions. The first, termed nucleophilic oxygen, is characterized by an O 1s binding energy of ~528.5 eV. It is active only in ethylene combustion<sup>[20]</sup>. The second type of oxygen, electrophilic oxygen, is active in epoxidation and is characterized by an O 1s binding energy of ~530.5 eV. The structure of the former is a well-known family of surface reconstructions, while the latter has long been attributed to oxygen on the unreconstructed surface<sup>[21]</sup> ( $O_{ads}$ ), in part due to scanning tunneling microscopy and computed phase diagrams. This assignment that is summarized in Figure 2.1 motivated computational studies<sup>[22]</sup> of the mechanism of ethylene epoxidation on silver. However, recent evidence suggests this assignment to be incomplete with respect to the molecular structure of the electrophilic oxygen species.<sup>[8-9]</sup>

In an effort to unambiguously identify the O 1s binding energy of oxygen on the unreconstructed surface, and to place bounds on its coverage under oxygen chemical potentials relevant for ethylene epoxidation, we have performed a series of UHV and NAP-XPS experiments coupled with ab initio calculations. Through this approach we find that the O 1s binding energy of  $O_{ads}$  is  $< 528$  eV on the Ag(110) surface, see Figure 3.2.1a and 3.2.1b, in agreement with our earlier results<sup>[9b]</sup> on the Ag(111) surface. The coverage of  $O_{ads}$  can reach 0.1 ML at 120 K. At temperatures relevant for epoxidation (423 K) the stabilization of surface reconstructions are removed and the measured maximum coverage is less than 0.04 ML, see Figure 3.2.1b, in agreement with the computed thermodynamic limit, see Figure 3.2.1c.

Our results demonstrate the electrophilic oxygen species shown to be active in ethylene epoxidation is not the  $O_{ads}$  often modeled computationally. We were able to identify a spectroscopic fingerprint for  $O_{ads}$  and develop a method of preparing high (0.1 ML) coverage of the species. With this information we are now in a position to test the reactivity of  $O_{ads}$  under artificially clean conditions and search for its presence in in situ experiments. There we find the critical function of the co-catalyst sulfur as described in section 2 of this report.

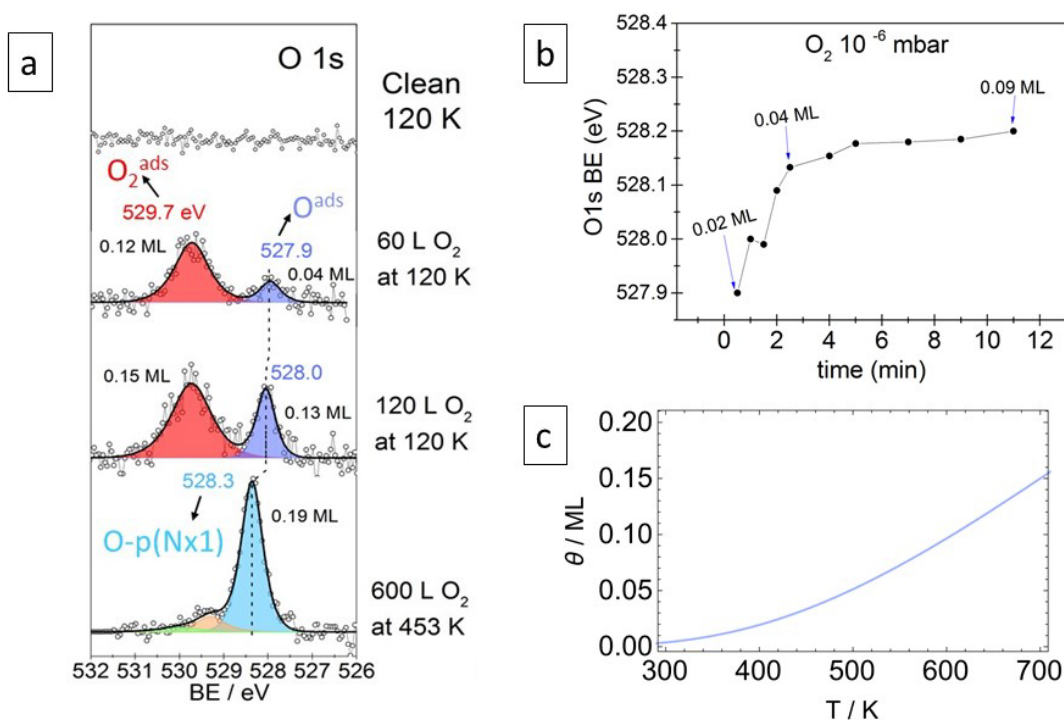


**Figure 3.2.1:** (a) O 1s spectrum of clean and oxygen covered Ag(110) surface. Temperature and oxygen dosing are indicated in the figure. (b) O 1s BE evolution with time measured in-situ for Ag(110) exposed to  $10^{-6}$  mbar O<sub>2</sub>. (c) Computed maximum  $O_{ads}$  coverage as a function of temperature.

## In-situ XPS at Atmospheric Pressure

In the research community, the discrepancy between the higher operating pressures applied in catalytic processes and the lower measurement pressures accessible during surface characterization is known<sup>[2]</sup> as the “pressure gap”. To bridge this gap beyond the capabilities of NAP-XPS, we have recently developed an experimental setup that provides chemical information on a molecular level under atmospheric pressure and in presence of reactive gases<sup>[5b]</sup> at elevated temperatures. Figure 3.2.3 summarizes the concept of our approach and a worked example. The concept is to separate a reaction volume from the vacuum environment by way of a silicon nitride grid—that contains an array of micrometer-sized holes—coated with a bilayer of grapheme. We here use the same technology than in a EC-cell developed previously<sup>[5a]</sup> in our group. Using this configuration, we have investigated the local electronic structure of catalysts by means of photoelectron spectroscopy, and in presence of gases at one atmosphere. The successful operation of this setup was demonstrated with the hydrogenation of propyne on Pd black catalyst (powder), see Figure 3.2.3b.

It is noted that we can compare the results of gas chromatography and XPS without having to extrapolate between the working pressures of the techniques. The data show that the as-prepared catalyst exists in a partly metallic and partly oxidized form. After activation in hydrogen the Pd is solely metallic. Under operation conditions where selective hydrogenation occurs, however, the Pd is present in a minority metallic form (cores) and a majority surface carbide form that allows for controlling selectivity. We here confirm the results of previous NAP XPS<sup>[23]</sup> to prevail also after completely removing the pressure gap without any adaptation necessary.

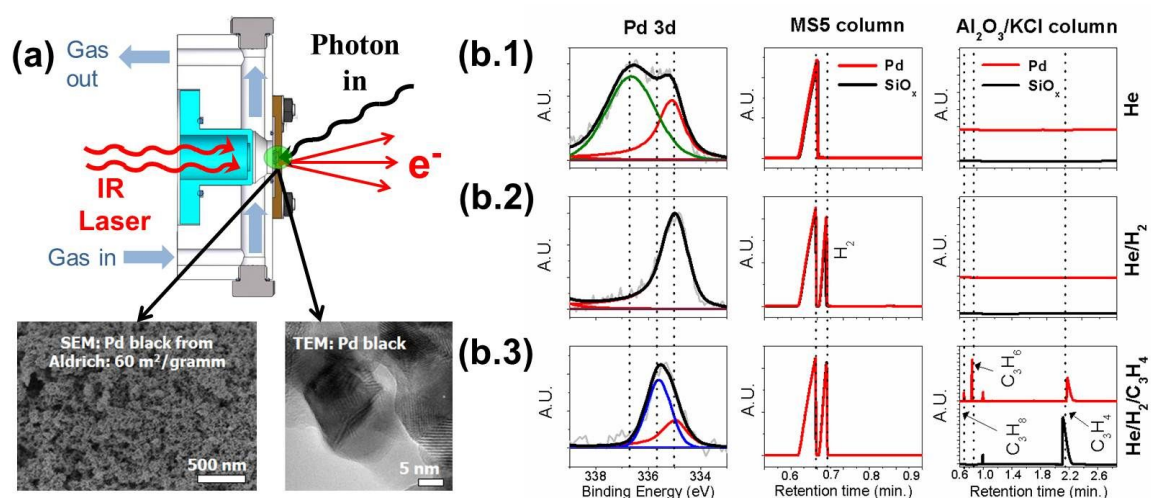


Figure 3.2.3: a) Gas reaction cell and SEM/TEM of Pd catalyst used b) Pd 3d XPS spectra and gas chromatography traces using a mol sieve MS5 column and Al<sub>2</sub>O<sub>3</sub>/KCl column: b.1) He, b.2) He/H<sub>2</sub>, and b.3) He/H<sub>2</sub>/C<sub>3</sub>H<sub>4</sub>.

## Operation of the EMIL Experiment

EMIL, the Energy Materials In-Situ Laboratory Berlin is a concerted effort of the Helmholtz-Zentrum Berlin and the MPG (Fritz-Haber-Institut and MPI for Chemical Energy Conversion) to install and operate a unique facility at the synchrotron source BESSY II that is dedicated to the synthesis and characterization of materials and devices for energy conversion, energy storage and energy efficiency. X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) are among the most versatile methods for the investigation of surfaces on the atomic scale, providing quantitative information about the elemental composition and chemical specificity. The FHI operates a state-of-the-art ambient pressure high kinetic energy X-ray photoelectron spectrometer (“AP-XPS”) at EMIL. With its modular design it is capable of being equipped with reaction cells optimized to study solid-gas and solid-liquid interfaces. Several of these reaction environments and cells have been constructed and put into operation within the last 2 years and are now available at EMIL.

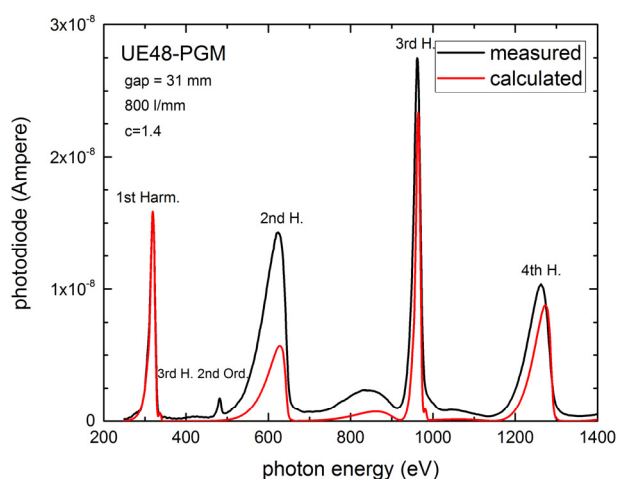


*Figure 3.2.4: Comparison of the measured and calculated photon flux of the soft X-ray undulator UE48 at a fixed gap of 31mm.*

A first milestone of the project has been reached by the first light from the soft X-ray undulator UE48 and the inauguration of the EMIL lab at the end of 2016. The EMIL beamlines offer a broad photon energy range from 80eV to up to 8000eV allowing the utilization of photoelectrons at high kinetic energy as a probe of the interfaces. Two canted

undulators serve as a source for two plane grating monochromators (PGM) and one liquid nitrogen cooled double crystal mono-

chromator (DCM) to make this wide photon energy range available in one overlapping focus. In combination with a small entrance aperture of the differentially pumped AP-XPS spectrometer a high operation pressure can be achieved that for instance allows to work at the vapor pressure of water (around 20mbar at room temperature). Currently, the soft X-ray branch of EMIL is under commissioning. The first results suggest that the performance is as designed (Fig. 3.2.4). The tender X-ray undulator is scheduled to be implemented in the storage ring BESSY in November 2017.

In order to explore the usefulness of the non-destructive depth profiling we performed with an existing HIKE endstation at BESSY some ex-situ tests of metal electrodes<sup>[24]</sup> subject for extensive times to OER conditions in acid environments. In Figure 3.2.5 results from HIKE XPS and a cross-sectional TEM investigation of a used Pt crystal are shown. Unexpectedly we see that up to 4 Pt species representing metal, a surface oxide, a divalent species and a tetravalent species co-exist and are detectable in varying abundance when probing through the overlayer structure seen as lighter contrast in the TEM image. Quantitative analysis reveals that the visual impression of a homogeneous dense overlayer is not correct. A layered sequence of oxide species would be a simplified description of the reacted sample. We verified that no beam damage occurs and point out that degradation in the UHV of the analysis chamber is intermixing with the depth profiling. These observations well justify the expense we make to be able to depth profile electrodes in operando within the EMIL experiment.

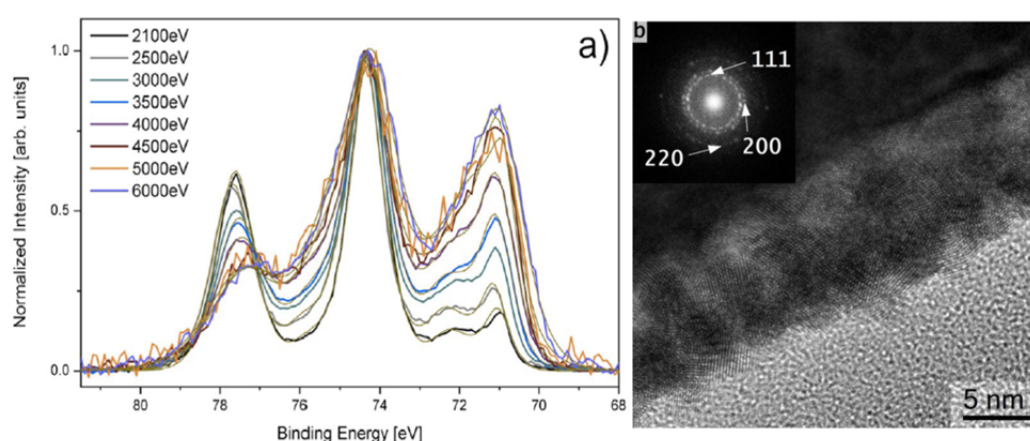


*Figure 3.2.5. Kinetic energy depth profiling (a) and a cross-sectional TEM preparation (b) of a  $Pt_xO_y$  overlayer grown on a Pt (111) crystal after 5 h of OER in 1 n  $H_2SO_4$  at  $10mA/cm^2$ . The change in the line profile of the HIKE XPS data is due to degradation of the resolution of the monochromator used. Note that the EMIL experiment will not have this strong distortion. The two spectra at each kinetic energy indicated show the first and cumulative profile respectively indicating that no beam damage occurs with this delicate sample.*

### 3.3 Electron Microscopy Group

The group operates two in-situ electron microscopes for observing structural dynamics at pressures in the mbar to atmospheric pressure range. One is a SEM for studies in the mesoscopic range and one is a TEM for near atomic resolution observations. In both instruments we can observe reaction products of the minimal amount of specimen and thus try to obtain structure-function relations.



The group invested much work in making the hardware more reliable and more sensitive, in particular for the TEM/MEMS holder combination. We collaborate with both commercial providers of holder namely DENS solution and PROTOCHIPS and have contributed significantly to the improvement of their products to our own benefit. This allows now observing also slow processes as they occur with samples at practical operation conditions where morphologies change on timescales of many h in agreement with reactor observation. An example is the restructuring of silver transforming in oxygen slowly under conditions of ethylene epoxidation and fast during methanol oxidation.

Using the SEM instrument we completed the observation and functional analysis of the growth mode of graphene<sup>[25]</sup> over Pt and Cu. The significant resonance of that work in the community arises from the fact that with these observations several speculative arguments were experimentally resolved. Most relevant was the visual elucidation of reaction mechanisms at the transition between graphene formation and multi-layer growth. The quantifications of time evolution of area, perimeter and layer number during growth experiments with practical conditions not only help the evolution of growth strategies but also allow for testing kinetic models.

### **Metal Redox Transformations**

In many oxidation reactions with metallic catalysts it is unclear if the active form of the catalyst prevails from the metallic precursor or gets oxidized during performance operation. Then the possibility occurs that not only thermodynamically stable phases but intermediate sub-oxides may form and constitute<sup>[26]</sup> the active form of the catalyst. We observed in multiple cases of Ni, Cu, Pt, Ag that at conditions where the metal is of similar stability than the stoichiometric oxide, the system starts undergoing dynamical restructuring<sup>[19]</sup> with surprising velocity and massive morphological changes.

In Figure 3.3.1 a copper foil during hydrogen oxidation at conditions of equal chemical potential is shown in mesoscopic resolution. The conditions were chosen such that convenient time frames with high resolution were obtained. One may estimate how deep the structural transformations are at 973 K with flat terraces representing metallic patches and rough areas being constituted of an oxide as found by EDX point analyses at still slower transformation speed.



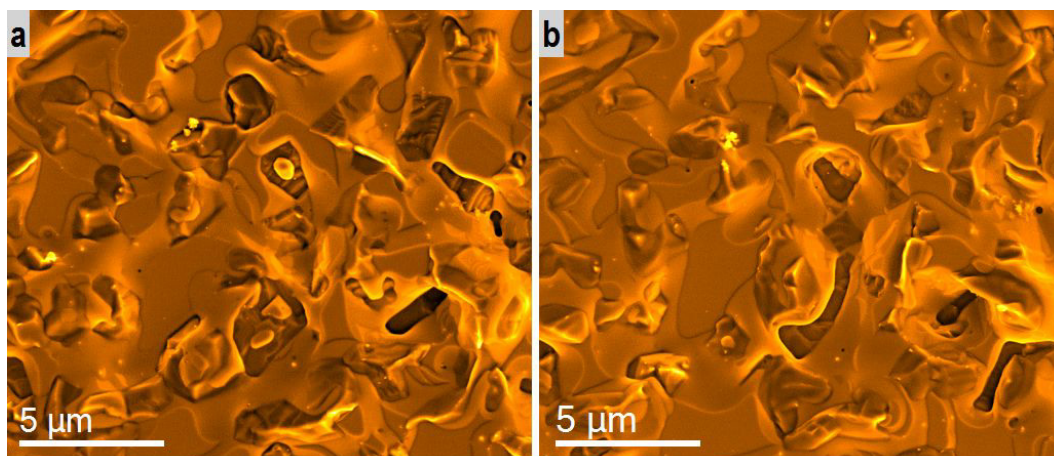


*Figure 3.3.1: (a) and (b) show in situ SEM images of a copper surface in a  $H_2/O_2$  (20:1) atmosphere at 0.2 mbar and 650 °C. Image (b) was recorded 8 minutes after image (a).*

More detailed impressions about the dynamical restructuring can be seen from a TEM study of the same system with examples shown in Figure 3.3.2. We observe a transition from metal to oxide and back. The in-situ diffraction analysis reveals the metal to  $Cu_2O$  reversible transition. The high crystallinity of the phases indicates that despite the transition time of seconds fully crystalline phases are interconverted. We see no indication of amorphous intermediate states. Target preparations of the SEM samples at a moving interface between metal and oxide examined in the TEM confirms this by revealing atomically sharp interfaces between  $Cu_2O$  and Cu metal. Compositional analysis by EDX and EFTEM disclosed, however, that the oxygen abundance is non-zero in the metal phase and exhibits large local variation in the crystallographically well-developed  $Cu_2O$  phase.

In summary, we see that the structural dynamics occurs between two well-defined structural motifs. They exist however, in compositionally large variability as one may expect by the rapid transformation events. Great care has thus to be executed when one uses scattering methods such as XRD or EXAFS to conclude about composition and reactivity in the Cu-O system. This work is currently complemented by NAP-XPS studies to reveal the electronic structures of the two phases in the dynamical state.

In the near future we will test a more powerful camera with the aim to improve our time resolution without sacrificing dynamical range and resolution. Should this test be successful we will apply for funding to buy this camera. We will further complete our extensive studies into stimulus artifacts and avoiding them by adequate preparation. A typical example of this study is the increase in resolution of the observation of zeolitic structures that are notoriously beam-sensitive. Here the combination of better preparation and careful observation using the

low-voltage options seems to allow substantial progress. We connect here to the work in the CP department on silica films<sup>[27]</sup> and try observing disorder phenomena at zeolitic interfaces.

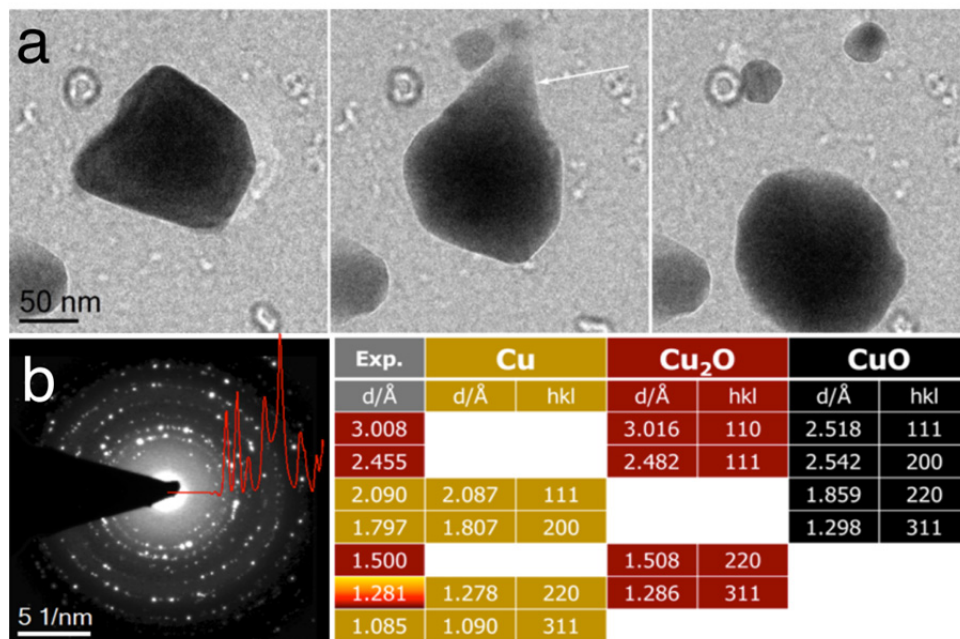


Figure 3.3.2 Cu nanoparticles during a cycle of dynamic transformation between metal (begin in (a)), Cu<sub>2</sub>O center in (a) and metal again right in (a). The transformation occurred within 2 s at 873 K and H<sub>2</sub>/O<sub>2</sub> 20:1 at a pressure of 200 mBar. In (b) the time averaged diffraction patterns are shown together with their analysis revealing the absence of CuO. We note that the transformation process is associated with a loss of facets that are reconstructed after the transformation. The data further show that besides motion relative to the marker structure top left also mass loss is associated with the transformation in agreement with the fact that oxidation of Cu causes metal atoms to move rather than oxygen atoms.

### 3.4 Solid State Electrochemistry Group

#### Silicon Deposited by Low Pressure Chemical Vapor Deposition on Carbonaceous Powdered Materials and Planar Current Collectors for Lithium Ion Batteries

The development of electrochemical devices with high energy density accompanied by long cycling life is essential to store energy produced by intermittent and renewable energy sources. Owing to the capacity of Si to charge up to ten times more Li than graphite, Si based anodes represent an attractive material for next generation lithium ion batteries. Specifically for this project, we have developed a Low Pressure Chemical Vapor Deposition (LP-CVD) reactor, allowing us to perform diverse surface treatments and

depositions in a single batch on both powder (graphite flakes) and planar (metallic foil) samples. The LP-CVD process represents a clean and highly reproducible route when compared to alternative chemical approaches, *e.g.*, precursor calcination, and allows the synthesis of a comprehensive series of material by appropriately adjusting the process. Silicon was deposited using several varying parameters, *e.g.*, temperature, deposition time and gas precursor mixtures, on numerous carbonaceous materials (graphite, multi-walled carbon nanotubes, carbon black) and on metallic current collectors. As an example of our achievements, Figure 3.4.1 shows the electrochemical performance in terms of delithiation capacity over several charge-discharge cycles of Si deposited on graphite (Fig. 3.4.1a) and Si deposited on metallic current collectors (Fig. 3.4.1b) considering, for both, an increasing Si deposition time. The metallic current collectors are purposely developed flat and clean Ti substrates equipped with TiN buffer layer to provide a sharp interface for the reaction with Li. In both cases, the delithiation capacity scales to the Si loading (Fig 3.4.1a insert) and Si film

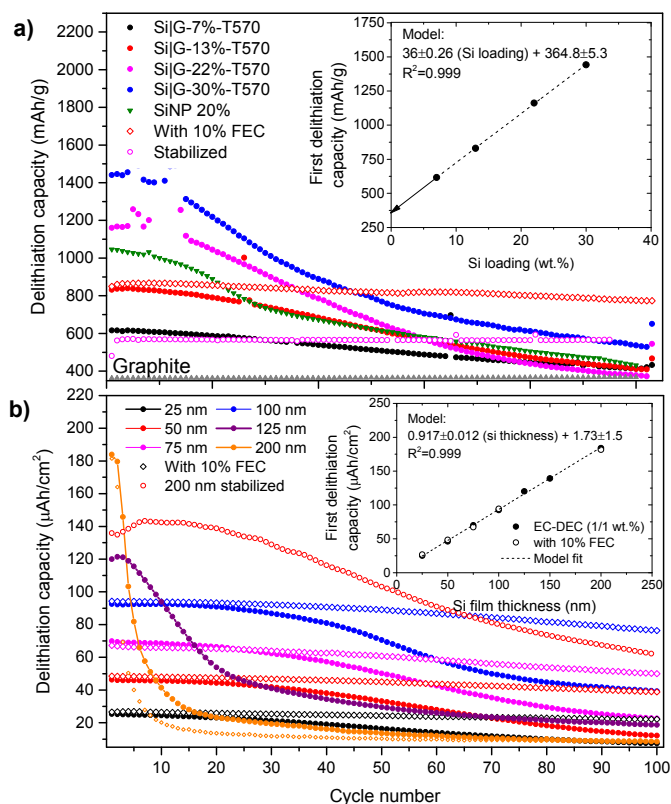


**Figure 3.4.1:** Delithiation capacity of Si deposited on a) graphite flakes and b) metallic current collectors. Insert shows the first delithiation capacity versus a) Si loading and b) Si thin films thickness.

thickness (Fig 3.4.1b insert) according to a first order polynomial model demonstrating the overall reproducibility, from the material synthesis to the electrochemical evaluation. The regressed parameters, which correspond to the specific capacity of the active materials, are equal to  $364.8 \pm 5.8$  and  $3600 \pm 260$  mAh/g and compare well with reported specific capacities of pristine graphite (372 mAh/g) and silicon (3578 mAh/g), respectively.

The stabilization of the capacity decay over several lithiation and delithiation cycles using additives (10% fluoroethylene carbonate, FEC) and an optimized electrochemical cycling protocol is significant as can be observed in Fig. 3.4.1 (open markers). The reasons for the differences in electrochemical performance are analyzed by post-mortem analysis of the anodes. As an example, Figure 3.4.2 shows a scanning electron microscopy image and elemental mapping of a post-mortem anode after 100 cycles, composed of amorphous silicon (20%wt.) and graphite, which

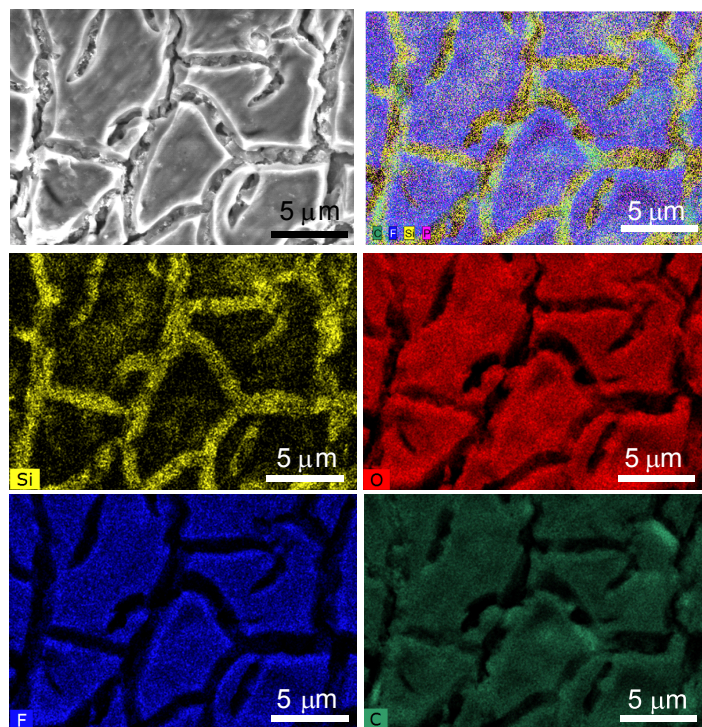


Figure 3.4.2: *Post-mortem elemental mapping of amorphous silicon based anode after 100 cycles of lithiation and delithiation.*

illustrates the severe and continuous electrochemical degradation process of the electrolyte, forming thick polygon islands of ca. 20 by 20  $\mu\text{m}$ . The degradation product of the electrolyte is, according to elemental analysis, mainly composed of F, O and C (Fig. 2, see color code) while Si is located below the polymer and well visible between the islands. Detailed results of this research are presented on AC posters 4.1 and 4.2.

### **Investigation of Charge Transfer at Interfaces Using the Contact-free and in situ Microwave Cavity Perturbation Technique**

Charge transfer at interfaces is of particular relevance in energy storage devices (lithium ion batteries), in energy conversion processes (electro-catalytic water splitting) and in heterogeneously catalyzed reactions, *e.g.*, the activation of hydrocarbons. Within the specific field



of selective oxidation catalysis, the investigation of charge carrier dynamics is of fundamental importance to disentangle the surface and bulk influence on the catalytic performance. Charge carrier properties of a bulk material are typically evaluated via DC or AC electrical conductivity methods, where electrode-material and grain boundaries resistance impede quantitative and sensitive electrical conductivity investigations. To circumvent these limitations, we are using a non-invasive and contact-free method<sup>[28]</sup> based on the microwave cavity perturbation techniques (MCPT) to measure *in situ* the dielectric properties of powder materials in a fixed-bed flow-through reactor. MoVTenNbOx in the orthorhombic M1 phase is an n-type semiconductor under reaction conditions and a promising selective oxidation catalyst for propane. We have demonstrated the formation of an active surface layer and a band bending related to the Fermi level pinning to  $V^{4+}/V^{5+}$  surface states using near-ambient pressure X-ray photoelectron spectroscopy. The *in situ* formation of a space charge layer is furthermore detected by MCPT, which gives the opportunity to relate the conductivity changes to the work function changes, evaluated from photoemission spectroscopy, in several gas atmospheres and conditions. Similarly, the concept of using a gas phase dependent band bending as a descriptor for the selective oxidation alkanes was also supported by the analysis of the selective oxidation of n-butane by the industrial vanadyl pyrophosphate catalyst. Currently, we are investing our efforts to evaluate the generalization of the above concept to a broader range of V-based and V-free catalysts. As an example, the ternary MoV-oxide in the M1 phase showed a conductivity scaling with the number of electrons formally transferred during the oxidation reactions, see AC poster 4.3. While a major part of heterogeneous selective oxidation catalysts are wide bandgap semiconductors, we aim to extend our analytical capabilities to more conductive samples, such as Cu supported on ZnO which is of particular relevance for methanol synthesis. As a first step, we have extended our methodology and defined experimental guidelines for using MCPT with conductive samples. Based on this, a series of Cu/ZnO catalysts was produced and investigated with MCPT to complement the *in situ* investigations of the electronic properties of this catalyst system, thereby favoring the development of a rational synthetic approach. This research, described on AC poster 4.3, is particularly focused to elucidate the direction of charge transfer between the different components of the catalysts, which is still under debate and, as well, to expand the reported literature results gathered from model systems to industrially relevant conditions. In parallel to the above investigations, we have pursued and completed the instrumental development of the MCPT setup by the design of several resonant cavities giving us the

ability to investigate *in situ* the frequency dependence of the conductivity of a material to gain insight into the nature of charge carriers, *e.g.*, free or bound charges. We have moreover completed the development of a microwave hall effect instrument that allows the simultaneous investigation of the charge carrier mobility and conductivity. The MHE setup was successfully validated and used to characterize a series of  $\text{Al}^{3+}$  promoted Cu/ZnO catalysts, with results presented on AC poster 4.4. For the first time we were able to verify the relation of charge carrier concentration to the activation of an adsorbed molecule ( $\text{CO}_2$ ). Increase of the number of charge carriers (found by evaluating the conductivity together with the Hall effect) at the site of activation by doping the ZnO co-catalyst increased the reaction rate and decreased the apparent activation energy to an extent where the activation became no longer rate-controlling and adsorption limitation occurred in the overall reaction as shown by a concomitant increase in the formal reaction order with increased doping.

#### 4. Future Developments

The Department intends to continue its activities along the lines indicated in sections 1 and 3. No major new activities are envisaged at present. A challenge to pursue arises with the beginning interest in solar fuel production. Here molecular structures of  $(\text{C-H}_2\text{-O})_n$  become of interest as fuels for IC engines with minimal particle and greatly reduced  $\text{NO}_x$  emissions. The synthesis of these fuels requires besides methanol from green sources ( $\text{CO}_2$  and renewable hydrogen) the access to a water-poor form of formaldehyde. Such a reaction is currently not available. The Department has access to the core systems that may form a solution by either dehydrogenating methanol or selectively hydrogenating CO. The Department is engaged in putting together a national research consortium (NAMOSYN). If this materializes we will engage in a project to explore the fundamentals of anhydrous formaldehyde production.

The collaboration with B. Roldán on copper chemistry and on setting up electrochemical TEM for her group will engage the Department. This ties in with the increasing effort in developing the combined ETEM/operando TEM instrument that would form a convenient methodical base for more facile and more advanced (electro)-catalytic investigations. In this context we wish to explore the potential and complementarity of X-ray microscopy at BESSY requiring however also operando or in-situ capabilities. Recent developments at HZB may enable more advanced instrumentation and a broader access to these techniques that we may jointly use with our array of electron-based microscopies. The development of a specimen holder plus its interfaces to the various instruments capable of being used in TEM instruments and at BESSY simultaneously could massively reduce application barriers. With HZB we

further continue our intense and fruitful collaboration in consolidating the chemical electron spectroscopy facilities as described in section 1.

We will need to replace our existing SEM instrument. It is with 13 years of continuous operation slowly at the end of its useful life and service becomes increasingly a problem. As this instrument is a core facility to the Department we will need a powerful replacement with field emission gun and proper lens system. This includes a modern EDX instrumentation, as local homogeneity of crystallites is a key analytical target required for functional analysis. We will also strive for extending the quality of the vacuum and the transfer system in order to reduce the still problematic sample contamination issue that wastes much time of instrument and operators. Further we will need to replace our oldest powder X-ray instrument as its mechanical precision is at its end. It has served for 20 years of continuous operation and was repaired several times. We would use the opportunity to experiment with modern 2D detectors in order to enhance the analytical precision. As we need to be able to analyze the line profiles of diffraction patterns we need to be careful with choices of detectors. The Department would welcome a supporting statement of the Fachbeirat for these instrument replacements.

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Wen, G., B. Wang, C. Wang, J. Wang, Z. Tian, R. Schlögl and D.S. Su: Hydrothermal Carbon Enriched with Oxygenated Groups from Biomass Glucose as an Efficient Carbocatalyst. *Angewandte Chemie International Edition* **56** (2), 600–604 (2017).

Willinger, E., A. Tarasov, R. Blume, A. Rinaldi, O. Timpe, C. Massué, M. Scherzer, J. Noack, R. Schlögl and M.G. Willinger: Characterization of the Platinum–Carbon Interface for Electrochemical Applications. *ACS Catalysis* **7** (7), 4395–4407 (2017).

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Xiong, H., K. Lester, T. Ressler, R. Schlögl, L.F. Allard and A.K. Datye: Metastable Pd ↔ PdO Structures During High Temperature Methane Oxidation. *Catalysis Letters* **147** (5), 1095–1103 (2017).

Yi, Y., G. Weinberg, M. Prenzel, M. Greiner, S. Heumann, S. Becker and R. Schlögl: Electrochemical corrosion of a glassy carbon electrode. *Catalysis Today*, in press. 

Zhu, B., C.H. Tang, H.Y. Xu, D.S. Su, J. Zhang and H. Li: Surface activation inspires high performance of ultra-thin Pd membrane for hydrogen separation. *Journal of Membrane Science* **526**, 138–146 (2017).

Zhu, Q., J.N. Kondo and T. Tatsumi: Co-reaction of methanol and ethylene over MFI and CHA zeolitic catalysts. *Microporous and Mesoporous Materials*, in press.

## Doctoral Thesis

Heenemann, M.: Charge Transfer in Catalysis Studied by In-situ Microwave Cavity Perturbation Techniques. Technische Universität Berlin 2017.

Li, X.: Synthesis, characterization and catalytic testing of metal tungstates as catalysts for activation of lower alkanes. Technische Universität Berlin 2017.

## 6. Invited Talks of the Members of the Department of Inorganic Chemistry

- Cap, Sébastien: Investigation of Silicon Based Anode for Lithium Ion Batteries. (Seminar, Silicon based anode research at the FHI, Fritz Haber Institute, Berlin, Germany, Dec 2015).
- Cap, Sébastien: Silicon Based Anode for Lithium Ion Batteries. (9th MAXNET Energy Meeting, Berlin, Germany, Feb 2016).
- Cap, Sébastien: Investigation of Silicon Based Anodes for Lithium Ion Batteries at the FHI. (Seminar, Helmholtz-Zentrum Berlin, Berlin, Germany, Jul 2016).
- Cap, Sébastien: In-Situ Spectroscopic Techniques in Electrochemistry: From Experimental Design to Data Analysis. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Jan 2017).
- Cap, Sébastien: Silicon-Based Materials as High Capacity Anodes for Next Generation Lithium Ion Batteries. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Frei, Elias: CO<sub>2</sub> Activation on Ni- and Cu-Catalysts. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Frei, Elias: CO<sub>2</sub> Activation - Catalysis on Interfaces. (3rd International Symposium on Catalysis for Clean Energy and Sustainable Chemistry (CCESC2016), Madrid, Spain, Sep 2016).
- Frei, Elias: Activation of Small Molecules: Ethylene and Oxygen. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Dec 2016).
- Frei, Elias: Activation of Small Molecules: Carbon Dioxide. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Jan 2017).
- Frei, Elias: CO<sub>2</sub> Activation - from Fundamental Understanding to Application. (Anorganisch-Chemisches Kolloquium, Universität Freiburg, Freiburg, Germany, Jan 2017).
- Frei, Elias: CO<sub>2</sub> Activation to Value Added Products. (Helmholtz-Kolleg Energy-Related Catalysis, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, Jul 2017).
- Girgsdies, Frank: Introduction to Powder X-Ray Diffraction. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Greiner, Mark: Epoxidation on Catalysts in Dynamic Meta-Stable States. (18th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany, Nov 2015).
- Greiner, Mark: Dynamics of Reactivity of Copper Interfaces. (2nd Annual APXPS - Workshop @ Berkeley Lab, Berkeley, CA, USA, Dec 2015).
- Greiner, Mark: Catalysts on the Edge of Stability. (49. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, Mar 2016).



- Hermann, Klaus: Computational Core Electron Spectroscopy: Challenges and Success. (Symposium, New developments in theoretical simulation of x-ray absorption spectra: Possibilities and applications, Berlin, Germany, Oct 2015).
- Hermann, Klaus: Molecular Switches and Machines: Electronic, Magnetic, Geometric. (CRF Seminar, Hong Kong Baptist University, Hong Kong, China, Apr 2016).
- Hermann, Klaus: Structure and Reactivity of Biocatalytic Centers: DFT Studies on Vanadium Oxo-Peroxo Species. (16th International Conference on Theoretical Aspects of Catalysis (ICTAC-16), Zakopane, Poland, Jun 2016).
- Hermann, Klaus: Translation, Rotation, Flexibility of a Cluster, Memories from Classical Mechanics. (CRF Seminar, Hong Kong Baptist University, Hong Kong, China, Oct 2016).
- Hermann, Klaus: Graphene and Other Overlayers Forming Interference Lattices: a Unified Theoretical Treatment. (Seminar, School of Physics, Shandong University, Jinan, Shandong, China, May 2017).
- Hermann, Klaus: Theoretical X-ray Spectroscopy, DFT Cluster Studies for Systems of Catalytic Relevance. (Seminar, Chemistry Department, Qufu Normal University, Qufu, Shandong, China, May 2017).
- Hermann, Klaus: Theoretical X-ray Spectroscopy, DFT Cluster Studies for Systems of Catalytic Relevance. (Seminar, Chemistry Department, Taian University, Taian, Shandong, China, May 2017).
- Hermann, Klaus: Classical Analysis of Molecular Motion: Stilbene as a Test Case. (CRF Seminar, Hong Kong Baptist University, Hong Kong, China, Jun 2017).
- Hetaba, Walid: 72 Years of Electron Microscopy at TU Wien. (EELS. My Life in Science, A Symposium on the occasion of the 65th birthday of Prof. Peter Schattschneider, Vienna, Austria, Nov 2015).
- Hetaba, Walid: Electron Microscopy at the FHI-Berlin - Chemical and Structural Analysis for Heterogeneous Catalysis. (Institutsseminar, Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria, Jun 2016).
- Knop-Gericke, Axel: Photoelectron-Spectroscopy Studies of Electrochemical Processes. (Physikalisch-Chemisches Kolloquium, Ludwig-Maximilians-Universität München, Munich, Germany, Oct 2015).
- Knop-Gericke, Axel: Photoelectron-Spectroscopy Studies of Electrochemical Processes. (SFB 1073 Atomic scale control of energy conversion, Doctoral Students' Seminar in Berlin, Berlin, Germany, Oct 2015).
- Knop-Gericke, Axel: In-Situ Studies of Electrochemically Active Gas-Solid and Liquid-Solid Interfaces. (Berlin-St. Petersburg Workshop on "Structure and Dynamics of Nanoscopic Matter", Berlin, Germany, Dec 2015).
- Knop-Gericke, Axel: The Electronic Structure of Iridium Based Oxygen Evolution Reaction Catalysts. (Skoltech-MSU-FHI-CEC Workshop, Lomonosov Moscow State University, Moscow, Russia, Mar 2016).

- Knop-Gericke, Axel: Solid-Gas Phase and Solid-Liquid Interfaces Studied by (Near) Ambient Pressure X-Ray Photoelectron Spectroscopy under Reaction Conditions. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Knop-Gericke, Axel: XPS Spectroscopy. (Lecture, IMPRS on Reactive Structure Analysis for Chemical Reactions, Mülheim an der Ruhr, Germany, Aug 2016).
- Knop-Gericke, Axel: How to Extend In-Situ Photoelectron Spectroscopy Studies of Electrochemically Active Gas-Solid Interfaces to Liquid-Solid Interfaces? (24th SILS Conference 2016, Bari, Italy, Sep 2016).
- Knop-Gericke, Axel: X-Ray Photoelectron Spectroscopy. (Summer School 2016, Physical Methods in Molecular and Heterogeneous Catalysis, Gelsenkirchen, Germany, Sep 2016).
- Knop-Gericke, Axel: CAT@EMIL. (BESSY II Foresight Workshop on Energy Materials Research, Helmholtz-Zentrum Berlin, Berlin, Germany, Oct 2016).
- Knop-Gericke, Axel: How to Extend In-Situ Photoelectron Spectroscopy Studies of Electrochemically Active Gas-Solid Interfaces to Liquid-Solid Interfaces? (X International Conference Mechanisms of Catalytic Reactions, MCR-X, Svetlogorsk, Kaliningrad, Russia, Oct 2016).
- Knop-Gericke, Axel: The Electronic Structure of Iridium Oxides Active in Water Splitting. (4th Ertl Symposium on Chemical Processes on Solid Surfaces: Water at Interfaces, Berlin, Germany, Oct 2016).
- Knop-Gericke, Axel: X-Ray Photoelectron Spectroscopy for Studying Functional Interfaces. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Knop-Gericke, Axel: The Electronic Structure of Electrochemically Active Interfaces. (AVS 63rd International Symposium and Exhibition, Nashville, TN, USA, Nov 2016).
- Knop-Gericke, Axel: NEXAFS Spectroscopy. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Dec 2016).
- Knop-Gericke, Axel: X-Ray Photoelectron Spectroscopy. (Lecture, Instrumentelle Analytik, Institut für Werkstoffwissenschaften und -technologien, Technische Universität Berlin, Berlin, Germany, Dec 2016).
- Lunkenbein, Thomas: Local Information Powers Heterogeneous Catalysis Research: A TEM Description of Local and Surface Structure. (SFB 840 Kolloquium, University of Bayreuth, Bayreuth, Germany, May 2016).
- Lunkenbein, Thomas: Local Structures in Heterogeneous Catalysis. (Seminar, Institute for Condensed Matter Chemistry of Bordeaux (ICMCB), Bordeaux, France, Mar 2017).
- Lunkenbein, Thomas: Exploring Structural Complexity in Heterogeneous Catalysis. (Anorganisch-Chemisches Kolloquium, Fakultät für Chemie, Universität Duisburg-Essen, Essen, Germany, Jul 2017).
- Schlögl, Robert: Catalysis – a Fundamental Perspective. (Seminar, Institute for Chemical and Bioengineering (ICB), ETH Zurich, Zurich, Switzerland, Oct 2015).

- Schlögl, Robert: Chemical Energy Conversion. (Siemens Council, New York, NY, USA, Oct 2015).
- Schlögl, Robert: Energiewende - Chancen und Herausforderungen für Unternehmen. (Wirtschaftsimpuls Ruhr. Energie mit Zukunft! Essen Economic Development Agency, Folkwang Museum, Essen, Germany, Oct 2015).
- Schlögl, Robert: Heterogene Katalyse-Wissenschaft und Anwendung. (2. RUHR-Symposium „Funktionale Materialien für die Katalyse“, CENIDE, Duisburg, Germany, Oct 2015).
- Schlögl, Robert: Catalysis for Energy. (Kick-Off-Meeting, International Center for Advanced Studies of Energy Conversion, ICASEC, Georg-August-Universität Göttingen, Göttingen, Germany, Nov 2015).
- Schlögl, Robert: Chemical Energy Conversion. (German-Israeli Cooperation Workshop on Microbial Biotechnology and Renewable Energy, Greifswald, Germany, Nov 2015).
- Schlögl, Robert: Chemie für die Energiewende. (Tag der Chemie, University of Oldenburg, Oldenburg, Germany, Nov 2015).
- Schlögl, Robert: CO<sub>2</sub> Utilization from Large-Scale Industrial Point Sources. (The 15th IERE General Meeting & German Forum: International Energy Systems in Transition - Perspectives from Science and Industry, Berlin, Germany, Nov 2015).
- Schlögl, Robert: Energiewende braucht Beratung: Die Rolle der Wissenschaft. (Senatssitzung der Max-Planck-Gesellschaft, Berlin, Germany, Nov 2015).
- Schlögl, Robert: The Nature of Active Sites in Selective Oxidation of Small Alkane Molecules. (GeCatS-Infotag „Katalytische Oxidation als Schlüsseltechnologie“, DECHEMA-Haus, Frankfurt, Germany, Nov 2015).
- Schlögl, Robert: Energiewende 2.0 – Eine Gemeinschaftsaufgabe. (SIEMENS AG, Erlangen, Germany, Dec 2015).
- Schlögl, Robert: In-Situ Electron Spectroscopy for Energy Applications. (2nd Annual APXPS Workshop @ Berkeley Lab, Berkeley, CA, USA, Dec 2015).
- Schlögl, Robert: Catalysis for Sustainable Energy. (CCI Annual Conference, Cardiff Catalysis Conference, Cardiff University, Cardiff, UK, Jan 2016).
- Schlögl, Robert: Requests from Chemistry for Future Electron Microscopy. (1st CHEMEM School on Chemical Electron Microscopy, Harnack House, Berlin, Germany, Jan 2016).
- Schlögl, Robert: The Role of Fossil Carbon in Energy Transformations. (Jahrestagung, Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany, Jan 2016).
- Schlögl, Robert: Elemente und Akteure der Systemtransformation (?). (E-world energy & water, Essen, Germany, Feb 2016).
- Schlögl, Robert: Ir Ox Electrochemistry: A Reaction Totally Dominated by Defects. (Lecture Series Winter Semester 2015 / 2016, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Feb 2016).

- Schlögl, Robert: Power to Liquids: A Challenge for Catalysis Science. (Workshop, Perspectives on Power-to-Liquids & Power-to-Chemicals, Fraunhofer ISE, Freiburg, Germany, Feb 2016).
- Schlögl, Robert: Concepts of Oxidation under Reaction Activities. (Lomonosov Moscow State University, Moscow, Russia, Mar 2016).
- Schlögl, Robert: Surface Chemistry of OER Electrodes. (18th Topical Meeting of the International Society of Electrochemistry, Gwangju, South Korea, Mar 2016).
- Schlögl, Robert: Towards a Sustainable Energy System - The German Model (?). (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Schlögl, Robert: Carbon to Energy: A Facile Link. (Australian Institute for Nanoscale Science and Technology (AINST), The University of Sydney, Sydney, Australia, Apr 2016).
- Schlögl, Robert: Designer Fuels from CO<sub>2</sub> – Neue Kraftstoffe aus CO<sub>2</sub>. (37. Internationales Wiener Motorensymposium, Vienna, Austria, Apr 2016).
- Schlögl, Robert: Energy Systems of the Future: Why Chemistry? (Nanotechnology & Catalysis Research Centre (NANOCAT), University of Malaya, Kuala Lumpur, Malaysia, Apr 2016).
- Schlögl, Robert: Towards a Sustainable Energy System - The German Model (?). (Manfred-Eigen-Nachwuchswissenschaftlergespräche 2016 der Deutschen Bunsen-Gesellschaft: Physical Chemistry of Solar Fuels Catalysis, Mülheim an der Ruhr, Germany, Apr 2016).
- Schlögl, Robert: Catalysis at the Synchrotron BESSY. (Synchrotron Beamline development for the Catalysis Industry in City of London, The Royal Society, London, UK, May 2016).
- Schlögl, Robert: Structure Sensitivity in Oxidative Coupling of Methane over MgO. (University of Virginia, Charlottesville, VA, USA, May 2016).
- Schlögl, Robert: Carbon2Chem - Das Projekt. (Pressekonferenz, Carbon2Chem, Duisburg, Germany, Jun 2016).
- Schlögl, Robert: Fundamentals and Challenges of CCU/CCS. (Aufaktworkshop: Technische Wege der Dekarbonisierung: CO<sub>2</sub>-Minderungsoptionen für Industrieprozesse, acatech, Berlin, Germany, Jun 2016).
- Schlögl, Robert: Opportunities and Challenges for Catalysis Research: Instrumental (?) Infrastructure. (DOE Basic Research Needs workshop on critical instrumentation for energy sciences, Rockville, MA, USA, Jun 2016).
- Schlögl, Robert: Chemical Energy Storage - Part of a Systemic Solution. (3rd Course of the Joint EPS-SIF International School on Energy, 69th Course of the International School of Solid State Physics: “Materials for Energy and Sustainability V”, Erice, Italy, Jul 2016).
- Schlögl, Robert: Energiewende und Chemie. (Strategieklausur Wacker Chemie, Munich, Germany, Jul 2016).

- Schlögl, Robert: Energiewende und Mobilität. (Workshop, OBRIST Engineering, Listenaus, Germany, Jul 2016).
- Schlögl, Robert: Microscopy and Interfacial Reactions. (Workshop on Scientific Directions for Future Transmission Electron Microscopy, RWTH Aachen University, Aachen, Germany, Jul 2016).
- Schlögl, Robert: Chemical Energy Conversion. (Inauguration, VILLUM Center for the Science of Sustainable Fuels and Chemicals, Humlebæk, Denmark, Aug 2016).
- Schlögl, Robert: Electrocatalysis. (Summer School 2016, Physical Methods in Molecular and Heterogeneous Catalysis, Wissenschaftspark, Gelsenkirchen, Germany, Sep 2016).
- Schlögl, Robert: Energy. Global. Digital. (ProcessNet-Jahrestagung und 32. DECHEMA-Jahrestagung der Biotechnologen 2016, Aachen, Germany, Sep 2016).
- Schlögl, Robert: Inorganic Materials for Sustainable Energy. (18. Vortragstagung der Wöhler-Vereinigung, Wöhler-Vereinigung für Anorganische Chemie, Gesellschaft Deutscher Chemiker (GDCh), Berlin, Germany, Sep 2016).
- Schlögl, Robert: Ir Oxide - a Prototypical Case for an OER Catalyst. (International Conference on Advances in Semiconductors and Catalysts for Photoelectrochemical Fuel Production (SolarFuel16), Berlin, Germany, Sep 2016).
- Schlögl, Robert: Utilization of Carbon Sources in Sustainable Energy Systems. (DGMK/acatech Workshop: Stoffliche Nutzung von Braunkohlen und Biomassen und deren Rolle bei der Ausgestaltung der Energiewende, Berlin, Germany, Oct 2016).
- Schlögl, Robert: Best Practice: Nachwuchsförderung. (Tag des wissenschaftlichen Nachwuchses, Technische Universität Chemnitz, Chemnitz, Germany, Nov 2016).
- Schlögl, Robert: Die Struktur des Energieproblems. (Rotary Club, Mülheim an der Ruhr, Germany, Nov 2016).
- Schlögl, Robert: Electrocatalytic Materials for Oxygen Evolution. (2016 MRS Fall Meeting, Boston, MA, USA, Nov 2016).
- Schlögl, Robert: Fundamental Aspects of Oxidation Catalysis - a Case for Academic-Industrial Collaboration. (ExxonMobil's ESEP Symposium 2016, Brussels, Belgium, Nov 2016).
- Schlögl, Robert: IrOx as OER Benchmark Towards Its Functional Understanding. (SLAC Workshop, Stanford University, Menlo Park, CA, USA, Dec 2016).
- Schlögl, Robert: Energiewende: Was wir wollen und was wir können. (Science Festival 2017, XLAB, Göttingen, Germany, Jan 2017).
- Schlögl, Robert: Energy Science in the MPG from Strategy to Physical Chemistry. (Workshop, Schaeffler Group, Herzogenaurach, Germany, Jan 2017).
- Schlögl, Robert: Potential Future Utilization of CO<sub>2</sub>. (Meeting, The Royal Society of Chemistry, London, UK, Jan 2017).
- Schlögl, Robert: Monomolekulare Kraftstoffe für Diesel- und Ottomotoren. (4. Internationaler Motorenkongress, Baden-Baden, Germany, Feb 2017).

- Schlögl, Robert: Sustainable CO<sub>2</sub> Utilization Opportunities and Challenges. (BIO-raffiniert IX, Fraunhofer UMSICHT, Oberhausen, Germany, Feb 2017).
- Schlögl, Robert: Synthetische Kraftstoffe. (Seminar, IEC, Technische Universität Bergakademie Freiberg, Freiberg, Germany, Feb 2017).
- Schlögl, Robert: Dynamics of Interfacial Reaction. (Seminar, Institute of Solid State Physics, Vienna University of Technology, Vienna, Austria, Mar 2017).
- Schlögl, Robert: Heterogene Katalysatoren: statisch oder dynamisch? (SFB 840 Kolloquium, University of Bayreuth, Bayreuth, Germany, Mar 2017).
- Schlögl, Robert: Selective Oxidation of C<sub>2</sub>-C<sub>4</sub> Alkanes on Oxide Catalysts. (50. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, Mar 2017).
- Schlögl, Robert: Towards a Sustainable Energy System - The German Model. (Symposium: Catalysed Energy Storage in Chemicals, CSIRO, Clayton, Melbourne, Australia, Apr 2017).
- Schlögl, Robert: Einführung: Kopernikusprojekte für die Energiewende - Status quo. (Zukunftskongress „Energieoffensive 2030“, BMBF, Berlin, Germany, May 2017).
- Schlögl, Robert: Ammonia Synthesis. (Lecture Series, Advanced Courses on Catalytic Reactions, IMPRS RECHARGE, Mülheim an der Ruhr, Germany, Jun 2017).
- Schlögl, Robert: CO<sub>2</sub> Harvesting. (Lecture Series, Advanced Courses on Catalytic Reactions, IMPRS RECHARGE, Mülheim an der Ruhr, Germany, Jun 2017).
- Schlögl, Robert: The Evolution of the Concepts of Active Sites in Heterogeneous Catalysis. (Workshop, The Theory and Practice of Catalysis, Telluride Science Research Center, Telluride, CO, USA, Jun 2017).
- Schlögl, Robert: Why Operando Studies in Catalysis. (North American Catalysis Society Meeting 2017 (NAM25), Denver, CO, USA, Jun 2017).
- Schlögl, Robert: Chemical Energy Conversion. (Darmstadt Symposium, The great transition: The importance of critical metals for green energy technologies, Darmstadt, Germany, Jul 2017).
- Schlögl, Robert: Role of Synthetic Fuels in Sustainable Energy System. (2nd International Conference on Power and Energy Engineering, Munich, Germany, Jul 2017).
- Schlögl, Robert: Transition Towards Sustainable Energy. (Lecture, Energy & Sustainability Summer School 2017, Leiden University, Leiden, The Netherlands, Jul 2017).
- Siebeky, Uta: Open Access Statistik an einem Max-Planck-Institut. (Herbsttagung der Bibliotheken der CPT-Sektion, Golm, Germany, Nov 2016).
- Siebeky, Uta: Unterstützung im Publikationsprozess am FHI. (XL. Bibliothekstagung der Max-Planck-Gesellschaft, Berlin, Germany, Apr 2017).
- Siebeky, Uta: Open Access und Publikationsprozess am FHI. (Frühjahrssitzung, Arbeitskreis Spezialbibliotheken Dresden, HZDR, Dresden, Germany, May 2017).

- Siebeky, Uta: Wie wird was wann wo gezählt? Open Access-Statistik. (Open Access-Workshop, Experten für Experten – No. 1, Berlin, Germany, Jun 2017).
- Teschner, Detre: Ir-Based Electrocatalysts for the Oxygen Evolution Reaction. (International FOXSI Conference 2016, Functional Oxide Surfaces and Interfaces, Vienna, Austria, May 2016).
- Trunschke, Annette: Structural and Dynamic Aspects of Site Isolation at the Surface of Selective Oxidation Catalysts. (251st ACS National Meeting & Exposition, Division of Catalysis Science and Technology: Surface Chemistry & Catalysis of Metal Oxides, San Diego, CA, USA, Mar 2016).
- Trunschke, Annette: Synthesis of Complex Metal Oxides. (Seminar, Lomonosov Moscow State University, Moscow, Russia, Mar 2016).
- Trunschke, Annette: Hydrothermal Synthesis of Bi-Functional Nanostructured Manganese Tungstate Catalysts for Selective Oxidation. (Faraday Discussion: Designing New Heterogeneous Catalysts, London, UK, Apr 2016).
- Trunschke, Annette: Infrared Spectroscopy. (Lecture Series, Physical Methods in Homogeneous and Heterogeneous Catalysis, IMPRS RECHARGE, Mülheim an der Ruhr, Germany, May 2016).
- Trunschke, Annette: Mechanistic Studies of Propane Oxidation over Vanadium Oxide Catalysts. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Trunschke, Annette: The Surface of Metal Oxide Catalysts: Quantitative Approaches towards Active Site Characterization. (Catalysis Group Seminar, Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA, USA, Jun 2017).
- Trunschke, Annette: Experimental Elucidation of the Complex Reaction Network in Propane Oxidation. (LCT Seminar, Laboratory for Chemical Technology, Ghent University, Ghent, Belgium, Jul 2017).
- Trunschke, Annette: Frustrated Surface Sites in Olefin Metathesis. (22nd International Symposium on Olefin Metathesis and Related Chemistry (ISOM XXII), Zurich, Switzerland, Jul 2017).
- Velasco Vélez, Juan: On the Way to Bridging the Gaps in Catalysis: A Perspective in X-Ray Photoelectron Spectroscopy. (Seminar, National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, May 2016).
- Velasco Vélez, Juan: Operando Soft X-Ray Photo Electron Spectroscopy Characterization of Interfacial Phenomena in Chemical Energy Conversion Processes at Atmospheric Pressure. (Seminar, Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA, USA, Dec 2016).
- Velasco Vélez, Juan: Soft X-Ray Photoelectron Spectroscopy Characterization of Interfacial Phenomena in Chemical Energy Conversion Related Processes at Atmospheric Pressure. (Physikalisches Kolloquium, Fakultät für Chemie und Physik, Technische Universität Bergakademie Freiberg, Freiberg, Germany, Apr 2017).
- Velasco Vélez, Juan: Sustainable Energy and Climate Change: The Role of the X-Ray in the Solution of the Renewable Energy Storage Puzzle. (Science Slam, The Long Night of

Ideas: Explore the international world of research, WissenschaftsForum, Berlin, Germany, May 2017).

- Velasco Vélez, Juan: Towards, the Uncovering of the Electrochemical Energy Conversion Conundrum by Means of Advanced X-Ray Spectroscopy Methods. (XXVI International Materials Research Congress (IMRC 2017), Material Characterization Symposia, Cancún, Mexico, Aug 2017).
- Willinger, Elena: Analysis of Local Structure by Atomic Pair Distribution Function. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Feb 2017).
- Willinger, Marc Georg: Chemical Electron Microscopy. (SFB 1073 Atomic scale control of energy conversion, Doctoral Students' Seminar in Berlin, Berlin, Germany, Oct 2015).
- Willinger, Marc Georg: In-Situ SEM: A Versatile Surface Science Tool for Catalysis. (Bruker Seminartage zur Mikroanalyse, Berlin, Germany, Oct 2015).
- Willinger, Marc Georg: Capturing the Dynamics of Heterogeneous Catalysts by Electron Microscopy. (Festkörperchemisches Seminar, Technische Universität Berlin, Berlin, Germany, Nov 2015).
- Willinger, Marc Georg: Chemistry Is the Physics of the Outer Electrons...and a Bit! (EELS. My Life in Science, A Symposium on the occasion of the 65th birthday of Prof. Peter Schattschneider, Vienna, Austria, Nov 2015).
- Willinger, Marc Georg: Chemical Electron Microscopy. (Conferencia, Facultad de Ciencias, Universidad de Cádiz, Cádiz, Spain, Dec 2015).
- Willinger, Marc Georg: Progress in Ultra-High Resolution Electron Microscopy for the Study of Advanced Materials. (Seminar, Centre for Research in Ceramics and Composite Materials (CICECO), University of Aveiro, Aveiro, Portugal, Dec 2015).
- Willinger, Marc Georg: The Power of Analytical Electron Microscopy: Examples from Catalysis and Biomineralization. (Institutsseminar, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, Jan 2016).
- Willinger, Marc Georg: In-Situ T(S)EM Applications and Prospect of In-Situ Technique Development for Catalyst Application. (Seminar, DENSsolutions, Delft, The Netherlands, Mar 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (Seminar, Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons, Jülich, Germany, Apr 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (Physikalisches Kolloquium, Department für Physik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany, Apr 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (NPRL mini-symposium, University of Birmingham, Birmingham, UK, Apr 2016).



- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (In Situ TEM Workshop, Trondheim, Norway, Jun 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (2016 Japan-Germany Joint Symposium on Advanced Characterization of Nanostructured Materials for Energy and Environment, Düsseldorf, Germany, Jun 2016).
- Willinger, Marc Georg: Electron Microscopy. (IMPRS: Recharge Summer School 2016, Physical Methods in Molecular and Heterogeneous Catalysis, Gelsenkirchen, Germany, Jul 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (The 16th European Microscopy Congress, Lyon, France, Aug 2016).
- Willinger, Marc Georg: Electron Microscopy. (IMPRS: Recharge Summer School 2016, Physical Methods in Molecular and Heterogeneous Catalysis, Gelsenkirchen, Germany, Sep 2016).
- Willinger, Marc Georg: Electron Microscopy in Catalysis. (YounGeCatS Summerschool, German Catalysis Society, Berlin, Germany, Sep 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (IV Russian-German Seminar on Catalysis, Bad Staffelstein, Germany, Sep 2016).
- Willinger, Marc Georg: Electron Energy Loss Spectroscopy (EELS). (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Oct 2016).
- Willinger, Marc Georg: Fundamentals of Transmission and Scanning Electron Microscopy. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Willinger, Marc Georg: Oscillatory Red-Ox Behavior of Active Metal Catalysts Observed by In-Situ Electron Microscopy. (4th Ertl Symposium on Chemical Processes on Solid Surfaces: Water at Interfaces, Berlin, Germany, Oct 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (Seminar, Leibniz Institute for Solid State and Materials Research (IWF), Dresden, Germany, Oct 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (CISCeM 2016, 3rd International Conference on In-Situ and Correlative Electron Microscopy, Saarbrücken, Germany, Oct 2016).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (GRK Summer School, Graduiertenkolleg 1896 In-Situ Microscopy with Electrons, X-rays and Scanning Probes, Bischofsgrün, Germany, Oct 2016).

- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (Workshop, JEOL F2 and Gatan: The new world for in-situ applications, Freising, Germany, Oct 2016).
- Willinger, Marc Georg: The Need for UHV TEM for In-Situ Studies of Heterogeneous Catalysts. (Workshop on Scientific Directions for Future Transmission Electron Microscopy, Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons, Jülich, Germany, Oct 2016).
- Willinger, Marc Georg: Catalysts by In-Situ Scanning and Transmission Electron Microscopy. (AVS 63rd International Symposium and Exhibition, Nashville, TN, USA, Nov 2016).
- Willinger, Marc Georg: Capturing the Dynamics of Heterogeneous Catalysts by Electron Microscopy. (Festkörperchemisches Seminar, Department of Chemistry, Technische Universität Berlin, Berlin, Germany, Nov 2016).
- Willinger, Marc Georg: The Need for In-Situ Microscopy. (Workshop on Cryo-FIB/SEM, Max Planck Institute of Colloids and Interfaces, Golm, Germany, Dec 2016).
- Willinger, Marc Georg: CVD Graphene Growth Dynamics, Stacking Sequence and Interlayer Coupling Revealed by In-Situ Scanning Electron Microscopy. (International Winterschool on Electronic Properties of Novel Materials (IWEPM), Kirchberg, Austria, Mar 2017).
- Willinger, Marc Georg: The Dynamics of Active Metal Catalysts Revealed by In-Situ Electron Microscopy. (Lecture, ETH Zurich, Zurich, Switzerland, Mar 2017).
- Willinger, Marc Georg: Real-Time Observation of Catalyst Dynamics by In-Situ Microscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Willinger, Marc Georg: Multi-Scale Observation of Catalyst Dynamics under Reactive Conditions. (Microscopy Conference 2017, Dreiländertagung, Lausanne, Switzerland, Aug 2017).
- Wrabetz, Sabine: Mikrokalorimetrische Untersuchungen zum dynamischen Verhalten von heterogenen Katalysatoren unter quasi-realen Reaktionsbedingungen. (Anwenderseminar „Methoden der Thermischen Analyse und Rheologie in der Entwicklung und Qualitätssicherung“, Würzburger Tage 2016, Würzburg, Germany, Apr 2016).
- Wrabetz, Sabine: Reactants Induced Dynamic Responses of Heterogeneous Catalysts Monitored by Adsorption Microcalorimetry. (ICTAC 2016, International Confederation for Thermal Analysis and Calorimetry, Orlando, FL, USA, Aug 2016).

## Department of Chemical Physics

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

|                      |                |
|----------------------|----------------|
| Markus Heyde         | (Habilitation) |
| Helmut Kühlenbeck    | (Habilitation) |
| Thomas Schmidt       |                |
| Shamil Shaikhutdinov |                |

**Guest scientists, staying for at least six months, paid by FHI:**

|                         |                      |                       |                      |
|-------------------------|----------------------|-----------------------|----------------------|
| Giulia Berti            |                      | Quishi Pan            |                      |
| Felix Feiten            | <i>until 12/2017</i> | Wolf-Dieter Schneider |                      |
| Francesca Genuzio       | <i>until 09/2016</i> | Jan Seifert           | <i>until 02/2017</i> |
| Daniel Gottlob          |                      | Georg Simon           |                      |
| Francisco Ivars Barcelo |                      | Heloise Tissot        | <i>until 05/2017</i> |
| David Kuhness           |                      | Eberhard Umbach       |                      |
| Helder Marchetto        |                      | Xuefei Weng           |                      |
| Dietrich Menzel         |                      | Hyun Jin Yang         |                      |
| Jagriti Pal             |                      |                       |                      |

**Guest scientists, staying for at least six months, paid from external funds:**

|                    |                                            |                        |                       |
|--------------------|--------------------------------------------|------------------------|-----------------------|
| Smardar Attia      | <i>CAU Kiel</i>                            | Nina Richter           | <i>BMBF</i>           |
| Jade Barreto       | <i>DFG</i>                                 | Thomas Risse           | <i>FU Berlin</i>      |
| Christin Büchner   | <i>DFG (CRC 1109)</i>                      | Swetlana Schauerermann | <i>CAU Kiel</i>       |
| Kristen Burson     | <i>AvH Fellow</i>                          | Jan Seifert            | <i>DFG (CRC 1109)</i> |
| Xiong Feng         | <i>CSC-Program</i>                         | Randall Snurr          | <i>AvH Awardee</i>    |
| Alexander Fuhrich  | <i>DFG (UniCat)</i>                        | Evan Spadafora         | <i>CAU Kiel</i>       |
| Leonhard Gura      | <i>ERC Cryvisil</i>                        | Fernando Stavale       | <i>DFG</i>            |
| Laxman Kankate     | <i>DFG (UniCat)</i>                        | Sefik Süzer            | <i>AvH Fellow</i>     |
| Meng-Fan Luo       | <i>National Central University, Taiwan</i> | Eman Zaki              | <i>DFG (CRC 1109)</i> |
| Patrick Marschalik | <i>ERC Cryvisil</i>                        | Zongfang Wu            | <i>AvH Fellow</i>     |
| Christoph Möller   | <i>DFG</i>                                 | Zechao Yang            | <i>ERC Cryvisil</i>   |
| Gina Peschel       | <i>DFG (UniCat)</i>                        |                        |                       |

|                                 |                              |
|---------------------------------|------------------------------|
| Graduate students:              | 21 (incl. 16 IMPRS students) |
| Technicians:                    | 10                           |
| Service Group PP&B:             |                              |
| Head: Heinz Junkes              | 5 Technicians, 2 Trainees    |
| Service Group                   |                              |
| Crystal Preparation Laboratory: |                              |
| Head: Shamil Shaikhutdinov      | 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.

Prof. Thomas Risse terminated his collaboration on EPR with the CP Department.

With Dr. Svetlana Schauermaann's move to Kiel the Single Crystal Microcalorimetry has been relocated to Kiel University.

Three Postdoctoral Associates have left the group to higher academic positions:

- Dr. Florencia Calaza (National University of the Littoral / Argentina)
- Dr. Kristen Burson (Hamilton College / USA)

The collaborations with two MPG partner groups were continued:

- 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

Both groups will have their evaluation in late 2017 and early 2018 respectively.

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

### Honors and Awards:

*Christin Büchner*

- Feodor Lynen Research Fellowship (2017)
- Otto-Hahn Medal (2017)

*Hans-Joachim Freund*

- Elected Foreign Honorary Member, American Academy of Arts and Sciences (2016)
- Dr. Honoris Causa, Karlsruhe Institute of Technology (KIT) (2016)
- Honorary Senator, Friedrich-Alexander-Universität Erlangen-Nürnberg (2016)

- Dr. Honoris Causa, Friedrich-Alexander-Universität Erlangen-Nürnberg (2017)
- Visiting Einstein Professor at University of Science and Technology of China (2017)

*Swetlana Schauermann*

- Dozentenstipendium des Fonds der Chemischen Industrie (Fellowship of the Association of Chemical Industry) (2012-2017)

**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)
- Member, International Advisory Board, Utrecht University Sustainability programme (since 2015)
- Scientific Member of the Senate and the Joint Committee of the German Science Foundation (Deutsche Forschungsgemeinschaft) (2015 - 2016)
- Member, Advisory Board, “Advances in Physics: X“ (since 2015)
- Member, Selection Committee of the Gottfried Wilhelm Leibniz-Program of the German Science Foundation (Deutsche Forschungsgemeinschaft) (since 2016)

*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:**

- International Department Workshop, Ringberg (2016)
- International Department Workshop, Döllnsee (2017)
- Symposium on the occasion of Helmut Kühlenbeck’s 60. Birthday (2017)

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

1. Scanning Probe Microscopy

*Group Leader: Markus Heyde*

*consultant: Wolf-Dieter Schneider*

2. Spectroscopy

*Group Leader: Helmut Kuhlenbeck*

3. Spectro-Microscopy (SMART)

*Group Leader: Thomas Schmidt*

*consultants: Dietrich Menzel, Eberhard Umbach*

4. Structure and Reactivity

*Group Leader: Shamil Shaikhutdinov*

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. 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 is an associate member to the Einstein Center within the Berlin universities. The evaluation has been in favor.

**The complete list of collaborations encompasses:**

- Collaboration H.-J. Freund, M. Sterrer, S. Shaikhutdinov, M. Heyde, Th. Schmidt:  
*SFB/CRC 1109: “Understanding of Metal Oxide / Water Systems at the Molecular Scale: Structural Evolution, Interfaces, and Dissolution”*
- Collaboration H.-J. Freund, J. Sauer and J. Paier:  
*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 Físicas (CBPF), Rio de Janeiro
- Collaboration with China:  
H.-J. Freund, M. Heyde and H.-J. 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
- Collaboration with France:  
S. Shaikhutdinov, J. Goniakowski and C. Noguera, Sorbonne Universités (UPMC), Paris  
H. Junkes and R. Lange, ITER Organisation, Cadarache
- Collaboration within Germany:  
H.-J. Freund, M. Heyde and N. Nilius, Universität Oldenburg, Oldenburg  
H.-J. Freund, M. Heyde, S. Shaikhutdinov, S. Schauer mann, H. Kuhlenbeck and J. Sauer, Humboldt-Universität zu Berlin, Berlin  
H.-J. Freund, H. Kuhlenbeck und V. Staemmler, Ruhr-Universität Bochum  
H.-J. Freund, H. Kuhlenbeck und Ch. Papp, Universität Erlangen-Nürnberg, Erlangen  
H. Junkes and H. Hafok, MPI für Radioastronomie, Radioobservatorium Effesberg



- 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 the Sweden:  
H. Junkes and T. Korhonen, ESS, Lund
- Collaboration with the UK:  
H. Junkes and M. Clarke, ISIS, Rutherford Appleton Laboratory, Oxfordshire
- Collaborations with the USA:  
H.-J. Freund, H. Kuhlenbeck and P.S. Bagus, University of North Texas, Denton  
H.-J. Freund, H. Kuhlenbeck, S. Shaikhutdinov 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 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

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

- After an effort of two years we succeeded to record the first action spectrum of Ne from a surface ( $\text{V}_2\text{O}_3(0001)$ ) using the FEL facility of the institute. Further instrument development is important for this project.

- The first high field EPR spectrum from defects in MgO has been recorded.
- Well-ordered silica films have been successfully investigated using the LEEM/PEEM instrument after considerable experimental difficulties and the crystal-glass transition has been observed and characterized with respect to the activation energy for the process. This represents important input for the on-going ERC Cryvisil Project.
- The silica film van-der-Waals bound to a Ru(0001) surface has been used to study the reaction of intercalated oxygen with hydrogen diffusing through the film in confined space. Apparent activation energies between the reaction in confined and open space reveal differences that may be related to differences in transition states. This will be explored in collaboration with theory group.
- Transferability of an amorphous silica film from a Ru(0001) to a Pt(111) substrate has been demonstrated. There is potential for device design based on 2D materials. An EU patent has been filed.
- A  $\text{GeO}_2$  film has been prepared and structurally characterized using STM and quantitative I/V-LEED studies as a monolayer film bound to a Ru(0001) substrate.
- First attempts to prepare and characterize well-defined models for the Phillips catalyst for ethane polymerization have been carried out. The known atomic positions in the amorphous silica film and its hydroxylation opens unique opportunities to study this complex reaction for the first time at the atomic level.
- A full experimental study of water (dissociative and molecular) adsorption at  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_3\text{O}_4(100)$  using STM, IRAS, TPD and LEED as well as large scale computational efforts have been successfully undertaken to contribute a key milestone to the joined efforts in SFB 1109 “water on oxides”. Results of previous studies need revision.
- Transition metal sulfide films have not gained a lot of attention in the past. We have successfully prepared a very well ordered  $\text{Fe}_3\text{S}_4$  film in (111) orientation. STM characterization has been carried out and a quantitative I/V-LEED study is under way.
- Instrument Development: The new beam splitter for SMART-2 is being tested, allowing for considerable increase in lateral resolution. The integration of an STM into the action spectroscopy instrument.

## 2. Progress Reports

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

### 2.1 Scanning Probe Microscopy Group

*Members: C. Büchner<sup>d</sup>, K. Burson<sup>c</sup>, M. Heyde<sup>a</sup>, B. Kell<sup>b</sup>, D. Kuhness<sup>c</sup>, A. L. Lewandowski<sup>d</sup>, J. Lu<sup>d</sup>, L.E. Pascua<sup>d</sup>, St. Stuckenholtz<sup>d</sup>, C. Stiehler<sup>d</sup>, G. Thielsch<sup>b</sup>, H.-J. Yang<sup>c</sup>, Z. Yang<sup>c</sup>, W.-D. Schneider<sup>e</sup>*

The main focus in our group is the atomic scale characterization of thin oxide film systems in the context of model catalysis by using scanning probe microscopy (SPM) techniques. Certainly the silica bilayer structures as well as their physical and chemical properties are highlights in our current research efforts. Nevertheless, we are still continuing long-time department endeavors in preparation of Au clusters on magnesia ultrathin films supported by Ag(001) supports to activate CO<sub>2</sub> into useful chemicals.

#### Investigation of CO<sub>2</sub> activation reaction on oxide supported Au catalyst

With the help of inelastic tunneling spectroscopy (IETS) techniques we hope to unravel the detailed reaction mechanism and steps involved in CO<sub>2</sub> activation over Au nanoparticles dispersed on ultrathin MgO films grown on Ag (100) in our scanning tunneling microscope (STM). This method allows studying the inner structure of molecular adsorbates with high resolution and high sensitivity. By monitoring the tunneling current and energy during the reaction, this technique allows selecting a particular reaction pathway and provides a combined study of spatial resolution at molecular level and energy resolution of molecular vibrational modes. The activation process involves transfer of electrons that results in a stable chemical entity and further to useful chemicals. Supported Au catalyst have been studied extensively and used as model catalyst for decades by researchers and in industry but the mechanism at the atomistic level still needs to be explored. A comprehensive study of the factors affecting the chemical reactivity of the system is needed to address the unexplained questions. In this project we are exploring the resolution limits and trying to optimize our current experimental setup. Once this instrument has reached our goals for the magnesia based model systems, we also intend to use this machine for addressing catalytically relevant questions on silica thin film systems.

<sup>a</sup> Group Leader; <sup>b</sup> Technician; <sup>c</sup> Postdoc; <sup>d</sup> PhD Student; <sup>e</sup> Consultant

## Transfer of 2D Silica Films

Bilayer silica films are a promising material for various technological applications. Their complex but tunable ring network allows size selective penetration of atoms and small molecules. This property indicates a potential use in filtration membranes or anticorrosion coatings. Furthermore, ultrathin silica films have larger band gaps than other commonly used 2D materials, indicating they may be a useful alternative to the insulating hexagonal boron nitride sheets used in nanotransistors.

In order to make silica bilayers accessible for the mentioned applications, we investigated the material's stability and subsequently developed a procedure to transfer the films. 2D SiO<sub>2</sub>, while grown in an ultra-high vacuum (UHV) chamber to prevent contamination, can withstand exposure to air and solvents such as water, ethanol and acetone. Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) taken after the exposure show no significant change in the film structure. Imaging the silica/water interface with a liquid cell atomic force microscopy (AFM) shows the characteristic 2D-amorphous network of rings, which maintain their arrangement under water. In view of related studies in the Structure and Reactivity group it was concluded that the silica bilayer films are chemically inert and particularly stable against spontaneous hydroxylation, although hydroxyl formation is commonly observed on surfaces of other silica modifications.

Mechanical exfoliation of the SiO<sub>2</sub> film from the Ru(0001) substrate can be achieved by spin-coating the 2D silica film with a polymer layer. LEED, AES and STM show that through this step, the entire silica layer is removed, indicating significant in-plane bonding strength. The silica-polymer stack can be placed on a new substrate and the polymer can be removed, e.g. by heating. LEED, AES and STM show the transferred SiO<sub>2</sub> bilayer on a Pt(111) crystal without indicating any changes in the film structure. In collaboration with the AC department, environmental scanning electron microscopy (ESEM) imaging corroborated the successful transfer on a cm-scale, without signs of typical transfer-related damage.

By demonstrating a successful transfer of a 2D SiO<sub>2</sub> film, technological applications are no longer limited to substrates that withstand the high temperatures required for growing 2D silica. This proof-of-concept now allows the incorporation of silica bilayers in nanoelectronic devices and to test their performance as a 2D insulator.

### **“Zig-Zag” Silica Film Structures**

Recently, we have prepared a new metastable silica film structure besides the well-known monolayer and bilayer films on Ru(0001). This new silica polymorph can be transformed upon annealing into a patched bilayer silica film. The detailed knowledge about this intermediate phase is of great importance, because it might allow us to gain further insights into the growth modes of silica films as well as a better understanding of structural transitions between crystalline and amorphous film structures. This new silica phase has a rectangular unit cell. High resolution STM images revealed zig-zag line-shapes. From low energy electron microscopy (LEEM) and LEED measurements taken by the group of Thomas Schmidt a glide mirror plane in the structural unit cell has been identified. In addition the group of Shamil Shaikhutdinov has measured infrared finger prints of such film preparations. Currently the group of Prof. Martin Schütz together with Prof. Joachim Sauer is working on reasonable structural models in accord with our experimental observations.

In addition to this new silica polymorph the group has started initial work on incorporating Mg atoms into our silica bilayer film systems. So far the department has introduced different network forming agents such as Al or Fe into silica films without changing the structure morphology. Here we try to incorporate with the Mg a network modifying agent where it is expected to affect the structure morphology significantly. Besides playing with network forming and modifying elements, we raised the question whether or not silica might be the only available thin film amorphous network. This has led us to the development of a new oxide film system based on germanium.

### **Growth and Characterization of Ultrathin Germania Films**

Germanium oxide surfaces are of interest, both due to the technological relevance of the material, and the expected complex structures analogous to silicon dioxide.  $\text{GeO}_2$  has a high refractive index, which is used in optical fibers, windows and lenses. Material composites of  $\text{GeO}_2$  and  $\text{SiO}_2$  are also utilized frequently. Recently,  $\text{GeO}_2$  has been suggested as potential electrode material for high density batteries. Based on the detailed investigations of  $\text{SiO}_2$  films in our group during the last years, we now produced and investigated  $\text{GeO}_2$  surfaces.

We have developed thin film growth procedures for atomically flat monolayer and partial coverage bilayer germania films supported on Ru(0001). Through carefully chosen annealing treatments, the bilayer films can be converted into monolayer films. Atomic resolution STM images show predominantly hexagonally ordered films with occasional mesopores. Different

film heights and characteristic line defects are observable. The honeycomb lattices are similar to silica monolayers and bilayers.  $[\text{GeO}_4]$  tetrahedral building blocks are corner connected via oxygen bridges.

The high-resolution real-space imaging by scanning tunneling microscopy (STM) was combined with a detailed structure study by LEED-IV (Low energy electron diffraction). Atomically flat monolayer germania films have been prepared allowing to resolve in clear and detailed STM images the individual network and domain boundary structures. Throughout the structural analysis, LEED measurements were taken over an energy range of 60 and 550 eV with steps of 1 eV. 42 diffraction spots were recorded and averaged over 6 symmetry equivalent spots, leading to a total energy range of 2500 eV. The experimental curves were compared to modeled diffraction pattern intensities from suggested test structures based on density functional theory (DFT) calculations in collaboration with Prof. Gianfranco Pacchioni. The individual preparation steps from the clean Ru(0001) substrate, the oxygen pre-covered Ru(0001) and finally the deposited germania films on Ru(0001) were separately analyzed. For the germania films the best agreement has been achieved with DFT structures where the germanium atoms sit preferentially on top and an fcc hollow sites of the Ru(0001) substrate.

To our knowledge, this is the first ultrathin film of germania. It makes the surface of this technologically important material accessible for surface science methods. Going forward, we are planning to study the structures of mixed  $\text{Ge}_x\text{Si}_{1-x}\text{O}_2$  films as well.

### **Silica Surface Structure Characterization by Liquid AFM: Ultrathin Film to Bulk**

Alongside the novel ultrathin silica polymorphs, bulk  $\text{SiO}_2$  is omnipresent in the animate and inanimate world as well as in technology. However, despite its archetypical nature with respect to physical and chemical properties like insulating character, chirality, transparency, glass formability or chemical inertness, little is known about the atomic structures at its surfaces. Even less is known about the surface structures when in contact with water. In fact, no real space experimental data on quartz or quartz glass atomic surface structure are currently available.

We use AFM in air, water and aqueous salt solution to resolve atomic scale surface structures of three silica polymorphs in contact with water. The interface with bulk water of the ultrathin 2D silica bilayer on Ru(0001) is compared to crystalline ( $\alpha$ -quartz(0001)) and amorphous bulk  $\text{SiO}_2$  interfaces with moist air and water. While the silica bilayer has been prepared in the

arid environment of ultrahigh vacuum, the bulk samples have been prepared by high temperature (1100°C, many hours) annealing in moist air or by wet chemical etching (acid or base etchants) at room temperature. In doing so, preparations above and below the structural phase transition from  $\alpha$ -quartz to  $\beta$ -quartz at 573°C are assessed. Especially for the etching recipe we would like to acknowledge fruitful discussion and communication with Paul Ohno and Prof. Franz M. Geiger (Northwestern University, Chicago, USA).

We established an easy to use high temperature annealing procedure for  $\alpha$ -quartz(0001) in air. This preparation produces nicely ordered terraced surfaces with atomic scale steps. AFM in moist air further reveals coverage of the resulting surfaces by three stripe domains which fade away or cease to be detectable during imaging in bulk water. Etched surfaces have so far proven less successful with disordered overlayers seemingly covering the surface. Additionally, the surface morphology is altered by numerous etch pits at dislocations. However, small scale, high resolution, liquid AFM data from both bulk crystal preparations show hexagonally ordered stripes or rows of rings, which match quartz bulk termination in their spacing and symmetry. An additional benefit and actual design goal of the described preparations is their transferability between crystalline quartz and amorphous silica, i.e. bulk glass. The surface structure of the latter remains completely unknown. Surfaces of the amorphous bulk silica samples have been prepared with analog high and low temperature procedures. As expected, the glass surfaces exhibit very low surface corrugation and morphologies without any sign of order. Structures in images recorded on small smooth surface sections are being analyzed in comparison to the crystalline surfaces. With our structural study we give insight into preparative aspects of bulk silica surfaces. New information could be gained with respect to the atomic scale structure of  $\alpha$ -quartz(0001) surfaces in contact with bulk water and moist air. This will help to remove ambiguities in data analysis in state of the art spectroscopic and wet chemical surface science studies on such surfaces and allow for informed comparison among techniques. Our findings are further expected to assist theorists in the development of more appropriate surface models.

### **Towards Resolving Dynamic Processes in Silica Surfaces**

The possibility to follow chemical reactions at surfaces by STM has been proven quite a few years ago by Prof. Joost Wintterlin and Prof. Gerhard Ertl. In a new project we would like to further develop this approach by designing and building a state of the art instrument dedicated to the resolution of dynamic processes in real space as a function of temperature on our silica bilayer films. For this purpose, we are developing a video rate STM that will be operated over

a large temperature range from cryogenic temperatures to approximately 1200 K. A compact, highly symmetric microscope design will be attached to a continuous flow cryostat. This combination optimizes the temperature stability, thermal drift and vibrational noise during scanning. Lissajous scanning mode are planned to ensure efficient high-speed movements of the piezo setup. A hybrid-electronics solution will be used for the video-rate measurements, which will be realized by a combination of a typical commercial SPM control unit (Nanonis control system) with custom-made high-speed electronics Versa Module Eurocard bus (VMEbus) technology. Furthermore, an atom-tracking program will be developed to automatically correct the thermal drift caused by the temperature ramp. This project is headed by Prof. Hans-Joachim Freund in the frame work of the CRYVISIL - ERC Grant (2016-2020).

## 2.2 Spectroscopy Group

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In the last ~2 years a surface action spectroscopy experiment was brought into operation at the free electron laser of the Fritz Haber Institute and a well ordered iron sulfide layer on Au(111) was prepared and studied.

### Surface action spectroscopy with neon messenger atoms

Action spectroscopy with rare gas messenger atoms is a method to measure vibrational spectra of gas phase aggregates. The aggregates are first decorated with rare gas atoms and then illuminated with infrared light of variable energy. Rare gas atoms may desorb when the infrared light is in resonance with a cluster vibration, and therefore the rare gas desorption rate as a function of the infrared energy represents a vibrational spectrum, which may be used to identify the cluster structure (A. Fielicke, A. Kirilyuk, C. Ratsch, J. Behler, M. Scheffler, G. von Helden, and G. Meijer, Phys. Rev. Lett. 93, 023401 (2004)). We have set up an experiment to apply this method to surfaces since the cluster structure is also a very relevant topic in model catalysis.

In surface action spectroscopy a surface covered with rare gas atoms (neon was used) is illuminated with infrared light, which stems from the Fritz Haber free electron laser in the present case. Rare gas atoms may desorb when the infrared light excites a vibration at the surface.

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The action spectrum, i.e. the rare desorption rate as a function of the infrared energy, is measured with a quadrupole mass spectrometer positioned in front of the sample.

Other common methods for surface vibrational spectroscopy are HREELS (high-resolution electron energy loss spectroscopy) and IRAS (infrared reflection absorption spectroscopy).

Both methods have disadvantages, which the action spectroscopy method does not have: the HREELS method suffers from a rather bad resolution and (in the case of ionic surface) intense multiple phonon losses which may cover other relevant vibrational losses, while IRAS requires normalization of a measured spectrum with a reference spectrum, which contaminates the spectral information with structures from the reference sample.

$\text{V}_2\text{O}_3(0001)/\text{Au}(111)$  has been selected for first test experiments. This oxide was chosen since it has well-characterized vanadyl groups at the surface, which can be used to test the surface sensitivity.

The action spectroscopy method could detect the surface vanadyl vibration and other surface vibrations, but turned out to be insensitive to bulk vibrations as concluded from a comparison of the action spectroscopy data with HREELS and IRAS spectra. The present understanding of the desorption process is that absorption of a single photon by a vibrational state at the surface induces the rare gas desorption via a transfer of energy from the excited state to the rare gas vs. surface vibration. This anharmonic coupling process requires an overlap of the vibrational wave functions, which explains the surface sensitivity of the method as well as its insensitivity to bulk or sub-surface vibrations, which do not involve a reasonable vibrational amplitude of surface atoms.

Action spectroscopy experiments performed for a  $\text{TiO}_2(110)$  single crystal surface have shown that there is also a thermal rare gas desorption channel. Absorption of FEL infrared light by a vibrational bulk state of this rather thick sample leads to a significant warming, which may induce neon desorption. We have used this desorption channel to study a polaronic trap state in  $\text{TiO}_2(110)$ , which is populated by UV light or hydrogen incorporation according to a recent infrared spectroscopy study (S. Sezen et al, Scientific Reports 4, 3808 (2014)). With action spectroscopy we could show that these paths are not relevant for the population of this state. The state appears to be permanently occupied, which may require a re-interpretation of its nature. We could draw this conclusion since the action spectroscopy method does not require normalization with a reference spectrum. This normalization process did probably destroy the relevant information in the case of the infrared spectroscopy study.

Some experiments have also been performed with adsorbed argon. However, it turned out that argon cannot easily be desorbed in an action spectroscopy experiment, which we attribute to the higher binding energy of argon atoms to the respective surfaces.

Until now, action spectroscopy data have been taken with a helium cooled fixed sample setup without sample transfer option. Recently we have commissioned a transferable sample holder for temperatures required to adsorb neon ( $< 8\text{K}$ ). With this sample holder it should be possible to also include the STM/AFM system attached to the chamber in experiments with FEL radiation.

### **Well-ordered iron sulfide layers on Au(111)**

Iron sulfides are a central component of the iron-sulfur world hypothesis of G. Wächtershäuser (Progress in Biophysics and Molecular Biology 58, 85-201 (1992)). This hypothesis assumes that the first steps in the evolution of life involve catalytic processes occurring at sub-marine iron sulfide compounds. A central component of this hypothesis is the activation of  $\text{CO}_2$  by iron sulfides towards the formation of simple organic molecules. Theoretical and experimental studies (A. Roldán, N. Hollingsworth, A. Roffey, H.-U. Islam, J. B. M. Goodall, C. R. A. Catlow, J. A. Darr, W. Bras, G. Sankar, K. B. Holt, G. Hogarth and N. H. de Leeuw, Chem. Commun. 51, 7501, 2015) have shown that greigite ( $\text{Fe}_3\text{S}_4$ ) is able to activate carbon dioxide in an aqueous environment. We have set up a project to prepare ordered iron sulfide layers since the transformation of carbon dioxide into more useful chemical compounds is a very relevant process from an environmental but also from an economic point of view. After several tries we could show that such layers can be prepared on Au(111) by deposition of iron in an atmosphere of  $\text{S}_2$  molecules which are produced by an electrochemical method. STM image reveals a homogeneous, well-ordered surface with a hexagonal symmetry, which is also found in LEED patterns of the film. The hexagonal lattice parameter of the layers as derived from the LEED images is near to that of  $\text{Fe}_3\text{S}_4(111)$ . I/V LEED curves of the layer have been measured and I/V LEED calculations are running at present. Parallel to this,  $\text{CO}_2$  activation experiments have been performed, which have not yet been successful. According to XPS data the layer is probably terminated by sulfur which may explain why carbon dioxide does only physisorb. However, it is possible to hydrogenate the layer which may offer routes to hydrogenation reactions.

## 2.3 Spectro-Microscopy Group (SMART)

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The activities of the group have been focused on (1) thin oxide film growth and (2) instrumental development. The chemical and structural properties of silica, iron silicate and germanium oxide films and the intercalation of reactive gases under the silica film have been studied *in situ* and *in real time* with the SMART microscope (SpectroMicroscope with Aberration correction for many Relevant Techniques) and the first version of SMART-II. 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).

### Silica on Ru(0001): Growth and Transformation

Combining low energy electron microscopy (LEEM) with local low energy electron diffraction ( $\mu$ LEED) and x-ray photoemission electron microscopy (XPEEM) with local x-ray photoemission electron spectroscopy ( $\mu$ XPS) enables a comprehensive study of the growth processes of the silica film, involving oxidation, structure formation and structural phase transition.

We followed the preparation and structure of bilayer silica films on the Ru(0001) surface as a function of temperature, heating rate and oxidation conditions. For the standard recipe, reproducible and well-established in our department, we deposit a bilayer equivalent of silicon on the Ru(0001)-(2x2)-3O surface at room temperature and subsequently heat this film in  $10^{-6}$  mbar of oxygen up to about 1200 K. Here we found a sequence of four different phases: (i) the starting film at RT is only weakly oxidized (due to the initial (2x2)-3O of the Ru support) and three dimensionally disordered. (ii) The annealing up to 625 K in oxygen completely oxidizes the silicon, but the film is still disordered. (iii) A further annealing in oxygen up to around 1070 K yields into the formation of the crystalline phase, corresponding to a (2x2) superstructure on Ru(0001). (iv) If now the annealing is continued the film converts into a vitreous phase, which is in fact a two-dimensional disordered system, but well defined perpendicular to the surface. Up to now, the transformation is irreversible. The time for this transformation is temperature dependent: the higher the temperature, the faster is the transformation, directly observed as an intensity change in the LEED pattern.

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An Arrhenius analysis of the transformations time yields in an activation energy of 4.2 eV, which can be explained by a Stone-Wales process as the determining step in the transformation.

A new structure was found when the standard recipe was slightly changed: after the annealing in oxygen starting from RT up to 1000 K (steps (i) and (ii), see above) the film was completely oxidized. In this situation, the oxygen pressure was reduced and the annealing was continued in UHV. As in the case for the standard recipe, the film becomes ordered upon further annealing, but in this case not with a (2x2) hexagonal structure, but with a much more complex, but well-ordered rectangular structure with three rotational domains on Ru(0001). The sharp LEED pattern exhibits further details: the structure is commensurate along the longer period, but incommensurate along the shorter period (about 7% compressed). This special structure was also found in IRAS and STM and exhibits special features like a regular arrangement of pore sizes larger than 6 Å as in the hexagonal silica bilayer structure. This special structure is stable unless it is annealed in oxygen which converts the film into a crystalline bilayer structure and with further annealing into the known vitreous film.

#### **Chemical reactions in confined space under SiO<sub>2</sub> bilayer supported on Ru(0001)**

We used SiO<sub>2</sub> bilayer films supported on Ru(0001) to investigate the intercalation of gases such as carbon monoxide, hydrogen and oxygen in the confined space between the silica film and the metallic substrate. The combination of LEEM/PEEM/LEED/XPS experiments allowed an understanding of the dynamic aspects of the process at the sub-micron level and enabled to study the influence of defects at mesoscopic scale. The real-time measurements have shown that it is possible to intercalate all three gases, although the process seems to occur in different ways for H<sub>2</sub>, O<sub>2</sub> and CO. In the case of O<sub>2</sub>, the intercalation occurs homogeneously across the surface without the formation of any special features or clear influence of defects on the silica film.

On the other hand, CO has proven to intercalate only under O-poor SiO<sub>2</sub>/Ru(0001) films, i.e. with low oxygen concentration at the supporting Ru(0001) surface which can be tuned during the sample preparation. In this case, intercalation occurs via formation of CO domains that can be easily identified both in LEEM and local XPS. The intercalation behaviour in this case depends on the integrity of the silica film. In the case of the completely closed film, CO permeates the bilayer until the sample is fully and homogeneously intercalated. On the contrary, in the case of films with mesoscopic holes which are formed by dewetting during

sample preparation, a fully CO intercalated sample could not be produced so far, resulting in CO patches surrounded by O-poor regions at the SiO<sub>2</sub>/Ru(0001) sample surface. Further measurements are planned to study desorption and also oxidation of the CO islands.

In the case of H<sub>2</sub>, its intercalation and reaction with O pre-adsorbed on the Ru(0001) interface were studied. Its importance lies on the fact that hydrogen can be used to control the amount of oxygen adsorbed on Ru under the SiO<sub>2</sub> bilayer, thus making it possible to alternate between the O-rich and O-poor phases, even at mild temperatures without compromising the integrity of the SiO<sub>2</sub> film. The oxygen removal occurs via reaction with H<sub>ads</sub> resulting from the dissociative adsorption of H<sub>2</sub> on Ru(0001) after intercalation, yielding the formation of H<sub>2</sub>O. This represents the first reported chemical reaction conducted in confined space in the SiO<sub>2</sub>/Ru(0001) system, to the best of our knowledge. Also, by performing the measurements at different temperatures we were able to obtain the activation energy for this chemical process. The value obtained (~0.3 eV) has proven to be lower than reported for bare basal and stepped Ru(0001) surfaces (0.55 and 0.5 eV, respectively). Although the origin of the difference is yet not well understood, it may reflect the effect of the silica film on the chemical reaction. It is important to stress out that, DFT calculations are being performed by collaborators (G. Pacchioni, University of Milano-Bicocca) in order to gain more insight on this effect. This might shed some light on the mechanistic aspect of the reaction under the effect of confinement.

### **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 used iron-silicate films grown on a Ru(0001) support. The film can be described as an iron-oxide layer (FeO-like) with a ML of silica on top forming a ( $\sqrt{3}\times\sqrt{3}$ )R30° reconstruction on the FeO-layer underneath which itself creates a Moiré structure on the Ru support.

The iron-silicate films were prepared on a Ru(0001) single crystal using two different preparation recipes: (a) the deposition of iron and silicon on a 3O-(2x2) covered substrate with subsequent oxidation and (b) first producing a complete iron-oxide layer followed by silicon deposition on top with an final oxidation step.

We were interested to study whether the way of preparation or the structure and thickness of the initial iron-oxide layer influence the properties of the resulting iron-silicate film. For

preparation (b) iron was deposited at 800 K at two different oxygen atmospheres ((i)  $2.0 \cdot 10^{-8}$  mbar and (ii)  $1.0 \cdot 10^{-7}$  mbar), resulting in differently oxidized iron-oxide layers with different thickness ((i) monolayer, (ii) bilayer). Both show the same Moiré LEED pattern typical for an FeO layer. After silicon deposition and final oxidation step at 900 K, XPS, LEEM-IV and LEED proof that the resulting iron-silicate film is identical with the film produced with preparation method (a). XPS, measured at different oxidation states of the iron-silicate layer, indicates an oxygen intercalation between the iron-oxide layer and the Ru-Substrate.

Both preparation recipes may be applied to complete and incomplete films. For preparation method (a) domains are formed, whereas silicon was found to bind preferentially on top of the iron oxide islands before covering the surrounding Fe-free Ru(0001) substrate. The additional silicon atoms form a pure bilayer of silica adjacent to iron-silicate islands. Interestingly the pure silica films also show the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  reconstruction on Ru(0001). Using preparation method (b) for both iron-oxide films (i) and (ii) iron migrates out of the initial iron-silicate islands in order to reduce the iron concentration what occurs already at relatively low temperatures (660 K). This iron diffuses into the area between the initial islands and forms iron-silicate domains in two different ways. For (i) small islands are formed on the iron-free areas, while for (ii) a growing rim surrounds the initial islands and thus enlarges the iron-silicate islands. These findings fit to the assumption that the iron-oxide layer of iron-silicate contains less iron atoms per unit cell as the initial FeO layer, for both monolayer and bilayer.

### **Germania on Ru(0001) and Pt(111)**

Germania ( $\text{GeO}_2$ ) is known as a catalyst for poly-ethylene-terephthalate (PET) polymerisation reactions. Also germania glass and germania-silica glass are widely used for optical fibres and non-linear optic devices. The experiments were performed with the first version of the SMART-2 instrument, using LEEM and  $(\mu\text{-})$ LEED as methods. This technique offers to study the morphology and structure of ultra-thin oxide films *in situ* and in real-time at mesoscopic scale (field of view of 1  $\mu\text{m}$  to 20  $\mu\text{m}$ ) with surface sensitivity of less than a nanometer.

We choose two different supporting substrates: (a) the  $3\text{O}-(2 \times 2)$ -Ru(0001) surface well known as an ideal support for silica monolayer and physisorbed bilayer and (b) the oxygen free Pt(111) surface. The comparison of the growth behaviour on both supports allows to study the effect of the different oxygen affinities of the substrate, whereas the lattice constants are quite similar (Ru(0001): 2,71 Å; Pt(111): 2,78 Å). We developed new preparation methods for ultra-thin germania films on Ru(0001) and Pt(111) surfaces using the

instrumental ability to directly observe the growth of ultra-thin oxide films *in situ* and in real-time.

On the Ru(0001) surface two different preparation recipes were used. In the first preparation recipe (A) the Ge was deposited on the bare Ru(0001) surface in UHV at 540 K and subsequently oxidized at higher temperatures (550 K - 700 K) in  $1 \cdot 10^{-6}$  mbar O<sub>2</sub>. In the second recipe (B) the Ge was deposited in oxygen atmosphere ( $1 \cdot 10^{-7}$  mbar) at RT onto the 3O-(2x2)-Ru(0001) surface. Then the partially oxidized Ge was oxidized at 550 K - 700 K in  $1 \cdot 10^{-6}$  mbar O<sub>2</sub>. On Pt(111) the germanium was deposited at RT in UHV and afterwards oxidized in  $1 \cdot 10^{-6}$  mbar O<sub>2</sub>. Due to the preparation conditions, it is possible to control the domain size of the GeO<sub>2</sub> films on Ru(0001). Preparation B on 3O-(2x2)-Ru(0001) forms very small domains in the range of a few nanometer. In contrast, preparation A yields large domain sizes up to micrometer. Because of the presence of oxygen, the diffusion of germanium on 3O-(2x2)-Ru(0001) is extremely low. That leads to the small GeO<sub>2</sub> domains on 3O-(2x2)-Ru(0001). For both preparation methods the resulting germania films show the same LEEM-IV curves and a sharp (2x2) LEED pattern, corresponding to an identical crystalline structure of the oxide film. Up to now there is no evidence for a vitreous germania phase on Ru(0001). On the Pt(111) surface germanium arranges in a ( $\sqrt{19} \times \sqrt{19}$ ) superstructure. The germanium starts to oxidize already at RT on Pt(111) and forms a (2x2) LEED pattern. This superstructure corresponds within a few percent to the intrinsic structure of the germania mono- and bilayer and is observed on both metal supports.

## SMART-2

This new aberrations-corrected LEEM-PEEM instrument SMART-2 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. The solution is the new beam splitter module with implemented apertures and slits which 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) existing central magnetic beamsplitter with aberration correction

and space charge reduction (operating in at test set-up) and (3) the new electrostatic Omega-filter (under construction).

The challenge for the construction of the new beamsplitter was the implementation of the optical design of the SMART-1 beamsplitter into the commercial set-up. New deflector and stigmator modules had to be added to align the beamsplitter to the optical axis, what has been quite critical at the original SMART-1 instrument. The newly designed vacuum system allows placing the important electron flux reducing apertures and energy slits in the intermediate image and back focal planes, respectively, what was not possible in the original SMART-1 design. The new beamsplitter module is currently tested and optimized in a special test set-up and will be implemented in the actual SMART-2 instrument as soon as the optimization is finished.

## 2.4 Structure and Reactivity Group

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The group has continued previous studies on preparation and structural characterization of thin silica films grown on metals as a template for fabrication of well-defined planar model systems which would be well-suited for “surface science” studies of chemical reactions on zeolitic materials. Another long-term project is aimed at understanding of CO oxidation reactions over metal-supported ultrathin transition metal oxide films and the role of the interface on reactivity. The latter systems are intimately related to the so-called “strong metal-support interaction” (SMSI) effects often observed for metal particles supported on reducible oxides. As a member of the collaborative research project CRC 1109 focused on interaction of water with oxides, the group carried out studies on water adsorption both on non-reducible (silica) and reducible (magnetite Fe<sub>3</sub>O<sub>4</sub>) oxides. Recently, we initiated surface science studies focused on fundamental understanding of the Phillips (Cr/SiO<sub>2</sub>) catalysts of ethylene polymerization that remains challenging since its discovery in early 1960’s. Finally, in attempt to rationalize recently reported superior activity of the ceria catalysts in the selective alkyne hydrogenation reactions, which is very unusual for oxide materials, we have carried out studies on interaction of hydrogen with CeO<sub>2</sub>(111) thin films.

### Towards planar models of zeolitic structures

The structural motif of well-ordered silica films grown on metals is a layer of corner-sharing

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[SiO<sub>4</sub>] tetrahedra like a silicate sheet in naturally existing phyllosilicates. The films can be prepared either as a monolayer, strongly bound to a metal support (e.g. on Mo(112) and Ru(0001) surfaces), or as a weakly bonded bilayer (on Ru(0001), Pt(111), and very recently on Pd(111)). Introduction of Al into the silicate framework results in aluminosilicate films, which become exposing bridging hydroxyl species similar to highly acidic zeolites. Doping a bilayer silicate film with Fe does not, however, lead to substitutional structures as observed for aluminosilicates, but to a layered Fe-silicate (SiO<sub>2.5</sub>/FeO(111)) film which mimic the Fe-rich clay mineral Nontronite.

In attempts to fabricate model systems of Fe-containing zeolites showing superior activity in number of reactions, we studied incorporation of iron into aluminosilicate films. Structural characterization performed by LEED, XPS, IRAS, and STM show that even at low concentrations Fe does not randomly substitute Si(Al) cations in the silicate framework, but segregates into a pure silicate (aluminosilicate) phase and an Fe-silicate phase. At high Fe/(Si+Al) molar ratios, the resulting films showed two phases depending on the annealing temperature. In both phases, the surface exposes a silicate layer and the bottom layer is dominated by FeO. The results suggest that the formation of in-frame Fe species in silicalites and zeolites is thermodynamically unfavourable.

In addition, we monitored the preparation of the Fe-containing silicate films and found that the Fe-silicate domains trigger the formation of the crystalline pure silicate, which propagates in the same orientation as a “crystallization wave” outwards the Fe-silicate. By using transition metal as a “seed” one may, therefore, improve crystallinity and lower the preparation temperature, which may be critical for future applications of the ultrathin silica films in nanotechnology.

### **CO oxidation on ultrathin transition metal oxide films and interfaces**

Ultrathin films of transition metal oxides (TMO) grown on metal substrates were found considerably active in the low temperature CO oxidation reaction. Our comparative study of various TMO films, fully covering metal supports, suggested the binding energy of the most weakly bound oxygen (WBO) as a good descriptor for the reactivity. The reaction rate is further enhanced at sub-monolayer coverage regime, i.e. by exposing TMO/metal interface, when only supported on Pt and not on Ag, thus suggesting that CO adsorption on the metal surface is another factor affecting the reaction. To shed more light on this issue, we performed comparative studies of FeO(111) films grown on Pt(111) and Au(111) as a function of oxide

coverage. On Pt(111) supported films, CO<sub>2</sub> production rate measured under O-rich conditions at nearly atmospheric pressures reached a maximum at ~ 40% coverage, whereas on Au(111) supported films, the activity is the highest at the close to 100% coverage. Structural characterization of the fresh and spent model catalysts revealed that the FeO(111) layer on Au(111) is fairly stable towards high pressure oxidation in the low coverage regime, but undergoes substantial reconstruction at near-monolayer coverages, resulting in poorly-defined structures. Comparison of structure-reactivity relationships showed the complex role of a metal support on reactivity. While a strong interaction with the Pt(111) surface stabilizes a planar, FeO(111)-derived structure for the active oxide phase, in the case of a more weakly interacting Au(111) surface, the reaction atmosphere induces structural transformations governed by the thermodynamic phase diagram of the iron oxide.

### **Surface structure of magnetite Fe<sub>3</sub>O<sub>4</sub>(111) and its interaction with water**

Although the (111) surface of Fe<sub>3</sub>O<sub>4</sub> (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination proposed based on structural and adsorption studies. In collaboration with the group of Prof. Sauer (HU Berlin) providing DFT results we could rationalize experimental IRAS and TPD results on CO adsorption, leading us to a unified picture in which the Fe<sub>3</sub>O<sub>4</sub>(111) surface is terminated by a <sup>1</sup>/<sub>4</sub> monolayer of tetrahedrally coordinated Fe<sup>3+</sup> ions on top of a close-packed oxygen layer as previously determined by analysis of I/V LEED results.

This finding led us to revisit the previously reported scheme for water adsorption on Fe<sub>3</sub>O<sub>4</sub>(111) based on assumption of a double metal terminated surface in our films. Additional IRAS and TPD results revealed the important role of defects for the initial stages of water adsorption. To this end, the proposed scenario includes water dissociation resulting in “monomeric” species which behave as anchors for molecular water, thus forming “dimer”, and further clusters at increasing coverage.

### **Electron stimulated hydroxylation of silicate surface**

Being siloxane (Si-O-Si) terminated on either side a double-layer silicate film is, in essence, inert towards water. Only tiny amounts of silanols (Si-OH) could be formed upon deposition of an ice-like (amorphous solid water, ASW) film and subsequent heating to room temperature. However, silanol coverage monitored by IRAS is considerably enhanced by low-energy (100 – 500 eV) electron irradiation of an ASW pre-covered silicate film. The degree of hydroxylation can be tuned by the irradiation parameters (beam energy, exposure) and the

ASW film thickness. The results are consistent with a generally accepted picture that hydroxylation occurs through hydrolysis of siloxane bonds in the silica network. DFT calculations performed by Sauer and co-workers showed that this may happen on Si-O-Si bonds, which are either parallel (i.e., in the topmost silicate layer) or vertical to the film surface (i.e., connecting two silicate layers). In the latter case, the mechanism may additionally involve the reaction with a metal support underneath. The observed vibrational spectra are dominated by terminal silanol groups ( $\nu(\text{OD})$  band at  $2763\text{ cm}^{-1}$ ) formed by hydrolysis of vertical Si-O-Si linkages. Film dehydroxylation fully occurs only upon heating to very high temperatures ( $\sim 1200\text{ K}$ ) and is accompanied by substantial film restructuring.

### **Planar model systems of the Phillips (Cr/SiO<sub>2</sub>) catalyst**

In attempts to prepare a well-defined planar model system of the Phillips ethylene polymerization catalysts that could be well-suited for surface-science studies, we employ Cr physical vapor deposition onto a hydroxylated silicate bilayer films. Structural characterization and adsorption studies were performed by infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD) suggested that hydroxyls groups serve as anchoring centers to Cr ad-atoms deposited at low temperatures to minimize their clustering. Monitored by IRAS, hydroxyls consumption correlates with the appearance of the new band at  $\sim 1010\text{ cm}^{-1}$  typical for Cr=O vibrations. In addition, CO titration experiments suggested also the presence of “naked” Cr sites, which may transform into mono- and di-chromyl species and their aggregates upon oxidation treatment. TPD experiments of ethylene adsorption at low temperatures under UHV conditions showed the formation of butane as one of the main products. The resultant surfaces are thermally stable, at least, up to  $400\text{ K}$  which allows to further investigate ethylene polymerization under more realistic conditions.

### **Interaction of hydrogen with CeO<sub>2</sub>(111)**

Cerium oxide (CeO<sub>2</sub>) has recently been found as a promising catalyst in the selective hydrogenation of alkynes to alkenes. Commonly, this reaction is considered to occur primarily on highly dispersed metal catalysts, and it was thought to be unlikely for oxides. We addressed interaction of hydrogen with CeO<sub>2</sub> using well-defined CeO<sub>2</sub>(111) surfaces as thin films. The experiments performed by x-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy and nuclear reaction analysis suggest that H<sub>2</sub> dissociates on CeO<sub>2</sub>(111) at elevated pressures and temperatures, and H atoms may migrate into the bulk of

a heavily reduced  $\text{CeO}_{2-x}(111)$  films and not on fully oxidized  $\text{CeO}_2(111)$ . Complemented with DFT calculations performed in Sauer group, the results show that oxygen vacancies are the key to H migration.

### 3. Publications of the Department of Chemical Physics

#### 2015 (late publications)

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* **92** (11), 1896–1902 (2015). 

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*Dostert, K.-H.*: Selectivity in Hydrogenation of  $\alpha,\beta$ -unsaturated Carbonyl Compounds on Model Palladium Catalysts. Humboldt-Universität zu Berlin 2015. 

*Liu, B.H.*: Preparation and Structure of Ultra-Thin Zinc Oxide Films on Pt(111), Ag(111) and Cu(111). Freie Universität Berlin 2015.

## 2016

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## Doctoral Thesis

*Büchner, C.*: Adding a Novel Material to the 2D Toolbox: Properties and Transfer of a Silica Bilayer. Humboldt-Universität zu Berlin 2016. 

*Dementyev, P.*: Adsorption calorimetry on two-dimensional model catalysts. Technische Universität Berlin 2016.

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*Abu-Haija, M., Y. Romanyshyn, A.H.H. Uhl, H. Kuhlenbeck and H.-J. Freund*: Carbon Dioxide Adsorption on V<sub>2</sub>O<sub>3</sub>(0001). *Topics in Catalysis* **60** (6-7), 413–419 (2017). 

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*Weng, X., K. Zhang, Q. Pan, Y. Martynova and H.-J. Freund*: Support Effects on CO Oxidation on Metal-supported Ultrathin FeO(1 1 1) Films. *ChemCatChem* **9** (4), 705–712 (2017).

### **Doctoral Thesis**

*Song, X.*: Vanadium doped TiO<sub>2</sub>(110) thin layers: preparation, structure, and reactivity - methanol partial oxidation. Freie Universität Berlin 2017.

#### 4. Invited Talks of the Members of the Department of Chemical Physics

- Büchner, Christin: 2D Silica Films - Structure, Properties and Transfer. (Joint Seminar on Solid State Physics, Universität Bremen, Bremen, Germany, Apr 2017).
- Burson, Kristen: Amorphous Materials: From Two-Dimensional Glass to Bubble Rafts. (Seminar, Williams College, Williamstown, MA, USA, Dec 2015).
- Burson, Kristen: Amorphous Materials: From Two-Dimensional Glass to Bubble Rafts. (Seminar, Hamilton College, Clinton, NY, USA, Dec 2015).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level. (1st International Symposium of Institute for Catalysis - Global Collaboration in Catalysis Science toward Sustainable Society, Hokkaido University, Sapporo, Japan, Oct 2015).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level. (AVS 62nd International Symposium and Exhibition, San Jose, CA, USA, Oct 2015).
- Freund, Hans-Joachim: Model Systems in Catalysis for Energy Economy. (ALC'15, 10th International Symposium on Atomic Level Characterizations for New Materials and Devices '15, Matsue, Shimane, Japan, Oct 2015).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level. (Seminar, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel, Nov 2015).
- Freund, Hans-Joachim: Model Systems in Catalysis for Energy Economy. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Freund, Hans-Joachim: Adsorption: Thermodynamics and Dynamics. (Lecture, Advanced Graduate School, Catalysis Research Center, Hokkaido University, Sapporo, Japan, Jan 2016).
- Freund, Hans-Joachim: Doped Oxides and the Oxide-Metal Interfaces: Reactivity at the Molecular Level. (10th International Workshop on Oxide Surfaces (IWOX-X), Dalian, Liaoyang, China, Jan 2016).
- Freund, Hans-Joachim: Model Catalysts at the Atomic Level: From Structure (Geometric and Electronic) to Reactivity. (Lecture, Advanced Graduate School, Catalysis Research Center, Hokkaido University, Sapporo, Japan, Jan 2016).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Surface and Subsurface Chemistry. (Lecture, The Institute of Physics, Chinese Academy of Sciences, Beijing, China, Jan 2016).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Surface and Subsurface Chemistry. (Lecture, School of Engineering, The University of Tokyo, Tokyo, Japan, Jan 2016).
- Freund, Hans-Joachim: Surface Characterization: Electron and Optical (IR) Spectroscopy. (Lecture, Advanced Graduate School, Catalysis Research Center, Hokkaido University, Sapporo, Japan, Jan 2016).

- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: An Approach at the Atomic Level. (International Conference on Concepts in Catalysis: From Heterogeneous to Homogeneous and Enzymatic Catalysts, Rome, Italy, Feb 2016).
- Freund, Hans-Joachim: Metal-Insulator-Metal (MIM) Structures for CO<sub>2</sub> Activation. (251st ACS National Meeting & Exposition, Division of Energy and Fuels: Novel Materials for Energy & Fuels, San Diego, CA, USA, Mar 2016).
- Freund, Hans-Joachim: Oxide Surface Chemistry: From Single Crystals to Supported Particles. (251st ACS National Meeting & Exposition, Division of Catalysis Science and Technology: Surface Chemistry & Catalysis of Metal Oxides, San Diego, CA, USA, Mar 2016).
- Freund, Hans-Joachim: Thin Film Oxide Systems for Electron Transfer Control. (251st ACS National Meeting & Exposition, Division of Colloid and Surface Chemistry: Computational & Experimental Advances Towards Design of Energy Efficient Catalysts, San Diego, CA, USA, Mar 2016).
- Freund, Hans-Joachim: A Metal-Insulator-Metal Electron Shuttle for CO<sub>2</sub> Activation. (9th Brazilian-German Workshop on Applied Surface Science, Maresias, Brazil, Apr 2016).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: An Approach at the Atomic Level. (Seminar, Research Centre for Gas Innovation, Department of Chemical Engineering, University of São Paulo, São Paulo, Brazil, Apr 2016).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: An Approach at the Atomic Level. (Faraday Discussion: Designing New Heterogeneous Catalysts, London, UK, Apr 2016).
- Freund, Hans-Joachim: Oxide Surface Chemistry: From Single Crystals to Supported Particles. (Lecture, Brazilian Center for Research in Physics (CBPF), Rio de Janeiro, Brazil, Apr 2016).
- Freund, Hans-Joachim: Model Catalysts: Characterization and Function at the Atomic Scale. (Gordon Research Conference, Catalysis - From Theory to Commercialization, New London, NH, USA, Jun 2016).
- Freund, Hans-Joachim: Oxide Film Based Metal-Insulator-Metal Systems to Control Charge Transfer and Chemical Reactivity. (76th IUVSTA Workshop, Thin Films, Surface Science, Applied Surface Science, Nanometer Structures Division, Structure of ultra thin films of oxides on metal surfaces, Avila, Spain, Jun 2016).
- Freund, Hans-Joachim: Scanning Probe Investigations on Model Catalysts: Henning Neddermeyer's Legacy from Our Time in Bochum. (International Workshop on "Recent Developments in Surface and Interface Science" on the Occasion of the 80th Birthday of Henning Neddermeyer, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany, Jun 2016).
- Freund, Hans-Joachim: Model Systems in Catalysis at the Atomic Level: The Role of the Oxide-Metal Interface. (Special Seminar, Department of Chemistry, University of California, Berkeley, CA, USA, Aug 2016).

- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level. (Special Seminar, Department of Chemistry, University of California, Irvine, CA, USA, Aug 2016).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Surface and Subsurface Chemistry. (20th International Vacuum Congress (IVC-20), Busan, Korea, Aug 2016).
- Freund, Hans-Joachim: Oxide Surface Chemistry: From Single Crystals to Thin Films. (Special Seminar, Department of Chemistry, University of California, Irvine, CA, USA, Aug 2016).
- Freund, Hans-Joachim: Two Dimensional Silica: From Crystal to Glass. (Special Seminar, Department of Chemistry, University of California, Irvine, CA, USA, Aug 2016).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Scale. (Hamburg Photon Science Colloquium, Hamburg, Germany, Oct 2016).
- Freund, Hans-Joachim: Structure-Reactivity Relations Through Charge Control at the Atomic Level in Heterogeneous Catalysis. (24th Solvay Conference on Chemistry: Catalysis in Chemistry and Biology, Brussels, Belgium, Oct 2016).
- Freund, Hans-Joachim: The Structure of Oxide Surfaces and its Interaction with Water. (4th Ertl Symposium on Chemical Processes on Solid Surfaces: Water at Interfaces, Berlin, Germany, Oct 2016).
- Freund, Hans-Joachim: Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-Dimensional Zeolites. (GDCh Lecture, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany, Nov 2016).
- Freund, Hans-Joachim: Surface Science Influenced by Dopants. (AVS 63rd International Symposium and Exhibition, Celebrating a Life in Surface Science: A Symposium in Honor of John T. Yates, Jr., Nashville, TN, USA, Nov 2016).
- Freund, Hans-Joachim: Adsorption. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Dec 2016).
- Freund, Hans-Joachim: Developing Concepts for Reactive Surface Systems at the Atomic Scale in the Realm of Catalysis. (Chemical Reactions at Surfaces, Gordon Research Conference, Barga, Italy, Feb 2017).
- Freund, Hans-Joachim: Iron Oxide, Silica and Modified Silica and its Interaction with Water. (International Symposium of the CRC 1109, Metal Oxide – Water System, Erkner, Germany, Feb 2017).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: An Approach at the Atomic Level. (Lecture Series: Fundamental Research in Energy and Sustainability Hour (FRESH Lecture), Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands, Feb 2017).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Level. (DPG-Frühjahrstagung, Dresden, Germany, Mar 2017).

- Freund, Hans-Joachim: Controlling Silica in its Crystalline and Amorphous States: A Problem in Surface Science. (253rd ACS National Meeting & Exposition, Presidential Symposium on Holy Grails in Chemistry, San Francisco, CA, USA, Apr 2017).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Level. (Seminar, Frontiers in Catalysis Science and Engineering, Pacific Northwest National Laboratory, Richland, WA, USA, Apr 2017).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Scale. (253rd ACS National Meeting & Exposition, Symposium on Elucidation of Mechanisms and Kinetics on Surfaces, San Francisco, CA, USA, Apr 2017).
- Freund, Hans-Joachim: Structure-Reactivity Relations Through Charge Control at the Atomic Level in Heterogeneous Catalysis. (253rd ACS National Meeting & Exposition, ACS Award in Surface Chemistry: Symposium in Honor of Cynthia M. Friend, San Francisco, CA, USA, Apr 2017).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Level. (PSI Catalysis Symposium, Paul Scherrer Institut, Villigen, Switzerland, May 2017).
- Freund, Hans-Joachim: Model Systems in Heterogeneous Catalysis at the Atomic Level. (Forum of Great Minds, USTC Hefei, Hefei, China, Jun 2017).
- Freund, Hans-Joachim: The Surface Science of Catalysis and More: Using Ultrathin Oxide Films as Templates. (Workshop, The Theory and Practice of Catalysis, Telluride Science Research Center, Telluride, CO, USA, Jun 2017).
- Freund, Hans-Joachim: Charge Control in Model Catalysis: The Decisive Role of the Oxide - Nanoparticle Interface. (International Workshop on Nanomaterials and Nanodevices, Beijing, China, Jul 2017).
- Freund, Hans-Joachim: The Surface Science of Catalysis and More: Using Ultrathin Oxide Films as Templates. (International Workshop on Nanomaterials and Nanodevices, Xi'an, China, Jul 2017).
- Freund, Hans-Joachim: Models for Heterogeneous Catalysts: Complex Materials at the Atomic Level. (Plenary Talk, IMRC 2017, XXVI International Materials Research Congress, Cancún, Mexico, Aug 2017).
- Heyde, Markus: From Resolving the Structure of Amorphous Materials Towards the Glass Transition. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Heyde, Markus: From Crystalline to Amorphous 2D Oxide Films. (NCM13, 13th International Conference on the Structure of Non-Crystalline Materials, Halifax, NS, Canada, Jul 2016).
- Heyde, Markus: From Crystalline to Amorphous Surface Structures by Atomic Force Microscopy. (Lecture Series Winter Semester 2016 / 2017, Modern Methods in Heterogeneous Catalysis Research, Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany, Nov 2016).
- Heyde, Markus: Surface Characterization by Atomic Force Microscopy. (Block course on Fundamentals of solids and their interfaces and surfaces, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Apr 2017).

- Heyde, Markus: Understanding Ultrathin Networks - 2D Silica and Beyond. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Heyde, Markus: From Crystalline to Amorphous Silica Films by Designing a New 2D Material. (20th Conference on Insulating Films on Semiconductors, Potsdam, Germany, Jun 2017).
- Ivars Barcelo, Francisco: Multifunctional Materials for Sustainable Heterogeneous Catalysis. (Seminar, Institute for Solar Fuels, Renewable Energies Division, Helmholtz Zentrum Berlin, Berlin, Germany, May 2016).
- Ivars Barcelo, Francisco: Developing Materials for Heterogeneous Catalysis Applications. (Seminar, Leibniz Institute for Catalysis, Rostock, Germany, Jun 2016).
- Junkes, Heinz: EPICS Archiver Appliance in Connection with a StrongBox Storage Gateway. (EPICS Collaboration Meeting, Experimental Physics and Industrial Control System, Spring 2015 (Southern Hemisphere), Melbourne, Australia, Oct 2015).
- Junkes, Heinz: ELN at the Fritz Haber Institute. (ELN Workshop, MPDL, Berlin, Germany, Mar 2016).
- Junkes, Heinz: Elektronisches Laborbuch. (33. DV-Treffen der Max-Planck-Institute, Göttingen, Germany, Oct 2016).
- Junkes, Heinz: EPICS on RTEMs 4.12. (EPICS Collaboration Meeting, Spring 2017, Osaka, Japan, May 2017).
- Kuhlenbeck, Helmut: Surface Studies of Thin Oxide Layers. (Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, Apr 2016).
- Kuhlenbeck, Helmut: Surface Studies of Thin Oxide Layers. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Kuhlenbeck, Helmut: Fundamentals of Surface Characterization by Low Energy Electron Diffraction. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Kuhlenbeck, Helmut: Vibrational Spectroscopy of Single Crystal Surfaces Using FEL Infrared Radiation Induced Neon Desorption. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Kuhlenbeck, Helmut: Examples of Vanadium in Model Catalysis:  $V_2O_3(0001)$ ,  $V_2O_5(001)$  and Vanadium in  $TiO_2(110)$ . (FHI/CP-USTC/CP Workshop on Surface Chemistry of Oxides, Hefei, China, Jun 2017).
- Marchetto, Helder: Aberration-Corrected PEEM and LEEM Surface Science Applications. (ASEAN Workshop on Photoemission Electron Spectroscopy and Microscopy (AWPESM2017), Nakhon Ratchasima, Thailand, May 2017).
- Marschalik, Patrik: Design of a High-Speed EPICS Interface: Resolving Glass Dynamics by Scanning Tunneling Microscopy. (Seminar, European Spallation Source, Lund, Sweden, Apr 2017).

- Menzel, Dietrich: Ultrafast Charge Transfer at BN Monolayers on Variably Coupled Substrates. (European Conference on Surface Crystallography and Dynamics (ECSCD-12), Trieste, Italy, Oct 2015).
- Pan, Qiushi: Surface Science Approach to the Philips (Cr/SiO<sub>2</sub>) Catalyst. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Pan, Qiushi: Surface Science Approach to the Phillips (Cr/SiO<sub>2</sub>) Catalyst. (253rd ACS National Meeting & Exposition, Symposium on Amorphous Catalytic Materials, San Francisco, CA, USA, Apr 2017).
- Prieto, Mauricio: Morphology and Structure of Silica Thin Films Unveiled by Spectromicroscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Risse, Thomas: Structure and Dynamics of Enzymes Using Site Directed Spin Labeling. (Second Berlin - St. Petersburg Workshop on Structure and Dynamics of Nanoscopic Matter, G-RISC, St. Petersburg, Russia, May 2016).
- Risse, Thomas: Charge Transfer Processes on Single Crystalline Alkaline Earth Oxide Films. (76th IUVSTA Workshop, Thin Films, Surface Science, Applied Surface Science, Nanometer Structures Division, Structure of ultra thin films of oxides on metal surfaces, Avila, Spain, Jun 2016).
- Risse, Thomas: EPR Spectroscopy of Spin Labeled Protein Single Crystals: Insights into Structure and Dynamics. (38th Discussion Meeting of the Fachgruppe „Magnetische Resonanzspektroskopie“, GDCh, Düsseldorf, Germany, Sep 2016).
- Risse, Thomas: Electron Transfer Processes on Single Crystalline Alkaline Earth Metal Oxide Films. (AVS 63rd International Symposium and Exhibition, Nashville, TN, USA, Nov 2016).
- Risse, Thomas: EPR Spectroscopy of Spin Labeled Protein Single Crystals: Insights into Structure and Dynamics. (Seminar, Institute of Physical Chemistry, Technische Universität Darmstadt, Darmstadt, Germany, Nov 2016).
- Schmidt, Thomas: Aberration Corrected Spectro-Microscopy: Oxide Film Growth, a Case Study. (18th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany, Nov 2015).
- Schmidt, Thomas: Morphology and Structure of Ultra-Thin Silica Films Unveiled by Spectro-Microscopy. (66th Yearly Meeting of the Austrian Physical Society, Vienna, Austria, Sep 2016).
- Schmidt, Thomas: Preparation and Structure of Ultrathin Silica Films Studied by LEEM and PEEM. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Schneider, Wolf-Dieter: Electron Transport in Thin Oxide Films: From Phonon-Polariton Excitations to Changes in the Quantum Structure of Oxide-Supported Gold Nanoparticles. (9th Brazilian-German Workshop on Applied Surface Science, Maresias, Brazil, Apr 2016).



- Schneider, Wolf-Dieter: Geordnete Strukturen auf atomarer und molekularer Skala: Elementare Schritte zu einer künftigen Nanotechnologie. (Wissenschaftlicher Abendvortrag, Deutsche Physikalische Gesellschaft, Berlin, Germany, May 2016).
- Schneider, Wolf-Dieter: Electron Transport in Thin Oxide Films: From Phonon-Polariton Excitations to Changes in the Quantum Structure of Oxide Supported Gold Nanoparticles. (From Solid State to BioPhysics VIII: From Basic to Life Sciences, Cavtat, Croatia, Jun 2016).
- Schneider, Wolf-Dieter: Electron Transport in Thin Oxide Films: From Phonon-Polariton Excitations to Changes in the Quantum Structure of Oxide Supported Gold Nanoparticles. (Superstripes 2016, Quantum in Complex Matter: Superconductivity, Magnetism and Ferroelectricity, Ischia, Italy, Jun 2016).
- Schneider, Wolf-Dieter: Some Facts and Thoughts About Imaging and Manipulation of Atoms and Molecules with a Scanning Tunneling Microscope. (Workshop of the Chemical Physics Department of the FHI, Schloss Ringberg, Kreuth, Germany, Sep 2016).
- Schneider, Wolf-Dieter: Atomic Structure of Supported Ultrathin Germanium Films. (Symposium on Surface and Nano Science 2017 (SSNS'17), Furano, Japan, Jan 2017).
- Schneider, Wolf-Dieter: Atomic Structure of Supported Ultrathin Germanium Films. (30th Symposium on Surface Science 2017 (3S'17), St. Moritz, Switzerland, Mar 2017).
- Shaikhutdinov, Shamil: Ultrathin Oxide Films on Metal Substrates: Structure and Reactivity. (Seminar, Paris Institute of Nanosciences, Paris, France, Mar 2016).
- Shaikhutdinov, Shamil: Ultrathin Oxide Films on Metal Substrates: Case Studies. (International FOXSI Conference 2016, Functional Oxide Surfaces and Interfaces, Vienna, Austria, May 2016).
- Shaikhutdinov, Shamil: Ultrathin Silica Films on Metal Substrates: Silicatenes. (Physics Boat Workshop 2016, Atomic structure of nanosystems from first-principles simulations and microscopy experiments (AS-SIMEX 2016), Helsinki, Finland/Stockholm, Sweden, May 2016).
- Shaikhutdinov, Shamil: Oxide Supported Nanoparticles: When Experiment Needs Theory. (Symposium, Theoretical Modelling of Nanoparticulate Materials: Theory catching up Experiment, University of Barcelona, Barcelona, Spain, Sep 2016).
- Shaikhutdinov, Shamil: Interaction of Water with Metal Supported Silicate Films. (4th Ertl Symposium on Chemical Processes on Solid Surfaces: Water at Interfaces, Berlin, Germany, Oct 2016).
- Shaikhutdinov, Shamil: Ultrathin Oxide Films on Metal Substrates. (2nd International Conference on Applied Surface Science (ICASS), Dalian, China, Jun 2017).
- Stiehler, Christian: The Impact of Molecular Adsorption on the Quantum Structure of Oxide-Supported Au Nanoparticles: CO<sub>2</sub> Adsorption and Activation. (Seminar, IMASC Energy Frontier Research Center, Department of Chemistry & Chemical Biology (AG Cynthia Friend), Harvard University, Cambridge, MA, USA, Dec 2015).

- Umbach, Eberhard: Large-Scale Reconstruction of Metal-Organic Interfaces Induced by Chemisorption and Surface Stress Change. (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Gaede Prize Talks, Regensburg, Germany, Mar 2016).
- Umbach, Eberhard: Influence of Surface Morphology on Organic Epitaxy and on Large-Scale Reconstructions of Metal-Organic Interfaces. (9th Brazilian-German Workshop on Applied Surface Science, Maresias, Brazil, Apr 2016).
- Umbach, Eberhard: “Macroscopic” Surface Reconstruction by Adsorption-Induced Stress at a Metal-Organic Interface. (Workshop of the Chemical Physics Department of the FHI, Schloss Ringberg, Kreuth, Germany, Sep 2016).
- Umbach, Eberhard: Zwischenbericht zur Sektorkopplung - Energiesysteme der Zukunft. (Jahrestagung des Themennetzwerkes Energie und Ressourcen, acatech, Berlin, Germany, Mar 2017).
- Weng, Xuefei: Interactions of Hydrogen with CeO<sub>2</sub>. (Seminar, Institute of Industrial Science, The University of Tokyo, Tokyo, Japan, Dec 2016).
- Werner, Kristin: H<sub>2</sub> on (and in?) CeO<sub>2</sub>(111) Thin Films. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Wu, Zongfang: Vibrational Spectroscopy of Single Crystal Surfaces Using FEL Infrared Radiation Induced Neon Desorption. (FHI/CP-USTC/CP Workshop on Surface Chemistry of Oxides, Hefei, China, Jun 2017).

## Department of Molecular Physics

## Department of Molecular Physics

**Director: Gerard Meijer**

### Staff scientists (as of August 2017)

André Fielicke  
Bretislav Friedrich  
Gert von Helden

Stefan Truppe  
Bernd Winter

### Post-doctoral scientists, staying for at least one year:

Alan Günther  
Claudia Kolbeck (*CRC 1109*)  
Mateusz Marianski (*MPG-EPFL*)  
Silvio Marx

Christian Schewe  
Jongcheol Seo  
Anne Stephansen (*Villum Fellow*)  
Daniel Thomas (*AvH Fellow*)

### Guest-group leaders:

Knut Asmis, Universität Leipzig  
Kevin Pagel, Freie Universität Berlin

### Guest scientists (temporary):

|                                          |                                                  |
|------------------------------------------|--------------------------------------------------|
| Ad van der Avoird ( <i>AvH Awardee</i> ) | Radboud Universiteit, Nijmegen, The Netherlands  |
| Mike Bowers ( <i>AvH Awardee</i> )       | University of California, Santa Barbara, CA, USA |
| Phil Bunker                              | NRC of Canada, Ottawa, Canada                    |
| Manfred Faubel                           | MPI Göttingen & Microliquids GmbH, Göttingen     |
| Somenat Garai                            | Universität Leipzig                              |
| Andreas Osterwalder                      | EPFL, Lausanne, Switzerland                      |
| Boris Sartakov                           | Russian Academy of Science, Moscow, Russia       |
| Bum Suk Zhao                             | Ulsan NIST, Ulsan, South Korea                   |

**Graduate students:** 11

**Under-graduate students:** 5

**Technicians:** 9

### Free-Electron Laser Facility:

Scientist in charge: Wieland Schöllkopf  
Engineer: Sandy Gewinner

## Recent Developments in the Department of Molecular Physics

Director: Gerard Meijer

### 1. General Remarks

The research in the Department of Molecular Physics focuses on the structure and the intra- and inter-molecular dynamics of molecular systems, from diatomic molecules to biological macromolecules, either in isolation or in interaction with their environment. For this, new experimental methods to manipulate and to control as well as to characterise and to spectroscopically investigate these molecular systems are developed and exploited.

Among the new methods and tools that have been developed and set up over the years, the infrared free electron laser (IR-FEL) facility arguably is the most prominent example. Since the last meeting of the Fachbeirat in November 2015, the research group on *Infrared Excitation of Gas-Phase Molecules and Clusters* of Gert von Helden, as well as the guest-groups of Knut Asmis, André Fielicke (up to April 2017 at the TU Berlin) and Kevin Pagel, have successfully made use of the unique capabilities of this facility in a variety of studies, presented in more detail below. Methods have also been developed and perfected to manipulate and to control the motion and the internal quantum states of neutral and charged molecules and clusters, in preparation for further spectroscopic investigations. In the research group *Interactions of Molecules with Fields* led by Bretislav Friedrich, novel routes to control molecules in electric, magnetic and optical fields – and any combinations thereof – are theoretically explored.

Following the re-appointment of Gerard Meijer as full-time Director of the Molecular Physics department per January 2017, three new scientific staff members have been attracted to the department:

- **Dr. André Fielicke** returned to the FHI on a permanent staff member position per April of 2017, leading the research group on *Spectroscopy and Chemistry of Metal Clusters and Cluster Complexes*.
- **Dr. Stefan Truppe** started per May of 2017 on a six-year, temporary position, setting up a research group on *Cold and Controlled Molecules*.
- **Dr. Bernd Winter** started per January 2017 as a permanent staff member, leading the research group on *Liquid Microjets*.

With the return of André Fielicke, we strengthen the in-house IR-FEL research, in particular the *in-situ* investigations of the chemistry that occurs on isolated clusters of a well-known atomic composition, in various charge states. With Stefan Truppe we have brought in a young molecular physicist who has hands-on experience with laser cooling and trapping of molecules, which – combined with the available expertise on the manipulation of molecules with electric and magnetic fields – yields new prospects for the production of dense samples of cold and controlled molecules. Bernd Winter has pioneered the use of photoelectron spectroscopy from liquid microjets, which has enabled new studies of the inter-molecular interactions in liquid water and aqueous solutions. Making use of the liquid microjets, we plan to perform detailed studies of gas-liquid and liquid-solid interfaces.

The ongoing and planned research projects are described below in sections I-III. A large experimental effort is devoted to research under the theme of “Molecular physics studies with infrared radiation”, described in Section I. In these studies, the IR optical properties and dynamics of molecules, clusters and cluster-adsorbate complexes are investigated in the gas-phase. Section II deals with “Controlled molecules”. The aim of these research projects is to develop experimental schemes to achieve full control over both the internal and external degrees of freedom of neutral molecules, and to exploit these schemes in investigations of the properties of (samples of) molecules. In Section III the new research line around the study of “Gas-liquid interfaces” is described.

## **2. Molecular Physics Studies with Infrared Radiation**

Free electron lasers operating in the infrared region of the spectrum, such as our own FHI-FEL, are ideally suited for a large variety of experiments in gas-phase molecular physics. On the one hand this is due to the available wavelength tuning range, extending from 2.5 to 250  $\mu\text{m}$ , thereby covering the full “molecular fingerprint” region, and the possibility of user-controlled wavelength scanning. The feature that really distinguishes IR-FELs from other lasers for applications in this research area is that they have the highest output energy per microsecond throughout the relevant wavelength range, which is the crucial factor when one wants to be able to resonantly pump as much energy as possible into an isolated molecule.

When FELs are used to excite neutral or charged gas-phase molecules or molecular complexes, the change in quantum state or the dissociation of complexes can be monitored as a function of excitation wavelength. These experiments require the absorption of only one or two photons and can then lead to, for example, the unravelling of the IR spectral properties of

important gas-phase molecules and ions or to an enhanced understanding of energy transfer in molecular systems. On the other hand, FELs can also be used to resonantly pump several hundred photons into a single gas-phase molecule. The internal energy can then become very high with temperatures reaching several thousand Kelvin. Most molecules will then dissociate by evaporating off small atomic or molecular fragments. Very tightly bound species, however, will undergo thermionic emission, i.e. they choose to “evaporate off” an electron instead. The resulting charged species can be easily detected, and monitoring them as a function of wavelength yields information on the IR spectrum of the neutral molecule.

The light output of the FHI-FEL comes in macropulses of up to 10  $\mu$ s duration at a repetition rate of typically 10 Hz. Each macropulse contains micropulses that are 300 fs to 5 ps long and spaced by 1 ns. The bandwidth is Fourier transform limited, implying a typical spectral resolution of several  $\text{cm}^{-1}$  for a central frequency of  $1000 \text{ cm}^{-1}$ . The FHI-FEL is therefore mainly restricted to studies in which vibrational resolution suffices. The available energies of about 100 mJ per macropulse make a variety of multiple photon excitation and double-resonance detection schemes possible. In all of our experiments we rely on mass-selective ion detection in the end, and the IR spectral information is obtained via the FEL induced change in the ion signal (“action spectroscopy”).

#### *Biological Molecules in the Gas Phase (Gert von Helden)*

Because of its speed and low sample consumption, mass spectrometry (MS) is the key gas-phase analytical technique to sequence the amino acid order in peptides and proteins. However, while this primary structure usually remains intact after transfer to the gas phase, the secondary or higher order structures of biological molecules can be severely affected by the absence of environment. An important question is in how far the secondary and higher order structures of biological molecules can be conserved after transfer from solution to the gas phase. If one can conserve higher order structures, highly sensitive gas-phase techniques could be used to address questions relevant to structural biology. Further, 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.

To address those questions, we use a combination of different experimental tools. A key technique is electrospray ionization (ESI) combined with mass spectrometry to isolate well-defined mass/charge selected molecular ions or complexes. Adding IR action spectroscopy

allows for the investigation of the secondary structure and ion mobility spectrometry (IMS) for the analysis of global shape (*i.e.*, higher order structures). Further, helium droplet isolation techniques can be employed to perform IR spectroscopy at ultralow (0.4 K) temperatures.

A key question we wanted to answer is the one stated above: *can the native structure of a protein be conserved upon transfer to the gas phase?* For this, we measured IR spectra of IMS-MS selected ions of the proteins Myoglobin and  $\beta$ -Lactoglobulin. In solutions, they are prototypical examples of  $\alpha$ -helical and  $\beta$ -sheet proteins, respectively. Using IMS-MS alone, we observe that when being sprayed from aqueous solution, low charge state proteins are compact, having sizes in the gas phase that are compatible with those in solution. Using IMS-MS alone, however, no information on the internal secondary structure is obtained. IR spectroscopy, on the other hand, clearly shows that for low charge states when being sprayed from aqueous solution, the native  $\beta$ -sheet structure of  $\beta$ -Lactoglobulin is retained. This observation can be considered as the first direct evidence for the conservation of the native structure of a protein in the gas phase.

In a different experiment, we investigate clusters of amino acids. Especially those composed of the amino acid Serine have puzzled researchers for more than a decade. It has been observed that Serine clusters form very stable octameric clusters which have the striking property that they strongly prefer homochirality, *i.e.*, when spraying a racemic mixture of L- and D-Serine, octameric clusters are formed that defy statistics and prefer to form octamers composed of either eight L-Serine or eight D-Serine molecules. Those observations have spurred experiment and theory, however, a convincing structure has not yet been found. We investigated anionic Serine octamer clusters and in particular those composed of eight Serine units complexed with two chloride ions –  $\text{Ser}_8\text{Cl}_2^{2-}$ .

Using IMS-MS, we found that pure L- or D-Serine forms a compact structure with a collision cross section (CCS) of  $189 \text{ \AA}^2$  (labeled I in Fig. *MPI*). When working with a racemic mixture, two structures are observed, one with the same CCS as observed for the enantiopure samples and one less compact structure with a CCS of  $201 \text{ \AA}^2$  (labeled II in Fig. *MPI*). Performing isotopic labeling experiments shows that the compact structure contains eight either L- or D-Serine molecules while the less compact structure II contains a statistical mixture of L- and D-units with a maximum at 4:4.



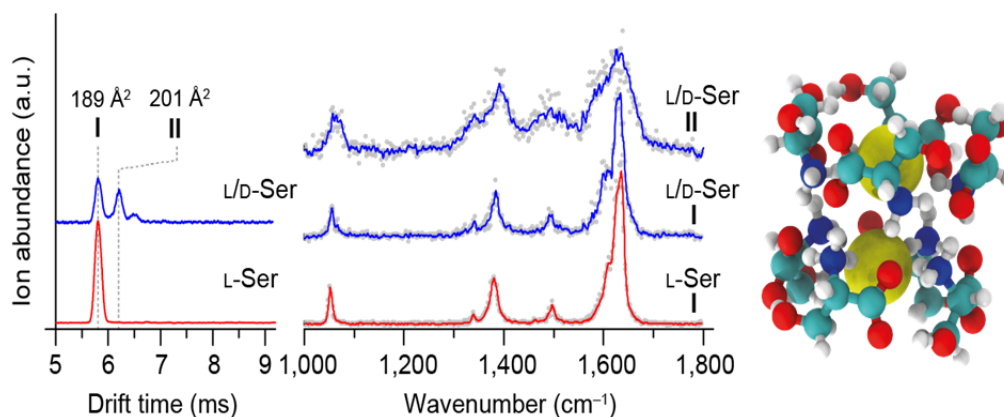


Fig. MPI: Left: IMS drift time distributions and derived cross sections for  $\text{Ser}_8\text{Cl}_2^{2-}$ . The trace in red is obtained from an enatiopure L-Serine sample while that in blue stems from a racemic sample. Center: the corresponding IR spectra. Shown on the right is the proposed structure for the homochiral  $\text{Ser}_8\text{Cl}_2^{2-}$  cluster, giving rise to peak I in the drift time distributions (Nat. Chem., DOI:10.1038/nchem.2821).

The IR spectra of the structures I and II are shown in the center of Fig. MPI. The spectra of I show four rather narrow lines. The spectrum of II shows bands at the same positions, however with significantly increased width. Inspection of the spectra shows that all clusters are composed of zwitterionic serine units. The reduced width in the spectra of I can be explained by a high symmetry of the cluster. Further analysis led us to the structure shown on the right side of Fig. MPI. The structure has D<sub>4</sub> symmetry in which all serine units are equivalent. The Cl<sup>-</sup> ions are tightly held in an electrostatic pocket provided by the -NH<sub>3</sub><sup>+</sup> units and all functional groups have hydrogen bonding partners. *Ab-initio* calculations support the stability and the calculated IR spectra match perfectly those observed in the experiment.

In a different experimental setup, we perform IR spectroscopy on mass/charge selected ions that are embedded in liquid helium droplets. In collaboration with Kevin Pagel (FU Berlin) and Peter H. Seeberger (MPI for Colloids and Interfaces), we investigate carbohydrate ions. The corresponding spectra are very sharp, rich in structure and sensitive to minute differences in carbohydrate structure. Very recently, we started exploring anions in that setup and results on proton bound carboxylate ions will be presented in a poster.

#### *Spectroscopy and Chemistry of Metal Clusters and Complexes (André Fielicke)*

The focus of the research is the characterization of gas-phase clusters, cluster complexes and molecular ions by different spectroscopic means. For this, use can be made of two experimental set-ups, one allowing for infrared spectroscopy of clusters and cluster

complexes using the FHI-FEL and a second one (that has recently been transferred back from the TU Berlin) to obtain photoelectron spectra (PES) of anionic species.

While the infrared experiments are performed to obtain structural information of the clusters and cluster complexes and to study reactions on the clusters' surface, the most recent PES experiments target the fundamentals of the interaction of an electron with a chiral environment. In essence, there is a forward-backward asymmetry in the spatial distribution of the photoelectrons emitted from chiral molecules upon irradiation with circularly polarized light, changing in sign with the chirality of the molecule and with the direction of the polarization of the light. In the past, photoelectron circular dichroism has been studied for neutral species using either ionization with VUV radiation at synchrotron facilities or via multiple photon ionization, by detecting the spatially integrated electron signal. The circular dichroism observed via the forward-backward asymmetry in the spatial distribution of photoelectrons, however, is orders of magnitude larger than the normal circular dichroism as measured in absorption and, furthermore, can also be detected for low density matter, like species isolated in a molecular beam. So far, such studies have focused on neutral stable molecules either directly brought in the gas-phase or entrained in molecular beams. The goal of this study is to investigate the photoelectron circular dichroism of anionic molecules and metal cluster complexes. In comparison to similar studies on neutral species in the gas phase, anionic species offer the possibility of prior mass selection and are technically less demanding due to the lower energy required for electron detachment *vs.* ionization. The latter allows for electron detachment by single photons in the visible or near-UV that can be obtained from off-the-shelf lasers. This drastically simplifies the experimental approach and potentially opens it up for analytical applications.

At present, complexes of metal anions with chiral molecules like fenchone and the chiral anion alaninate have been investigated. The experiments use a tunable ns OPO laser system covering the 215-2000 nm range, such that an overview on the valence band structure can be obtained or the behavior of very slow electrons via detachment close to the threshold can be studied. Electron kinetic energy and spatial distributions are analyzed using velocity map imaging (VMI). This project is funded by the DFG (FI 893/6).

In the FEL based studies we have focused on two topics related to small molecule activation, i) the activation of molecular hydrogen by transition metal doped aluminum clusters and ii) the activation of carbon dioxide by anionic metal clusters.

The first topic is a continuation of our collaboration with Ewald Janssens (KU Leuven, Belgium). In our earlier studies on hydrogen complex formation of Co, Rh, V doped Al clusters we have shown that dissociative binding is promoted by the transition metal dopand. While these conclusions are drawn based on the IR spectra in the frequency range of characteristic vibrations of the atomic hydrogen ligands ( $800\text{-}2100\text{ cm}^{-1}$ ), we now applied Ar tagging of cold clusters to probe the initial structure of the doped Al clusters via spectroscopy in the far-IR ( $210\text{-}500\text{ cm}^{-1}$ ).

The second topic centers on the activation and functionalization of carbon dioxide by anionic transition metal clusters. In collaboration with Tatsuya Tsukuda (Tokyo University, Japan) we have studied  $\text{CO}_2$  binding by rhodium and cobalt clusters. While the IR spectra identify an intact  $\text{CO}_2^-$  entity for the rhodium complexes, on the cobalt clusters a band corresponding to the presence of a carbonyl is observed, indicating a dissociative binding into CO and O. Ultimately, it would be of interest to study secondary reactions of the activated  $\text{CO}_2$  and therefore we have included platinum into these studies, which is known to also (size-dependently) activate  $\text{CH}_4$ . In collaboration with Stuart Mackenzie (University of Oxford, UK) we have started studying the reaction of  $\text{CO}_2$  with small platinum cluster anions, showing interesting size and coverage dependent behavior with some sizes dissociating  $\text{CO}_2$  like cobalt while for others the  $\text{CO}_2^-$  unit is observed. Ongoing quantum chemical calculations shall reveal the role of the energetics and barriers for the fate of the  $\text{CO}_2$  reactant.

In the near future we intend to extend the capabilities of the IR-UV two-color ionization technique that we have shown to be a very successful approach for determination of IR spectra of strongly bound neutral clusters. As these studies require a UV photon close in energy to the ionization energy of the cluster of interest, we are setting up a tunable vacuum-UV laser systems based on 4-wave mixing in rare gases. This shall allow studies of, for instance, neutral metal oxide clusters and boron clusters were, depending on their size, rather different structural motives are predicted like ribbons, pseudoplanar sheets or cages.

*Guest-group at MP: Knut Asmis (Universität Leipzig)*

The Asmis guest-group at the FHI makes use of 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 measured 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 part of the IR spectral range (200-6000 cm<sup>-1</sup>). Apart from the radiation from the FHI-FEL, a table-top OPO/OPA laser system is used.

The group currently consists of Somenath Garai (postdoc) and Sreekanta Debnath (PhD student, January 2015 – , funded by the DFG Collaborative Research Center 1109 “Understanding of Metal Oxide/Water Systems at the Molecular Scale”). During the last two years two group members left the group; Xiaowei Song (AvH Fellow) accepted a job in industry in April 2016 and Matias Fagiani successfully defended his PhD thesis at the FU Berlin in January 2017.

As part of the CRC 1109 we studied the vibrational spectroscopy of small Al-, Fe- and Si-oxide cluster ions and their interaction 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. Highlights include our work on  $[\text{Al}_3\text{O}_4(\text{D}_2\text{O})_{1-4}]^+$ ,  $[\text{Fe}_3\text{O}_4(\text{H}_2\text{O})_{1-4}]^+$ ,  $[\text{Fe}_3\text{O}_3(\text{H}_2\text{O})_{0-2}]^+$  and  $[\text{Fe}_4\text{O}_5(\text{H}_2\text{O})_{0-2}]^+$  in the O-H/D stretching as well as in the mid- and far-IR region, performed in collaboration with the theory group of J. Sauer (HU Berlin). For  $[\text{Al}_3\text{O}_4(\text{D}_2\text{O})_{1-4}]^+$ , for example, we find that dissociative water adsorption is favored in all cases. The unambiguous assignment of the vibrational spectra of these gas phase model systems allows identifying characteristic spectral regions for O–D and O–H stretching modes of terminal ( $\mu_1$ ) and bridging ( $\mu_2$ ) hydroxyl groups in aluminum oxide/water systems, which sheds new light on controversial assignments for solid  $\text{Al}_2\text{O}_3$  phases. Other studies focus on the IRPD spectroscopy of  $[\text{FeClOH}(\text{H}_2\text{O})_{0-4}]^-$  as well as silica-containing anions and are aimed at understanding the formation of Fe-oxo-hydroxy and silica oligomers, respectively. The interaction of titanium oxide anions with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was at the focus of a longstanding and fruitful collaboration with the group of D. Neumark (UC Berkeley).

Our work in the field of ion solvation was continued and focused on the characterization of salt microhydration as well as protonated water clusters. As part of a collaboration with Prof. Ling Jiang (Dalian Institute of Chemical Physics, CAS; former AvH Fellow in the MP department) we studied  $[\text{Mg}(\text{NO}_3)(\text{H}_2\text{O})_{0-12}]^+$  clusters and characterized the transition from a bidentate  $\text{Mg}(\text{O}_2\text{NO})^+$  binding motif, over a monodentate one and all the way to a solvent shared ion pair. As part of our collaboration with the AvH awardee Mark Johnson (Yale University) we revisited the vibrational spectroscopy of the protonated water pentamer and its fully deuterated isotopologue and this led to new insights into the Grotthuss mechanism of proton transfer in water.

Finally, we continued our work on boron-containing clusters and characterized the unusual structure of  $B_{13}^+$ , which behaves as a molecular ball bearing, as well as some larger cluster cations in collaboration with André Fielicke (FHI) and the theory group of Thomas Heine (Universität Leipzig).

*Guest-group at MP: Kevin Pagel (Freie Universität Berlin)*

Complex oligosaccharides – often referred to as glycans – are biomacromolecules that play an essential role in virtually all living organisms. They are involved in vital processes such as protein folding, cell recognition, and information transfer. In contrast to linearly linked biopolymers such as oligonucleotides and proteins, however, glycans are branched and stereochemically complex, which represents a major challenge for their characterization. The currently most widely used technique for the characterization of glycans is mass spectrometry (MS). With this technique, reliable information about the composition of the molecule can be obtained for very small sample quantities, but it provides little data on the underlying regio- and stereochemistry of the glycosidic bonds. The research of the Pagel group is dedicated towards the design and development of novel analytical tools, which can help to overcome this inherent problem of isomerism. Within the last two years especially two techniques have been in focus.

The first approach is based on the combination of ion mobility spectrometry and mass spectrometry (IMS-MS). With this technique, analyte ions can be distinguished not only based on their mass and charge, but also by their size and shape. The obtained drift times can furthermore be used to calculate the rotationally-averaged collision cross section (CCS) of an ion in a specific drift gas. This CCS is a molecular property, which under controlled conditions is independent of instrument parameters and can therefore be used as an additional identification parameter allowing an easier and more reliable structural assignment. In the last two years we developed a comprehensive calibration framework, which can be used to accurately determine CCSs using commercially available travelling wave IMS-MS instruments. In addition, a database in which reference CCSs can be deposited and used for a more reliable structural identification has been established. In collaboration with the group of Peter H. Seeberger (MPI for Colloids and Interfaces), we have shown very systematically that detailed information on the branching and three-dimensional structure of oligosaccharides can be obtained using IMS-MS. A series of further evaluations has provided evidence that not only intact glycans, but also glycan fragments, for example from larger glycans or glycopeptides, can be used for the identification of structural features. Taken together, this

work provides the basis for a new and simple strategy for the analysis and sequencing of glycans and glycoconjugates and should be developed further within the next years with a focus on applications.

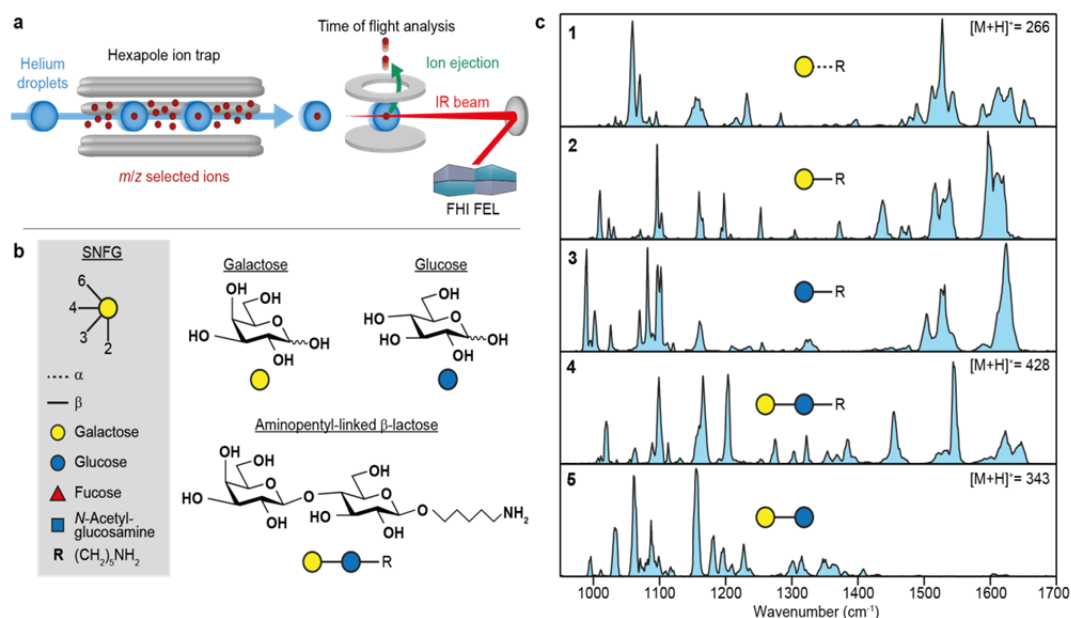


Figure MP2: a) Schematic diagram of the experimental setup. Ions in the gas phase are mass-to-charge selected and accumulated inside an ion trap. Traversing helium droplets can pick up trapped ions, which immediately cools them to 0.37 K. Subsequently, the doped droplets are irradiated with IR radiation of a defined wavelength using the free-electron laser. b) Representative structures of selected carbohydrates and their corresponding symbol nomenclature (SNFG). c) IR spectra of the mono- and disaccharides  $\alpha$ -galactose (1),  $\beta$ -galactose (2),  $\beta$ -glucose (3),  $\beta$ -lactose (4) and free lactose (5). (Angew. Chem. Int. Ed., DOI: 10.1002/anie.201702896)

The second approach is gas-phase infrared (IR) spectroscopy. These experiments are performed in collaboration with the group of Gert von Helden and make use of the FHI-FEL. While being already widely established for the structural analysis of peptides and proteins, gas phase spectroscopy has been sparsely utilized for oligosaccharide analysis. This is largely a result of the relatively low information content obtained in standard spectroscopy experiments. At room temperature, the gas-phase IR spectra of glycans are typically characterized by very broad, indistinctive vibrational bands. This spectral broadening is not only due to temperature *per se*, but also a result of the multiple photon absorption mechanism underlying these experiments. We very recently overcame this problem by cooling the investigated ions prior to the experiment by encapsulating them in superfluid helium nanodroplets (Figure MP2). Under these conditions, oligosaccharide ions yield well-resolved and highly diagnostic IR fingerprints in which even minute structural variations such as the

stereochemistry of a single OH group are reflected. As such, this technique is capable of unambiguously identifying all conceivable structural details in oligosaccharides. Investigating ionic species furthermore provides the exceptional potential to use gas-phase IR spectroscopy to trap and structurally characterize short-lived cationic intermediates that occur during oligosaccharide synthesis. This will provide a better understanding of the currently only empirically understood reaction mechanisms that govern glycosidic bond formation. First experiments directed towards this end are currently underway.

The most promising perspective for future research clearly lies in the combination of IMS-MS and cold-ion spectroscopy for oligosaccharide analysis. Combined into one experimental setup, this will enable the simultaneous measurement of  $m/z$ , CCS and IR fingerprint of a given glycan and its gas-phase fragments. In combination with a database that contains reference values from well-known compounds, these multi-dimensional datasets will help to unambiguously identify unknown biological oligosaccharides on a high-throughput scale with very little sample consumption. Even though technically elaborate, there is also a potential for commercialization of a slightly altered experimental setup using IMS-MS and tagging spectroscopy with commercially available bench top OPO lasers. There is already an ongoing discussion with instrument manufacturers and it is anticipated that a first prototype for such experiments will be developed at the FHI within the next years.

### **3. Controlled Molecules**

Getting full control over both the internal and external degrees of freedom of neutral, gas-phase molecules has been an important goal in molecular physics during the last decades. Almost twenty years ago by now, we experimentally demonstrated that appropriately designed arrays of time-varying electric fields in a so-called “Stark decelerator” can be used to fully control the transverse as well as the longitudinal (forward) velocity of molecules in a beam. Since then, the ability to produce focused packets of state-selected accelerated or decelerated molecules has made many new experiments possible. Decelerated beams of molecules have been used in crossed molecular beam and surface scattering experiments, they have been used for high-resolution spectroscopy and they have been used to load molecules into traps. In these traps, electric or magnetic fields are used to keep the molecules confined in a region of space where they can be studied in complete isolation from the environment. Trapping of ammonia molecules in a quadrupole electrostatic trap has been demonstrated first, but trapping various other molecules in more versatile geometries like, for instance, on a chip or in a molecular synchrotron has been demonstrated as well. The long interaction time

afforded by the trap has been exploited to measure the lifetime of metastable states, for instance.

During the last years, it has been demonstrated that laser cooling – the work-horse to control atoms – can also be used for a subset of molecules, that have a specific electronic and ro-vibrational energy level structure. We will be exploring the possibilities that the combined manipulation with optical fields and with electric and magnetic fields holds to achieve ultimate control over molecules.

#### *Interactions of Molecules with Fields (Bretislav Friedrich)*

Over the reporting period, the research group carried out work on (i) interactions of molecules with external electric, magnetic and optical fields as well as on mutual interactions of a pair of molecules subject to such external fields; (ii) quantum computing with polar paramagnetic molecules. In addition, the research group embarked on two DFG-funded projects: (iii) analytic solvability and eigenenergy-surface topology of problems related to molecules subject to electromagnetic fields (jointly with Burkhard Schmidt, Freie Universität Berlin); (iv) configurations of molecular complexes formed and detected in He nanodroplets (jointly with Alkwin Slenczka, Universität Regensburg).

We examined how the electric dipole–dipole interaction potential between two polar  $^2\Sigma$  molecules – which are inherently paramagnetic – creates entangled pair-eigenstates and how these are affected by the Zeeman interaction between the molecules and a superimposed magnetic field. The electric dipole–dipole intermolecular potential couples Zeeman levels that fulfill selection rules imposed by the electric dipole–dipole operator. This coupling alters the Zeeman levels of the pair-eigenstates in general and modifies the mutual alignment of the two molecular rotors in particular. We are reminded of the coupling of the Zeeman levels of a single polar paramagnetic molecule by a superimposed electric field, whose interaction with the body-fixed electric dipole of the polar molecule plays the role of the electric dipole–dipole interaction (although under different selection rules). However, the pair-eigenstates exhibit a behavior quite different from that of single-molecule eigenstates. For instance, we find that the field-free pair-eigenstates are the maximally entangled Bell states. The application of a magnetic field is akin to effecting a Bell measurement that results in destroying the pair’s entanglement.

We made use of the above features to propose a prototype design for a universal quantum computer based on an array of trapped  $^2\Sigma$  molecules. We showed that by subjecting the array



to combinations of concurrent homogeneous and inhomogeneous electric and magnetic fields, the entanglement of the array's Stark and Zeeman states can be tuned and the qubit sites addressed. Two schemes for implementing an optically controlled CNOT gate were proposed and their feasibility discussed in the face of the broadening of spectral lines due to dipole-dipole coupling and the inhomogeneity of the electric and magnetic fields. In addition, we carried out an analysis of an array consisting of polar  $^1\Sigma$  molecules and showed that up to a negligible error, the ground state of the array can be considered as the unentangled qubit basis state.

Like the harmonic oscillator, the quantum pendulum is key to the understanding of a number of prototypical problems in chemistry and physics. However, unlike the harmonic oscillator problem, the planar pendulum one is not analytically solvable, *i.e.*, its Schrödinger equation does *not* possess algebraic solutions that cover the entire spectrum of the problem's Hamiltonian. Instead, the problem is only conditionally quasi-exactly solvable, *i.e.*, its algebraic solutions only exist for finitely many eigenvalues of the pendular Hamiltonian (quasi-exact solvability, QES), and, moreover, only obtain if the problem's interaction parameters satisfy a particular set of conditions (conditional quasi-exact solvability, C-QES). We showed that the planar pendulum system possesses symmetries isomorphic with those of the  $C_{2v}$  point group and found that the four analytic solutions that we had reported earlier exhibit these symmetries. Furthermore, we found thirty-six new analytic solutions and determined that even and  $2\pi$ -periodic solutions correspond to the  $A_1$  symmetry, odd and  $2\pi$ -periodic solutions to  $A_2$ , even and  $2\pi$ -antiperiodic solutions to  $B_1$ , and odd and  $2\pi$  antiperiodic solutions to  $B_2$  symmetry. As recognized in our previous work, the intersections (genuine or avoided) of the pendulum's eigenenergy surfaces, spanned by the problem's dimensionless interaction parameters  $\eta$  and  $\zeta$ , can be characterized by a single integer index  $\kappa$  (the topological index) and that the values of  $\kappa$  correspond to the conditions of analytic solvability. During the reporting period we determined that the parabolic surfaces running through the loci of the intersections for a given  $\kappa$  (parabolas of conditional quasi-exact solvability) arise due to the structure of the tri-diagonal matrices representing the symmetry-adapted pendular Hamiltonian: if and only if  $\kappa$  is an odd/even positive integer can the tri-diagonal matrices, each of which corresponds to one of the problem's four irreducible representations, be broken into finite-dimensional matrices and infinite-dimensional remainders, whereby the finite-dimensional matrices can be diagonalized, at least in principle, analytically, with solutions that are periodic/antiperiodic in  $2\pi$ . The dimensions of the finite

block matrices add up to the topological index  $\kappa$ , which, therefore, equals the number of analytic solutions. Although we can find, in principle, infinitely many analytic solutions, we cannot find all solutions analytically. In particular, the solutions that remain out of reach are those that correspond to either  $\eta$  or  $\zeta$  equal to zero (*i.e.*, no analytic solutions to the spheroidal wave equation or the Mathieu equation obtain). For non-integer  $\kappa$ , the tri-diagonal matrices are infinite and, therefore, not amenable to analytic diagonalization. We also treated – in a similar manner – the planar pendulum’s anti-isospectral counterpart, the Razavy problem. In our future work, we plan to exploit the Quantum Hamilton-Jacobi theory that amounts to taking supersymmetric quantum mechanics to the complex plane.

Exploring the features of a high-resolution spectrum of impurities embedded in a superfluid He environment has so far generated more questions than answers. In particular, little is known about the processes of formation and solvation of molecular complexes inside a He nanodroplet. As model systems, we examine the Phthalocyanine (Pc) based molecular complexes such as Pc-(H<sub>2</sub>O) and (Pc)<sub>2</sub> prepared and probed in superfluid helium nanodroplets. The experimental technique of choice is high-resolution electronic spectroscopy capable of resolving the structure of complexes of well-defined stoichiometry. A superimposed Stark field aids in identifying the various isomeric variants of the complexes formed. A simultaneous theoretical analysis based on quantum chemistry computations serves to affirm the structural information on the clusters as revealed by the optical Stark spectra. To this end, global structure optimization based on the DoDo genetic algorithm followed by a local CC2 treatment is used to furnish the dipole moments for the ground and first electronically excited states along with the gas phase geometries/moments of inertia for a number of theoretically predicted configurations. Further, for benchmarking and key insights on smaller systems we use the bosonic Time-Dependent Density Functional Theory (TD-DFT) as a means of simulating the experiment from scratch. The effective moments of inertia/rotational constants of the complexes in the helium droplet environment are determined via the recently developed angulon theory and used to generate simulated Stark spectra for each theoretical configuration.

#### *Atom Optics and Quantum Reflection of Molecular Beams (Wieland Schöllkopf)*

We have been extending our studies on matter wave optics, which are carried out with a dedicated molecular-beam diffraction apparatus at the FHI, originally built at the Max-Planck-Institut für Strömungsforschung in Göttingen, Germany. With its high angular resolution ( $\sim 100 \mu\text{rad}$ ) the apparatus allows to resolve small-angle diffraction patterns of

atomic, molecular and cluster beams. We have investigated quantum reflection and diffraction from solid micro-structured gratings made out of different materials and of various shapes, in collaboration with Prof. B.S. Zhao and his group at the Ulsan National Institute of Science and Technology, South Korea. In 2016 and 2017 four Korean students have been joining our lab for periods ranging from a few weeks to several months.

Quantum reflection of atoms or molecules from a solid, *i.e.*, the reflection of a particle's wave-function at the attractive particle-surface Casimir-van der Waals potential can only be observed at extremely low incident kinetic energies. We employ grazing incidence of a highly collimated molecular beam onto a reflection grating to achieve an extremely small perpendicular component of the incident momentum. This allows us to observe quantum reflection of He atoms, small He clusters, or D<sub>2</sub> molecules typically at the percent level. Beams that are quantum reflected from a grating exhibit clearly resolved diffraction patterns.

Matter-wave diffraction and interference represent an analogy to the corresponding effects in classical optics. In a series of experiments we have investigated the validity of two basic principles well known from classical optics; the reciprocity principle and Babinet's principle. Reciprocity states that observed signals do not change upon interchanging source and detector in a scattering experiment. It is a basic principle that holds in various fields including optics and acoustics. Babinet's principle, known from classical optics, states that diffracting objects of complementary shape, e.g. a slit and a bar of the same width, cause identical diffraction intensities (except for the forward or zero-order direction).

We investigated both principles in matter-wave grating diffraction. We found the reciprocity principle to hold robustly. It applies even for emerging-beam-resonance conditions when, at Rayleigh angles of incidence, another diffraction beam emerges from the grating plane. We have also found Babinet's principle to hold for conditions where the atom-surface interaction is negligible. However, we observed a break down of Babinet's principle under emerging-beam-resonance conditions as well as for very small incidence angles and for diffraction beams scattered at very small angles with respect to the grating surface. We attribute this behavior to the effect of the surface potential on the atomic or molecular wavefunction.

In the future, we want to search for inelastic grating diffraction. The idea here is that an incoming particle, such as the He trimer, can be brought to an excited internal state upon scattering from the grating. As a result, the kinetic energy will be reduced by exactly the excitation energy. Consequently, the de Broglie wavelength of the outgoing trimer will be

larger. Thus, the diffraction angles of inelastic peaks, when observed, can reveal accurate information on the internal excitation energy of  $\text{He}_3$ . A precise determination of the latter is of special interest, because there is only one excited state in  $\text{He}_3$  and it is known to be an Efimov state. A precise measurement of the Efimov state's energy can serve as an important benchmark for quantum chemistry calculations of the He-He interaction potential.

#### *Cold and Controlled Molecules (Stefan Truppe)*

During the last years, it has been experimentally shown that a certain group of molecules, in particular the diatomic halides, can be laser-cooled, something that was long considered impossible for molecules because of their complex internal structure. In 2010, the SrF molecule was the first molecule to be laser-cooled by the group of Dave DeMille (Yale University) and various other groups then followed suit, laser cooling similar molecules. As a postdoc in the group of Ed Hinds and Michael Tarbutt at Imperial College, London, Stefan Truppe was involved in the design and setting up of a cryogenic, buffer-gas beam of CaF molecules, that he then used in laser cooling, slowing and trapping experiments. The first laser cooling results on CaF were obtained at the end of 2015 and frequency-chirped laser slowing of CaF was demonstrated a year later. In the first months of this year, a reliable Magneto Optical Trap (MOT) of CaF molecules was demonstrated, holding 25.000 CaF molecules, sub-Doppler cooled to 52 microKelvin – a real break-through in the field. The production of sub-Doppler cooled samples of diatomic molecules will be the starting point for many experiments to come in the next years, and some of the long-held promises and expectations in the field of Cold and Controlled Molecules can now be experimentally studied.

We are currently designing a cryogenic, buffer-gas laser ablation source to produce intense, slow beams of diatomic halides at the FHI, which we will subsequently bring further under control with a combination of laser light and external fields. In particular, we plan to use the molecular synchrotron, that we have demonstrated and used previously, as the ideal trap to store bunches of laser-cooled diatomic halides.

#### **4. Gas-liquid Interfaces**

In the MP department we are setting up a new research line, aimed at improving our understanding of gas-liquid interfaces. We will make use of liquid microjets in vacuum, a field pioneered by Manfred Faubel and co-workers at the Max-Planck-Institut für Strömungsforschung in Göttingen and brought to fruition by him in collaboration with many

others, amongst whom Bernd Winter. We will combine the available expertise in the MP department in the field of molecular beams and laser detection methods with the expertise on liquid microjets and on photo-electron spectroscopy thereof to obtain a more complete picture of the gas-liquid interface.

*Liquid Microjet Photoelectron Spectroscopy (Bernd Winter)*

An experimental setup for photo- and Auger-electron spectroscopy from vacuum liquid microjets will be operational in the MP department by the end of 2017 for investigating the electronic structure of liquids, mostly aqueous solutions. With this setup we access valence and core-level electronic structure, and also electronic relaxation (autoionization) processes. Studies described in the following build on our previous liquid-jet works on aqueous solutions with soft-X-rays at BESSY.

Some of the topics we want to investigate at the FHI are (1) the solutions' work functions, (2) the interactions of a molecular beam with an aqueous-solution surface, and (3) the forward-backward asymmetry in the photoelectron (PE) angular distribution from chiral molecules dissolved in water, when using circularly polarized light. Additionally, we plan to develop a vacuum liquid-ammonia microjet with the goal achieving high concentrations of solvated electrons in the solution, enabling to experimentally study the liquid-to-metal transition. Moreover, (4) we continue to explore the electronic structure of transition-metal-oxide nanoparticles in aqueous solutions which is one of our scientific goals within the DFG Collaborative Research Center, CRC 1109, on "Metal Oxide/Water Systems". Furthermore, (5) we have an ongoing interest in the non-local relaxation processes that are induced upon core-level ionization. This spectroscopy can be used to determine hydrogen-bond strengths, and the processes are uniquely sensitive to ion pairing. These latter works are embedded within the DFG Research Unit FOR 1789, on "Intermolecular and Interatomic Coulombic Decay (ICD)". Except for (1), experiments require EUV, XUV light, or soft X-rays with variable polarization; our first liquid-jet PECD measurements will be conducted at a soft-X-ray beamline at PETRA, DESY, in March 2018. For (1) we will perform in-house studies, using a monochromatized high-intensity EUV light source (He II  $\alpha$  = 40.8 eV); a light-focusing capillary needs to be developed as to achieve focal size on the order of the liquid-jet diameter.

*Work Function Measurements:* We will study the effect of a bias voltage applied to a liquid jet which requires careful elimination of electric fields due to any other components. From the

low-energy electron cutoff energy we can determine work functions, and quantify electrokinetic charging. Based on this information bulk- and interfacial solution binding energies can be determined more accurately than previously. This is because contributions from work function, surface dipoles, and from solvation-induced electronic-structure changes to spectral shifts can be distinguished.

*Liquid – Gas Dynamics:* We explore how well-characterized cold molecular beams interact with an aqueous surface in vacuum for advancing our understanding of the occurring chemical and physical processes. Applying liquid-jet PE spectroscopy as well as several complementary techniques we aim at tackling the different steps in a gas – liquid scattering event by separately studying the scattering, the ad-/absorption, and the surface structure. This is a longer-term project, and a first experiment is currently being set up where we explore the feasibility of directing a state-selected metastable CO beam and a CO<sub>2</sub> molecular beam on a cylindrical liquid water microjet. Once the experimental conditions are characterized we will use a flat liquid-water jet (providing a more suitable planar scattering surface), and our goal is to quantify the interactions between the molecular beam and the solution surface on the microscopic level. This includes detection of the scattering angular distributions, and characterization of the scattered molecules by various spectroscopic techniques, as well as photoelectron-spectroscopy measurements of the solution surface. Aforementioned CO<sub>2</sub> studies will be performed for an amine-based aqueous solution. Specifically, we aim at detecting the products in the solution resulting from the CO<sub>2</sub> + monoethanolamine (industrially used for CO<sub>2</sub> capture) reaction by PE spectroscopy. In an initial experiment with soft X-rays at BESSY we use however a gas-streamer unit which applies a high local CO<sub>2</sub> pressure around the laminar liquid jet.

*Photoelectron Circular Dichroism (PECD):* This is a relatively novel effect capable to detect chiral molecules with high sensitivity. This requires determination of the ‘chiral’ asymmetry parameter obtained for circularly polarized light. Experimentally, this parameter can be accessed in a geometry that detects electrons in the direction (or opposite) direction of the k-vector of the light. For liquid solutions, this is a challenging task, and our new Liquid-Jet PES setup is designed to capture these angles which are not in the dipole plane. Main motivations for carrying out aqueous phase PECD measurements are to understand how hydration affects the magnitude of the PECD, and a related question is to what extent the solvation shell would be chiral. Another important aspect is how PECD differs for bulk versus interfacial solvation. At present, no other approach than the one presented here has been experimentally realized.

An obvious desire though is to develop a liquid-jet velocity-map imaging (VMI) spectrometer. This is a challenging task (mainly due to the poor conductivity of water and the high vapor pressure of water), and we are beginning to design such a device.

*Nanoparticles and Nucleation Processes:* Our interest is in the electronic structure of the interface between transition-metal-oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) nanoparticles (NP) and the surrounding aqueous solution. This work aims to advance our understanding of dissociative (liquid) water adsorption at catalytic transition-metal oxide surfaces. Here, we record photoemission spectra for resonant excitation at both the oxygen 1s and the metal 2p edges to detect the interfacial products resulting from  $\text{H}_2\text{O}$  dissociation. In addition, we investigate the early-stage nucleation processes (upon pH increase) that lead to particle formation. We specifically detect the photoelectrons from the occurring metal-oxide oligomers before particles begin to form. One experimental challenge in these experiments is to induce the neutralization reactions (addition of  $\text{OH}^-$ ) milliseconds before recording the PE spectra. This requires an efficient (turbulent) mixing of two microjets which is a whole and active research area itself; we will perform studies along these lines as well.

*Inter-Coulombic Decay (ICD) and Electron-Transfer Mediated Decay (ETMD):* We want to demonstrate that electron-transfer mediated decay is a potentially important novel spectroscopy for detecting ion pairing. The other non-local auto-ionization process, ICD, will be studied, for instance, in  $\text{OH}^-$  and ADP / ATP (in the presence of  $\text{Mg}^{2+}$  and / or  $\text{Ca}^{2+}$ ) aqueous solutions. Our interest in the former solution is to infer the hydration structure which is related to the fast migration / diffusion mechanism of the hydroxide anion. The second system is studied to fully characterize the electronic structure of the reactant and product state of the ATP hydrolysis in aqueous solution, a key reaction in living cells.

## 5. Publications of the Department of Molecular Physics

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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* **17** (39), 25714–25724 (2015).



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*Schön, D., J. Xiao, R. Golnak, M.F. Tesch, B. Winter, J. Velasco Vélez and E.F. Aziz:* Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells. *The Journal of Physical Chemistry Letters* **8** (9), 2087–2092 (2017).



Seidel, R., M.N. Pohl, B. Winter and E. Aziz: Advances in liquid phase soft-x-ray photoemission spectroscopy: A new experimental setup at BESSY II. *Review of Scientific Instruments* **88** (7), 073107 (2017).

Seo, J., W. Hoffmann, S. Warnke, X. Huang, S. Gewinner, W. Schöllkopf, M.T. Bowers, G. von Helden and K. Pagel: An infrared spectroscopy approach to follow  $\beta$ -sheet formation in peptide amyloid assemblies. *Nature Chemistry* **9** (1), 39–44 (2017).

Seo, J., S. Warnke, K. Pagel, M.T. Bowers and G. von Helden: Infrared spectrum and structure of the homochiral serine octamer-dichloride complex. *Nature Chemistry*, in press.

Seo, J., W. Hoffmann, S. Malerz, S. Warnke, M.T. Bowers, K. Pagel and G. von Helden: Side-chain effects on the structures of protonated amino acid dimers: A gas-phase infrared spectroscopy study. *International Journal of Mass Spectrometry*, in press.

Song, X., M.R. Fagiani, S. Gewinner, W. Schöllkopf, K.R. Asmis, F.A. Bischoff, F. Berger and J. Sauer: Gas-Phase Vibrational Spectroscopy of the Aluminum Oxide Anions  $(\text{Al}_2\text{O}_3)_{1-6}\text{AlO}_2^-$ . *ChemPhysChem* **18** (8), 868–872 (2017).

Song, X., M.R. Fagiani, S. Gewinner, W. Schöllkopf, K.R. Asmis, F.A. Bischoff, F. Berger and J. Sauer: Inside Cover: Gas-Phase Vibrational Spectroscopy of the Aluminum Oxide Anions  $(\text{Al}_2\text{O}_3)_{1-6}\text{AlO}_2^-$ . *ChemPhysChem* **18** (8), 866–866 (2017).

Truong, N.X., B.K.A. Jaeger, S. Gewinner, W. Schöllkopf, A. Fielicke and O. Dopfer: Infrared Spectroscopy and Structures of Boron-Doped Silicon Clusters  $(\text{Si}_n\text{B}_m)$ ,  $n = 3-8$ ,  $m = 1-2$ . *The Journal of Physical Chemistry C* **121** (17), 9560–9571 (2017).

Warnke, S., W. Hoffmann, J. Seo, E.D. Genst, G. von Helden and K. Pagel: From Compact to String—The Role of Secondary and Tertiary Structure in Charge-Induced Unzipping of Gas-Phase Proteins. *Journal of the American Society for Mass Spectrometry* **28** (4), 638–646 (2017).

### **Doctoral Thesis**

Fagiani, M.R.: Cryogenic Ion Vibrational Spectroscopy of Gas-Phase Clusters: Structure, Anharmonicity and Fluxionality. Freie Universität Berlin 2017.

### **Master's Thesis**

Malerz, S.: Structural Investigation of Amyloid Oligomers via IM-MS and Infrared-Spectroscopy. Freie Universität Berlin 2017.

Manz, C.: Automated Analysis of Complex Oligosaccharides via Ion Mobility-Mass Spectrometry. Freie Universität Berlin 2017.

### **Bachelor's Thesis**

Kirschbaum, C.: Untersuchung von isomeren Lipiden mittels Ionenmobilitäts-Massenspektrometrie. Freie Universität Berlin 2017.

## 6. Invited Talks of the Members of the Department of Molecular Physics

- Asmis, Knut R.: Infrared Spectroscopy of Cold Microhydrated Sulfate Dianions. (Molecular and Ionic Clusters, Gordon Research Conference, Ventura, CA, USA, Jan 2016).
- Asmis, Knut R.: Infrared Spectroscopy of Cold Microhydrated Sulfate Dianions. (20th Symposium on Atomic, Cluster and Surface Physics 2016 (SASP 2016), Davos, Switzerland, Feb 2016).
- Asmis, Knut R.: Ion Microhydration Probed by Cryogenic Ion Trap Vibrational Spectroscopy. (251st ACS National Meeting, Decoding the Spectroscopic Signatures of Large Amplitude Motions, San Diego, CA, USA, Mar 2016).
- Asmis, Knut R.: Ion Microhydration Probed by Cryogenic Ion Trap Vibrational Spectroscopy. (European Conference on Trapped Ions (ECTI 2016), Arosa, Switzerland, Aug 2016).
- Asmis, Knut R.: Spectroscopic Snapshots of the Proton Transfer Mechanism in Water. (PTC-Kolloquium, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Bonn, Germany, Nov 2016).
- Asmis, Knut R.: Spectroscopic Snapshots of the Proton Transfer Mechanism in Water. (International Symposium of the CRC 1109, Metal Oxide - Water Systems, Erkner, Germany, Feb 2017).
- Asmis, Knut R.: Spectroscopic Snapshots of the Proton Transfer Mechanism in Water. (2nd MOLIM (Molecules in Motion) Training School, Campus Universitaire à Orsay, Université Paris-Saclay, Orsay, France, Mar 2017).
- Asmis, Knut R.: Spectroscopic Snapshots of the Proton Transfer Mechanism in Water. (Theoretical Chemistry Colloquia, Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Bochum, Germany, Apr 2017).
- Asmis, Knut R.: Unusual Properties of Boron-Containing Clusters Probed by Cryogenic Ion Trap Vibrational Spectroscopy. (International Conference on Chemical Bonding (ICCB), Kauai, HI, USA, Jun 2017).
- Debnath, Sreekanta: Gas Phase Vibrational Spectroscopy of Titanium Oxide Anions: Structure-Reactivity Relationship. (115th General Assembly of the German Bunsen Society for Physical Chemistry, Rostock, Germany, May 2016).
- Debnath, Sreekanta: Vibrational Spectroscopy of Microhydrated Magnesium Nitrate Cations  $[\text{MgNO}_3(\text{H}_2\text{O})_{0-12}]^+$ : Evolution of Characteristic Binding Motifs. (116th General Assembly of the German Bunsen Society for Physical Chemistry, Kaiserslautern, Germany, May 2017).
- Fielicke, André: Far-Infrared Spectroscopy of Metal Cluster Rare-Gas Complexes. (DPG-Frühjahrstagung 2016, Atomic, Molecular, Plasma Physics and Quantum Optics Section (SAMOP), Hannover, Germany, Feb 2016).
- Fielicke, André: Far-Infrared Spectroscopy for the Structure Determination of Strongly Bound Clusters: Metals and Semiconductors. (CECAM Workshop, Structure prediction of nanoclusters from global optimization techniques: computational strategies and connection to experiments, Pau, France, Jul 2016).

- Fielicke, André: Shedding IR Light on Gas-Phase Metal Clusters: Insights into Structures and Reactions. (Future of Chemical Physics, AIP Publishing Horizons conference, Oxford, UK, Aug 2016).
- Fielicke, André: Vibrational Spectroscopy of Metal Cluster Complexes with a Free Electron Laser: Investigating the Chemistry on a Small Surface. (Seminar, Instituto de Investigaciones en Materiales, National Autonomous University of Mexico, Mexico, Mexico, Nov 2016).
- Fielicke, André: Vibrational Spectroscopy of Metal Cluster Complexes with a Free Electron Laser: Investigating the Chemistry on a Small Surface. (Nanotech Congress 2016, International Topical Meeting on Nanostructured Materials and Nanotechnology, Puerto Vallarta, Mexico, Nov 2016).
- Fielicke, André: Shedding IR Light on Gas-Phase Metal Clusters: Insights into Structures and Reactions. (Seminar, Department of Physics and Astronomy, University of Leuven, Leuven, Belgium, Jan 2017).
- Fielicke, André: Far-Infrared Spectroscopy of Gas-Phase Metal Clusters. (Gaseous Ions: Structures, Energetics & Reactions, Gordon Research Conference, Ventura, CA, USA, Feb 2017).
- Fielicke, André: Spectroscopy of Metal Complexes; from Small Molecule Activation to the Imprinting of Chirality in Metal Clusters. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Friedrich, Bretislav: How Did the Tree of Knowledge Get Its Blossom? The Rise of Physical and Theoretical Chemistry with an Eye on Berlin and Leipzig. (Seminar, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, Universität Leipzig, Leipzig, Germany, Oct 2015).
- Friedrich, Bretislav: Clara Haber, nee Immerwahr (1870-1915): Life, Work and Legacy. (Permanent Representation of the Federal Republic of Germany to the OPCW (Organization for the Prohibition of Chemical Weapons), The Hague, The Netherlands, Nov 2015).
- Friedrich, Bretislav: Supersymmetry of the Molecular Stark Effect. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Friedrich, Bretislav: Not Just a Branch but the Blossom of the Tree of Knowledge: The Rise – and Blossoming – of Physical and Theoretical Chemistry. (The Learned Society of the Czech Republic, Prague, Czech Republic, Mar 2017).
- Friedrich, Bretislav: A Brief History of the Fritz Haber Institute. (A presentation for the Worshipful Company of Saddlers and guests, Haber Villa, Berlin, Germany, May 2017).
- Haak, Henrik: Konzeption und Konstruktion von Projekt: Mobile Beamer. (Seminar, Department Dynamics at Surfaces, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany, Oct 2015).
- Helden, Gert von: Infrared Spectroscopy of Peptides and Proteins Embedded in Helium Droplets. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).



- Helden, Gert von: VUV Photodissociation of Conformer Selected Protein Ions. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Helden, Gert von: Peptides and Proteins in Liquid Helium Droplets. (Molecular and Ionic Clusters, Gordon Research Conference, Ventura, CA, USA, Jan 2016).
- Helden, Gert von: Infrared Spectroscopy of Mass/Charge Selected Biomolecules in Liquid Helium Droplets. (Hauptvortrag, DPG-Frühjahrstagung, Hannover, Germany, Feb 2016).
- Helden, Gert von: IR Spectroscopy of Biomolecules after Ion Mobility Selection and in Liquid Helium Droplets. (Seminar, Radboud University, Nijmegen, The Netherlands, Feb 2016).
- Helden, Gert von: Amino Acid Metaclusters Probed by Ion Mobility Spectrometry and IR Spectroscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Helden, Gert von: The Structures of Amino Acid and Peptide Aggregates Studied by IR Spectroscopy. (Conference on Molecular Nanostructures 2017, Ascona, Switzerland, Mar 2017).
- Helden, Gert von: Investigating Biological Molecules by a Combination of ESI, MS, IMS, IR and HENDI. (Advancing Mass Spectrometry for Biophysics and Structural Biology, Ann Arbor, MI, USA, Jul 2017).
- Helden, Gert von: Homochiral Serine Octamer Anions: Infrared Spectrum and Structure of the Chloride Adduct. (254th ACS National Meeting & Exposition, Division of Physical Chemistry: Gaseous Ion Chemistry & Surface Reactions, Washington, DC, USA, Aug 2017).
- Heyne, Georg: Fundamentals of Electronic Measurements. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Meijer, Gerard: Open Access of Scientific Publications (in The Netherlands). (13th Berlin Open Access Conference, Building capacity for the transformation, Berlin, Germany, Mar 2017).
- Meijer, Gerard: Challenges in Scholarly Communication. (XL. Bibliothekstagung der Max-Planck-Gesellschaft, Berlin, Germany, Apr 2017).
- Meijer, Gerard: Open Access of Scientific Publications. (International Symposium on Molecular Beams (ISMB2017), Nijmegen, The Netherlands, Jun 2017).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-MS. (5th Symposium on Structural Proteomics, Halle, Germany, Nov 2015).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-MS. (Seminar, Physical Chemistry department (ISIC), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland, Dec 2015).

- Pagel, Kevin: Wenn Zucker fliegen lernen: Ionenmobilitäts-Massenspektrometrie von komplexen Kohlenhydraten. (BioClub at Freie Universität Berlin, Berlin, Germany, Feb 2016).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-MS. (Department Seminar, Manchester Institute of Biotechnology, The University of Manchester, Manchester, UK, Feb 2016).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-MS. (Award Lecture - Mattauch-Herzog-Förderpreis, DGMS 2016 – 49th annual conference of the German Society for Mass Spectrometry, Hamburg, Germany, Feb 2016).
- Pagel, Kevin: Wenn Zucker fliegen lernen: Ionenmobilitäts-Massenspektrometrie von komplexen Kohlenhydraten. (Symposien, Ergebnisse des Leopoldina-Förderprogramms X, Halle, Germany, Feb 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (9th international conference on Isolated Biomolecules and Biomolecular Interactions, Oxford, UK, Apr 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Seminar, BASF, Ludwigshafen, Germany, Apr 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Analytica Conference 2016, Munich, Germany, May 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Seminar, Leibniz-Institut für Analytische Wissenschaften - ISAS - e. V., Dortmund, Germany, May 2016).
- Pagel, Kevin: Sugars in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (OC-Kolloquium, Fachbereich Chemie, Universität Hamburg, Hamburg, Germany, May 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (GDCh Seminar, Fakultät für Chemie und Mineralogie, University Leipzig, Leipzig, Germany, Jun 2016).
- Pagel, Kevin: Ion Mobility-Mass Spectrometry - How Does It Work and What Is It Good For? (Ion Mobility Interest Group Meeting, ASMS 2016: 64th Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, USA, Jun 2016).
- Pagel, Kevin: Sugars in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Seminar, Max Planck Institute for Medical Research, Heidelberg, Germany, Jul 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (21st International Mass Spectrometry Conference (IMSC 2016), Toronto, ON, Canada, Aug 2016).

- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (The Polish-German Conference on Organic Chemistry, Warsaw, Poland, Oct 2016).
- Pagel, Kevin: Gas-Phase Infrared Spectroscopy of Proteins and Protein Assemblies. (6th Symposium on Structural Proteomics (6SSP), Dortmund, Germany, Nov 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Seminar, Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Frankfurt, Germany, Dec 2016).
- Pagel, Kevin: Glycomics in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (OC Kolloquium, Institute of Organic and Biomolecular Chemistry, Faculty of Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany, Jan 2017).
- Pagel, Kevin: Sugars in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (Seminar, Research Center Borstel - Leibniz Center for Medicine and Biosciences, Borstel, Germany, Mar 2017).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-Mass Spectrometry. (Sixth symposium of the RIKEN-Max Planck Joint Research Center for Systems Chemical Biology, Naha, Okinawa, Japan, Apr 2017).
- Pagel, Kevin: Structural Analysis of Biomolecules in the Gas Phase. (Award Lecture, ANAKON 2017, Fachgruppe Analytische Chemie, GDCh, Tübingen, Germany, Apr 2017).
- Pagel, Kevin: Ion Mobility Mass Spectrometry. (Structural Mass Spectrometry Workshop, Rehovot, Israel, May 2017).
- Pagel, Kevin: Sugars in a Wind Tunnel - Ion Mobility-Mass Spectrometry of Isomeric Glycans and Glycopeptides. (19th Carbohydrate Symposium EUROCARB, Barcelona, Spain, Jul 2017).
- Pagel, Kevin: Separation of Oligosaccharide and Glycopeptide Isomers using Ion Mobility-Mass Spectrometry. (254th ACS National Meeting & Exposition, Division of Carbohydrate Chemistry: Advances in Glycan Structure & Dynamics, Washington, DC, USA, Aug 2017).
- Pohl, Marvin Nicolas: Intermolecular Proton and Electron Transfer in Aqueous Solution. (LiXS 2017 “Liquid-Xray-Spectroscopy”, Paris, France, Jan 2017).
- Santambrogio, Gabriele: Cold Molecules for Precision Measurements. (Seminar, Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy, Feb 2016).
- Santambrogio, Gabriele: Molecules on a Chip for High-Resolution Spectroscopy. (Seminar, University College London, London, Great Britain, Mar 2016).
- Santambrogio, Gabriele: High-Resolution Spectroscopy in the Mid Infrared. (Cluster Research Laboratory, Toyota Technological Institute and East Tokyo Laboratory Genesis Research Institute, Tokyo, Japan, Nov 2016).
- Schlecht, Patrick and Teßmar, Christian: Computer-Aided Measurement Technology: ADC, DAC and Network. (Block Course on Methods of modern interface and surface

science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).

- Schöllkopf, Wieland: The FHI Free-Electron Laser Facility: Status and Future Prospects. (18th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany, Nov 2015).
- Schöllkopf, Wieland: The Infrared Free-Electron Laser at the Fritz Haber Institute: A Tool for IR Spectroscopy of Molecules, Clusters, and Solids. (Seminar, State Key Laboratory of Physical Chemistry of Solid Surfaces, (AG Shi-Gang Sun), Xiamen University, Xiamen, China, Mar 2016).
- Schöllkopf, Wieland: The Infrared Free-Electron Laser at the Fritz Haber Institute: A Tool for IR Spectroscopy of Molecules, Clusters, and Solids. (Seminar, School of Chemistry and Material Science, Department of Chemical Physics, (AG Xingan Wang), University of Science and Technology of China, Hefei, China, Mar 2016).
- Schöllkopf, Wieland: The Infrared Free-Electron Laser at the Fritz Haber Institute: A Tool for IR Spectroscopy of Molecules, Clusters, and Solids. (Seminar, Department of Chemistry, (AG Fengyan Wang), Fudan University, Shanghai, China, Mar 2016).
- Schöllkopf, Wieland: Latest Results and Developments at the FHI FEL Facility. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Seo, Jongcheol: The Homochiral Anionic Serine Octamer: An Infrared Spectroscopic Study. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Song, Xiaowei: Vibrational Spectroscopy of Titanium Oxide Anions Structure-Reactivity Relationship. (Molecular and Ionic Clusters, Gordon Research Seminar, Ventura, CA, USA, Jan 2016).
- Winter, Bernd: Aqueous Solutions: Ultrafast Proton and Electron Dynamics, and Nature of Bonding Revealed from Photoemission Spectroscopy. (Seminar, Department of Physical Chemistry, Fritz Haber Institute, Berlin, Germany, Jan 2017).
- Winter, Bernd: Electronic Structure of Small Iron Oxide Molecular Frameworks and Their Precursors in Aqueous Solution. (International Symposium of the CRC 1109, Metal Oxide – Water Systems, Erkner, Germany, Feb 2017).
- Winter, Bernd: Local and Non-Local Electronic and Nuclear Relaxation Processes in Aqueous Solutions. (IWP-RIXS-2017 “International Workshop on Photoionization & Resonant Inelastic X-ray Scattering”, Aussois, France, Mar 2017).
- Winter, Bernd: Photoelectron Spectroscopy of Liquids. (Spring School on Condensed Phase Spectroscopy, Helmholtz-Zentrum Berlin, Berlin, Germany, Mar 2017).
- Winter, Bernd: Photoemission Spectroscopy from Aqueous Solutions: Ultrafast Proton and Electron Dynamics. (The next generation for Low Density Matter (NGLDM) – workshop on AMO and cluster research at MAX IV, Lund, Sweden, Mar 2017).
- Winter, Bernd: Photoemission from Aqueous Solutions: Electronic Structure. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).

- Winter, Bernd: Photoemission from Aqueous Solutions: Electronic Structure. (Seminar, Institute of Organic Chemistry and Biochemistry, The Czech Academy of Sciences, Prague, Czech Republic, May 2017).

## Department of Physical Chemistry

**Department of Physical Chemistry****Director: Martin Wolf****Staff scientists:**

Kramer Campen  
 Markus Eiswirth  
 Tobias Kampfrath *until 6/2017*  
 Takashi Kumagai  
 Alexey Melnikov *until 6/2016*

Alexander Mikhailov *until 06/2017*  
 Melanie Müller *since 5/2017*  
 Alexander Paarmann  
 Laurenz Rettig *since 2/2016*  
 Mohsen Sajadi

Gerhard Ertl (Emeritus)

**Scientists, staying for at least six months, paid by FHI:**

Vasileios Balos *since 7/2017*  
 Lukas Braun  
 Maciej Dendzig *since 6/2017*  
 Laura Foglia *until 4/2016*  
 Karsten Horn *until 12/2016*  
 Matthias Koch *since 8/2016*  
 Chenfang Lin *since 8/2017*  
 Sebastian Mährlein

Lukáš Nádvorník *since 11/2016*  
 Ilya Razdolski  
 Natalia Martín Sabanés *since 9/2017*  
 Christian Schewe *until 12/2016*  
 Martin Thämer  
 Hendrik Vita *until 7/2016*  
 Yoav William Windsor *since 2/2017*

**Scientists, staying for at least six month, paid from external funds:**

|                                      |                         |                                        |                   |
|--------------------------------------|-------------------------|----------------------------------------|-------------------|
| Delroy Baugh <i>until 8/2016</i>     | <i>UCLA</i>             | Francoise Lapointe <i>until 4/2016</i> | <i>Quebec/MPG</i> |
| Majed Chergui <i>until 3/2017</i>    | <i>AvH</i>              | Fumito Mori <i>until 12/2015</i>       | <i>VW</i>         |
| Franz Geiger <i>until 8/2017</i>     | <i>Northwestern/AvH</i> | Jeffrey Noel                           | <i>AvH</i>        |
| Marc Herzog <i>until 1/2016</i>      | <i>EU/DFG</i>           | Amartya Sarkar <i>until 12/2015</i>    | <i>VW/MPG</i>     |
| Harald Kirsch                        | <i>SFB 1109</i>         | Vasily Temnov <i>until 12/2016</i>     | <i>AvH</i>        |
| Janina Ladenthin <i>since 1/2017</i> | <i>SFB 951/JST</i>      | Yujin Tong                             | <i>SFB 658</i>    |

|                    |                             |
|--------------------|-----------------------------|
| Graduate students: | 32 (14 from external funds) |
| Master students:   | 5                           |
| Trainees:          | 7                           |
| Technicians:       | 11                          |

**Max Planck Research Group: Structural and Electronic Surface Dynamics**

**Head:** Ralph Ernstorfer

|                     |
|---------------------|
| 6 post doc          |
| 3 graduate students |
| 1 master student    |

**Max Planck Research Group: Electronic Dynamics**

**Head:** Julia Stähler  
*(maternity leave 11/2016 - 8/2017)*

|                        |
|------------------------|
| 4 post doc             |
| 8 graduate students    |
| 1 bachelor student     |
| 1 scientific assistant |

**Service Group Mechanical Workshop**

**Head:** Petrik Bischoff

|                  |               |
|------------------|---------------|
| 19 staff members | 1 apprentices |
|------------------|---------------|

## **Recent Developments in the Department of Physical Chemistry**

**Director: Martin Wolf**

### **1. General Remarks**

**1.1** Research of the Department

**1.2** Recent Research Highlights

### **2. Progress Report**

#### **2.1 Ultrafast Dynamics of Solids: Electrons, Phonons and Spins**

2.1.1 Excited State Spectroscopy and Ultrafast Dynamics of the Electronic System

2.1.2 Photoinduced Phase Transitions in Strongly Correlated Materials

2.1.3 Mid-infrared Nonlinear Optical Spectroscopy of Phonon Polaritons

2.1.4 Nonlinear THz Spectroscopy of Lattice Dynamics

2.1.5 Terahertz Spin Transport

2.1.6 Ultrafast Spin Dynamics in Epitaxial Metallic Multilayers

#### **2.2 Molecular Processes at Interfaces and in Condensed Phase**

2.2.1 Dynamics of Individual Molecules at Surfaces

2.2.2 Local Photochemistry and Near-Field Induced Processes

2.2.3 Nonlinear Vibrational Spectroscopy of Interfacial Molecular Structure

2.2.4 Reactions at Electrochemical Interfaces

2.2.5 Nonlinear THz Spectroscopy of Liquids

2.2.6 Theoretical Investigations of Molecular Machines

### **3. Research Projects Funded from Outside Sources**

### **4. Publications of the Department of Physical Chemistry**

### **5. Invited Talks of Members of the Department**

#### **Max Planck Research Group: Structural and Electronic Surface Dynamics**

**Head: Ralph Ernstorfer**

#### **Max Planck Research Group: Electronic Dynamics**

**Head: Julia Stähler**



## 1. General Remarks

Since June 2017 the Department of Physical Chemistry has moved into the new building on the FHI campus and now all members of the department enjoy working together and communicating with each other in one building. Unfortunately, a part of the lab space is still not operational due to technical problems with the cooling water system. We hope that at the time of the Fachbeirat the experimental research infrastructure will finally be fully operational.

Several changes have occurred among the group leaders of the department since the last meeting of the Fachbeirat:

- *Dr. Julia Stähler* has started her Max Planck Research Group (MPRG) in January 2016 and is now expanding her experimental infrastructure by a versatile high-repetition rate laser system for her studies on interfacial electron dynamics
- Since February 2016 *Dr. Laurenz Rettig* is leading the research group on ultrafast dynamics of correlated materials employing XUV based time-resolved ARPES. With the successful implementation of his Emmy Noether Group he will expand these activities by combining time-resolved ARPES with x-ray diffraction experiments and dedicated sample growth using pulsed laser deposition (PLD).
- In January 2017 *Dr. Mohsen Sajadi* started a new research group on ultrafast molecular dynamics in liquids driven by high-field THz pulses.
- *Dr. Melanie Müller* has started in May 2017 her new research group to develop ultrafast scanning probe microscopy for studies of local carrier and molecular dynamics at surfaces.
- *Prof. Tobias Kampfrath* received an offer for a full professorship at the Freie Universität Berlin and has started on this position in July 2017. He will operate his group in our department for approximately two more years until his laboratory space is available at the FU Berlin.
- *Dr. Alexey Melnikov* moved to a position at the University of Halle in July 2016, but continues his research on spin and magnetization dynamics using the dedicated experimental setup at the FHI. Once the collaborative research center TRR 227 between Berlin and Halle on ultrafast spin dynamics will be established these activities shall move to Halle.
- After his retirement *Prof. Alexander Mikhailov* is associated as guest scientist both with the department and the Hiroshima University in Japan.

The Mechanical Workshops, headed by *Petrik Bischoff*, are still associated with the PC department whereas the Electronic Lab is now connected to the Molecular Physics Department. The machine infrastructure and organization of the workshop has been further improved and the high quality output is well received by all scientists.

During the last two years a remarkable number of younger scientists in the department received awards and distinguished research grants, for example, from the European Research Council (ERC), the German Research Foundation (DFG) and the Japanese Science and Technology Agency (JST). This is considered as an indicator demonstrating the success of the department in the promotion and guidance of younger scientists in their career development:

*Ralph Ernstorfer* (ERC consolidator grant 2015), *Tobias Kampfrath* (ERC consolidator grant 2016, full professor at Freie Universität Berlin 2017), *Takashi Kumagai* (JSTS PRESTO grant 2017, Gerhard Ertl Young Investigator Award 2016), *Claude Monney* (SNF professorship University of Fribourg 2017), *Laurenz Rettig* (DFG Emmy Noether Research Group 2017), *Julia Stähler* (Max Planck Research Group (MPRG) 2015, Gaede Award 2016 of the German Vacuum Society 2016, Edith Flanigen Award 2016), *Lutz Waldecker* (Carl Ramsauer Award of the Physical Society Berlin 2016, Feodor Lynen Fellowship 2016, AvH), *Nicolai Paßler* (Physics Study Award 2017 of the Physical Society Berlin).

Furthermore, the PC department is hosting several winners of the Alexander von Humboldt and the Friedrich Wilhelm Bessel Research Award as well as winners of the Alexander von Humboldt Research Fellowships.

## **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 the coupling between various (electronic, spin and lattice) degrees of freedom and mechanistic insights into selected dynamic phenomena like ultrafast phase transitions, excited state dynamics or single molecule reactions at surfaces. We follow the strategy 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 in the department is performed by small teams with specific, often complementary expertise, creating various synergies between the different groups.

*Structure:* The research topics of the department focus on two main directions.

*(I) Ultrafast dynamics of elementary processes* in solids and at interfaces with specific focus on the interactions between electrons, phonons and spins: This line of research addresses the dynamics of elementary processes on their relevant time scales, employing ultrafast laser spectroscopy (with, typically, femtosecond time resolution). Both existing and newly developed spectroscopic techniques are used to study the electronic structure, excited state dynamics, optically induced phase transitions and low-energy excitations including lattice dynamics and spin dynamics in solids and at interfaces.

*(II) Molecular processes at interfaces and in condensed phase* systems including gas-solid, liquid-solid as well as electrochemical interfaces and liquids: Here 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. Furthermore, nonlinear optical sum-frequency and high field THz spectroscopy provides insights into the molecular structure at interfaces and into the dynamics of liquids. In particular, with these activities we implement the new direction of the FHI for the evolution of the institute into the next decade towards atomistic studies of processes at complex interfaces (i.e. beyond gas-solid in UHV) including liquid-solid, liquid-gas and electrochemical interfaces.

The Department of Physical Chemistry currently supports the following research groups:

#### **Ultrafast Dynamics of Solids: Electrons, Phonons and Spins**

- Dynamics of Correlated Materials (*Laurenz Rettig*)
- Ultrafast Scanning Probe Microscopy (*Melanie Müller*)
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)
- Time-resolved Second Harmonic Generation Spectroscopy (*Alexey Melnikov*)

#### **Molecular Processes at Interfaces and in Condensed Phase**

- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- THz Driven Molecular Dynamics (*Mohsen Sajadi*)
- Complex Chemical and Biological Systems (*Alexander Mikhailov*)

#### **Max-Planck-Research Groups (MPRG)**

- Structural and Electronic Surface Dynamics (*Ralph Ernstorfer*)
- Electron Dynamics (*Julia Stähler*)

Both the MPRG of *Ralph Ernstorfer* and *Julia Stähler* are embedded in the department by various collaborations and their research on ultrafast structural dynamics and interfacial electron dynamics, respectively, nicely complements corresponding research topics of other groups.

*New developments:* In the last few years the department has started to address several new research topics, which are often linked to the development of new techniques, and several new research groups have been initiated. One example is the research group of *Alexander Paarmann* who exploits the potential of the FHI free electron laser (FEL) for spectroscopy in solids (in particular surface phonon polaritons) and develops laser synchronization with the FEL. In the future this will have a strong impact on interfacial molecular spectroscopy at the FEL using nonlinear optics enabling studies of *e.g.* electrochemical interfaces.

More recently the department has put increasing emphasis on liquids and their interfaces: This includes studies of (i) liquid-solid or liquid-gas interfaces and electrochemical processes employing nonlinear vibrational sumfrequency spectroscopy with specific designed sample cells in the group of *Kramer Campen* and (ii) THz driven molecular dynamics in liquids using high field THz pulses to excite low frequency (*e.g.* rotational or librational) modes in the new group of *Mohsen Sajadi*. The activities based on high-field THz generation will be further boosted by an upgrade of the existing high power laser system at the FHI enabling several new experiments including application to solids in the group of *Tobias Kampfrath*.

Furthermore several new scanning probe setups are currently being developed for studies of light-induced single molecule processes on and for local spectroscopy and transport measurements at the nanoscale. Our goal is to bring together the expertise from (spatial averaging) optical spectroscopy together with local probes. This includes a project developing ultrafast scanning probe microscopy in the new group of *Melanie Müller* and a project developing a setup for a nanoscale integrated circuit single molecule transport measurements in low-temperature STM by *Matthias Koch*.

*Promotion of younger scientists:* Guidance and promotion of younger scientists in their career development is an important goal of the department, and is implemented by several measures (*e.g.* within the IMPRS graduate school, PhD student days and department workshops, regular status discussions, the nomination for awards or invited talks). As one specific measure, junior group leaders and advanced postdocs are guided to obtain experience in grant applications and to become also project leaders in ERC, DFG or JST funded projects. In particular, establishing an independent junior research group with substantial own funding is a

major achievement and career step for younger scientists. Recently the department has been very successful in this regard and currently five such research groups are funded:

- Max Planck Research Group & ERC Group of *Ralph Ernstorfer*
- ERC Group of *Tobias Kampfrath*
- DFG Emmy Noether Group of *Laurenz Rettig*
- Max Planck Research Group of *Julia Stähler*

In addition, several group leaders have projects as PIs in DFG funded collaborative research centers (Sfb 658, Sfb 951, Sfb 1109), one DFG research unit (FOR 1700) or have received individual research grants funded by DFG or JST (see section 3 for a complete list of all projects). The department has been strongly involved in the development of the concept for a new collaborative research center between Berlin and Halle (TRR 227) on Ultrafast Spin Dynamics. Several members of the department are PIs in this initiative.

## 1.2 Recent Research Highlights

The following topics are a selection of research achievements as well as instrument developments in the department, obtained in the last two years:

- Semiconducting transition metal dichalcogenides (TMDCs) exhibit a hidden spin texture in the electronic ground state despite the inversion symmetry of the crystal structure. Employing spin-selective optical excitation combined with time- and angle-resolved photoemission spectroscopy (trARPES) with XUV probe pulses, the preparation of spin-, valley- and layer-polarized excited states in bulk WSe<sub>2</sub> crystals has been demonstrated suggesting opto-spintronic applications of these materials [Phys. Rev. Lett. **117**, 277201 (2016)].
- Using XUV trARPES, we studied the ultrafast dynamics of a spin density wave (SDW) in Chromium. Surprisingly, the suppression of the SDW gap in the electronic structure can be well understood in a thermal picture driven by the hot thermalized electronic heat bath. This shows that for phases governed by the temperature of a single (e.g. electronic, phononic) sub-system concepts from thermodynamic equilibrium are still applicable [Phys. Rev. Lett. **117**, 136801 (2016)].
- An advanced femtosecond XUV laser source at 500 kHz repetition rate has been implemented for trARPES providing access to band mapping of excited state and scattering processes throughout the full Brillouin zone with unprecedented sensitivity. In a first application the transient electronic band structure during the photo-induced (8x2)  $\leftrightarrow$

(4x1) transition of Indium nanowires on Si(111) has been elucidated providing detailed insights into excitation mechanism and timescales of this Peierls type transition. Moreover, the distinct dynamic changes of the bandstructure can be correlated with bond formation and the structural changes in real space.

- Using THz emission spectroscopy, ultrafast photoinduced charge transfer from Se to Bi atoms was revealed at the surface of the three-dimensional topological insulator Bi<sub>2</sub>Se<sub>3</sub>. The results show that previously suggested models of photocurrent generation in Bi<sub>2</sub>Se<sub>3</sub> require refinement. This experiment renders THz emission spectroscopy to be an ultrafast surface-specific probe [Nature Commun. **7**, 13259 (2016)].
- Ultrafast manipulation of an electronic band gap was achieved in the layered semiconductor Ta<sub>2</sub>NiSe<sub>5</sub> which exhibits an excitonic insulating ground state: By tuning the excitation density, the electronic band gap can be either decreased due to enhanced dynamical screening, or enlarged around the  $\Gamma$  point of the Brillouin zone, where the order parameter of the excitonic insulating phase is the strongest. The band gap enhancement is related to an increase of the exciton condensate density and persists for approximately 1 ps until the quasiparticle distribution thermalizes across the band gap [Phys. Rev. Lett., **119**, 086401 (2017)].
- Femtosecond electron diffraction provides snapshots of the atomic structure atom motion in a crystal. From the momentum- and time-resolved inelastic scattering signal of WSe<sub>2</sub>, a momentum-resolved picture of the phonon dynamics was obtained enabling to directly visualize transient non-thermal phonon populations in momentum space [Phys. Rev. Lett., **119**, 036803 (2017)].
- Surface phonon polaritons (SPhPs) in polar dielectric crystals provide a novel platform for mid-infrared low-loss nanophotonics. Using the FHI infrared free-electron laser, the nonlinear response of localized surface phonon polaritons in sub-diffractive nanostructures has been studied as well as propagating polaritons using prism coupling [Nano Letters **16**, 6954 (2016) & ACS Photonics **4**, 1048 (2017)].
- Atomic-scale heterostructures of polar dielectric crystals, so-called crystal hybrids, offer a new pathway for active tuning the frequency of mid-infrared phonon polaritons, which was demonstrated for GaN/AlN superlattices.
- Spin-polarized currents can arise from a temperature gradient across a ferromagnetic/normal-metal interface, also known as the spin-dependent Seebeck effect. The ultrafast,

non-thermal counterpart of this effect was demonstrated, whereby the spin-dependent transmittance for non-thermalized, high-energy hot carriers leads to generation of ultrashort spin current pulses with a duration defined by the hot carrier thermalization time [Phys. Rev. Lett. **119**, 017202 (2017)].

- Ultrashort spin current pulses can induce magnetization dynamics by spin transfer torque when injected into a ferromagnet opening the time domain for probing non-uniform magnetization dynamics. Laser-excited spin current pulses injected into a ferromagnetic Fe film were found to excite inhomogeneous high-frequency spin wave dynamics up to 0.6 THz, indicating that the perturbation of the ferromagnetic magnetization is confined to only 2 nm [Nature Commun. **8**, 15007 (2017)].
- A conceptually new emitter of broadband THz electromagnetic pulses has been developed consisting of metallic thin film of a heavy-metal (HM) layer on top of a ferromagnetic (FM) layer. Excitation with a 10 fs laser pulse triggers spin transfer from the FM into the HM layer where the spin flux is converted into a transverse charge current, which acts as a source of an ultrashort electromagnetic pulse covering the frequency range from 0.5 to 30 THz without gap. The spintronic source outperforms state-of-the-art semiconductor emitters in terms of bandwidth, efficiency and cost [Nature Photonics **10**, 483 (2016)].
- Single-molecule force-induced chemistry is an emerging field and the microscopic reaction mechanisms are so far poorly understood. Using low-temperature non-contact atomic force microscopy force-induced tautomerization of a single porphycene molecule on Cu(110) has been directly observed. The mechanism and energetics of this reaction was revealed by combining atomic force spectroscopy and density functional theory calculations [Nature Chemistry **6**, 41 (2016)].
- Controlling a photo-switchable molecule on surfaces provides a novel way to attain photo-active functional interfaces. Photo-induced tautomerization in single porphycene molecules has been directly studied on Cu(111) by using low-temperature scanning tunneling microscopy combined with a wavelength tunable laser. It was revealed that the reaction occurs via substrate-mediated indirect charge transfer mechanism and vibrational excitation of the porphycene plays a crucial role [Nano Lett. **16**, 1034 (2016)].
- Excited electrons observed with two-photon photoemission spectroscopy can be trapped at the vacuum/amorphous solid water interface in unoccupied electronic states with lifetimes of tens of seconds. The energy release in the electron trapping process is sufficient to cause chemical reactions; namely a two-electron reaction occurring with water, splitting

water molecules and forming hydroxide anions at the amorphous solid water/vacuum interface [J. Phys. Chem. C. **121**, 7379 (2017)].

- Low-frequency dynamics of molecular liquids is believed to have large impact on the outcome of chemical reactions. Strong THz electric field pulses have been employed to drive orientational dynamics in polar liquids leading a transient optical anisotropy that is significantly enhanced as compared to optical pump pulses. This observation is a hallmark of the torque the THz electric field exerts on the permanent dipole moments of the solvent molecules. Our approach provides insights into the character of THz absorption resonances, the coupling between low-frequency modes, namely librational and reorientational motions and the sign of the polarizability anisotropy of the solvent molecules [Nature Commun. **8**, 14963 (2017)].
- Probing the mechanism of electrochemical reactions experimentally is challenging because it requires detecting species that typically exist in small concentrations and have very short lifetimes. Using a thin layer electrochemical cell it is possible to initiate, using a femtosecond laser pulse, the hydrogen evolution reaction at a Au and Pt electrode and track the progress of the reaction both optically and electrically with femtosecond time resolution.
- Understanding water structure at electrode/aqueous interfaces is a necessary first step in a mechanistic description and understanding of essentially all aqueous phase electrochemistry. A previously unobserved, population of hydrophobic interfacial water, namely water molecules with one OH group pointing towards the electrode, has been experimentally characterized at the Au electrode/water interface and its abundance varying with applied bias [Angew. Chemie, **56**, 4211 (2017)].
- The intermolecular interaction of interfacial water has been typically investigated experimentally by examination its OH stretch vibration, i.e. changes of the *intermolecular* potential were characterized by probing an *intramolecular* vibration. For the first time, an intermolecular mode of interfacial water, the libration, has been studied. Interestingly, the effect of the interface is to stiffen water's rotational potential while virtually all other structural properties are similar to the bulk liquid [PCCP **18**, 18424 (2016)].
- We have constructed a vibrationally resonant sum frequency (VSF) spectrometer with a novel phase referencing scheme that improves the signal to noise ratio over conventional VSF by > 15 times. This collinear, time-domain, heterodyned, balance detected VSF setup provides phase information cannot be obtained in conventional (homodyne) approaches.



- The complete stochastic thermodynamics in a complex chemical nano-machine, the channeling enzyme tryptophan synthase, has been reconstructed for the first time based on experimental data, entropy production and flow and considering the interactions between the tryptophans subunits [J. Chem. Phys. **146**, 025101 (2017)].

## 2. Progress Report

### 2.1 Ultrafast Dynamics of Solids: Electrons, Phonons and Spins

Elementary processes in solids and at interfaces such as vibrational or electronic excitations, electron transfer, and the coupling and energy exchange between electronic, lattice and spin degrees of freedom are the underlying microscopic processes of much more complex non-equilibrium phenomena. The study of the non-equilibrium, ultrafast dynamics of such fundamental processes provides mechanistic insights into various phenomena like structural and electronic phase transitions, dynamics and relaxation of excited states, or processes driven by spin-lattice or exchange coupling. 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 Excited State Spectroscopy and Ultrafast Dynamics of the Electronic System

A detailed analysis of the electronic structure is of fundamental importance for understanding various physical and optical properties of solids. Angle-resolved photoemission spectroscopy (ARPES) is well established to provide a detailed view on the occupied electronic structure, however, the unoccupied band structure remains inaccessible for conventional ARPES. Furthermore, the dynamics of typically short-lived excited state cannot be resolved. To overcome these limitations, the department has developed and commissioned a novel high-repetition rate apparatus for XUV-based time-resolved ARPES (trARPES) in close collaboration between the group of *Laurenz Rettig* and the MPRG of *Ralph Ernstorfer* (see also MPRG report). In this setup a home-built 20 fs OPCPA laser system running at 500 kHz is used to drive High-Harmonic Generation (HHG) in Argon to generate XUV photons at  $\sim 22$  eV, which provides sufficiently high photon energy to cover the complete first Brillouin zone (BZ) of most solid state materials. Owing to this exceptionally high repetition rate, which exceeds typical HHG systems by  $\sim 2$  orders of magnitude, the spectroscopy of transiently populated excited states in the normally unoccupied band structure becomes feasible. Such excited state spectroscopy extends static Fermi-surface mapping to time domain studies of transiently populated excited states throughout the whole BZ, which has previously been only explored close to the BZ center using time-resolved photoemission at low photon energies (see Fig. 1a). Using this system, the conduction band dispersion in the quasi-2D transition-metal dichalcogenite (TMDC) semiconductor WSe<sub>2</sub> could be probed in the whole BZ up to 3.1 eV above the valence band maximum (Fig. 1b). This allows to directly

observe and quantify the indirect band gap of the surface layer of WSe<sub>2</sub>. Furthermore, the excellent time-resolution  $< 40$  fs enables the analysis of the ultrafast intervalley scattering of resonantly excited excitons from the K to the  $\Sigma$  valley due to phonon emission on the timescale of  $\sim 15$  fs.

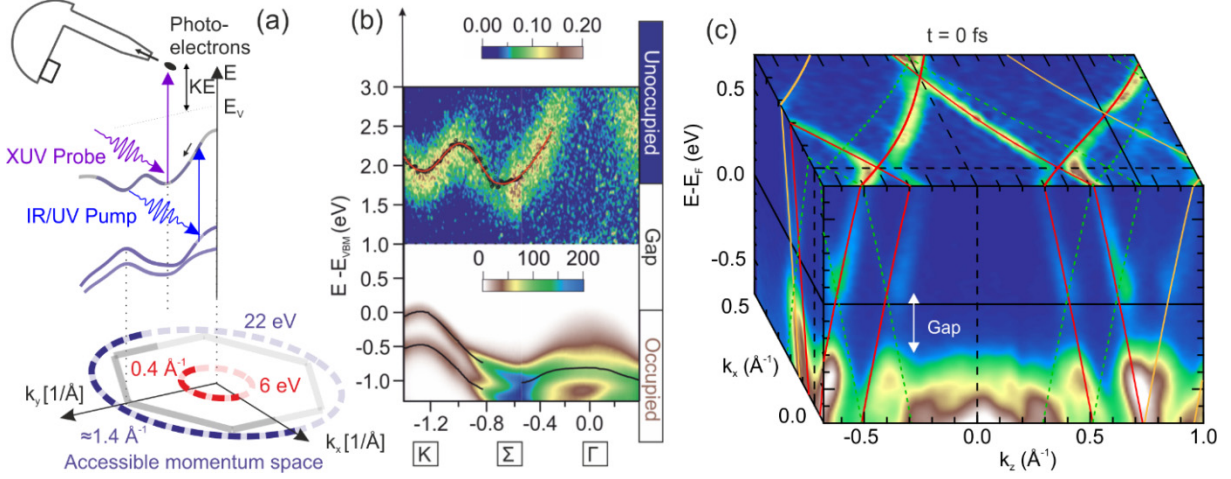


**Figure 1:** Excited state spectroscopy using XUV trARPES. (a) HHG-based trARPES with photon energies exceeding 20 eV allow access to the complete BZ of most materials, as exemplarily shown for the hexagonal BZ of the layered TMDC semiconductor WSe<sub>2</sub>. (b) At 100 fs after excitation by 3.1 eV pump photons, the complete valence and conduction band dispersion and the indirect band gap of bulk WSe<sub>2</sub> can be simultaneously observed in a large energy range both below and above the Fermi energy. (c) In the CDW material TbTe<sub>3</sub>, the unprecedented data quality achievable with the novel high-repetition rate XUV trARPES setup allows comparison to tight binding band structure calculations (lines) and reveals signatures of the CDW ordering such as energy gaps and spectral weight transfer into shadow bands (dashed green lines) in the ground and excited state band structure in the whole BZ.

Furthermore, in a collaboration with the ARTEMIS facility at Rutherford Appleton Lab, the extreme surface sensitivity in trARPES using 20 eV XUV laser pulses allowed the observation of a hidden spin- and valley polarization induced by circularly polarized light excitation even in the centro-symmetric bulk material [1]. The high spin polarization of this transient population and the subsequent spin relaxation during the intervalley relaxation has been demonstrated by spin- and time-resolved ARPES experiments.

The capabilities of our novel setup are further demonstrated in the quasi 2-dimensional charge density wave (CDW) material TbTe<sub>3</sub>. The excellent data quality achievable with this high-repetition rate system allows us to investigate the whole ground and excited state band structure close to the Fermi level. Signatures of the CDW ordering such as the opening of energy gaps and spectral weight transfer into shadow bands can be identified and quantified, and compared to theoretical tight binding band structure calculations (Fig. 1c).

[1] R. Bertoni, *et al.*, Phys. Rev. Lett. **117**, 277201 (2016).

### 2.1.2 Photoinduced Phase Transitions in Strongly Correlated Materials

The coupling of electronic to lattice and spin degrees of freedom in solids gives rise to various ordering phenomena and phase transitions in strongly correlated materials. The study of non-equilibrium dynamics of such materials following ultrafast photoexcitation can provide novel insights into the mechanisms and couplings leading to such ordered phases and eventually to ultrafast phase transitions. The high-repetition rate XUV trARPES setup is ideally suited to study the excited state dynamics and transient electronic structure during photoinduced phase transitions starting from an ordered, well defined ground state. In the quasi-2D CDW system  $\text{TbTe}_3$ , the group of *Laurenz Rettig* could identify the photo-induced closing of the charge-density wave gap and the concomitant suppression of shadow band spectral weight in the whole Brillouin zone (see Fig. 1c) and follow the dynamics of the CDW order parameter, extracted from the transient energy gap size and shadow band intensity, for a large range of fluences. Moreover, the analysis of the CDW gap dispersion along different directions in momentum space reveals a transient enhancement of the nesting conditions in the excited state, which results in a persistent finite CDW energy gap size in the transient metallic state [1].

Another prototypical system exhibiting a Peierls-type insulator-to-metal transition are quasi one-dimensional Indium nanowires on  $\text{Si}(111)$ . The ultrafast electron dynamics upon the optically driven structural phase transition from the low-temperature (8x2) to the high-temperature (4x1) phase has been studied, concomitant with an insulator-to-metal transition (Fig. 2). Starting from the 8x2 phase the gradual evolution of the electronic structure into the 4x1 phase could be followed by XUV trARPES on a femtosecond time scale. Remarkably, three distinctive time scales were found: (i) the insulator-to-metal transition associated with the gap closing at the 8x2 BZ boundary is observed already after 200 fs, while (ii) the Indium derived  $m_1$  band at the BZ center shifts from above to below the Fermi level within 500 fs. Both processes occur faster than the structural transition into the 4x1 phase, as manifested (iii) by the splitting of the  $m_2$ - $m_3$  bands, which is completed after 700 fs (Fig. 2e). Such distinct timescales of the insulator-to-metal and structural transitions clearly differ from expectations for a "standard" Peierls-like scenario. The momentum space distribution of excited carriers observed by trARPES served as an input for *ab initio* calculations with realistic initial conditions (collaboration with University of Paderborn). From these simulations, which well reproduce the three timescales found in the experiment (see Fig 2e), we conclude that the depopulation of antibonding orbitals by photoexcited holes is the main driving force

triggering the photoinduced structural phase transition. Furthermore, the combined experimental and theoretical approach allows to elucidate the real-space dynamics of bond formation and breaking during the ultrafast transition.

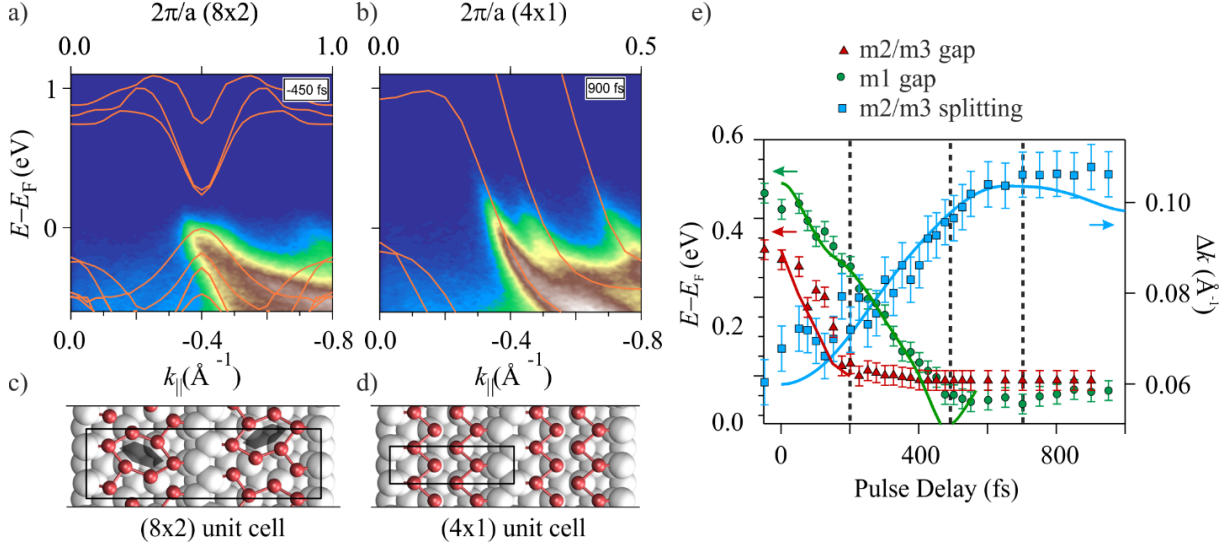


**Figure 2:** Ultrafast phase transition in In/Si(111) nanowires. (a,b) Energy/momentum maps of the trARPES intensity (a) before and (b) 900 fs after photoexcitation, overlaid by GW band structure calculations of the 8x2 and 4x1 phase, respectively. (c,d) Unit cell of the 8x2 and 4x1 phase. (e) Time dependence of the metal insulator transition (m2/m3 gap, red triangles), the closing of the m1 band gap (green circles) and the m2/m3 band splitting (blue squares), showing distinctly separate timescales for the three features. Solid lines are results of an ab-initio molecular dynamics simulation.

Complementary ordering phenomena involving electron and spin degrees of freedom are present in magnetically ordered systems, where the role of structural degrees of freedom is minimized. The dynamics of the spin-density wave (SDW) transition in Chromium has been investigated using XUV trARPES, and by comparison with a mean field model the group was able to quantitatively extract the evolution of the SDW order parameter through the ultrafast phase transition, and show that it is governed by the transient temperature of the thermalized electron gas [2]. In contrast, the transient suppression of long-range collinear anti-ferromagnetic order in the rare-earth intermetallic  $\text{GdRh}_2\text{Si}_2$ , observed by the time-dependent suppression of the exchange splitting of a Si-derived ferromagnetic surface state, proceeds on a much slower timescale of  $\sim 10$  ps. This slow demagnetization of the 4f antiferromagnet is limited by the angular momentum transfer between localized 4f and delocalized 5d electrons, due to the absent 4f orbital momentum in Gd. This conclusion is corroborated by the much faster demagnetization in the isostructural  $\text{SmRh}_2\text{Si}_2$  compound with a finite 4f orbital momentum, which proceeds on a much faster timescale of less than 500 fs.

[1] L. Rettig, *et al.*, Nature Commun. **7**, 10459 (2016).

[2] C. W. Nicholson, *et al.*, Phys. Rev. Lett. **117**, 136801 (2016).

### 2.1.3 Mid-Infrared Nonlinear Optical Spectroscopy of Phonon Polaritons

Surface polaritons are the key building block of nanophotonics, since these excitations provide sub-diffractive light localization accompanied by significant optical field enhancements. Many previous studies have focused on surface plasmon polaritons at noble metal surfaces. Recently, an alternative approach was introduced using surface phonon polaritons (SPhPs) which can be excited in the mid-infrared at the surface of polar dielectric materials, where optical phonon resonances lead to the negative dielectric permittivity required for the surface polariton formation. Particularly, the active tuning of the phonon polariton resonances in nanometer and atomic scale structures represents a major goal in modern nanophotonics. The group of *Alexander Paarmann* is studying such systems with newly developed experimental techniques, employing the free-electron laser (FEL) at the FHI as an intense and tunable infrared light source.

Light localization in nanophotonic structures is typically accompanied by considerable enhancements of the local electric fields, which can be conveniently probed using nonlinear optical techniques such as second harmonic generation (SHG). While SHG spectroscopy is well-established in the visible spectral region, the group has now established this technique also in the mid-infrared using the FEL. Subsequent experiments on sub-diffractive nanostructures demonstrated a drastic enhancement of the SHG yield for localized SPhP resonances, opening the field of mid-infrared nonlinear nanophotonics based on SPhPs [1]. Additionally, a versatile prism coupling approach has been implemented based on the Otto geometry, enabling the systematic study of SPhP resonances in polar dielectric heterostructures [2].

With these unique experimental methods at hand, various strategies for active control of phonon polaritons in nanoscale systems are now explored. Already for single AlN thin films (10-100 nm) on SiC substrates, strongly coupled modes were observed, providing a simple way for tuning the frequency of phonon polaritons. The major focus of this work, however, lies on atomic scale heterostructures of polar dielectrics, so-called crystalline hybrids. Here, phonon polariton hybridization has been predicted for layer thicknesses reaching to the atomic scale. A first model study of AlN/GaN heterostructures indeed demonstrates the emergence of hybrid phonon polariton modes in these systems, as well as monolayer-level control of their frequencies, linewidths, and polar strengths, see Fig. 3. Hereby, the drastic improvement of sensitivity and contrast provided by SHG phonon spectroscopy over linear optical techniques (reflectivity) enables a clear assignment of the hybrid modes.

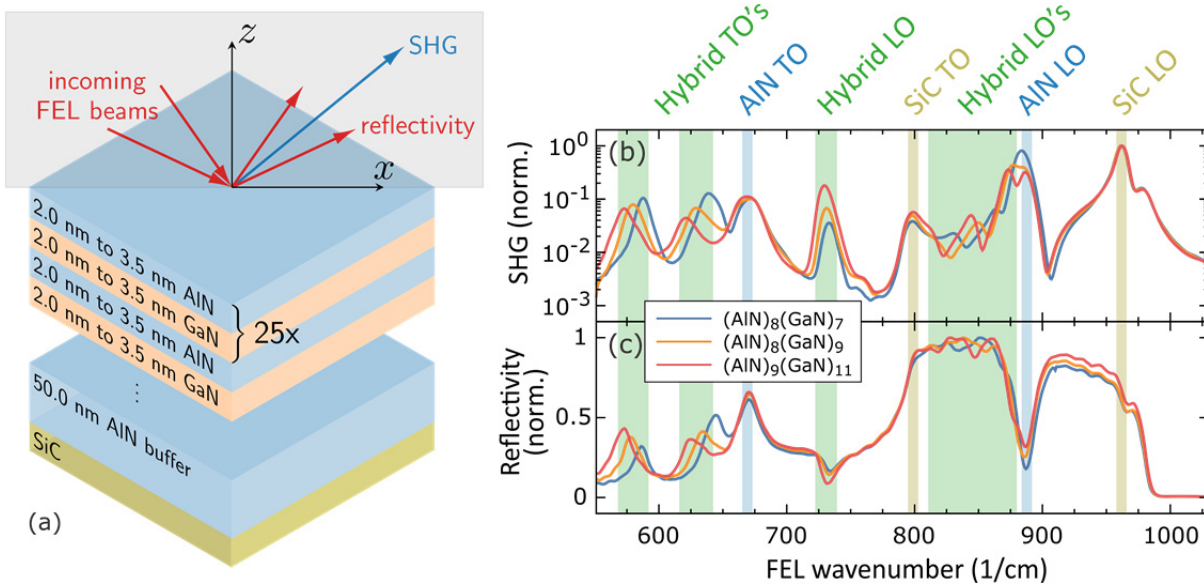


**Figure 3:** Control over phonon polariton hybridization on the atomic scale. (a) Schematic of the experiment and the atomic scale AlN/GaN heterostructure. Experimental second harmonic (b) and reflectivity (c) spectra of AlN/GaN superlattice structures with different AlN and GaN layer thicknesses. Several hybrid modes (green shaded) can be observed to shift with the layer thicknesses, while the SiC substrate (yellow shaded) and the AlN buffer layer (blue shaded) features are unaffected.

Furthermore, a table top near-infrared laser oscillator synchronized to the FEL was recently implemented together with a timing infrastructure providing synchronization to the FEL with better than 100 fs precision (see FEL report for more details). A balanced optical cross correlator based on mid-infrared/near-infrared sum-frequency generation (SFG) allowed a first measurement of the FEL timing drift and jitter, whereby the jitter is found to be on the order of only 100 fs (rms). These measurements also reveal peculiar details of the FEL temporal pulse structure, highly relevant for prospective time-resolved FEL-pump near-infrared probe spectroscopy. Additionally, the group also develops the infrastructure for FEL-based SFG spectroscopy for studies of far-infrared surface vibrations, for instance, metal-oxide formation in electrochemical systems.

[1] Razdolski *et al.*, Nano Letters **16**, 6954 (2016).

[2] Passler *et al.*, ACS Photonics **4**, 1048 (2017).

#### 2.1.4 Nonlinear THz Spectroscopy of Lattice Dynamics

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 and 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 current state of the art THz pulses can be generated in the lab with an electric-field amplitude of  $\sim 1$  MV/cm it is now possible to even drive and control such resonances on sub-

picosecond time scales [1]. The THz frequency range is thus of central relevance from a fundamental-scientific point of view but is also application-related as current information technology may soon approach data rates in the THz range. It is thus required to develop techniques to manipulate information carriers (such as electronic currents, 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

- 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 push physical effects so far studied at low frequencies into the THz range. Currently, a strong focus lies on fundamental spintronic effects such as the recently discovered ultrafast spin Hall effect and the spin-type Seebeck effects. These studies are conducted in the framework of the ERC Consolidator Grant project of *Tobias Kampfrath*.
- To develop new spectroscopic tools which permit, for example, control over elementary motions such as lattice vibrations and the detection of ultrafast spin currents (“ultrafast spin amperemeter”), with interface sensitivity.

Some recent examples on lattice control by THz pulses are illustrated below:

*Ultrafast spin-lattice coupling:* The coupling of lattice vibrations and ordered electron spins in magnetic solids is highly underresearched, despite its fundamental and applied relevance for ultrafast spin manipulation (femtomagnetism) and transport of spin angular momentum (spintronics and spin caloritronics). For example, the fundamental process of spin-lattice equilibration is far from being understood, even for model systems such as the ferrimagnet yttrium iron garnet  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  (YIG), a central material in the field of magnonics. Estimates of the underlying time constants extend over as many as 6 orders of magnitude from  $\sim 1 \mu\text{s}$  down to  $\sim 1 \text{ ps}$ .

To probe spin-lattice coupling in YIG, the THz physics group developed a pump-probe scheme in which an intense 20 THz pump pulse is used to resonantly excite optical phonons and the impact on the spin subsystem is monitored by measuring the transient Faraday effect over multiple time scales from femtoseconds to milliseconds (see Fig. 4a). The magnetic order is quenched on an ultrafast time scale of 1 ps and a slower scale of 0.1  $\mu\text{s}$ . The ultrafast component is extremely surprising because decoherence of spin precession in YIG is known to occur over much longer times of 0.1  $\mu\text{s}$  and more. Supported by measurements covering a



broad temperature range and by analytical and numerical calculations, the following consistent interpretation results: The THz pump pulse rapidly heats the YIG crystal lattice, thereby leading to additional stochastic modulation of the exchange interaction of the two ferrimagnetically coupled spin sublattices. On a 1 ps time scale, this modulation induces transfer of angular momentum between the spin sublattices and, thus, energy transfer from the phonon to the spin system.

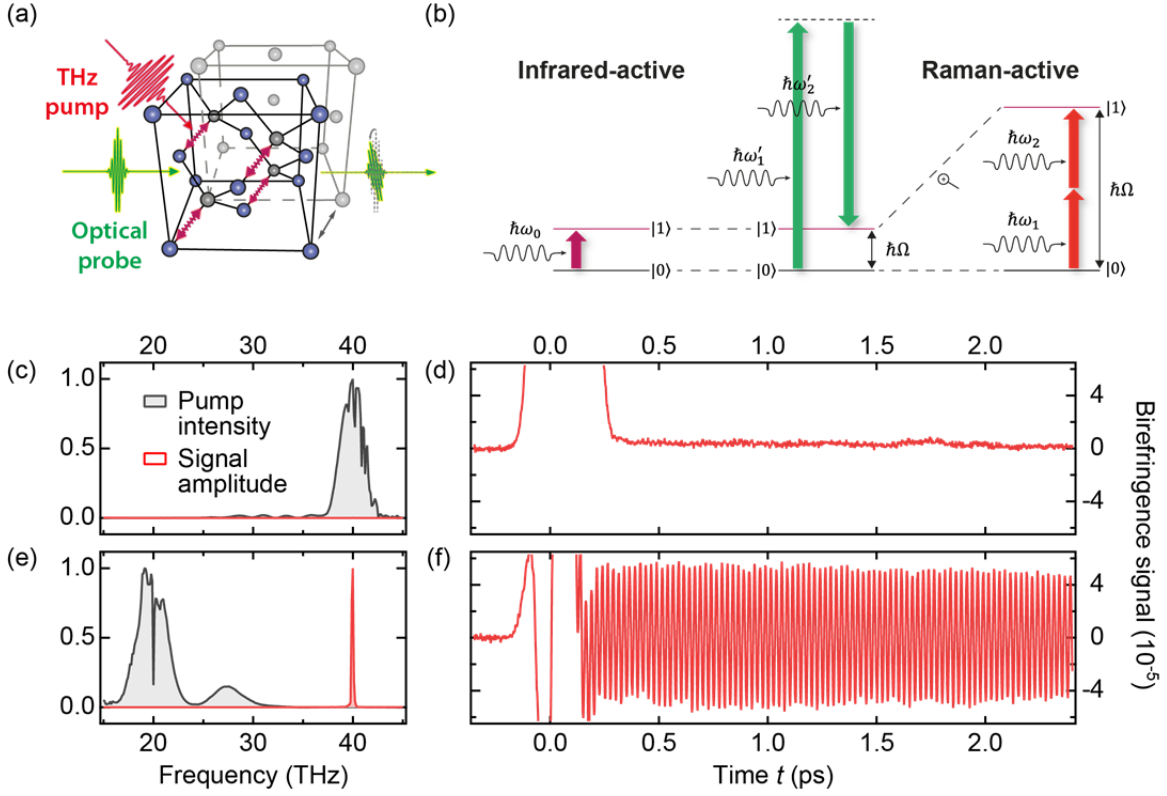


**Figure 4:** Excitation of coherent optical phonons by THz sum-frequency excitation. (a) Pump-probe scheme for driving and probing of coherent lattice vibrations in diamond or any other solid by femtosecond laser pulses. (b) Possible excitation pathways of a phonon with frequency  $\Omega$  (from left to right): by one-photon absorption (1PA) with  $\omega_0 = \Omega$ , stimulated Raman scattering using two spectral components of the pump field with  $\omega'_1 - \omega'_2 = \Omega$ , and by sum-frequency Raman excitation with  $\omega_1 + \omega_2 = \Omega$ , which can also be considered as two-photon absorption (2PA) by a transition across adjacent vibrational levels. (c) A pump spectrum resonant with the 40 THz optical phonon of diamond. (d) Resulting optical birefringence as a function of time. (e,f) Analogous to (c,d), but with the pump spectrum overlapping with half the phonon resonance frequency.

Note that the resulting quasi-equilibrium state is constrained by conservation of spin angular momentum and only accessible by ultrafast stimuli. This novel state finally decays by transfer of angular momentum and energy between phonons and spins on a 100 ns scale. In summary, our results reveal that the speed of spin-phonon relaxation in ferrimagnetic insulators with two spin sublattices depends on the dynamic observable one refers to. While energy transfer is dominated by exchange interaction and proceeds on picosecond time scales, angular-momentum equilibration is significantly slower and can easily extend to  $\sim 0.1 \mu\text{s}$ .

*Novel pathway to lattice control:* The above experiment on YIG relies on resonant excitation of infrared (IR)-active phonons with THz radiation. To drive IR-inactive yet Raman active phonons, stimulated Raman scattering (SRS) has been the method of choice so far. In SRS, a light pulse containing frequencies  $\omega'_2$  and  $\omega'_2 = \omega'_1 + \Omega$ , both at roughly  $2\pi \cdot 500\text{THz}$ , generates a force that coherently drives the lattice at the difference frequency  $\omega'_1 - \omega'_2 = \Omega$  (see Fig. 4b). Such rectification of optical fields is, however, often accompanied by unwanted electronic excitation due to one-photon and two-photon absorption (2PA), which is particularly severe in materials with small electronic band gaps. To avoid these issues, a novel scheme of coherent lattice control has been developed: the two incident frequencies are chosen such that their *sum*  $\omega_1 + \omega_2 = \Omega$  is resonant with the target mode (Fig. 4b). This process can also be considered as 2PA by a transition across adjacent vibrational levels [2].

The IR-inactive yet Raman-active 40 THz optical phonon of diamond served as test system of our idea. The underlying pump-probe experiment is schematically shown in Fig. 4a. For a pump pulse centered about the phonon resonance (Fig. 4c), the optical probe signal (Fig. 4d) did not exhibit any indications of coherent lattice vibrations. However, when the pump center frequency is tuned to half of the 40 THz phonon frequency (20 THz), an oscillatory signal (Fig. 4f) is observed whose Fourier transform peaks at 40 THz (Fig. 4e).

This is a clear signature of the phonon intended to drive. In subsequent experiments, it could be shown that by tuning the carrier-envelope phase of the phase-locked THz pump pulse, we were able to shift the phonon oscillation phase at will. In addition to their fundamental relevance, our findings are important for action spectroscopy at the FHI free-electron laser as they open up a way to extend this method from IR-active to IR-inactive yet Raman-active vibrational modes of molecules [2].

[1] T. Kampfrath, K. Tanaka, K.A. Nelson, Nature Photon. **7**, 680 (2013).

[2] S. Maehrlein, A. Paarmann, M. Wolf, T. Kampfrath, Phys. Rev. Letter, in press (2017)

### 2.1.5 Teraherz Spin Transport

Future electronic device architectures will potentially employ the electron spin (and not only the electron charge) as an information carrier. Successful implementation of such spin-based electronics (spintronics) requires the transfer of spin angular momentum through space, preferably at speeds exceeding that of today's computers, that is, at THz frequencies. Currently, the group of *Tobias Kampfrath* studies the high-frequency (THz) behavior of only recently discovered fundamental spintronic effects that enable the generation and detection of

spin currents. While the spin-dependent Seebeck effect (SDSE) and the spin Seebeck effect (SSE), respectively, refer to the transport of spin angular momentum by electrons and spin waves induced by a temperature gradient, the inverse spin Hall effect (ISHE) refers to the conversion of a spin current into a transverse charge current.

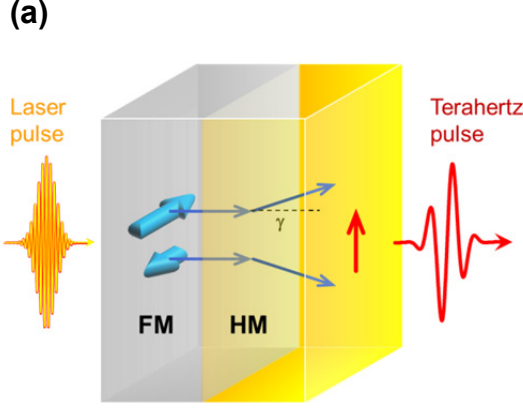
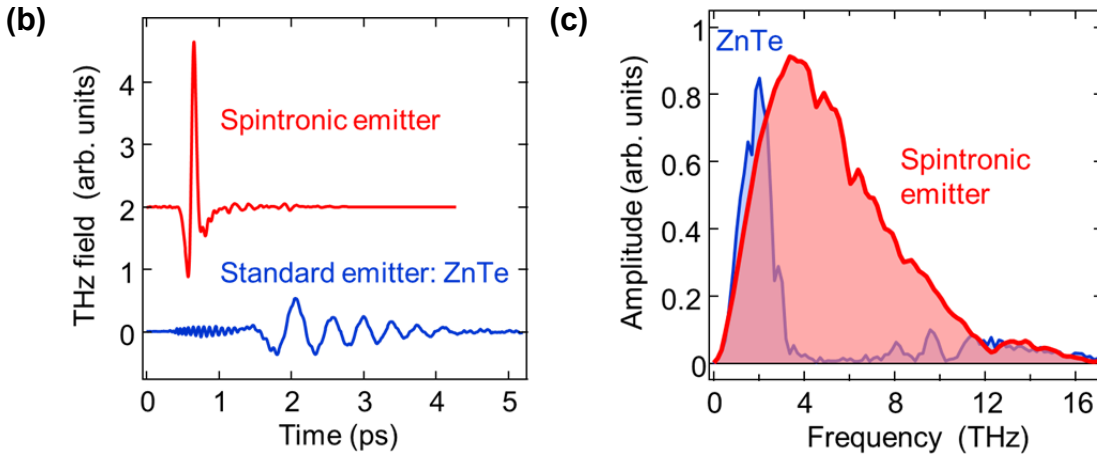


**Figure 5:** (a) Emission of free-space THz electromagnetic pulses from an optically excited ferromagnet (FM)/heavy-metal (HM) bilayer. The femtosecond pump launches injection of a spin current from the FM into the HM layer, where it is converted into a transverse charge current by the inverse spin Hall effect (ISHE). The time-dependent current gives rise to the emission of an electromagnetic pulse at THz frequencies. (b) THz signals as measured by electro-optic sampling. A spintronic W/Fe/Pt trilayer yields a THz signal with higher amplitude, shorter duration and (c) larger bandwidth than state-of-the-art emitters such as a 300  $\mu\text{m}$  thick ZnTe(110) crystal.



**THz spin transport:** To test the speed limit of the SDSE and ISHE, a THz emission experiment was conducted as schematically shown in Fig. 5a. Here, a femtosecond pump pulse is used to launch ultrafast spin transport from a ferromagnetic (FM) thin film into an adjacent heavy-metal (HM) layer through an ultrafast version of the SDSE. The longitudinal spin current is in part converted into a transverse charge-current burst by the ISHE, resulting in the emission of a THz electromagnetic pulse [1]. A typical THz waveform emitted by a Fe/Pt metal film of only 5 nm thickness driven by pulses of 10 fs duration from a simple laser oscillator is shown by Fig. 5b. An inversion procedure allows extraction of the ultrafast current generating the measured THz signal [2]. These results imply that the SDSE has a response time of less than 30 fs, pointing to an extremely fast generation process of the spin current, a point that is currently under study.

The above results have important applications. First, one can use the THz emission signal to obtain a relative estimate of the strength of the ISHE and the strength of the SDSE for a given HM and FM material respectively. The newly developed characterization method is straightforward because it works in a contact-free manner with standard thin film samples. In contrast, electronic approaches require relatively tedious preparation steps such as microstructuring and contacting. Second, FM/HM bilayer and trilayer stacks can be used as novel emitters of THz radiation which outperform standard emitters such as a 300  $\mu\text{m}$  ZnTe crystal in terms of peak amplitude, THz pulse shortness (Fig. 5b) and bandwidth (Fig. 5c). In particular, the metallic spintronic emitters do not suffer from attenuation as is the case in semiconductor emitters owing to their Reststrahlen band (see e.g. the ZnTe spectrum in Fig. 5c). By upscaling the emitter diameter to 7.5 cm and the pump-pulse energy to 5 mJ, we were able to generate THz electric fields with peak amplitudes of as high as 300 kV/cm over the spectral range from 1 to 10 THz. These field strengths facilitate nonlinear control over matter on the sub-picosecond time scale, also in the 5-10 THz frequency range, which was challenging to access up to now [3].

*Interface sensitivity:* THz emission experiments on Fe/Pt bilayers were also conducted as a function of the film thickness. Remarkably, these measurements showed that the charge current generating the THz pulse flows in an only 1 nm thick Pt sheet directly at the Fe/Pt interface [1]. This result attests to a significant surface sensitivity of the emitted THz waveform and shows that THz spectroscopy is capable of addressing both the bulk (as done in the overwhelming majority of works to date) and interfaces of condensed matter.

Another THz emission experiment took advantage of this high degree of interface sensitivity in which the THz group was able to optically launch and detect THz currents flowing at the surface of the topological insulator  $\text{Bi}_2\text{Se}_3$  by. It was found that excitation by a laser pulse (duration 10 fs, photon energy 1.55 eV) shifts electron density from the Se atoms toward the Bi atoms. The data indicate that this shift current flows predominantly in the first  $\sim 2$  nm of the surface region [2]. In addition, the results show that previously suggested scenarios based on optically induced changes in the electron group velocity are not operative or at least result in much less efficient photocurrents than previously assumed.

[1] T. Seifert, *et al.*, Nature Photon. **10**, 483 (2016).

[2] L. Braun, *et al.*, Nature Commun. **7**, 13259 (2016).

[3] T. Seifert, *et al.*, Appl. Phys. Lett. **110**, 252402 (2017).

### 2.1.6 Ultrafast Spin Dynamics in Epitaxial Metallic Multilayers

Ultrafast spin dynamics induced by transport of photoexcited spin polarized carriers is of fundamental interest for applications in 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. 6b). The spin dynamics is probed by time-resolved second harmonic generation (SHG) [1] and magneto-optical Kerr effect (MOKE) [2]. One particular focus lies on the development of generation, control, and detection techniques for ultrashort spin current pulses [1] and studies of their induced spin transfer torque acting on a ferromagnet (FM) [2]. The spin transfer torque is an elegant and promising way to excite ultrafast magnetization dynamics: When spin-polarized hot carriers propagating in a non-magnetic (NM) spacer reach a FM layer, the magnetization experiences an ultrafast torque confined to the NM/FM interface and starts rapidly moving out of the equilibrium at terahertz rates.

In metals, spin currents can be produced by temperature gradients in a bulk FM or across interfaces known as the spin-dependent Seebeck effect. Recently, the ultrafast, non-thermal counterpart of this effect has been demonstrated [1]. It is based on the spin-dependent transmittance of FM/NM interface for non-thermalized laser-excited hot carriers at energies  $E$  considerably different from the Fermi energy  $E_F$  (see Fig. 6a): The large Fe/Au interface transmittance for majority electrons at  $E > E_F + 0.3$  eV provides a spin flux from Fe to Au forming a spin current pulse with a polarization set by the direction of magnetization in the Fe emitter  $\mathbf{M}_E$ . Its duration is determined by the hot carriers thermalization time on the order of 200 fs: once the hot carriers relax towards  $E_F$  the transmission difference vanishes and thus the hot carriers emission stops. Experimentally, hot carriers were excited by 14 fs, 800 nm laser pulses in a layered Fe/Au/Fe/MgO(001) structure (Fig. 6b) leading to generation of  $\sim 250$  fs-long spin current pulses (Fig. 6d) detected by SHG which is sensitive to breaking of the inversion symmetry due to the spin current pulses in the Au. The study of spin current reflected from the Au/Fe interface has shown that the component polarized orthogonally to the magnetization of Fe collector  $\mathbf{M}_C$  is lost upon the reflection and thus the spin current becomes polarized anti-parallel to  $\mathbf{M}_C$  [1]. Subsequent picosecond precessional dynamics of  $\mathbf{M}_C$  excited by the spin transfer torque in the collector has been monitored with MOKE [2]. Owing to interfacial confinement of the spin transfer torque, several standing spin wave modes with frequencies up to 0.6 THz are excited (Fig. 6d, e). Spectral analysis of the excited

modes (Fig. 6c) allows for an estimation of the spin accumulation depth due to confinement of the spin transfer torque at the interface. The spin accumulation depth is found to be below 2 nm in Fe.

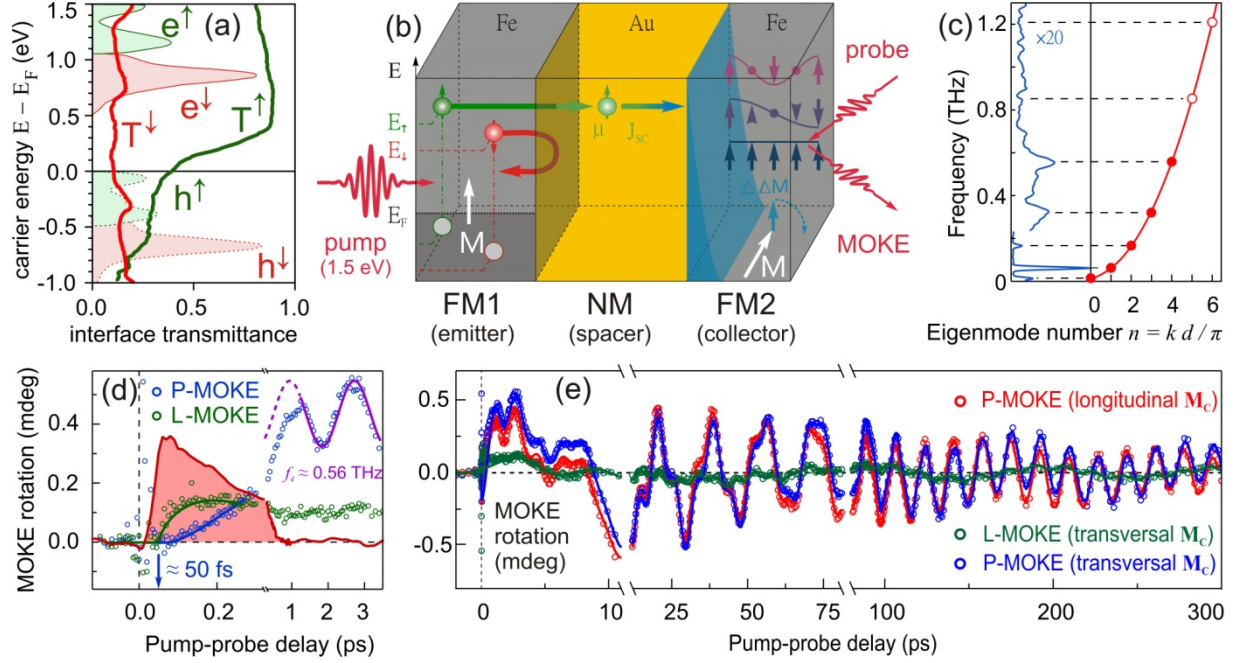


**Figure 6:** (a) Calculated momentum-averaged transmittance of the Fe/Au interface for majority ( $T^\uparrow$ ) and minority ( $T^\downarrow$ ) carriers moving from Fe to Au [1]. Shaded areas reproduce schematically the spectrum of primary carriers are excited by the 1.5 eV pump. (b) Experimental approach: Since only majority electrons at  $E > E_F + 0.3$  eV have large interface transmittance, a spin-current pulse is generated by laser excitation of a ferromagnetic emitter layer on the left-hand side with the duration limited to the electron thermalization time. This pulse exerts a torque on a ferromagnetic collector layer, which triggers ultrafast spatially non-uniform spin dynamics including the excitation of high-frequency standing spin-wave modes, which are subsequently probed magneto-optically. (c) Fourier spectrum of the MOKE signal (left) and spin waves dispersion calculated analytically (right). The frequencies of the standing spin waves in a 14 nm-thick Fe film are shown with red symbols. Along with the uniform precession ( $n=0$ ), four higher modes are shown which were detected in the experiment (full dots). [2] (d) Transient MOKE rotation on the ultrashort timescale [2]. The rapid onset of the longitudinal component (green circles) is followed by a slower increase of the polar one (blue circles) due to the magnetization precession. The red shaded area reproduces the SC pulse as measured with SHG [1]. The purple line illustrates the 4<sup>th</sup> spin wave eigenmode. (e) Transient MOKE rotation on longer timescales [2]. Polar (P-) and longitudinal (L-) MOKE effects are separated. Solid lines are the results of the fitting procedure with a set of exponentially decaying oscillations, with their frequencies given by the analytical equation [2]. The pronounced similarity between the two P-MOKE traces (red and blue dots) demonstrates the robustness of the measurements.

These findings shed light on the properties of the ultrafast laser-driven spin currents and elucidate their interaction with a non-collinear magnetization in thin ferromagnetic films. The results demonstrate the extreme ability of spin-current pulses to excite non-uniform spin dynamics, as compared to other ultrafast mechanisms, such as the heat-induced quenching of magnetic anisotropy. Moreover, the density of magnetic moment transferred across the Au/Fe interface per pulse is found to amount  $\sim 7 \mu_B/\text{nm}^2$ , which shows a high promise for the magnetization switching in thin FM layers.

[1] A. Alekhin *et.al.*, Phys. Rev. Lett. **119**, 017202 (2017).

[2] I. Razdolski *et.al.*, Nature Commun. **8**, 15007 (2017).

## 2.2 Molecular Processes at Interfaces and in Condensed Phase

Understanding molecular dynamics at gas-solid, liquid-solid interfaces and in the liquid phase is of fundamental importance for surface chemistry, electrochemistry and biological processes. Fundamental studies in this area are performed by several groups in the department with complementary microscopic and spectroscopic techniques, enabling high spatial resolution using scanning probe microscopy, chemical identification using vibrational spectroscopy, and ultrafast dynamics using nonlinear optical spectroscopy.

### 2.2.1 Dynamics of Individual Molecules at Surfaces

Studies on single-molecule structures and dynamics at surfaces provide important information for a microscopic understanding of surface reactions and for development of molecular scale electronics. The group of *Takashi Kumagai* investigates chemistry and physics of single molecules on well-defined surfaces using several low-temperature scanning probe techniques including scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM), and tip-enhanced Raman spectroscopy (TERS) under UHV conditions. These methods enable direct observation and manipulation of single atoms and molecules on surfaces and eventually the local control of reactions. The group has investigated intramolecular hydrogen-atom transfer (tautomerization) reactions and recently focused, in particular, on force-induced processes ('mechanochemistry'), tunneling dynamics in hydrogen transfer reactions, and single-molecule photochemistry at metal surfaces.

*Force-induced tautomerization in single porphycene molecules:* Beside thermal, electronic and optical excitation to activate chemical processes an externally applied force provides an alternative way to perturb a chemical system and eventually induce a reaction. However, dedicated studies for such a mechanical activation are rare and the underlying microscopic mechanisms remain poorly understood *at the single-molecule level*. Recently, force-induced tautomerization in a single porphycene molecule was demonstrated on a Cu(110) surface at 5 K combining nc-AFM and density functional theory (DFT) calculations [1]. Force spectroscopy quantifies the force needed to trigger tautomerization with sub-molecular spatial resolution (see Fig. 7). DFT calculations show how the reaction pathway and barrier for the tautomerization are modified upon approach of a copper tip to the porphycene and reveal the atomistic origin of the process. Interestingly, it could be shown that a chemically inert tip



whose apex is terminated with a xenon atom cannot induce the tautomerization reaction due to a weak interaction with porphycene and the strong relaxation of the Xe atom on the tip as contact to the molecule is formed.

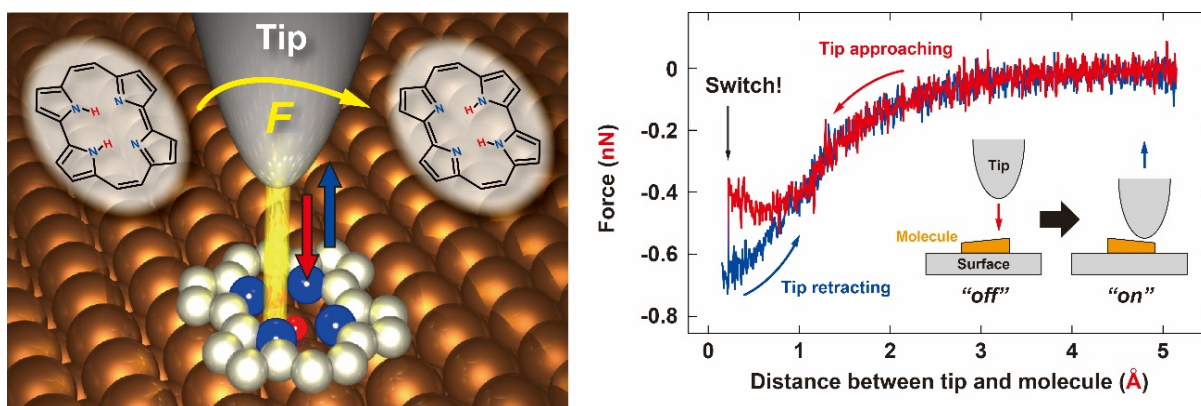


**Figure 7:** Force-induced *cis* ↔ *cis* tautomerization in a single porphycene molecule on Cu(110) at 5 K. Left: Schematic of the experiment with nc-AFM. The tip is brought toward and retracted from the porphycene while detecting the interaction acting between the tip apex and the molecule. Right: Force curve measured over the porphycene. The sudden drop of the force in the approaching curve corresponds to the moment of one tautomerization event underneath the tip.

*Quantum tunneling of hydrogen atoms* plays a crucial role in many physical, chemical and biological processes. Although tunneling of a single particle has been examined extensively in various one-dimensional potentials, many-particle tunneling in high-dimensional potential energy surfaces remains poorly understood. The direct observation of a double hydrogen atom transfer (tautomerization) within a single porphycene molecule on a Ag(110) surface was recently demonstrated using a STM. Below ~14 K the tautomerization rate is temperature-independent and a large kinetic isotope effect (~100) is observed upon substituting the hydrogen atoms by deuterium. This clearly indicates a dominant contribution of quantum tunneling in the reaction. Additionally, detailed analysis reveals a sequential (step-wise) tunneling process of the H-atoms, rather than a concerted one. It is also found that the tautomerization rate is increased by vibrational excitation via an inelastic electron tunneling and that the STM tip can be used to manipulate the tunneling dynamics through modification of the potential landscape.

[1] J. Ladenthin *et al.*, Nature Chem. **8**, 935 (2016).



### 2.2.2 Local Photochemistry and Near-Field Induced Processes

*Tip-enhanced photochemistry:* Photochemistry can lead to enhanced selectivity and different reaction products compared to thermally-induced chemistry. Using low-temperature scanning tunneling microscopy combined with a wavelength tunable light source the direct observation of photoinduced tautomerization in single porphycene molecules on a Cu(111) surface has been demonstrated [2]. It is found that the thermodynamically stable *trans* configuration of the porphycene is converted to the metastable *cis* configuration in a unidirectional fashion through photo-irradiation, whereas the backward *cis*  $\rightarrow$  *trans* conversion can be induced by heating the surface (Fig. 8). The wavelength dependence of the tautomerization cross section exhibits a steep increase around 2 eV, indicating that excitation of the Cu *d*-band electrons and the resulting hot carriers play a dominant role in the photochemical process. Additionally, a pronounced isotope effect in the cross section ( $\sim 100$ ) is observed when the transferred hydrogen atoms are substituted with deuterium, indicating a significant contribution of zero-point energy in the reaction. Combined with the study of inelastic tunneling electron-induced tautomerization with the STM, we proposed that the tautomerization occurs via excitation of molecular vibrations after photoexcitation. Currently we investigate near-field coupled process where the photo-induced tautomerization is largely enhanced in the presence of a metallic tip under photo-irradiation. It is found that the tip-enhanced process is particularly enhanced by using an Au tip (Fig. 8, lower panel), which is explained by localized plasmon excitation in the STM junction.

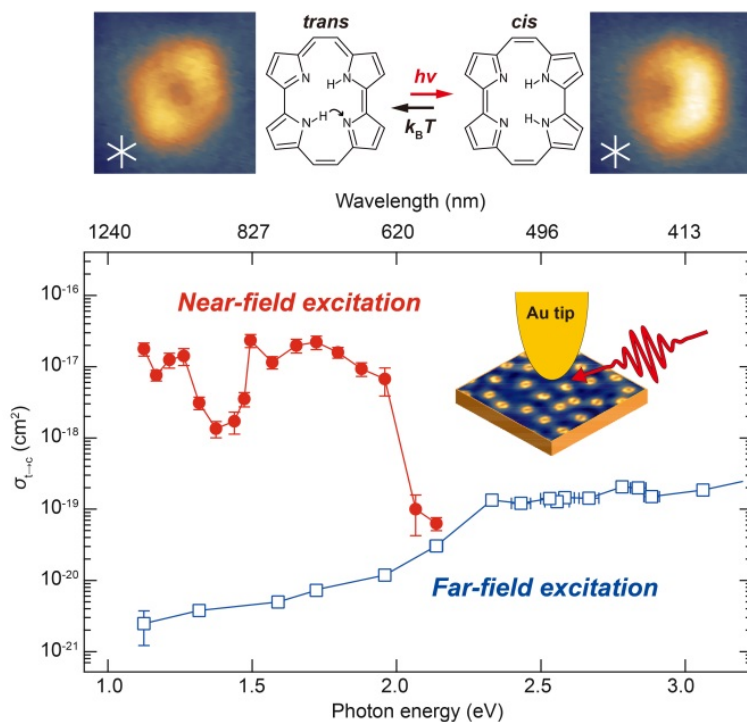


**Figure 8:** Upper panel: STM images and chemical structures of the trans and cis porphycene on a Cu(111) surface. The conversion can be selectively induced either by irradiation or by thermal activation. Lower panel: Cross section of the trans  $\rightarrow$  cis tautomerization a function of photon energy in the presence and absence of an Au tip, denoted as near-field and far-field excitation, respectively.

*Development of low-temperature optical scanning probe microscopy (SPM):* Many important physical, chemical, and biological processes are based on light driven processes in molecular systems. For molecules at interfaces such processes will critically depend on the local environment. In particular, optical excitations of molecules mediated by metallic nanostructures have a wide range of applications such as surface-enhanced Raman spectroscopy (SERS), enhanced molecular luminescence, and photo-catalysis. Similarly, tip-enhanced Raman spectroscopy (TERS) has recently emerged as a powerful tool of single-molecule spectroscopy. In order to probe locally the coupling of single adsorbates to optical excitation and detect (inelastic) scattered light with high efficiency, we have designed a new low-temperature *optical* scanning probe microscope. In this setup a motorized *in-situ* parabolic mirror and a lens with a sufficiently high numerical aperture have been installed on the low-temperature SPM stage in proximity to the tip apex. This will enable various experiments such as single-molecule TERS, near-field optical excitation, photoluminescence spectroscopy, and possibly ultrafast spectroscopy in combination with THz or femtosecond laser excitation. The new system is currently being implemented in the new SPM laboratory and first preliminary experiments are carried out.

*Development of ultrafast THz-STM combined with optical near-field photoexcitation:* The new group of Melanie Müller is currently developing a THz-pulse gated STM which will be combined with optical photoexcitation of few-femtosecond laser pulses. Building on the

previously demonstrated gating technique of the STM tunneling bias by an ultrashort THz-pulse, the concept of plasmonic nanofocusing of broadband surface plasmon polaritons (SPPs) will be employed to enable versatile ultrafast optical excitation of the tip-sample junction. Nanofocused SPPs can be used to trigger nonlinear photoemission from the tip apex with higher quantum efficiency compared to direct apex illumination [2], as shown in the MPRG of Ralph Ernstorfer, thus promising less thermal load on the tip-sample junction and increased excitation efficiency of the sample. As a first step in this direction, a home-built room-temperature STM at ambient conditions has been constructed, providing easy and flexible optical access to explore the suitability of SPP nanofocusing for ultrafast STM. Such experiments may provide access to spatio-temporal dynamics of nanostructures and molecules at surfaces on their natural length and time scales.

[1] H. Böckmann *et al.*, Nano Lett. **16**, 1034 (2016).

[2] M. Müller *et.al.*, ACS Photonics **3**, 611-619 (2016).

### 2.2.3 Nonlinear Vibrational Spectroscopy of Interfacial Molecular Structure

Probing most liquid interfaces requires using appropriate photons as probes and interface-specific nonlinear optical, *i.e.* sum frequency (SF), spectroscopy that is vibrationally (VSF) or electronically (ESF) resonant. The group of *Kramer Campen* studies molecular-scale structure and ultrafast structural dynamics at liquid-solid, liquid-air and gas-solid interfaces using SF spectroscopy, both in and out of equilibrium. To explore equilibrium structural fluctuations at liquid interfaces additional pulsed infrared excitation is added and the temporal evolution of interfacial vibrationally-labeled ensembles followed. Non-equilibrium conditions that drive redox chemistry are investigated by steady-state approaches, *i.e.* electrochemical interfaces under reactive conditions, as well as ultrafast charge transfer induced by femtosecond laser pulses. Some recent examples of such structural studies and method development are illustrated below:

*(Electrified) Liquid-Solid Interfaces:* Prior work has shown that the liquid water/ $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  interface exhibits surface aluminol (*i.e.*  $(\text{Al})_2\text{-OH}$ ) groups that are *non-H-bonded*, *i.e.* part of this surface is microscopically hydrophobic even as it macroscopically wets. However, how such groups exist in contact with liquid water ( $\text{H}_2\text{O}(l)$ ) and their influence on surface chemistry is not well understood. By adding an additional IR pulse to a VSF probe it was shown that the vibrational relaxation of this type of aluminol depends sensitively on solution chemistry. In collaboration with theorists at the University of Potsdam it has been clarified that the mechanism of vibrational relaxation is through coupling to

neighboring *H-bonded* surface aluminols and subsequently to molecular water. This mechanism depends sensitively on  $\alpha$ - $\text{Al}_2\text{O}_3$  crystal face and the solution chemistry and thus explains the dramatic changes in dynamics observed with changing solution chemistry and the low reactivity of the (0001) relative to other  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces in contact with  $\text{H}_2\text{O}(l)$ .

Along similar lines a VSF study of the water structure at the  $\text{H}_2\text{O}(l)/\text{Au}$  electrode interface as a function of bias has identified a previously unobserved population of interfacial water molecules that have one OH group pointing towards the gold electrode [1]. Because these OH groups are only weakly H-bonded they are expected to play a significant role in aqueous electrochemistry. Curiously, and counter to simple electrostatics, the density of this type of interfacial water increases as the surface potential became more positive (see Fig. 9).

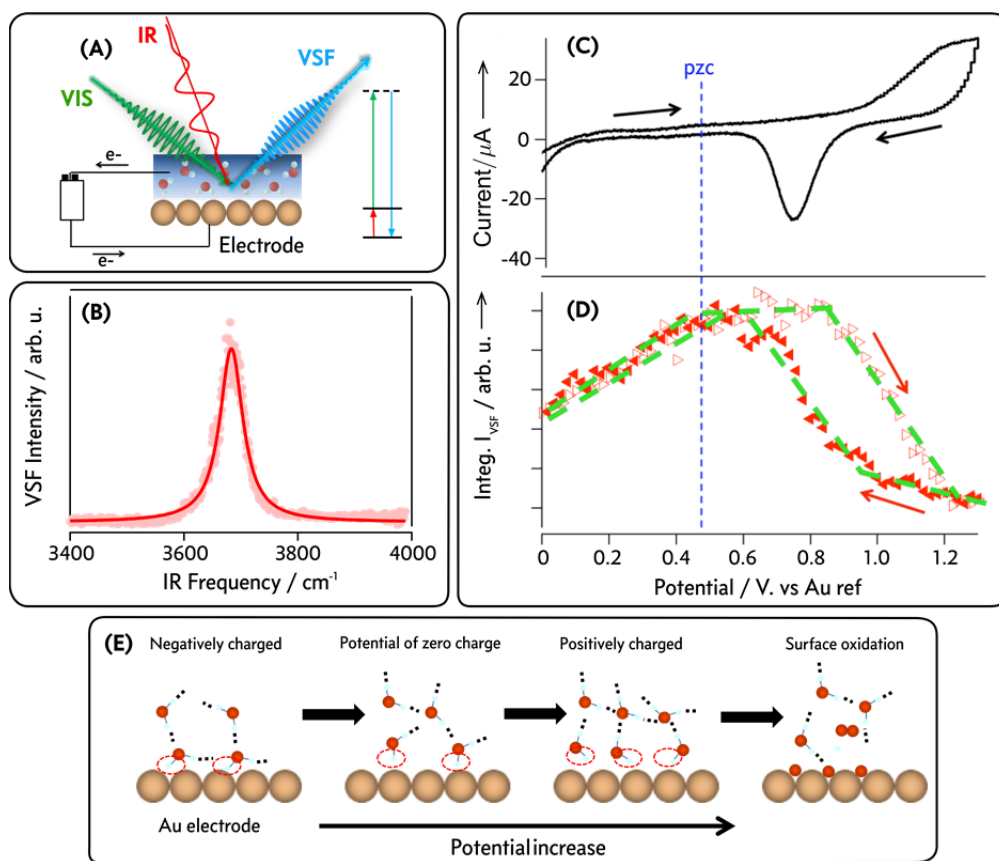


**Figure 9:** (A) Thin-film VSF spectro-electrochemical set-up used to probe water structure at the Au electrode/water interface [1]. (B) The VSF spectral response of water with one OH group pointing towards the electrode at open-circuit potentials. (C) Cyclic voltammogram in our thin-film spectro-electrochemical cell. (D) Integrated VSF intensity of the feature in (B) as a function of bias. (E) Cartoon of water structure consistent with observations in (B) and (D).

Creating self-assembled monolayers (SAMs) of bistable optically switchable chromophores on electrodes is a pathway towards a variety of next-generation, gated, switchable sensors. While quantitative characterization of such chromophores is relatively straightforward in solution, gaining such insight in a SAM at an electrified liquid- solid interface is more

challenging. Systematic VSF measurements of a Spiropyran based SAM on Au electrodes were conducted and it was shown how the composition of its photo stationary state(s) and kinetics of photo switching vary as a function of bias [2].

*H<sub>2</sub>O(l)-Air Interface:* The first measurement of the libration mode of interfacial water was reported, which is blue-shifted by 160 cm<sup>-1</sup> from bulk liquid water [3]. This indicates that the rotational potential of interfacial water is stiffened relative to bulk water in a manner similar to that on cooling ambient liquid water to form ice. Curiously, many other more local indicators of water structure (like hydrogen bond distance or angle) show only small changes between ambient bulk water and the air-water interface.

Contradicting classical, Debye-Hückel derived, theory, over the last 25 years, chemical kinetics measurements and surface sensitive spectroscopy have clarified that large, relatively polarizable anions tend to partition favorably to the H<sub>2</sub>O(l)/air interface. Despite this insight challenging questions remain: *e.g.* (i) what role does anion polarizability play in adsorption and (ii) what effect does the interface have on ion pair formation? Both questions have been addressed for the example of perchlorate at the H<sub>2</sub>O(l)/air interface. From bulk concentrations of 0-1 M the interfacial polarizability of perchlorate differs from bulk and continues to evolve with increasing concentration. Above 1 M bulk concentration interface induced ion pairing sets in. While in bulk water ion pairing occurs in solutions more concentrated than 11 M, at interfaces such effects occur at an order of magnitude lower concentration.

*Gas-Solid Interface:* A complete understanding of water-oxide interaction should encompass all water pressures from the single molecule to the liquid. The group also worked on the low-pressure end of this range. In collaboration with theoreticians from the University of Potsdam it was demonstrated that for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 1 $\bar{1}$ 02 surface, with sub-monolayer coverages of water in UHV, a population of OH bonds exists that is sufficiently anharmonic that the proton is delocalized [4]. Extending this approach to the Al<sub>2</sub>O<sub>3</sub> 11 $\bar{2}$ 0 surface an unusual arrangement of surface metal atoms was found that allow strong bidentate coordination of adsorbed OH groups and explains this surfaces high reactivity.

*Building a better SF Spectrometer:* Current work is limited by detecting only the emitted SF intensity, not the SF field (phase resolved), and by the relatively intense powers required for the incident fields. Overcoming the first limitation is important in correctly describing spectral line shapes while dramatically increasing signal to noise would both allow the direct probing of weakly adsorbing species (*e.g.* Zundel or Eigen cations in interfacial water) and/or allow

application of weaker continuum sources to collect broadband spectra spanning multiple decades in the infrared in a single shot. Recently both limitations have been addressed by building a collinear, time-domain, heterodyned, balance detected sum frequency spectrometer

- [1] Tong *et al.* Angw. Chem., **56**, 4211-4214 (2017).
- [2] Garling *et al.*, J. Phys.: Cond. Matt., **29**, 41 (2017).
- [3] Tong *et al.*, Phys. Chem. Chem. Phys., **18**, 18424-18430 (2016).
- [4] Wirth *et al.*, Phys. Chem. Chem. Phys., **18**, 14822-14832 (2016).

#### 2.2.4 Reactions at Electrochemical Interfaces

Gaining molecular level insight into the chemistry at electrochemical interfaces requires the development of interface specific molecular spectroscopy for detection of small concentrations of interfacial species, with the interface under bias, in the presence of much larger amounts of similar moieties in the electrolyte. Furthermore, during electrochemical reactions intermediates often exist in small concentrations and have ultrashort lifetimes. The group of *Kramer Campen* is on the way to address these challenges by performing vibrational and electronically resonant sum frequency (VSF or ESF) spectroscopy in thin-film and meniscus spectro-electrochemical cells and by employing fs laser driven ultrafast perturbation of the electrode potential to initiate electron transfer and tracking the resulting products.

*Electrooxidation of Au.* Understanding the mechanism of the oxygen evolution reaction on metal electrodes is challenging because often the electrode oxidizes in the same potential range as water, i.e. when the chemistry of interest is happening the electrode surface is often covered by a nm thick layer of poorly defined (hydr)oxide. The Au-O vibrational response (of oxide surface phonons) has been characterized *in-situ* under bias. These results suggest, contrary to thermodynamic expectations for idealized surfaces, that the Au surface is covered by a gold hydroxide phase at potentials at which the oxygen evolution sets in.

*Oxygen Evolution Reaction (OER) on Hematite.* Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a promising photoanode material for water splitting applications due to its relatively small bandgap and natural abundance. The role of electronic surface states in the OER at the Hematite photoanode has proven controversial: it's unclear whether they are trapped carriers, actively stabilize OER intermediates or neither. So far preliminary ESF measurements at the liquid water-hematite interface were conducted that reveal a previously unobserved intra-bandgap state. The bias-dependent spectral response suggests that this surface state must be depopulated for OER.

**Hydrogen Evolution Reaction (HER) on Au and Pt:** As neither protons nor water adsorb strongly on Au, theory suggests that the hydrogen evolution reaction on Au electrodes proceeds via an interfacial solvated electron. Because solvated electrons have relatively short lifetimes in water, understanding this chemistry requires the ability to start the HER at a well-defined time and then monitor the appearance of intermediates with high time resolution. Recently an experiment was developed in which, beginning with an Au electrode in contact with water, the HER is initiated by injecting photoexcited electrons from the electrode into the water conduction band using an intense femtosecond UV pulse. The fate of these (solvated) electrons are tracked both electrically, using a two-color laser induced perturbation of the open circuit potential, and by optical spectroscopy (see Fig. 10). Both types of probes suggest that, upon laser excitation, a delocalized solvated electron is generated that lives for 200 fs before localization. Some fraction of these localized solvated electrons relax back to the electrode on picosecond timescales, with a strongly potential dependent dynamics, while the remainder diffuses away from the surface and eventually drive chemistry.

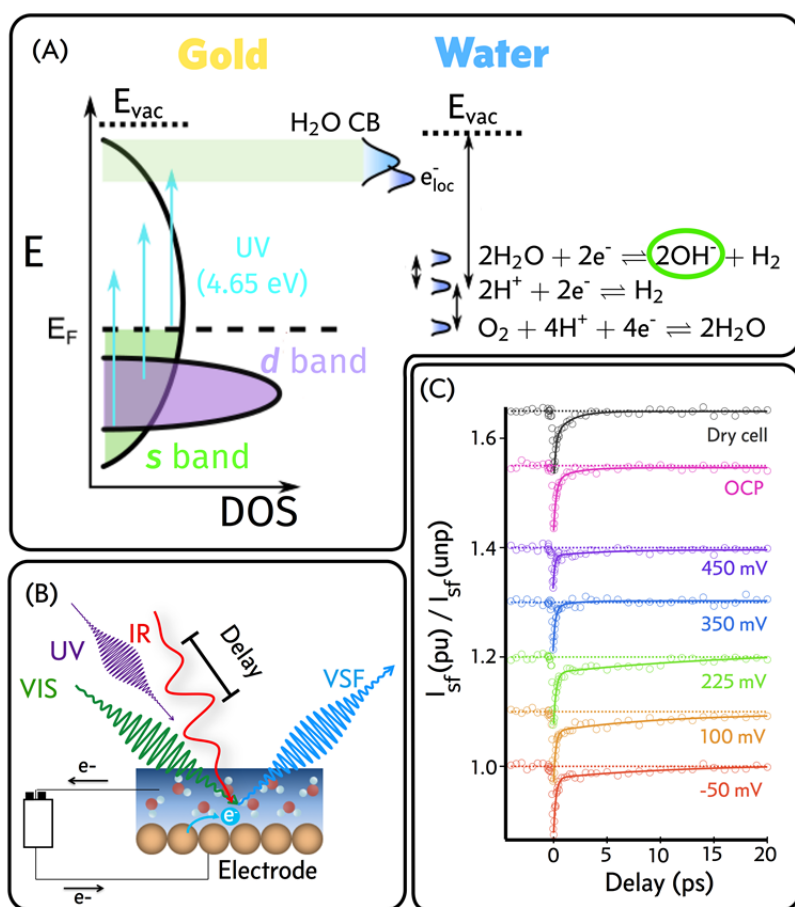


**Figure 10:** (A) Scheme for an experiment in which a fs UV pulse is used to adiabatically transfer an electron into the conduction band of water from which it drives chemistry (B) Experimental scheme illustrating the generation of an interfacial solvated electron and its characterization with a sum frequency probe pulse pair (C) Data from a normalized UV pump / SF probe scheme (mixing of 4  $\mu$ m and 800 nm light). The results clearly show the 100 fs lifetime of the delocalized electron and the potential dependent ps lifetime of the localized solvated electron.

In contrast to gold hydrogen adsorbs more strongly on platinum leading to dramatically higher electrocatalytic efficiency of the HER. However exactly how the HER proceeds on Pt is not clear: there is no mechanism that explains the dramatic dependence of the HER rate on pH, Pt crystal face, and electrolyte. Part of the challenge is that hydrogen adsorbs on Pt at potentials more oxidizing than hydrogen evolution and the relationship of this under potential deposited hydrogen to the HER is not clear. To help address this question an experiment was built whereby a femtosecond visible pulse was used to initiate electron transfer and the Pt-H surface probed by VSF. The results illustrate that, on sub ps time scales, Pt-H population is generated at the interface, presumably from molecularly adsorbed water, and that on a few picosecond time scale the Pt-H population decreases, presumably due to the generation of H<sub>2</sub>.

### 2.2.5 Nonlinear THz Spectroscopy of Liquids

Low-frequency collective dynamics in molecular liquids are believed to have large impact on the outcome of chemical and biological processes. These complex motions include hindered rotations (librations) and translations and reorientational diffusive relaxation processes. The collective nature of these motions is a consequence of the intermolecular interactions and the coupling between different types of molecular motions, in particular, intermolecular modes. The group of *Mohsen Sajadi* aims at understanding the nature of these collective dynamics and mapping the potential energy of the intermolecular interactions, using linear and nonlinear THz spectroscopy.

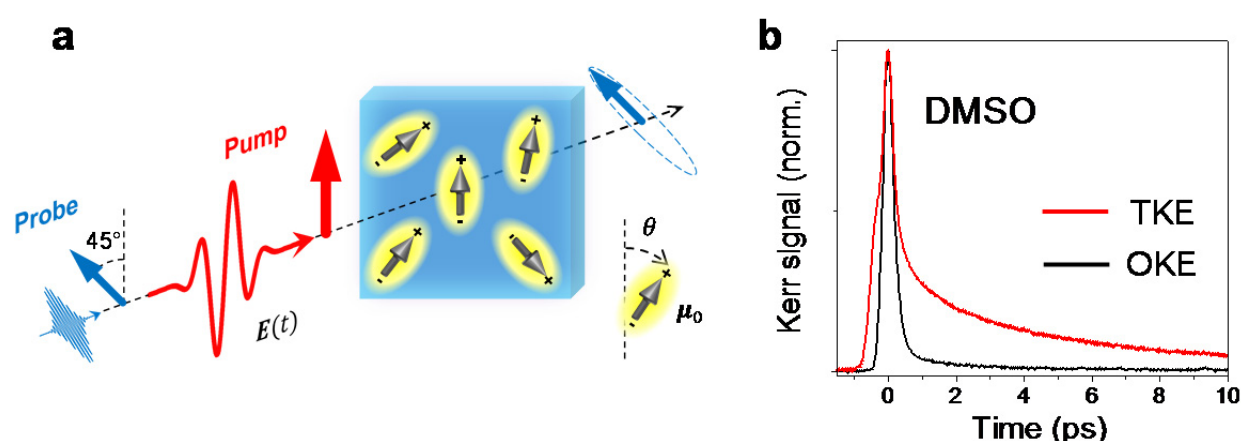


**Figure 11:** (a) An intense THz or optical pump pulse induces birefringence in a polar liquid which is measured by an optical probe pulse that becomes elliptically polarized upon propagation through the medium. (b) TKE (red line) and OKE (black line) signals of DMSO are normalized to the instantaneous electronic contribution.

*Direct observation of the intermolecular mode coupling in liquids:* Strong THz electric-field pulses have been applied to drive orientational dynamics in polar liquids leading a transient optical anisotropy induced by the torque of the THz field exerted on the permanent dipole



moments of the solvent molecules. The THz induced optical birefringence is monitored by an optical pulse as shown schematically in Fig. 11a. This THz Kerr effect (TKE) is significantly enhanced as compared to off-resonant optical excitation (OKE) as exemplified for the dipolar liquid dimethyl sulfoxide (DMSO, Fig. 11b). The amplitude enhancement in the TKE implies a direct coupling of the THz electric field to the permanent dipole moment of the liquid. Note that, optical pulses interact with the induced electronic dipoles where the nuclear dynamics is frozen during the light-matter interaction. Here, we use intense THz pulses to drive orientational molecular dynamics in polar liquids such as dimethyl sulfoxide or acetonitrile by coupling directly to their low-frequency resonances.

This approach provides insights into the character of THz absorption resonances, the coupling between low-frequency modes, namely librational and reorientational motions and the sign of the polarizability anisotropy of the solvent molecules. In light of a simple but quite general model and for excitation at different THz frequencies, it can be shown that the observed enhancement arises from the coupling between two intermolecular modes in the liquids, namely the resonantly excited librational (hindered rotational) motions and the optically resolved reorientational relaxation in the liquid. Here, the enhanced part of the TKE signal is assigned to the single molecule reorientational relaxation while the excited mode is the librational mode of DMSO.

Currently this approach of comparing transient optical anisotropy induced by THz and optical excitation has been expanded to liquid water. As water is highly polar, strong coupling of the THz electric field and the permanent dipole moment occurs. Such studies will provide insights into the coupling between the intermolecular modes associated with the hydrogen bonding network of water.

[1] M. Sajadi, M. Wolf, and T. Kampfrath, *Nature Commun.* **8**, 14963 (2017).

### **2.2.6 Theoretical Investigations of Molecular Machines**

The group of *Alexander Mikhailov* continued theoretical studies of molecular protein machines, with the emphasis on understanding conformational dynamics and kinetics of their operation cycles, and studies of their hydrodynamic effects.

The enzyme tryptophan synthase represents an extensively experimentally investigated chemical nano-machine. Based on the available experimental data, a stochastic model for the operation of tryptophan synthase has been constructed and it became possible, for the first time, to reconstruct its complete stochastic thermodynamics, quantifying energy dissipation,

entropy and information production in all steps within the operation cycle, as well as the information and entropy flow within the enzyme [1].

In a collaboration with the Max Delbrück Center (MDC) in Berlin and the Kanazawa university in Japan the molecular motor dynamin has been extensively studied. This protein forms filaments that coil around a membrane tube (see Fig. 12) and, through the motor operation, induce its constriction and breakup. Using the structural data from X-ray diffraction studies and FRET experiments at MDC in Berlin together fast atomic force microscopy (AFM) imaging at about 10 frames/s at the Bio-AFM Research Center in Kanazawa and reduced coarse-grained simulations, the full molecular-dynamics and the operation mechanism of this molecular machine has been explored.

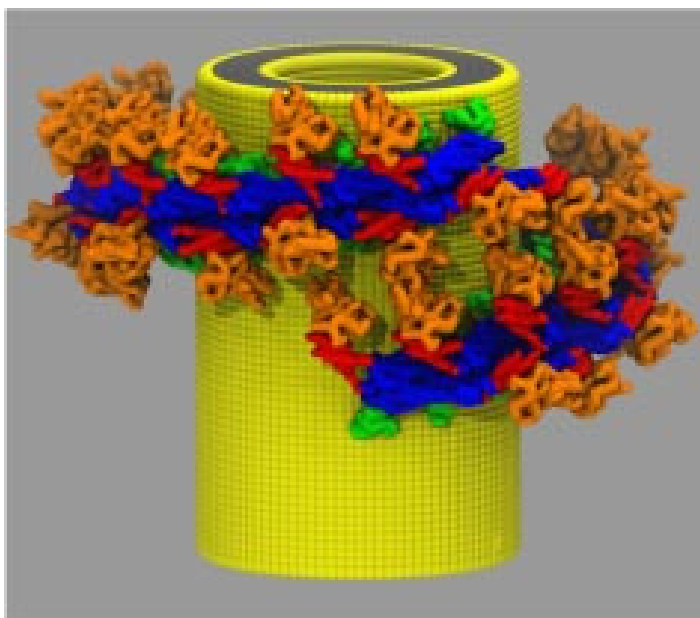


**Figure 12:** The dynamin filament coils itself around the membrane tube and, by constriction, induces its breakup.

When active proteins are cyclically changing their conformations this results in fluctuating non-thermal flows in the cytoplasm and fluctuating strains in the elastic network of a cell. Systematic investigations of these effects were performed in viscoelastic media that represent active gels and in biological membranes populated by active protein inclusions [2] and presented in a review [3]. Furthermore, Alexander Mikhailov has also written together with Gerhard Ertl a book on *Chemical Complexity: Self-Organization Processes in Molecular Systems* [4].

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[4] A.S. Mikhailov and G. Ertl, *Chemical Complexity: Self-Organization Processes in Molecular Systems* (Springer, Berlin, 2017)

### 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, until 6/2017).

#### 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:

- ERC Consolidator Grant #482843 “*FLATLAND: Electron-lattice-spin correlations and many-body phenomena in 2D semiconductors and related heterostructures*” (electron, phonon, and spin dynamics in van der Waals heterostructures investigated with trARPES, femtosecond electron diffraction and microscopy, from 10/2016).

#### 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 11/2015).

#### 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 ultrathin oxide films with STM and AFM, from 7/2015).

**Takashi Kumagai:**

- JST funded project on "*Eluciation of microscopic mechanism of catalytic effects via localized plasmon excitation*", within the PRESTO program on "Science and Creation of Innovative Catalysts" (surface reactions induced by localized plasmon excitation, low-temperature STM/ncAFM, from 10/2016)

**Tobias Kampfrath:**

- ERC consolidator grant TERAMAG, "*Ultrafast spin transport and magnetic order controlled by terahertz electromagnetic pulses*" (control of spin currents and spin dynamics by intense THz electromagnetic fields, from 07/2016).
- 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 7/2016).
- 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).

**Alexander Mikhailov:**

- Volkswagen Foundation, international project "*Self-organizing networks of interacting machines*" (design and analysis of the networks of molecular machines), until 12/2016.

**Laurenz Rettig**

- DFG Emmy Noether grant (RE 3977/1-1), "*Beyond time constants: Quantifying interactions in correlated materials by complementary ultrafast time-domain approaches*" (combined time-resolved ARPES and time-resolved diffraction experiments in strongly correlated materials across phase transitions, setup of Pulsed-Laser-Deposition (PLD) for oxide films, from 9/2017).

## **Julia Stähler**

- DFG 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*” (photoinduced electron transfer, two-photon photoemission spectroscopy of electronic states, from 7/2015).

#### 4. Publications of the Department of Physical Chemistry

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##### Doctoral Thesis

Bogner, L.: Ultrafast Relaxation Dynamics after Optical Excitation of Hybrid Inorganic/Organic Systems. Freie Universität Berlin 2015.

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Alekhin, A.: Ultrafast hot carrier driven magnetization dynamics. Freie Universität Berlin 2016.

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Gerke, F.: Probing of surface adsorbates during the electro-oxidation of gold by vibrational SFG spectroscopy. Freie Universität Berlin 2016.

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Waldecker, L., T. Vasileiadis, R. Bertoni, R. Ernstorfer, T. Zier, F.H. Valencia, M.E. Garcia and E.S. Zijlstra: Coherent and incoherent structural dynamics in laser-excited antimony. *Physical Review B* **95** (5), 054302 (2017).

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## Doctoral Thesis

Krecinic, F.: Ultrafast electron diffraction and imaging using ionized electrons. Freie Universität Berlin 2017.

Müller, M.: Femtosecond low-energy electron imaging and diffraction using nanotip photoemitters. Freie Universität Berlin 2017.

## **Master's Thesis**

*Eisbach, M.:* Entropy, Dissipation and Information in Models of Interacting and Coarse Grained Systems. Technische Universität Berlin 2017.

*Müller, P.:* A 2D Spatial Light Modulator for femtosecond THz light modulation. Technische Universität Berlin 2017.

*Zahn, D.:* Structural dynamics of transition metal dichalcogenide heterostructures studied by ultrafast high-energy electron diffraction. Freie Universität Berlin 2017.



## 5. Invited Talks of the Members of the Department of Physical Chemistry

### Invited Talks of the Members of the Department of Physical Chemistry

- Braun, Lukas: Ultrafast Spin- and Charge-Currents in Topological Insulators and Their Transport to Adjacent Ferromagnetic Layers. (Institutsseminar, Nano-Systems from Ions, Spins and Electrons, Max Planck Institute of Microstructure Physics, Halle, Germany, Nov 2016).
- Campen, R. Kramer: Probing of Surface Vibrational Modes with Optical SFG. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Campen, R. Kramer: Probing Molecular Structure and Chemistry at Electrochemical Interfaces in Real Time. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Ernstorfer, Ralph: Development of a 500 kHz XUV Source Based on an OPCPA. (Seminar, Rutherford Appleton Laboratory, Didcot, UK, Oct 2015).
- Ernstorfer, Ralph: Photocurrents and Structural Dynamics in Nanomaterials Probed by Femtosecond Electron Pulses. (4th International Workshop on Ultrafast Nanooptics (UNO-4), Bad Dürkheim, Germany, Oct 2015).
- Ernstorfer, Ralph: Structural and Electronic Dynamics in Transition Metal Dichalcogenides: Accessing Coupling and Correlation Effect by Time-Resolved Techniques. (BESSY II - THz to Soft X-ray Workshop, Helmholtz-Zentrum Berlin, Berlin, Germany, Dec 2015).
- Ernstorfer, Ralph: Accessing Electron-Phonon Interaction with Time-Resolved Diffraction and XUV-Based trARPES. (Seminar, Philipps-Universität, Marburg, Germany, Jan 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides. (Physikalisches Kolloquium, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, Feb 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides. (SIMES Seminar, Stanford Institute for Materials & Energy Sciences, SLAC, Stanford University, Stanford, CA, USA, Feb 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: From Electron-Phonon Coupling to Spin- and Pseudospin-Polarized Excited States. (Physical Seminar, Department of Chemistry, University of Rochester, Rochester, NY, USA, Feb 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: From Electron-Phonon Coupling to Spin- and Pseudospin-Polarized Excited States. (Seminar, ICFO The Institute of Photonic Sciences, Castelldefels, Barcelona, Spain, Feb 2016).
- Ernstorfer, Ralph: Femtosecond Electrons Probing Ultrafast Phenomena in Nanostructures by Diffraction and Imaging. (SPIE Photonics West - OPTO: Ultrafast Phenomena and Nanophotonics XX, San Francisco, CA, USA, Feb 2016).

- Ernstorfer, Ralph: Accessing Electronic and Structural Dynamics with Time-Resolved Electron Diffraction and High Repetition Rate XUV-trARPES. (Kolloquium, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, Mar 2016).
- Ernstorfer, Ralph: Spin- and Pseudospin-Polarized Excited States in Bulk WSe<sub>2</sub>. (Hauptvortrag, DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Ernstorfer, Ralph: Accessing Many-Body Effects and Coupling Phenomena in Transition Metal Dichalcogenides by Time-Resolved ARPES and Diffraction. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Ernstorfer, Ralph: Dynamics of Electrons, Spins and Phonons in Transition Metal Dichalcogenides. (1st WP2-Domain Workshop on Beyond CMOS, NEREID, NanoElectronics Roadmap for Europe: Identification and Dissemination, Espoo, Finland, May 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (Graz Advanced School of Science, Physics Colloquium of the University of Graz and the Graz University of Technology, Graz, Austria, Jun 2016).
- Ernstorfer, Ralph: A Momentum-Resolved View of Electronic and Structural Dynamics in WSe<sub>2</sub>. (Seminar, 1. Physical Institute, Georg-August-Universität Göttingen, Göttingen, Germany, Jul 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (MPSD-Seminar, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, Jul 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (Physikalisches Kolloquium, Institute for Nuclear Physics, Johannes Gutenberg University Mainz, Mainz, Germany, Jul 2016).
- Ernstorfer, Ralph: A Momentum-Resolved View of Electronic and Structural Dynamics in WSe<sub>2</sub>. (CRC 1242 Kick-Off-Meeting, Non-Equilibrium Dynamics of Condensed Matter in the Time Domain, University of Duisburg-Essen, Bad Honnef, Germany, Nov 2016).
- Ernstorfer, Ralph: Ultrafast Electronic and Structural Dynamics on the Nanoscale. (The 32nd Annual Symposium on Chemical Physics, University of Waterloo, Waterloo, ON, Canada, Nov 2016).
- Ernstorfer, Ralph: Ultrafast Point-Projection Electron Imaging and Diffraction. (StEM Workshop at Ringberg Castle, Kreuth, Germany, Jan 2017).
- Ernstorfer, Ralph: Accessing Micro- and Mesoscopic Ultrafast Electron Dynamics in Low-Dimensional Materials. (DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Spatio-Temporal Multiscale Optical Spectroscopy Meets Functional Materials, Dresden, Germany, Mar 2017).
- Ernstorfer, Ralph: A Momentum-Resolved View on Electrons, Phonons and Their Coupling in Nanoscale Materials. (Kolloquium des Fachbereichs Physik, Freie Universität Berlin, Berlin, Germany, May 2017).

- Ernstorfer, Ralph: Momentum-Resolved View on Electrons, Phonons and Their Coupling in WSe<sub>2</sub> through Ultrafast Techniques. (Workshop on Spectroscopy and Dynamics of Photoinduced Electronic Excitations, ICTP, Trieste, Italy, May 2017).
- Ernstorfer, Ralph: Accessing Microscopic Coupling in Solids with Momentum-Resolving Ultrafast Techniques. (Laser- und Quantenoptikseminar, Technische Universität Kaiserslautern, Kaiserslautern, Germany, Jun 2017).
- Ernstorfer, Ralph: Momentum-Resolved View on Electrons, Phonons and Their Coupling in WSe<sub>2</sub>. (10th International Symposium on Ultrafast Surface Dynamics, Inzell, Germany, Jun 2017).
- Ernstorfer, Ralph: Nonthermal Structural Dynamics Probed by Momentum-Resolved Femtosecond Electron Diffraction. (ARD-ST3 Annual Workshop, DESY, Zeuthen, Germany, Jul 2017).
- Horn, Karsten: Graphene and Some of Its Interfaces – Electronic Structure. (3rd Erlangen Symposium on Synthetic Carbon Allotropes 2015, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany, Oct 2015).
- Horn, Karsten: Zehn Jahre Forschung an Graphen: ein Rück- und Ausblick. (Workshop, Graphenschichten: Abscheideverfahren und Eigenschaften, European Society of Thin Films, Dresden, Germany, Nov 2015).
- Horn, Karsten: Forschung an Graphen – ein Rück- und Ausblick. (Lecture, Leibniz-Institut für innovative Mikroelektronik, Frankfurt (Oder), Germany, Apr 2016).
- Horn, Karsten: Graphene and Its Relatives, and Their Fascinating Electronic Properties. (6th International Conference on NANOstructures and nanomaterials Self-Assembly (NANOSEA), Catania, Italy, Jul 2016).
- Kampfath, Tobias: Spintronics and Femtomagnetism with THz Radiation. (Photon Science Seminar, Paul Scherrer Institut (PSI), Villigen, Switzerland, Oct 2015).
- Kampfath, Tobias: Terahertz Spectroscopy: From Ultrafast Probing Toward Control of the Motion of Electrons, Ions and Spins. (Workshop, SFB 1073 Atomic scale control of energy conversion, Doctoral Students' Seminar in Berlin, Berlin, Germany, Oct 2015).
- Kampfath, Tobias: Terahertz Spectroscopy: From Ultrafast Probing Toward Control of the Motion of Electrons, Ions and Spins. (Physikalisches Kolloquium, Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany, Nov 2015).
- Kampfath, Tobias: Spintronics with Terahertz Radiation. (Magnetism Three-Kings-Meeting, Deutsche Physikalische Gesellschaft, Bad Honnef, Germany, Jan 2016).
- Kampfath, Tobias: Terahertz Magnetism. (TELBE Kick-Off Meeting, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, Feb 2016).
- Kampfath, Tobias: Tutorial: Terahertz Spectroscopy. (Edgar-Lüscher-Seminar, Klosters, Switzerland, Feb 2016).
- Kampfath, Tobias: Probing and Controlling Ultrafast Magnetism with Terahertz Radiation. (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Focus Symposium,

Ultrafast non-equilibrium dynamics in quantum materials, Regensburg, Germany, Mar 2016).

- Kampfrath, Tobias: Intense Terahertz Pulses: Probing the Dynamics of Electrons, Phonons and Spins. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Kampfrath, Tobias: Terahertz Spintronics. (Colloquium, Cluster of Excellence PRISMA, Johannes Gutenberg University Mainz, Mainz, Germany, Jun 2016).
- Kampfrath, Tobias: Probing and Controlling Ultrafast Magnetism with Terahertz Radiation. (International Workshop on “Terahertz Science, Nanotechnologies and Applications”, Erice, Sicily, Italy, Jul 2016).
- Kampfrath, Tobias: Ultrathin Spintronic Metallic Multilayers as Efficient Emitters of Broadband Terahertz Electromagnetic Pulses. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Kampfrath, Tobias: Novel Emitters of Terahertz Radiation Based on Spintronic and Nanophotonic Concepts. (Leading Light Symposium with Kobus Kuipers, Amsterdam, The Netherlands, Oct 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (61st Annual Conference on Magnetism and Magnetic Materials (MMM), New Orleans, LA, USA, Oct 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Seminar, 1. Physical Institute (AG Stefan Mathias), Georg-August-Universität Göttingen, Göttingen, Germany, Nov 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Physikalisches Kolloquium, Grenz- und Oberflächenphysik (AG Markus Münzenberg), Ernst Moritz Arndt Universität Greifswald, Greifswald, Germany, Dec 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Seminar, Magnetism and Spintronics (AG Mathias Weiler), Walther-Meißner-Institute for Low Temperature Research, Bavarian Academy of Sciences and Humanities, Garching, Germany, Jan 2017).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (MPSD Seminar, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, Jan 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Allgemeines Physikalisches Kolloquium, Physikalisches Institut (AG Rudolf Bratschitsch), Westfälische Wilhelms-Universität Münster, Münster, Germany, Jan 2017).
- Kampfrath, Tobias: The Thinner, the Better: Broadband Terahertz Emitters Made of Spintronic Metal Films. (German Terahertz Conference 2017, Bochum, Germany, Mar 2017).

- Kampfrath, Tobias: Ultrafast Spin Interactions Revealed with Terahertz Radiation. (DPG-Frühjahrstagung, Focus Session, Non-Equilibrium Dynamics in Light-Driven Materials: Theory Meets Experiment, Dresden, Germany, Mar 2017).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Optical Terahertz Science & Technology Conference (OTST 2017), London, UK, Apr 2017).
- Kampfrath, Tobias: Ultrafast Spincaloritronics Enables Efficient Emitters of Terahertz Radiation. (SPINCALORITRONICS VIII, Conference 2017, Regensburg, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Kolloquium der Fakultät für Physik, Physik Dünner Schichten und Nanostrukturen, Universität Bielefeld, Bielefeld, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Torque on Spins and Molecules: New Insights into Magnets and Liquids. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Physikalisches Kolloquium, Fachbereich Physik, Technische Universität Kaiserslautern, Kaiserslautern, Germany, Jul 2017).
- Kumagai, Takashi: Direct Observation of H-Bond Dynamics Using Scanning Probe Microscopy. (CRC 1073 Workshop, Berlin, Germany, Oct 2015).
- Kumagai, Takashi: Direct Observation and Control of H-Bond Dynamics Using Scanning Probe Microscopy. (Seminar, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, Nov 2015).
- Kumagai, Takashi: Direct Observation of H-Bond Dynamics Using Scanning Probe Microscopy. (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Kumagai, Takashi: Heat-/Electron-/Photo-/Force-Induced Tautomerization in a Single Molecule. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Surface and Interface Science Laboratory, RIKEN, Saitama, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Kyushu University, Fukuoka, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Institute for Molecular Science, Okazaki, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Yokohama City University, Yokohama, Japan, Jan 2017).

- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Atomic, Molecular & Optical Physics Laboratory, RIKEN, Saitama, Japan, Jan 2017).
- Kumagai, Takashi: Structure and Dynamics of Single Molecules Studied by Scanning Tunneling Microscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Ladenthin, Janina: Force-Induced Tautomerization in a Single Molecule. (Seminar, Department of Physics (AG Katharina J. Franke), Freie Universität Berlin, Berlin, Germany, Nov 2016).
- Ladenthin, Janina: Force-, Heat-, and Electron-Induced Tautomerization of Single Porphycene Molecules Investigated with SPM. (Seminar, IBM Research, Zurich Research Laboratory, Rüschlikon, Switzerland, May 2017).
- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Seminar, Department of Physics (AG Katharina J. Franke), Freie Universität Berlin, Berlin, Germany, Oct 2015).
- Mährlein, Sebastian: Lattice Induced Ultrafast Phenomena. (Zhu group seminar, Department of Chemistry (X.-Y. Zhu), Columbia University, New York, NY, USA, Oct 2016).
- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Nanooptics Seminar, CIC nanoGUNE, Donostia – San Sebastian, Spain, Feb 2017).
- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Attoscience and Ultrafast Optics group seminar, ICFO The Institute of Photonic Sciences, Castelldefels, Barcelona, Spain, Mar 2017).
- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Seminar, IBS Center for Correlated Electron Systems, Seoul National University, Seoul, South Korea, Jul 2017).
- Mährlein, Sebastian: Ultrafast Spin Dynamics Driven by Pure Phonon Excitation. (8th International Conference on Metamaterials, Photonic Crystals and Plasmonics (META 2017), Seoul, South Korea, Jul 2017).
- Melnikov, Alexey: Excitation and Propagation of Spin Currents in Fe/Au/Fe/MgO(001): Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescale. (Seminar, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany, Oct 2015).
- Melnikov, Alexey: Ultra-Short Spin Current Pulses in Metallic Multilayers: Non-Thermal Spin-Polarized Seebeck Effect and the Role of Interfaces in Fe/Au/Fe/MgO(001). (Workshop, Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans, France, Oct 2015).
- Melnikov, Alexey: Ultrashort Spin Current Pulses in Metallic Multilayers: Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescales. (Seminar, Max-Born-Institut, Berlin, Germany, Oct 2015).

- Melnikov, Alexey: Ultrafast Spintronics Roadmap: From Femtosecond Spin Current Pulses to Terahertz Non-Uniform Spin Dynamics via Nano-Confined Spin Transfer Torques. (SPIE Optics and Photonics 2016, San Diego, CA, USA, Aug 2016).
- Melnikov, Alexey: Ultrafast Spintronics Roadmap: From Femtosecond Spin Current Pulses to Terahertz Non-Uniform Spin Dynamics via Nano-Confined Spin Transfer Torques. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (Department of Physics, Kyoto University, Kyoto, Japan, Oct 2015).
- Mikhailov, Alexander S.: Design Principles of Molecular Machines. (The AIMR International Symposium 2016, Tohoku University, Sendai, Japan, Feb 2016).
- Mikhailov, Alexander S.: Design Principles of Molecular Machines. (International Symposium, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan, Mar 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (71th Annual Meeting (2016), The Physical Society of Japan, Special joint Biophysics Session, Sendai, Japan, Mar 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (Seminar, Tokyo Metropolitan University, Tokyo, Japan, Nov 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator  $\text{Ta}_2\text{NiSe}_5$ . (Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany, Apr 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator  $\text{Ta}_2\text{NiSe}_5$ . (Seminar, Department of Mathematics and Physics (AG Claudio Giannetti), Università Cattolica del Sacro Cuore, Brescia, Italy, May 2016).
- Mor, Selene: Ultrafast Electronic Band Gap Control in an Excitonic Insulator. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Paarmann, Alexander: Phonon-Driven Ultrafast Demagnetization in a Ferrimagnetic Insulator. (EMN Meeting on Ultrafast Research, Las Vegas, NV, USA, Nov 2015).
- Paarmann, Alexander: Ultrafast Demagnetization in a Ferrimagnetic Driven by Optical Phonons. (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Feb 2016).
- Paarmann, Alexander: Nonlinear Phonon Spectroscopy Using the FHI IR-FEL. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Paarmann, Alexander: Nonlinear Mid-Infrared Solid State Spectroscopy Using Free-Electron Lasers. (United States Naval Research Laboratory, Washington, DC, USA, Jun 2016).

- Paarmann, Alexander: Nonlinear Phonon Spectroscopy with Infrared Free-Electron Lasers. (Colloquium, U.S. Naval Research Laboratory, Washington, DC, USA, Jun 2016).
- Paarmann, Alexander: Novel Concepts for Narrowband THz Excitation of Large Amplitude Lattice Motions. (Workshop on an accelerator based source for nonlinear THz science @ SwissFEL, Brugg-Windisch, Switzerland, Sep 2016).
- Paarmann, Alexander: Surface Phonon Polaritons for Mid-Infrared Nonlinear Nanophotonics. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Paarmann, Alexander: Coherent Phonon Spectroscopy Using TELBE: Challenges and Opportunities. (TELBE User Meeting at the HZDR, Dresden, Germany, Feb 2017).
- Paarmann, Alexander: Second Harmonic Phonon Spectroscopy: A New Tool for Studying Phonon Polaritons. (Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany, May 2017).
- Paarmann, Alexander: Mid-Infrared Nonlinear Nanophotonics Using Surface Phonon Polaritons. (BerliNano, 4th mini workshop in Berlin on nanophysics and related nanosciences, Physical Chemistry Department of the Fritz Haber Institute, Berlin, Germany, Jun 2017).
- Paarmann, Alexander: Nonlinear Phonon Spectroscopy Using Infrared Free Electron Lasers. (FELIX Colloquium, Radboud University, Nijmegen, The Netherlands, Jun 2017).
- Paarmann, Alexander: Mid-Infrared Nonlinear Nanophotonics in Anisotropic Dielectrics Using Surface Phonon Polaritons. (8th International Conference on Metamaterials, Photonic Crystals and Plasmonics (META 2017), Seoul, South Korea, Jul 2017).
- Puppini, Michele: Excited-State Band Mapping with XUV-Based trARPES. (Workshop on Time-resolved Photoelectron Spectroscopy, Trieste, Italy, Jan 2017).
- Puppini, Michele: Excited-State Mapping with XUV-Based trARPES. (Seminar, Laboratory of Ultrafast Spectroscopy, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland, Mar 2017).
- Puppini, Michele: Excited-State Mapping with XUV-Based trARPES. (Seminar, Departement Physik, ETH Zurich, Zurich, Switzerland, Mar 2017).
- Razdolski, Ilya: Nonlinear Surface Photonics in Hybrid Magnetic Structures. (META'16, 7th International Conference on Metamaterials, Photonic Crystals and Plasmonics, Malaga, Spain, Jul 2016).
- Sajadi, Mohsen: Intermolecular Interactions in Liquids: Insight from Nonlinear THz Spectroscopy. (23rd Iranian Conference on Optics and Photonics (ICOP 2017), Tarbiat Modares University, Teheran, Iran, Jan 2017).
- Seifert, Tom: Spin Transport and Spin-Orbit Interaction at Terahertz Frequencies: Spectroscopy and Applications. (Hauptvortrag, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Ultrafast spin currents for spin-orbitronics: from metals to topological insulators, Regensburg, Germany, Mar 2016).



- Seifert, Tom: Ultrafast Spin Transport in Magnetic Thin Films Probed by Terahertz Spectroscopy. (Workshop, Spin Caloric Transport (SPP 1538), Bad Honnef, Germany, Mar 2016).
- Seifert, Tom: Efficient Metallic Spintronic Emitters of Ultrabroadband Terahertz Radiation. (EMN Meeting on Terahertz, Energy Materials Nanotechnology, San Sebastian, Spain, May 2016).
- Seifert, Tom: The Thinner, the Better: Nanometer-Thick Efficient Spintronic Emitters of Terahertz Radiation. (Kickoff mini workshop, BerliNano, Berlin, Germany, Dec 2016).
- Seifert, Tom: Terahertz Spectroscopy of Femtosecond Spins Currents in Magnetic Heterostructures. (DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Antiferromagnetic Spintronics, Dresden, Germany, Mar 2017).
- Seifert, Tom: The Thinner, the Better: Nanometer-Thick Spintronic Terahertz Emitters. (NanoOstrava 2017, Terahertz technology and nanostructures in photonics and electronics, Ostrava, Czech Republic, May 2017).
- Seifert, Tom: Spin Orbit Interaction at Terahertz Speeds: Probing and Driving Spins at Highest Frequencies. (Spin Dynamics in Nanostructures, Gordon Research Conference, Les Diablerets, Switzerland, Jul 2017).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (19. Deutsche Physikerinnentagung, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (IV. Physical Institute (AG Claus Ropers), Georg-August-Universität Göttingen, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (Institute Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria, Nov 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Colloquium, Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany, Dec 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Special Seminar, Department of Chemistry, University of California, Berkeley, CA, USA, Dec 2015).
- Stähler, Julia: Real Time Measurement of the Vertical Binding Energy during the Birth and Lifetime of a Solvated Electron. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Jan 2016).
- Stähler, Julia: Many Body Effects in Ultrafast Spectroscopy: Polarons, Excitons & Correlated Electrons. (Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany, Jan 2016).

- Stähler, Julia: Ultrafast Dynamics of Many Body Effects in Solids and at Interfaces: Polarons, Excitons & Correlated Electrons. (Prize Talk, Gaede Prize Symposium, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (Colloquium, Department of Chemistry, Technical University of Munich, Munich, Germany, Apr 2016).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (International conference, Internal Interfaces 2016, Marburg, Germany, May 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (SFB 951 Colloquium, Humboldt-Universität zu Berlin, Berlin, Germany, Jun 2016).
- Stähler, Julia: Understanding Ultrafast Exciton Dynamics in ZnO and at Its Surfaces: Potential and Hazard of Impurities. (Gruppenseminar, Institut für Experimentelle Physik II (AG Marius Grundmann), Universität Leipzig, Leipzig, Germany, Jun 2016).
- Stähler, Julia: Photoinduced Transient Band Gap Enhancement in the Excitonic Insulator Ta<sub>2</sub>NiSe<sub>5</sub>. (International conference on dynamic pathways in multidimensional landscapes, Berlin, Germany, Sep 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (Award Ceremony of the Edith Flanigen Award 2016, CRC 1109, Berlin, Germany, Oct 2016).
- Vempati, Sesha Pavan Kumar: Frontier Molecular Orbitals of CO<sub>2</sub> on ZnO Surfaces: Time-Resolved Photoelectron Spectroscopy. (Seminar, Indian Institute of Science Education and Research Mohali, Mohali, India, Feb 2017).
- Vempati, Sesha Pavan Kumar: Hybrid Systems for Optoelectronic Applications and Photoelectron Spectroscopy. (Seminar, Material Research Center, Indian Institute of Science, Bengaluru, India, Mar 2017).
- Winta, Christopher: Second Harmonic Phonon Spectroscopy. (Group Seminar, Department of Physics (AG Wolfgang Kuch), Freie Universität Berlin, Berlin, Germany, Apr 2017).
- Wolf, Martin: Ultrafast Dynamics of Exciton Formation and Charge Transfer at Hybrid Interfaces. (1st funCOS International Workshop (FOR 1878), Erlangen, Germany, Nov 2015).
- Wolf, Martin: Ultrafast Dynamics of Photo-Induced Surface Reactions. (The 1st Sino-German Young Scientist Symposium on Structures & Dynamics at Surfaces, Beijing, China, Nov 2015).
- Wolf, Martin: Ultrafast Dynamics of Photoexcited Insulators Probed by Time- and Angle-Resolved Photoemission. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).

- Wolf, Martin: Dynamics in Complex Environments. (Photoionization & Photodetachment, Gordon Research Conference, Barga, Italy, Feb 2016).
- Wolf, Martin: Challenges and Prospects of Femtosecond Time-Resolved ARPES. (International Focus Workshop, Prospects and Limitations of Electronic Structure Imaging by Angle Resolved Photoemission Spectroscopy, Dresden, Germany, Apr 2016).
- Wolf, Martin: Ultrafast Bandgap Dynamics and Insulator-to-Metal Transitions Probed by Time-Resolved ARPES. (SPIE Defense + Commercial Sensing 2016, Baltimore, MD, USA, Apr 2016).
- Wolf, Martin: Ultrafast Electron Dynamics and Solvation at Interfaces. (Nilsson Symposium, Stockholm University, Stockholm, Sweden, May 2016).
- Wolf, Martin: Ultrafast Electronic Dynamics in Surface Reactions and 2D Materials. (Allgemeines Physikalisches Kolloquium, Fachbereich Physik, Westfälische Wilhelms-Universität Münster, Münster, Germany, May 2016).
- Wolf, Martin: Ultrafast Electronic Dynamics in Quasi 2D Materials Probed by Femtosecond Time-Resolved ARPES. (Ultrafast Dynamics at the Nanoscale 2016, Okinawa, Japan, Jul 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics in Low-Dimensional Materials Probed by Time-Resolved ARPES. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics in Quasi 2D Materials Probed by Time-Resolved ARPES. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Low Energy Excitations in Light-Driven Materials. (Physikalisches Kolloquium, Fakultät für Physik und Astronomie, Julius-Maximilians-Universität Würzburg, Würzburg, Germany, Nov 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Nonlinear Optical Spectroscopy of Interfaces and Solids. (Kolloquium SFB 1083, Fachbereich Physik, Philipps-Universität Marburg, Marburg, Germany, Nov 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Insulator to Metal Transitions Probed by trARPES. (Workshop on Time-resolved Photoelectron Spectroscopy, Trieste, Italy, Jan 2017).
- Wolf, Martin: Transient Electronic Band Structure Mapping by Time-Resolved ARPES: The In/Si(111) (8x2)  $\leftrightarrow$  (4x1) Phase Transition. (Workshop, Physics at the borderline between 1D and 2D, Bad Honnef, Germany, Mar 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics and Nonlinear Optical Spectroscopy at Interfaces. (APS March Meeting 2017, New Orleans, LA, USA, Mar 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics and Structural Phase Transitions Probed by Time-Resolved ARPES. (Optics Seminar, Department of Applied Physics (Group Tony Heinz), Stanford University, Menlo Park, CA, USA, Apr 2017).

- Wolf, Martin: The Forefront of Time-Resolved Photoemission: From the Past to the Future. (10th International Symposium on Ultrafast Surface Dynamics, Inzell, Germany, Jun 2017).
- Wolf, Martin: Ultrafast Electronic Structure Changes During Photoinduced Phase Transitions: The Dynamics of the In/Si(111) (8x2)  $\leftrightarrow$  (4x1) Transition. (16th International Conference on the Formation of Semiconductor Interfaces (ICFSI-16), Hannover, Germany, Jul 2017).
- Wolf, Martin: Ultrafast Dynamics of Excited States and Light Induced Processes at Surfaces. (Plenary Session, 33rd European Conference on Surface Science (ECOSS-33), Szeged, Hungary, Aug 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics Probed by Time-Resolved ARPES. (International School and Workshop on Electronic Crystals (ECRYS-2017), Cargèse, France, Aug 2017).

## **Max Planck Research Group for Structural and Electronic Surface Dynamics**

**Head: Ralph Ernstorfer**

### **Group members**

|                    |                                                                    |
|--------------------|--------------------------------------------------------------------|
| Roman Bertoni      | <i>(Postdoc, until 12/2015)</i>                                    |
| Johannes Feldl     | <i>(Master student, until 09/2016)</i>                             |
| Faruk Krecinic     | <i>(Postdoc)</i>                                                   |
| Jannik Malter      | <i>(Bachelor student)</i>                                          |
| Melanie Müller     | <i>(PhD student, until 08/2016, Postdoc, 09/2016 – 04/2017)</i>    |
| Michele Puppin     | <i>(PhD student, until 06/2016)</i>                                |
| Dong Shuo          | <i>(Postdoc)</i>                                                   |
| Thomas Vasileiadis | <i>(PhD student)</i>                                               |
| Lutz Waldecker     | <i>(PhD student, until 09/2015, Postdoc, 10/2015 – 03/2016)</i>    |
| Patrick Xian       | <i>(Postdoc)</i>                                                   |
| Daniela Zahn       | <i>(Master student, until 05/2017, PhD student, since 07/2017)</i> |

### **Research Projects Funded from Outside Resources**

- European Research Council Consolidator Grant (ERC-CoG #482843): “FLATLAND: *Electron-lattice-spin correlations and many-body phenomena in 2D semiconductors and related heterostructures*”. Start date: 10/2016.
- 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. 2<sup>nd</sup> funding period: 01/2017-31/2020.  
Project graduate student: Christopher Nicholson.

## 1. Scientific Scope

The ground state properties of complex materials as well as the reaction pathways of photo-excited states are governed by many-body phenomena and the mutual dependence of electron, spin and lattice subsystems. Ultrafast techniques provide access to these fundamental correlations and coupling phenomena as femtosecond light pulses allow for subsystem-specific excitations and time-resolved observation of the same or another subsystem's response.

We develop and employ complementary ultrafast probes sensitive to the ultrafast response of electrons and atomic structure in nanoscale materials. Most recently, we completed the development of a high-repetition rate extreme ultraviolet (XUV) laser and demonstrated the potential of this light source for mapping the excited state structure and dynamics in the entire Brillouin zone by time- and angle-resolved photoemission spectroscopy (trARPES), see Fig. 1. Femtosecond electron diffraction (FED) reveals the level of vibrational excitation and

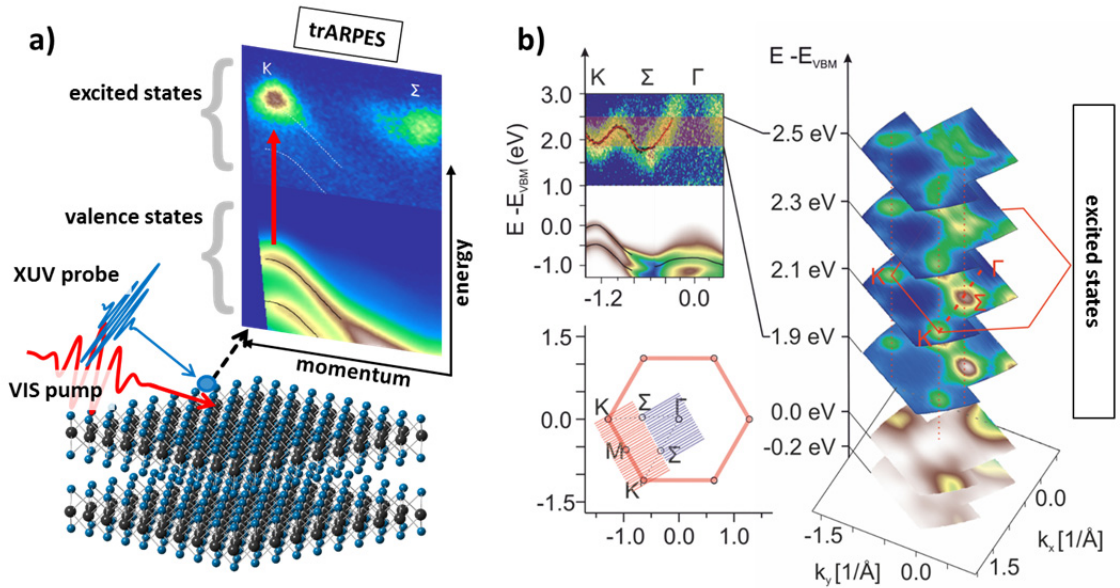


**Figure 1: Excited state spectroscopy with XUV-trARPES.** a) Principle of trARPES exemplified for excited state snapshots of WSe<sub>2</sub>. Electrons are excited with a short visible laser pulse in resonance with a vertical transition (red arrow) at the K points of the Brillouin zone. The color plot shows the distribution of excited states in energy and momentum (along a linear cut through the  $\Sigma$  and K valleys) at temporal overlap of pump and probe pulses. b) Excited state map of WSe<sub>2</sub> taken 100 fs after optical excitation with 3.1 eV photons. After this time, the excited state population has spread over an extended region of the excited state structure and are photoemitted with a 20 fs XUV with 21.7 eV photon energy. For a given sample orientation, the employed electron spectrometer detects the electronic structure above and below the band gap along a line in the Brillouin zone, see left panels. By rotation of the sample, a 3D snapshot (resolved in  $k_x$ ,  $k_y$  and energy) of the excited state distribution is obtained, see right panel. This experimental approach extends the concept of band structure mapping by ARPES to transiently populated excited states. See posters PC 3 and PC 4.

we recently demonstrated the investigation of ultrafast phonon dynamics with momentum resolution. In addition to these reciprocal space techniques, we utilize ultrashort low-energy electron wave packets for the microscopy of charge migration and 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.

## **2. Research Activities**

### **2.1 Electronic Excited State Mapping and Dynamics with XUV-Based trARPES**

Angle-resolved photoemission spectroscopy with extreme ultraviolet (XUV) and soft x-ray radiation is the key experimental method for the determination of the electronic structure of crystals and molecules. In collaboration with the *Dynamics of Correlated Materials* group headed by Laurenz Rettig, we developed a high-repetition rate femtosecond XUV laser which allows the time- and angle-resolve photoemission spectroscopy (trARPES) of excited electronic states (poster PC 3). The experimental scheme is illustrated in Fig. 1a: a femtosecond visible laser pump pulse excites a small fraction of the valence electrons to the conduction band. The distribution and evolution of the excited states in energy and momentum space is observed through subsequent photoemission with a short XUV probe pulse. Fig. 1a shows exemplary data for the layered semiconductor WSe<sub>2</sub>, optically excited by a vertical transition at the K point in the Brillouin zone (red arrow). At temporal overlap of pump and probe pulses, the excited state distribution at the K point as well as the onset of population build-up in the  $\Sigma$  valley of the conduction band is visible.

The trARPES experiments records photoemission signal resolved in four dimensions, i.e., time, energy, and both parallel momentum components. Fig. 1b shows the excited state distribution in  $E$ ,  $k_x$  and  $k_y$  at a fixed time of 100 fs after optical excitation of WSe<sub>2</sub> with 3.1 eV photons. This data set is constructed from individual two-dimensional acquisitions of the excited state spectrum along linear cuts through the irreducible part of the Brillouin zone, as illustrated on the left side of Fig. 1b. This proof-of-concept experiment demonstrates the extension of valence band structure mapping with ARPES to transient excited states (see poster PC 4). The new XUV-trARPES apparatus was additionally employed for studying ultrafast phase transitions of atomic indium wires on silicon substrates and to the charge

density wave material  $\text{TbTe}_3$ , see sections 2.1.1 and 2.1.2 in the PC report and posters PC 1 and PC 2.

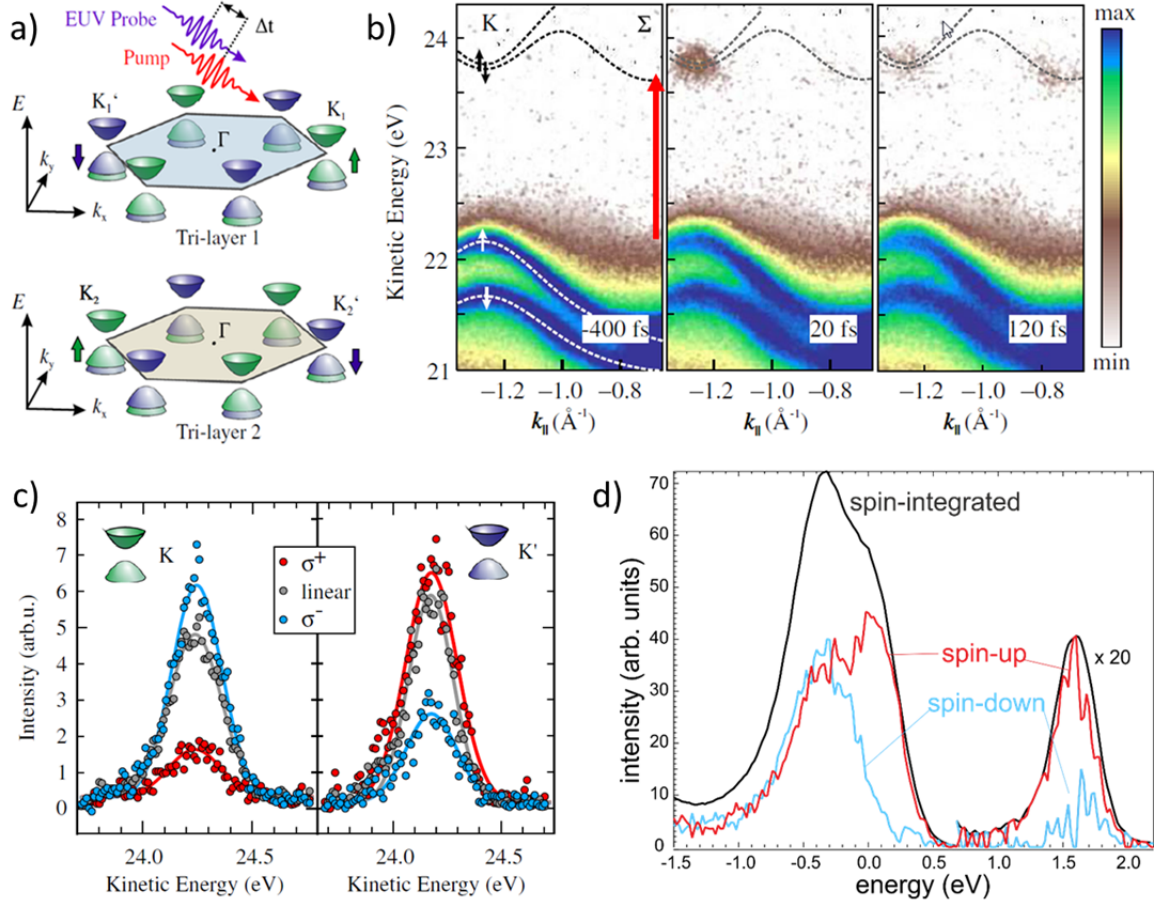


**Figure 2:** Observation of spin- and valley-polarized excited state in inversion-symmetric bulk  $\text{WSe}_2$ . a) Sketch of the electronic band structure in the  $K$  valleys. As these states have pronounced 2D character, the spin-valley correlation known from symmetry-broken TMDC monolayers [1–3] is present in each  $\text{WSe}_2$  tri-layer. Time- and angle-resolved photoemission spectroscopy (trARPES) provides access to the transient electronic structure of the topmost tri-layer. b) TrARPES maps before (left), during (middle) and 120 fs after resonant excitation at the  $K$  point (red arrow) showing the build-up of excited state population. c) The excited state signal in the  $K$  valleys shows a pronounced circular dichroism which is inverted in the  $K'$  valleys. d) Additionally, the spin-polarization of the excited states is directly evidenced by spin-resolved trARPES. Figures a)-c) adapted from [4]. See poster PC 3.

The technology enabling this type of photoemission spectroscopy is the XUV laser, which is based on a high-repetition rate, high-power optical parametric chirped pulse amplifier (OPCPA) developed in the department [5]. The near-infrared amplifier output is frequency up-converted to the 14<sup>th</sup> harmonic by sequential processes, i.e., second harmonic generation in a nonlinear crystal followed by High-Harmonic Generation (HHG) in an Ar gas jet. After spectral filtering of a single harmonic with 21.7 eV photon energy, a 0.5 MHz train of XUV pulse with a duration of 20 fs and a photon flux up to  $10^{12}$  ph/s is available at the sample. Details of this technological development are discussed on poster PC 4.



## 2.2 Spin-Polarized Excited States in Inversion-Symmetric Transition Metal Dichalcogenides

Layered semiconducting transition metal dichalcogenide (TMDC) materials like  $\text{WeSe}_2$  exhibit fascinating properties arising from many-body interactions and the resulting spin texture promises new device concepts ranging from optoelectronic to spintronic applications. The strong spin-orbit coupling in combination with the highly anisotropic bonding and the lack of inversion symmetry within individual layers of these materials result in unusual spin-valley correlation in the electronic structure [2,6]: for monolayers (ML) of these materials, the valence band at the corners of the hexagonal Brillouin zone (K and K' points) exhibits spin-split bands separated by up to 500 meV with alternating spin polarization between neighboring valleys [2]. This coupling of spin polarization and valley index allows for the optical preparation of spin- and valley-polarized excited states in monolayers [1,3,7]. In thicker TMDC samples like bi-layers, however, inversion symmetry is restored due to the 2H layer stacking. Consequently, all electronic states in these centrosymmetric materials are spin-degenerate. However, it has recently been predicted that spin-polarized states may exist in a range of materials as a consequence of atomic site asymmetry despite the global inversion-symmetry of the crystal [8]. This hidden spin texture has been experimentally observed with spin-resolved photoemission spectroscopy [9,10]. Employing trARPES with spin-selective optical excitation, we demonstrated that the spin-polarized excited state populations can be generated [4].

## 2.3 Electron-Lattice Interaction Beyond the Two-Temperature Approximation

The energy exchange between electronic and vibrational degrees of freedom in a solid is typically described in the framework of the two-temperature approximation, i.e. the assumption of Fermi-Dirac and Bose-Einstein distribution functions for electrons and phonons, respectively. We challenge this approximation and its predictive power for microscopic energy flow for several prototypical materials. By probing the phonon population dynamics with  $\sim 100$  fs resolution after impulsive excitation of the electrons with time-resolved electron diffraction [11], we quantify the electron-phonon coupling strength and compare to values obtained with first-principles calculations (J. Vorberger, Helmholtz-Zentrum Dresden-Rossendorf). Even for a simple metal like aluminium, we find that the assumption of thermal phonon distributions is insufficient as the electron-phonon energy

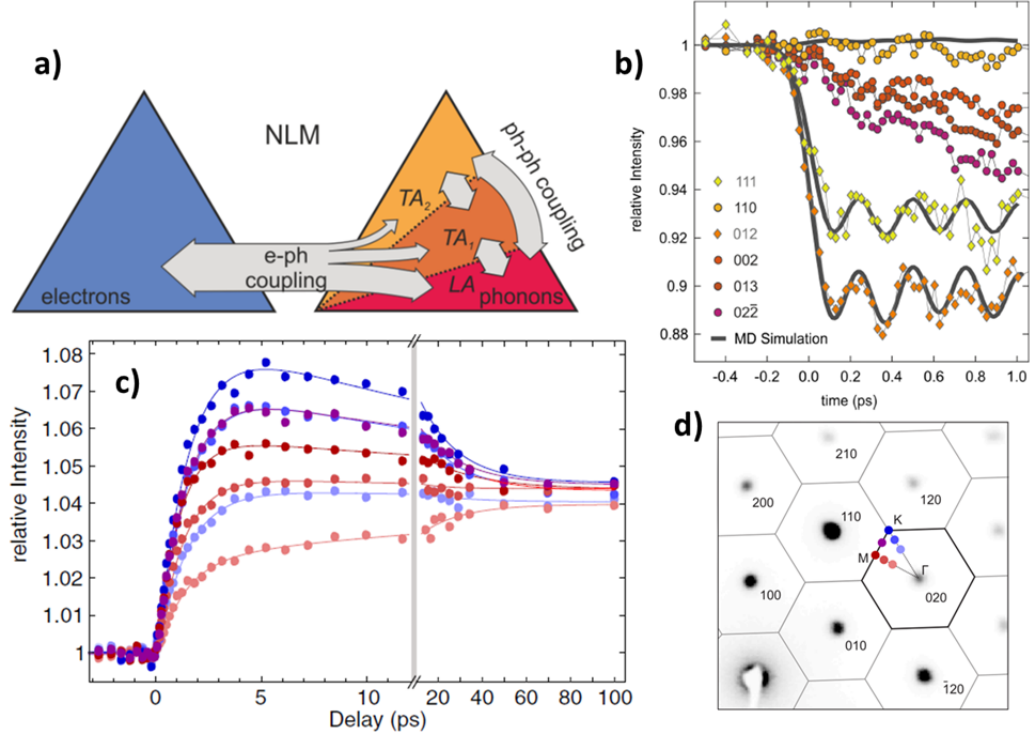


**Figure 3: Ultrafast nonthermal phonon dynamics in aluminium, antimony and WSe<sub>2</sub>.** a) Schematic depiction of the nonthermal lattice model (NLM) proposed for an accurate description of the energy exchange between electrons and phonons in Al [12]. b) Simultaneous detection of coherent optical phonon dynamics ( $A_{1g}$  mode, reflected by the 111 and 012 superlattice peaks) and incoherent phonon build-up. Again, a NLM is proposed and verified by comparison with first principle calculations [13]. c)&d) Momentum-resolved view on transient phonon populations in multilayer WSe<sub>2</sub>. The analysis of the momentum-resolved inelastic scattering signal (colored dots in d) reveals a pronounced  $q$ -dependence of the dynamics and amplitude of the phonon population shown in c). This information is compared to the momentum-resolved electron-phonon coupling strength obtained from theory [14]. See poster PC 23.

exchange rates are underestimated by a factor two [12]. This is caused by the preferential coupling of electrons to the high-energy longitudinal phonons. We proposed a nonthermal lattice model (NLM), which treats coupling to the three phonon branches individually as depicted in Fig. 3a, as a minimal model capable of a quantitative description of electron-lattice relaxation.

For the semi-metal antimony, we extract the ultrafast dynamics of coherent and incoherent phonons from a single measurement from the temporal evolution and superlattice peaks and conventional Bragg peaks, respectively, see Fig. 3b. We differential energy flow from the electron to optical and acoustic phonons, and show that the electron-phonon coupling calculated from ab initio theory (Martin Garcia, Univ. Kassel) quantitatively is in good agreement with experiment as long as an NLM is employed for data analysis [13].

A direct momentum-resolved view on nonthermal phonon distributions can be obtained from the inelastic scattering background, as demonstrated before for x-ray diffraction [15] and

MeV FED [16]. We measure the momentum-dependent phonon dynamics in multilayer WSe<sub>2</sub> induced by optical excitation of the A exciton resonance, see Fig. 3c&d and [14]. The excited electrons relax to the conduction band minimum within the  $\Sigma$  valleys. We observed a rapid build-up of phonons corresponding to the M and K points in the Brillouin zone. These phonons connect 2<sup>nd</sup>- and 3<sup>rd</sup>-next  $\Sigma$  valleys in the electronic structure. Our measurements reveal that the electron relaxation is governed by intervalley rather than intravalley scattering processes [14], in agreement with ab initio calculations (Angel Rubio and co-workers, MPSD Hamburg).

## 2.4 Nanoscale Energy Flow in Heterostructures

Recently, we extended our FED studies to nanoscale heterostructures to study energy flow across heterostructure interfaces from the phonon perspective (for details, see poster PC 25). As 2D-2D heterostructure model system, we manually stack multilayers of WS<sub>2</sub> and WSe<sub>2</sub>, see Fig. 4a&b. By tuning the photon energy of the pump pulses, the distribution of the initial electronic excitation can be controlled and the resulting structural dynamics in both materials can be extracted from the superposition diffraction pattern shown in Fig. 4b. In this semiconductor heterostructure with type-II band alignment, we find the electronic coupling to be highly efficient in spatially distribution the excitation energy.

In collaboration with the group of Richard Palmer (Swansea University), we investigate electron-phonon coupling and structural dynamics in size-selected Au<sub>923</sub> clusters and their electronic and vibrational coupling to various substrate materials, see Fig. 4c&d. We compare

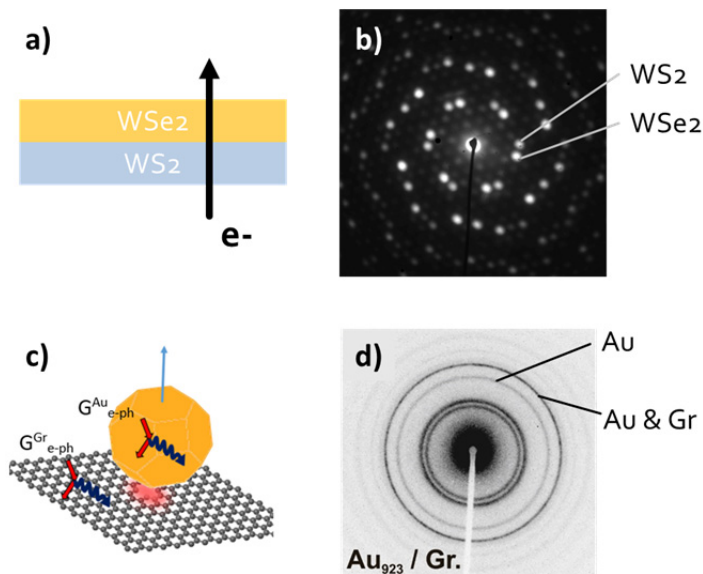


**Figure 4: Investigation of nanoscale energy flow in heterostructures with FED.** a&b) FED reveals the phonon population dynamics in the individual compounds of a 2D-2D multilayer heterostructure through the time-dependent changes of the respective sub-lattice peaks shown in b). c&d) The photo-induced lattice dynamics of size-selected Au<sub>923</sub> nanoclusters are investigated for different support films. See poster PC 25.

the same clusters on metallic, light-absorbing substrates (few-layer graphite or amorphous carbon) and on transparent silicon nitride films. The initial energy distribution as well as the resulting energy flow differ significantly for both scenarios, and we quantify the interfacial Kapitza conductance from the time-resolved data. Most importantly, we observe ultrafast surface disordering of the Au clusters induced by hot electron in the clusters. We describe this observation in terms of a modified electron friction model and discuss its potential implication for the enhanced photocatalytic activity of metal clusters [17].

## 2.5 Microscopy of Ultrafast Photocurrents in Nanoobjects: Towards Femtosecond Electron Holography

We developed femtosecond point-projection microscopy (fsPPM) as novel microscopic technique to visualize photoinduced charge migration in nanostructures, e.g., semiconductor nanowires [19]. This technique employs the emission of a single electron wave packet from metal nanotips by few fs laser pulses and visualizes time-dependent changes in the electric field distribution in the vicinity of a free-standing nanostructure. The temporal resolution is

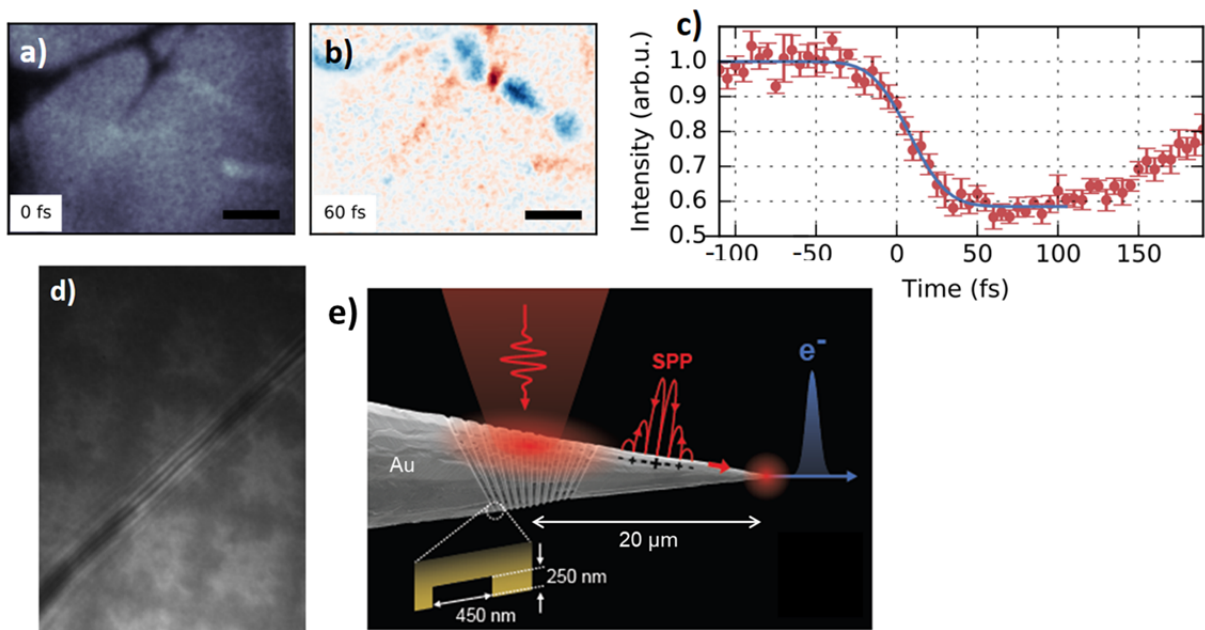


**Figure 5: Microscopy of photocurrents with femtosecond low-energy electron wave packets.** a) FsPPM image of 50 nm diameter Ag nanowires (bright) supported by a carbon mesh (black) at temporal overlap of optical pump and electron probe pulses. b) The transient space charge fields accompanying photoemission induced by the optical pulse is visible by the difference image taken at 60 fs delay and a pre-time zero image. c) The fastest temporal evolution of electron intensity shows dynamics shorter than the integral of Gaussian function with 40 fs FWHM. d) Hologram of a Ag nanowire recorded with in-line geometry. e) Illustration of non-local emission of sub-10 fs electron wave packets by propagating surface plasmon polaritons (SPP) from the apex of a gold tip [18]. See poster PC 24.

below 40 fs, as demonstrated by the measuring the space charge fields accompanying photoemission from Ag nanowires, see Fig. 5a-c. To advance this technique further in terms of spatial and temporal resolution, in collaboration with the group of Markus Raschke (Univ. of Colorado) we demonstrated the non-local photoemission of electrons from the apex induced by a surface-plasmon polariton (SPP) generated  $\sim 20\text{ }\mu\text{m}$  away by illumination of a chirped grating [18], see Fig. 5d. The SPP duration at the apex is below 8 fs, resulting in 5 fs short single-electron wave packets emitted through multiphoton emission. In the future, we intend to utilize this plasmon-triggered electron point-source to develop femtosecond low-energy in-line holography. Our experimental setup is conceptually identical to the electron holography approach developed by the Fink group at the University Zurich, which recently has been demonstrated to be capable of imaging single molecules [20] or single charges [21]. The mechanical stability of our setup has been sufficiently improved to record holograms from metal nanowires, see Fig. 5d. In the future, we intend to utilize holographic recording in time-resolved experiments.

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### **3. Current cooperation partners**

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Richard Palmer, Nanoscale Physics Research Laboratory, University of Birmingham, UK.

Valerio Pruneri, ICFO Barcelona, Spain.

Markus Raschke, Nano-Optics Group, University of Colorado, USA.

Angel Rubio and Hannes Hübener, Theory Department, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg.

Jan Vorberger, Helmholtz-Zentrum Dresden-Rossendorf, Germany.

Simon Wall, Ultrafast Optical Dynamics of Solids, ICFO Barcelona, Spain.

#### 4. Publications (August 2015 - July 2017)

*L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio, and R. Ernstorfer:* A Momentum-Resolved View on Electron-Phonon Coupling in Multilayer WSe<sub>2</sub>. *Phys. Rev. Lett.* **119**, 036803 (2017). Open access: arXiv:1703.03496.

*L. Waldecker, T. Vasileiadis, R. Bertoni, and R. Ernstorfer; T. Zier, F.H. Valencia, M.E. Garcia, and E.S. Zijlstra:* Coherent and incoherent structural dynamics in laser-excited antimony. *Phys. Rev. B* **95**, 54302 (2017). Open access: arXiv:1608.03486.

*R. Bertoni, C.W. Nicholson, L. Waldecker, H. Hübener, C. Monney, U. De Giovannini, M. Puppín, M. Hoesch, E. Springate, R.T. Chapman, C. Cacho, M. Wolf, A. Rubio, and R. Ernstorfer:* Generation and evolution of spin-, valley- and layer-polarized excited carriers in inversion-symmetric WSe<sub>2</sub>. *Phys. Rev. Lett.* **117**, 277201 (2016). Open access: arXiv:1606.03218.

*C. Monney, M. Puppín, C.W. Nicholson, M. Hoesch, R.T. Chapman, E. Springate, H. Berger, A. Magrez, C. Cacho, R. Ernstorfer, and M. Wolf:* Revealing the role of electrons and phonons in the ultrafast recovery of charge density wave correlations in 1T-TiSe<sub>2</sub>. *Phys. Rev. B* **94**, 165165 (2016). Open access: arXiv:1609.08993.

*T. Paasch-Colberg, S.Y. Kruchinin, Ö. Sağlam, S. Kapser, S. Cabrini, S. Mühlbrandt, J. Reichert, J.V. Barth, R. Ernstorfer, R. Kienberger, V.S. Yakovlev, N. Karpowicz, and A. Schiffrin:* Sub-cycle optical control of current in a semiconductor: from multiphoton to tunneling regime. *Optica* **3**, 1358 (2016).

*M. Müller, V. Kravtsov, A. Paarmann, M.B. Raschke, and R. Ernstorfer:* Nanofocused plasmon-driven sub-10 fs electron point source. *ACS Photonics* **3**, 611 (2016). Open access: arXiv:1512.07037.

*L. Waldecker, R. Bertoni, and R. Ernstorfer; J. Vorberger:* Electron-Phonon Coupling and Energy Flow in a Simple Metal beyond the Two-Temperature Approximation. *Phys. Rev. X* **6**, 021003 (2016).

*L. Waldecker, T.A. Miller, M. Rude, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer, and S. Wall:* Decoupled optical response and structural transition in phase change materials. *Nature Materials* **14**, 991 (2015). Open access: arXiv:1412.0901.

### **Doctoral Thesis**

*M. Puppin*: Time- and angle-resolved photoemission spectroscopy on bidimensional semiconductors with a 500 kHz extreme ultraviolet light source. FU Berlin, 2017.

*M. Müller*: Femtosecond low-energy electron imaging and diffraction using nanotip photoemitters. FU Berlin, 2016.

*L. Waldecker*: Electron-lattice interactions and ultrafast structural dynamics of solids. FU Berlin, 2015.

### **Master's Thesis**

*D. Zahn*: Structural dynamics of transition metal dichalcogenide heterostructures studied by ultrafast high-energy electron diffraction, FU Berlin, 2017.

*J. Feldl*: A 500 kHz high harmonics generation XUV light source for photoelectron spectroscopy, LMU München, 2016.

### **Bachelor Thesis**

*J. Malter*: Characterization of a nanotip electron source for femtosecond point-projection microscopy, FU Berlin, 2017.



## 5. Invited Talks (August 2015 - July 2017)

- Ernstorfer, R.: *Nonthermal structural dynamics probed by momentum-resolved femtosecond electron diffraction*, ARD WORKSHOP, DESY, Zeuthen, Germany, July 2017.
- Ernstorfer, R.: Accessing microscopic coupling in solids with momentum-resolving ultrafast techniques, Quantum Optics Seminar, University Kaiserslautern, Germany, June 2017.
- Ernstorfer, R.: Momentum-Resolved View on Electrons, Phonons and Their Coupling in WSe<sub>2</sub>. Talk presented at the Ultrafast Surface Dynamics 10, Inzell, Germany, June 2017.
- Ernstorfer, R.: Momentum-Resolved View on Electrons, Phonons and Their Coupling in WSe<sub>2</sub> Through Ultrafast Techniques. Talk presented at the Workshop on Spectroscopy and Dynamics of Photoinduced Electronic Excitations, ICTP, Trieste, Italy, May 2017.
- Ernstorfer, R.: A Momentum-Resolved View on Electrons, Phonons and Their Coupling in Nanoscale Materials. Kolloquium des Fachbereichs Physik, Freie Universität Berlin, Berlin, Germany, May 2017.
- Ernstorfer, R.: Accessing micro- and mesoscopic ultrafast electron dynamics in low-dimensional materials. Topical Talk presented at the DPG Spring Meeting 2017, Dresden, March 2017.
- Ernstorfer, R.: Ultrafast point-projection electron imaging and diffraction. Talk presented at the StEm Workshop 2017, Ringberg Castle, Jan 2017.
- Ernstorfer, R.: Ultrafast Electronic and Structural Dynamics on the Nanoscale. Lecture at the 32nd Annual Symposium on Chemical Physics, University of Waterloo, Waterloo, ON, Canada, Nov 2016.
- Ernstorfer, R.: A Momentum-Resolved View of Electronic and Structural Dynamics in WSe<sub>2</sub>. Talk presented at the CRC 1242 Kick-Off-Meeting, Non-Equilibrium Dynamics of Condensed Matter in the Time Domain, University of Duisburg-Essen, Bad Honnef, Germany, Nov 2016.
- Ernstorfer, R.: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. MPSD-Seminar, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany, Jul 2016.
- Ernstorfer, R.: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. Physikalisches Kolloquium, Institut für Kernphysik, Johannes Gutenberg Universität, Mainz, Germany, Jul 2016.
- Ernstorfer, R.: A Momentum-Resolved View of Electronic and Structural Dynamics in WSe<sub>2</sub>. Seminar at the I. Physical Institute, Georg-August-Universität Göttingen, Göttingen, Germany, Jul 2016.
- Ernstorfer, R.: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. Talk presented at the Physics Colloquium of the University of Graz and the Graz University of Technology. Graz, Austria. 2016-06-21.

- Ernstorfer, R.: *Dynamics of Electrons, Spins and Phonons in Transition Metal Dichalcogenides*. Talk presented at 1<sup>st</sup> WP2-Domain Workshop on Beyond CMOS, NEREID (NanoElectronics Roadmap for Europe: Identification and Dissemination). Espoo, Finland. 2016-05-16 - 2016-05-17.
- Ernstorfer, R.: *Accessing Electronic and Structural Dynamics with Time-resolved Electron Diffraction and High Repetition Rate XUV-trARPES*. Talk presented at Kolloquium, Helmholtz-Zentrum Dresden-Rossendorf. Dresden, Germany. 2016-03-17.
- Ernstorfer, R.: *Spin- and Pseudospin-Polarized Excited States in Bulk WSe<sub>2</sub>*. Hauptvortrag presented at DPG-Frühjahrstagung. Regensburg, Germany. 2016-03-06 - 2016-03-12.
- Ernstorfer, R.: *Electronic and Structural Dynamics in Solids: from Electron-phonon Coupling to Spin- and Pseudospin-polarized Excited States*. Talk presented at Physical Seminar, Department of Chemistry, University of Rochester. Rochester, NY, USA. 2016-02-22.
- Ernstorfer, R.: *Femtosecond Electrons Probing Ultrafast Phenomena in Nanostructures by Diffraction and Imaging*. Talk presented at SPIE Photonics West - OPTO: Ultrafast Phenomena and Nanophotonics XX. San Francisco, CA, USA. 2016-02-18.
- Ernstorfer, R.: *Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides*. Talk presented at SIMES Seminar, Stanford Institute for Materials & Energy Sciences, SLAC, Stanford University. Stanford, CA, USA. 2016-02-16.
- Ernstorfer, R.: *Electronic and Structural Dynamics in Solids: from Electron-phonon Coupling to Spin- and Pseudospin-polarized Excited States*. Talk presented at Seminar, ICFO The Institute of Photonic Sciences. Castelldefels (Barcelona), Spain. 2016-02-04.
- Ernstorfer, R.: *Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides*. Talk presented at Physikalisches Kolloquium, Christian-Albrechts-Universität zu Kiel. Kiel, Germany. 2016-02-02.
- Ernstorfer, R.: *Accessing Electron-Phonon Interaction with Time-resolved Diffraction and XUV-based trARPES*. Talk presented at Seminar, Philipps-Universität. Marburg, Germany. 2016-01-22.
- Ernstorfer, R.: *Structural and Electronic Dynamics in Transition Metal Dichalcogenides: Accessing Coupling and Correlation Effect by Time-resolved Techniques*. Talk presented at BESSY II - THz to Soft X-ray Workshop, Helmholtz-Zentrum Berlin. Berlin, Germany. 2015-12-07 - 2015-12-08.
- Ernstorfer, R.: *Photocurrents and Structural Dynamics in Nanomaterials Probed by Femtosecond Electron Pulses*. Talk presented at 4th International Workshop on Ultrafast Nanooptics (UNO-4). Bad Dürkheim, Germany. 2015-10-18 - 2015-10-22.
- Ernstorfer, R.: *Development of a 500 kHz XUV Source Based on an OPCPA*. Talk presented at Seminar, Rutherford Appleton Laboratory. Didcot, UK. 2015-10-02.
- Ernstorfer, R.: *Investigating Correlation and Coupling Phenomena in Solids with Ultrafast Diffraction and Photoelectron Spectroscopy: Which Physical Quantities Can we*

Access? Talk presented at the Workshop of the Institut für Quantumoptik (IQO), Leibniz Universität Hannover. Hannover, Germany. 2015-09-11.

- Puppín, M: *Excited-state mapping with XUV-based trARPES*. Seminar at École polytechnique fédérale de Lausanne, March 2017
- Puppín, M: *Excited-state mapping with XUV-based trARPES*. Seminar at Physics Department, Zurich University, March 2017
- Waldecker, L.: *Femtosecond Electrons Probing Ultrafast Structural Dynamics of Solids*. Talk presented at the LAP Seminar, Max-Planck-Institut für Quantenoptik. Garching, Germany. Jul 2015
- Waldecker, L.: Elektron-Gitter Wechselwirkungen und ultra-schnelle Struktur­dynamik in Festkörpern. Carl-Ramsauer Prize talk, University of Potsdam, Germany. Nov 2016

**Max Planck Research Group for Electron Dynamics:  
Transient Functionality at Interfaces**

**Head: Julia Stähler**

*(maternity leave: 11/2016-08/2017)*

**Group members**

**Current:**

|                        |                                   |
|------------------------|-----------------------------------|
| Stefano Calati         | <i>(PhD student)</i>              |
| Angelika Demling       | <i>(PhD student)</i>              |
| Lukas Gierster         | <i>(PhD student)</i>              |
| Sarah B. King          | <i>(Postdoc, Humboldt Fellow)</i> |
| Selene Mor             | <i>(PhD student)</i>              |
| Boubacar Tanda Bonkano | <i>(PhD student)</i>              |
| Sesha Vempati          | <i>(Postdoc)</i>                  |

**Former:**

|                       |                                              |
|-----------------------|----------------------------------------------|
| Katharina Broch       | <i>(Postdoc, until 12/2016)</i>              |
| Lea Bogner            | <i>(PhD student, until 12/2015)</i>          |
| Jan-Christoph Deinert | <i>(PhD student, until 01/2016)</i>          |
| Laura Foglia          | <i>(PhD student, until 12/2015)</i>          |
| Marc Herzog           | <i>(Postdoc, until 01/2016)</i>              |
| Ines Mayan            | <i>(Bachelor student, until 12/2015)</i>     |
| Clemens Richter       | <i>(scientific assistant, until 01/2016)</i> |

**Research Projects Funded from Outside Resources**

- DFG 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***” (photoinduced electron transfer, two-photon photoemission spectroscopy of electronic states, from 07/2015).

## 1. Scientific Scope

The current technological progress in seemingly different fields (e.g. light harvesting, optoelectronics, data processing, energy storage, catalysis...) relies on non-equilibrium phenomena that occur at the interfaces of different materials and on electronic time and energy scales, i.e. femtoseconds (fs) and electronvolts (eV). Examples span from ultrafast charge transfer processes initiating chemical reactions at electrochemical interfaces to quasiparticle interactions in strongly correlated systems triggering, for instance, insulator-to-metal phase transitions.

The group aims at the next step towards exploitation of ultrafast science beyond the research on non-equilibrium dynamics of matter by *utilizing* the transient properties of photoexcited systems. While the established methods for the investigation of non-equilibrium dynamics provide valuable insight into the excited state properties of matter, this new approach will *make use* of these properties to manipulate the functionality of materials and material combinations on the ultrafast timescale.

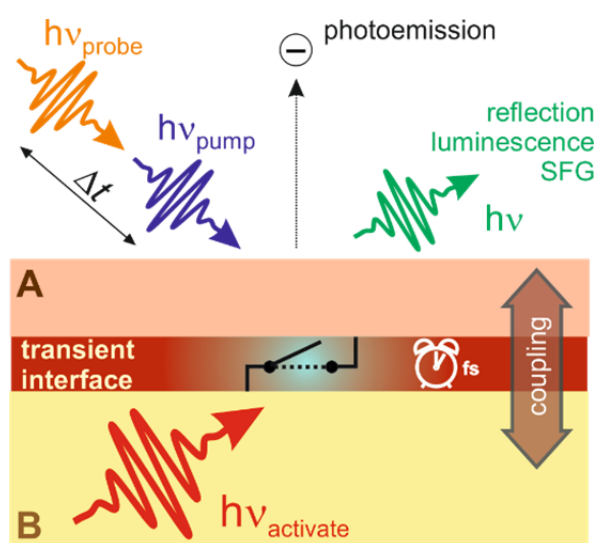


**Figure 1: Concept of transient functionality at interfaces (TRAFIC).** The functionality of the interface between material A and B is modified by an activation pulse  $h\nu_{\text{activate}}$ . The time-dependent properties of this transient interface are monitored by a complementary set of femtosecond time-resolved spectroscopies.

“Conventional” ultrafast spectroscopy is often performed in a pump-probe scheme, where a first laser pulse ( $h\nu_{\text{pump}}$ ) is used to bring the sample into non-equilibrium conditions and a second, time-delayed pulse ( $h\nu_{\text{probe}}$ ) to probe the transient properties of the system by, for instance, photoelectron, linear or non-linear optical spectroscopy (Figure 1, top). We plan to use an additional, third laser pulse ( $h\nu_{\text{activate}}$ ) in order to modify the properties and, thus, the functionality of the interface on an ultrafast timescales. This transient functionality at interfaces (TRAFIC) will be achieved in multiple ways: (i) modification of charge/exciton

density, (ii) chemical activation of adsorbed molecules, (iii) time-dependent changes of the electronic structure.

Since the last Fachbeirat evaluation, we have extended our complementary set of “conventional” state-of-the-art ultrafast spectroscopies. It now comprises: time- and angle-resolved (two-photon) photoelectron spectroscopy (tr-ARPES / tr- & ar-2PPE), transient reflection/transmission and time-resolved electronic sum frequency generation (tr-eSFG) based on a white light supercontinuum (WLC), time-resolved photoluminescence (tr-PL, single photon counting & optical down conversion) enabling the investigation of bulk materials, surfaces, and interfaces under ultrahigh vacuum to ambient conditions. It should be noted that we succeeded in setting up the first fs-time-resolved eSFG setup based on a WLC that is *applicable to solid state samples*. [1] These techniques were used to explore several different model systems ranging from electrochemical interfaces to strongly correlated low-dimensional materials as outlined in the following. These research highlights set the stage for TRAFIC once the third, strong activation laser pulse ( $h\nu_{\text{activate}}$ ) can be added. A new powerful laser system with tunable repetition rate was installed in May 2017, but still requires further service to achieve its specifications.

## **2. Development of the Group**

The Electron Dynamix Group has undergone several important changes in the last two years. Firstly, three PhD students and one long-standing postdoc left the group around the turn of the year 2015/16 and could only be replaced in late 2016 after an intensive search and interview time for suitable candidates. Secondly, Julia Stähler’s maternity leave unexpectedly started one month earlier than specified by law (health condition) in November 2016 and ended as planned in August 2017. Lastly, the move of the laboratory to the new building in spring 2016 extended the experimental space for the group, but also, naturally, interrupted experiments. Although generally efficient and successful, the new lab is still in its infancy (e.g. water leakage, unexpected power shut-downs). The above challenges were faced and conquered with pragmatic, optimistic, and diligent attitude by all group members: The new PhD students have learned the ropes, the experiments mostly are up and running. As soon as child care is available, Julia Stähler will be able to return to a full time schedule.

### 3. Research Activities

#### 3.1 Interfacial Electron Dynamics in Polar Solvents

Excess electrons in polar solvent environments play a crucial role in various different fields in physics, chemistry, and biology. Through the interaction with the molecular dipole moment, polaronic states form, in which the electron is stabilized (solvated) in a molecular cavity. In the vicinity of a metal surface, such states are particularly relevant for electrochemical reactions. We use tr- & ar-2PPE to investigate the formation, lifetime, and decay of solvated electrons and especially focus on their reactivity. In these experiments, as illustrated in figure 2(A), a first femtosecond (fs) laser pulse ( $h\nu_{\text{pump}}$ ) injects excess electrons from the metal and the second, time-delayed laser pulse ( $h\nu_{\text{probe}}$ ) is used to photoionize the sample. The ejected photoelectrons are then analyzed with regard to their kinetic energy and momentum parallel to the surface and, thus, provide information about the transient population and degree of localization of normally unoccupied states. One example of the multifaceted dynamics occurs in DMSO layers adsorbed on Cu(111) (figure 2(B)). Very similar to previous studies on amorphous solid water (ASW), alcohol, and ammonia layers on various metal surfaces [2-12], the excess electrons initially populate a delocalized state and increasingly localize with time, as indicated by the flattening dispersion depicted in the bottom panel. At the same time, the electronic state  $e_s$  shifts down to lower energies due to the rearrangement of the surrounding polar molecules. We find the evolution of this interfacial electronic state to be localized within the first two monolayers of DMSO and, moreover, show that it persists for even larger coverages. [13]

Recently, we could show that a long-lived state with a lifetime of several seconds exists at the vacuum interface of ASW. As illustrated in figure 2(C), the enormous lifetime of these trapped electrons even enables water splitting: under illumination with UV light, the signature of the trapped electrons  $e_T$  vanishes in a similar fashion as the work function  $\Phi$  rises (bottom panel), indicating that an anionic species is formed that suppresses further electron trapping at the interface. The unusually long excited state lifetime in combination with the large binding energy gain upon electron trapping enables the *dielectron hydrogen evolution reaction*, which exhibits large activation barriers. [12] In very recent experiments, we were able to observe a similarly long-lived state at the DMSO/vacuum interface that shows clear indications of chemical reactivity with molecular oxygen. [14]

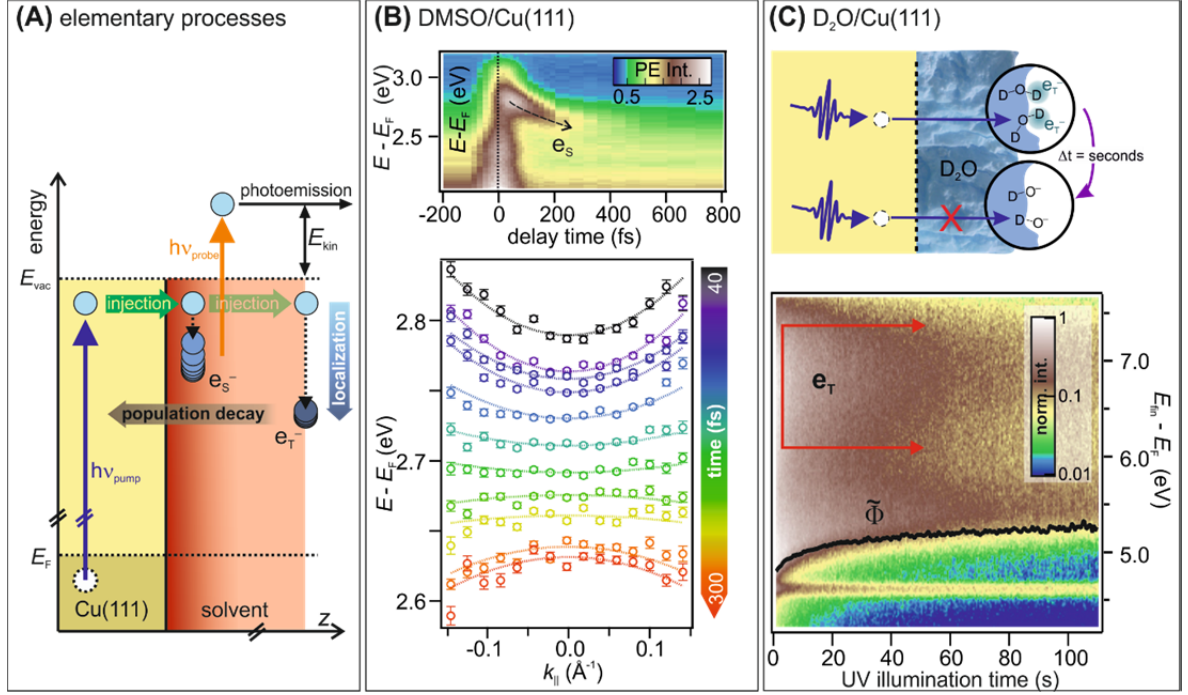


**Figure 2: Electron solvation, decay, and reactivity near solvent/metal interfaces.** (A) Experimental scheme for *tr*-2PPE and elementary processes:  $h\nu_{\text{pump}}$  optically excites the metal and thereby injects electrons into the solvent layers. Two different types of electronic states are formed: Near the metal, the excess electron population decays on femtosecond timescales while it survives 14 orders of magnitudes longer at the vacuum interface. The dynamics are probed by a second laser pulse after an adjustable time delay: The transient electron population is excited above the vacuum level and detected using a hemispherical electron analyzer. (B) Ultrafast polaron formation near the DMSO/Cu(111) interface probed by 2PPE: Intensity in false colors as a function of time and intermediate state energy with respect to the Fermi level  $E_F$  (top). Angle-resolved measurements show the time-dependent change of the dispersion, indicating increasing electron localization (bottom). (C) Long-lived electrons at the ice-vacuum interface react with  $D_2O$  to form  $OD^-$  (top), a reaction that causes a work function rise and reduction of  $e_T^-$  intensity as a function of UV exposure (bottom).

### 3.2 Ultrafast Charge Transfer-Induced $CO_2$ Activation on ZnO(10-10)

The man-made excess of  $CO_2$  in the atmosphere is undoubtedly one important cause of global warming. Unfortunately,  $CO_2$  also is energetically very stable and needs to be activated before it can be chemically transformed to, for instance, useful hydrocarbons (solar fuels). Catalytic surfaces can help to enhance reaction rates. On ZnO(10-10),  $CO_2$  adsorbs in a tridentate (figure 3B) form [15] and both activated and non-activated species are observed. [16] We find a substantial work function increase of 1.2 eV for the full  $CO_2$  monolayer up to 5.7 eV, which can be explained by its partial reduction upon adsorption and the corresponding dipole moment. This charge redistribution at the surface leads to surface band bending, causing surface photovoltage (SPV) effects when the sample is optically excited as illustrated in figure 3A.



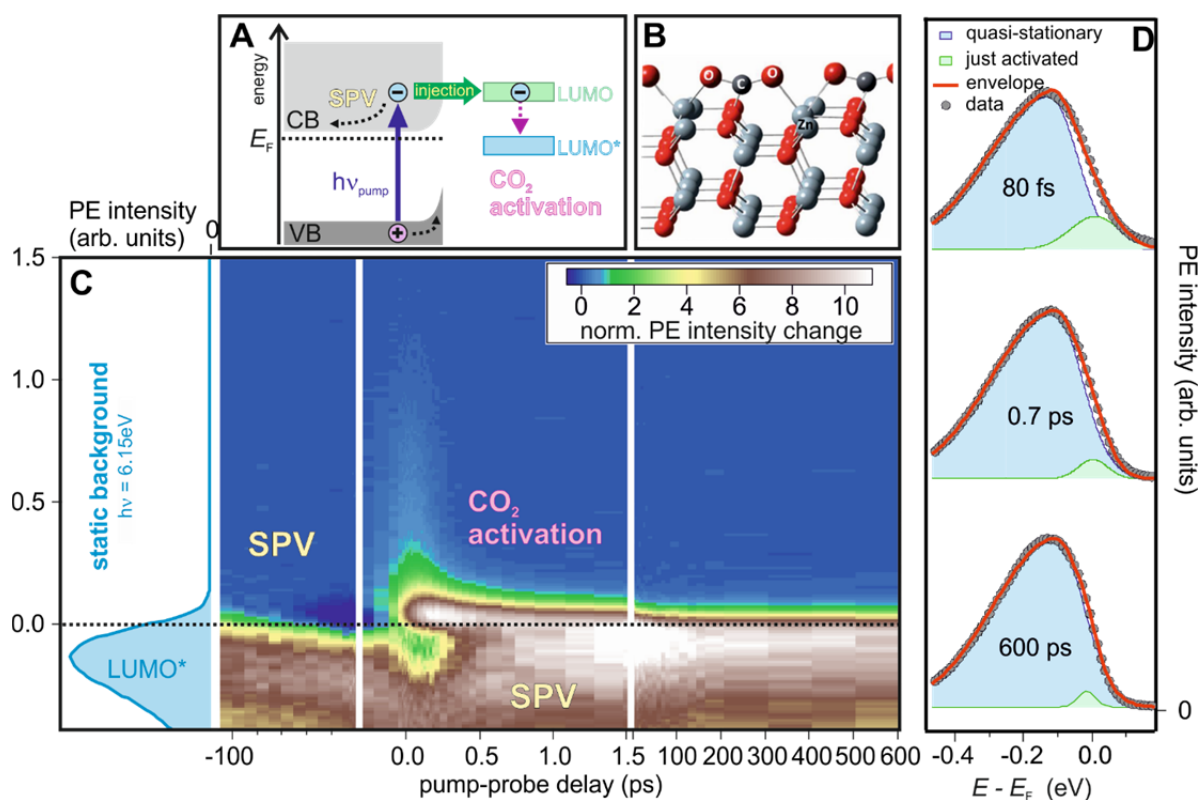


**Figure 3: Ultrafast dynamics at the  $\text{CO}_2/\text{ZnO}(10\text{-}10)$  interface.** (A) Across band gap excitation causes surface photovoltage and  $\text{CO}_2$  activation dynamics. (B) Adsorption motif modified from [15] (C) Photoinduced changes to the static (left) photoelectron spectra. The  $\text{CO}_2$  activation is evidenced by the transient electron population above  $E_F$ , shifting downwards within 1.4 ps. (D) Data analysis: The asymmetric Gaussian signature of activated  $\text{CO}_2$  molecules (blue) shifts in energy due to surface photovoltage effects. The transiently populated LUMO of newly activated molecules (green) lies at higher energies and relaxes as time proceeds.

Static photoemission (figure 3C, left) shows a (partially) occupied state just below the Fermi energy  $E_F$ , which we assign to the formally LUMO of the gas phase molecules, termed  $\text{LUMO}^*$  for the activated, adsorbed species. The false color plots in figure 3C show the photoinduced change of photoelectron intensity after subtraction of the static background as a function of pump-probe time delay. The dynamics can be explained by (i) a shifting of  $\text{LUMO}^*$  at positive and negative delays due to SPV similar to what has been recently observed for GaAs(110) [17] and (ii) a transient population of the LUMO of non-activated  $\text{CO}_2$  molecules as illustrated in figure 3A. Data analysis (figure 3D) yields a charge transfer-induced activation time of 1.4(2) ps. [18] This work, which was initiated through a collaboration with Elias Frei and Robert Schlögl from the AC department, thus demonstrates the possibility of  $\text{CO}_2$  activation through photoinduced charge transfer to the molecules at a catalyst surface. This is the proof-of-principle of monitoring photo-electrochemical reactions in real time.

### 3.3 Charge Carrier & Exciton Dynamics in ZnO

Beyond catalysis, ZnO is also a very promising material in the field of optoelectronics, in particular in combination with organic materials to form inorganic/organic hybrid systems. Unfortunately, ZnO also is a remarkably difficult material, which is highlighted by decades of research and partially conflicting results not only with regard to ultrafast dynamics (see, e.g. [19-21]). In order to achieve a complementary understanding, the group used the entire canon of experimental techniques to investigate a defined set of ZnO samples to ensure comparability of the results. We started with a thorough analysis of the electron and exciton dynamics at the ZnO(10-10) and ZnO(000-1) surfaces [22-25] in previous work using tr-ARPES and 2PPE, showing that these expose subsurface-bound excitons that form within 20-40 fs and decay in 100 ps. This report, however, highlights the most recent results on the carrier and exciton dynamics in bulk ZnO. [26]

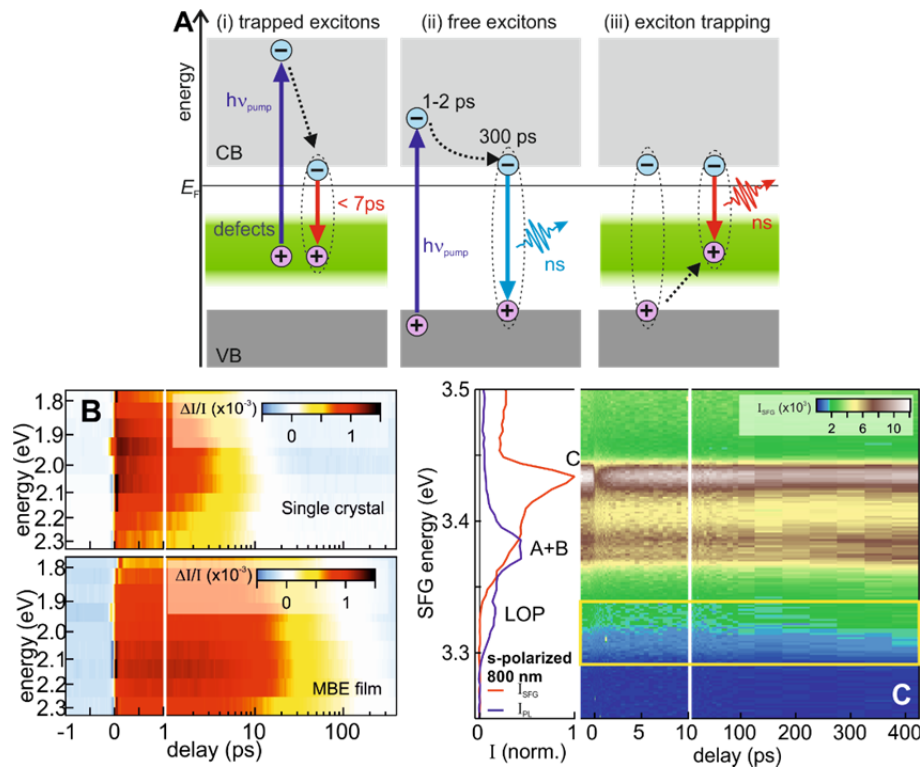


**Figure 4: Exciton dynamics in bulk ZnO.** (A) Illustration of the observed elementary processes: (i) Photoexcitation from in-gap defect states is followed by recombination within only 7 ps. (ii) Across band gap excitation is followed by carrier cooling and exciton formation within 300 ps. (iii) Free excitons with ns lifetimes are trapped at defect sites, leading to ns defect emission despite the 7 ps recombination rate. (B) Transient transmission using a WLC clearly shows faster dynamics in the single crystal sample compared to the MBE (molecular beam epitaxy) film with lower defect density. (C) tr-eSFG displays fast dynamics near the band edge due to carrier relaxation. The slow component (yellow box) reflects the formation dynamics of the free exciton.

By femtosecond time-resolved transmission experiments using a WLC (figure 4B), we found that the optical response is dominated by depletion of the in-gap defect band as illustrated in figure 4A(i), which decays within 7 ps after photoexcitation. Interestingly, and seemingly in

contrast, the corresponding (defect) light emission continues for nanoseconds as evidenced by tr-PL (not shown). In addition to these defect-related dynamics, across band gap excitation was observed, yielding hot carrier relaxation times at the band edges on the order of a few ps (figure 4A(ii)). These results were confirmed by tr-eSFG, which is bulk-sensitive in non-centrosymmetric ZnO (figure 4C). Beyond the good agreement between linear and non-linear optical spectroscopy, the eSFG experiments furthermore show, in agreement with previous work, [27] that the bulk exciton forms within 300 ps. Its nanosecond lifetime is reflected in complementary time-resolved photoluminescence<sup>1</sup> experiments, strongly suggesting that free excitons are trapped at defect sites as illustrated in figure 4A(iii) and explaining the apparent discrepancy between optical and PL time constants. This first comprehensive study of the ultrafast carrier and exciton dynamics in ZnO, and at its surfaces, provides unprecedented insight into the elementary processes occurring upon photoexcitation of this material and demonstrate the severe impact of defects on the lifetimes and relaxation pathways. [26]

### 3.4 Ultrafast Phenomena in Layered Materials

The technological relevance of low-dimensional materials was evident already before the ascent of graphene. The miniaturization and optimization of layered functional elements (solar cells, transistors, LEDs etc.) requires advanced control and understanding of the involved materials. As any functionality involves non-equilibrium quasiparticle dynamics, ultrafast spectroscopy is a perfect tool to achieve these goals.

Ta<sub>2</sub>NiSe<sub>5</sub> is a layered, orthorhombic, quasi-1D small band gap semiconductor (Figure 5A) that undergoes a transition to a monoclinic phase upon cooling across  $T_C = 328$  K. The low temperature phase is, moreover, characterized by a wider band gap, which is why the transition is termed semiconductor-to-insulator transition. Due to the low dielectric constant of Ta<sub>2</sub>NiSe<sub>5</sub> and the anomalous flattening and broadening of the valence band (VB), the low temperature phase of Ta<sub>2</sub>NiSe<sub>5</sub> is suspected to be an excitonic insulating phase. [28-32] In an excitonic insulator the exciton binding energy  $E_B$  exceeds the gap size  $E_G$  such that spontaneous exciton formation occurs, followed by exciton (boson) condensation, leading to a wider band gap  $E_G + 2\Delta$  (figure 5B).

We investigated the transient changes to the electronic band structure and the ultrafast electron dynamics in Ta<sub>2</sub>NiSe<sub>5</sub> using tr-ARPES in different parts of the surface Brioullin zone. As shown in figure 5D, photoexcitation below the critical fluence  $F_C = 0.2$  mJ/cm<sup>2</sup> leads

to a depletion and shifting of the

<sup>1</sup> In cooperation with Sylke Blumstengel, Humboldt University Berlin.

VBs towards  $E_F$ , i.e. a shrinking of the band gap. This band gap renormalization is a common effect in semiconductors and is due to the photoinduced change of the screening of the Coulomb interaction. However, upon crossing the threshold fluence, we observe a band gap *widening* through a downward shift of the topmost VB at  $\Gamma$  (red, figure 5D), while the other bands continue to shift upwards (green, yellow). This exotic behavior can be explained by the excitonic insulating phase through Hartree-Fock calculations<sup>2</sup> and demonstrates the possibility to control the band gap of materials on the ultrafast timescale. [33]

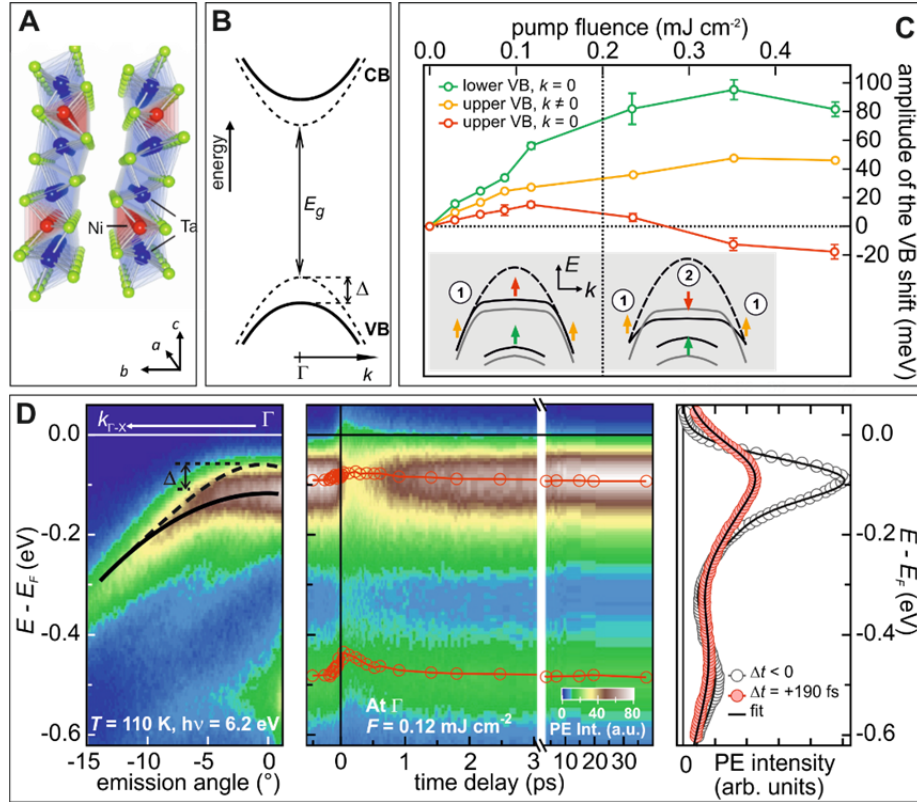


**Figure 5: Ultrafast electronic band gap control in Ta<sub>2</sub>NiSe<sub>5</sub>.** (A) Material crystal [28] and (B) electronic structure. (C) Fluence dependence of VB shifts. Upper valence band region of Ta<sub>2</sub>NiSe<sub>5</sub> at low temperature as observed by ARPES (left), pump-induced dynamics at  $\Gamma$  for below threshold excitation (center), photoelectron spectra before and after excitation (right).

Complementary to strongly correlated, low-dimensional materials such as Ta<sub>2</sub>NiSe<sub>5</sub>, thin, insulating oxide films are useful to electronically decouple materials from each other or to chemically protect electrodes. The group has, therefore, started to investigate the SiO<sub>2</sub> bilayer in collaboration with Hajo Freund and Thomas Schmidt's group in the CP department. The silica bilayer is found to form a specific, chemically inert structure when grown on Ru(0001) [34-36] and UPS experiments at SMART [37] already gave insights into the occupied

<sup>2</sup> In cooperation with Martin Eckstein (Univ. Erlangen-Nürnberg), Denis Golež and Philipp Werner (Univ. Fribourg).

electronic structure. In order to elucidate the properties of the (unoccupied) conduction band and the interplay with the significant image potential of the metal substrate, we use time- and angle-resolved 2PPE. As expected, we find quantum well-like states in the region of the SiO<sub>2</sub> conduction band with energy separations, lifetimes, and dispersions that clearly suggest a strong impact of the image potential. In forthcoming work, we will test in how far these states can serve as a mediator between adsorbed species and the Ru(0001) in terms of electronic coupling.

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#### **4. Current cooperation partners**

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## 5. Publications (August 2015 – August 2017)

*Foglia, L., L. Bogner, M. Wolf and J. Stähler:* Localization-dependent charge separation efficiency at an organic/inorganic hybrid interface. *Chemical Physics Letters* **646**, 25–30 (2016).

*Foglia, L., M. Wolf and J. Stähler:* Ultrafast dynamics in solids probed by femtosecond time-resolved broadband electronic sum frequency generation. *Applied Physics Letters* **109** (20), 202106 (2016).

*King, S.B., D. Wegkamp, C. Richter, M. Wolf and J. Stähler:* Trapped Electrons at the Amorphous Solid Water/Vacuum Interface as Possible Reactants in a Water Splitting Reaction. *The Journal of Physical Chemistry C* **121** (13), 7379–7386 (2017).

*Stähler, J. and P. Rinke:* Global and local aspects of the surface potential landscape for energy level alignment at organic-ZnO interfaces. *Chemical Physics* **485-486**, 149–165 (2017).

*Mor, S., M. Herzog, D. Golež, P. Werner, M. Eckstein, N. Katayama, M. Nohara, H. Takagi, T. Mizokawa, C. Monney, and J. Stähler:* Ultrafast electronic band gap control in an excitonic insulator. *Physical Review Letters* **119** (8), 086401 (2017).

*Wegkamp, D. and J. Stähler:* Ultrafast dynamics during the photoinduced phase transition in VO<sub>2</sub>. *Progress in Surface Science* **90** (4), 464–502 (2015).

### Doctoral Thesis

*Bogner, L.:* Ultrafast Relaxation Dynamics after Optical Excitation of Hybrid Inorganic/Organic Systems. Freie Universität Berlin 2015.

*Deinert, J.-C.:* Zinc Oxide Surfaces and Interfaces: Electronic Structure and Dynamics of Excited States. Technische Universität Berlin 2016.

*Foglia, L.:* Ultrafast dynamics and energy loss channels at a hybrid organic inorganic interface. Technische Universität Berlin 2015.

### Bachelor Thesis

*Mayan, I.:* Charakterisierung amorpher Eisschichten auf der Cu(111)-Oberfläche mittels thermischer Desorptions- und Photoelektronenspektroskopie: Mittlere freie Weglänge niederenergetischer Elektronen in amorphem Eis. Universität Potsdam 2015.



## 6. Invited Talks (August 2015 - August 2017)

- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (19. Deutsche Physikerinnentagung, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (IV. Physical Institute (AG Claus Ropers), Georg-August-Universität Göttingen, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (Institute Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria, Nov 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Colloquium, Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany, Dec 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Special Seminar, Department of Chemistry, University of California, Berkeley, CA, USA, Dec 2015).
- Stähler, Julia: Real Time Measurement of the Vertical Binding Energy during the Birth and Lifetime of a Solvated Electron. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Jan 2016).
- Stähler, Julia: Many Body Effects in Ultrafast Spectroscopy: Polarons, Excitons & Correlated Electrons. (Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany, Jan 2016).
- Stähler, Julia: Ultrafast Dynamics of Many Body Effects in Solids and at Interfaces: Polarons, Excitons & Correlated Electrons. (Prize Talk, Gaede Prize Symposium, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (Colloquium, Department of Chemistry, Technical University of Munich, Munich, Germany, Apr 2016).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (International conference, Internal Interfaces 2016, Marburg, Germany, May 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (SFB 951 Colloquium, Humboldt-Universität zu Berlin, Berlin, Germany, Jun 2016).
- Stähler, Julia: Understanding Ultrafast Exciton Dynamics in ZnO and at Its Surfaces: Potential and Hazard of Impurities. (Gruppenseminar, Institut für Experimentelle Physik II (Marius Grundmann), Universität Leipzig, Leipzig, Germany, Jun 2016).
- Stähler, Julia: Photoinduced Transient Band Gap Enhancement in the Excitonic Insulator Ta<sub>2</sub>NiSe<sub>5</sub>. (International conference on dynamic pathways in multidimensional landscapes, Berlin, Germany, Sep 2016).

- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (Award Ceremony of the Edith Flanigen Award 2016, CRC 1109, Berlin, Germany, Oct 2016).

**Cancelled/declined due to maternity leave:**

- Stähler, Julia: Ultrafast Dynamics at Inorganic/Organic Hybrid Interfaces. (Molecular Interactions & Dynamics, Gordon Research Conference (GRC), Easton, MA, USA, Jul 2016
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Stähler, Julia: DIET15 (15<sup>th</sup> conference on Desorption Induced by Electronic Transitions), Shanghai, China, Oct 2017
- Stähler, Julia: Chemistry Colloquium, Johannes Kepler University, Linz, Austria, Oct 2017
- Stähler, Julia: CMD26 (26<sup>th</sup> EPS Condensed Matter Division Conference), Groningen, Netherlands, Nov 2016
- Stähler, Julia: Kick-off meeting Sfb 1242, Bad Honnef, Germany, Nov 2016
- Stähler, Julia: Department Seminar, Cornell University, Dept. of Chemistry and Chemical Biology, Ithaca, NY, USA, Nov 2016
- Stähler, Julia: COST general meeting, Action CM1401 (Chem. & Mol. Sci. & Techn.) Non-thermal desorption from cold surfaces Workshop, Faro, Portugal, Jan 2017
- Stähler, Julia: March Meeting of the American Physics Society, New Orleans, LA, USA, Mar 2017
- Stähler, Julia: ECSCD-13 (European Conference on Surface Crystallography and Dynamics), San Sebastian, Spain, Jun 2017
- Stähler, Julia: ICFSI 16 (International Conference on the Formation of Semiconductor Interfaces), Hanover, Germany, Jul 2017
- Stähler, Julia: RACI (Royal Australian Chemical Institute) National Centenary Conference, Melbourne, Australia, Jul 2017
- Stähler, Julia: Summer Workshop of Theoretical Chemistry at TU Munich "Frontiers of Multi-scale Modelling in Materials, Energy & Catalysis III", Germany, Jul 2017
- Stähler, Julia: E-MRS Fall Meeting, Warsaw, Poland, Sep 2017
- Stähler, Julia: FEMTO13 (13th Femtochemistry Conference - Frontiers of ultrafast phenomena in Chemistry, Biology, and Physics) Cancun, Mexico, Aug 2017
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator Ta<sub>2</sub>NiSe<sub>5</sub>. (Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany, Apr 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator Ta<sub>2</sub>NiSe<sub>5</sub>. (Seminar, Department of Mathematics and Physics (AG Claudio Giannetti), Università Cattolica del Sacro Cuore, Brescia, Italy, May 2016).

- Mor, Selene: Ultrafast Electronic Band Gap Control in an Excitonic Insulator. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Vempati, Sesa Pavan Kumar: Frontier Molecular Orbitals of CO<sub>2</sub> on ZnO Surfaces: Time-Resolved Photoelectron Spectroscopy. (Seminar, Indian Institute of Science Education and Research Mohali, Mohali, India, Feb 2017).
- Vempati, Sesa Pavan Kumar: Hybrid Systems for Optoelectronic Applications and Photoelectron Spectroscopy. (Seminar, Material Research Center, Indian Institute of Science, Bengaluru, India, Mar 2017).

## Theory Department

**Theory Department****Director: Matthias Scheffler****Staff scientists:**

|                      |             |                     |
|----------------------|-------------|---------------------|
| Carsten Baldauf      |             | Christian Carbogno  |
| Luca M. Ghiringhelli | <i>BMBF</i> | Sergey V. Levchenko |
| Mariana Rossi        |             | Matthias Rupp       |
| Igor Ying Zhang      |             |                     |

Claudia Draxl (Max Planck Fellow)  
 Alexander M. Bradshaw (Emeritus)

**Guest scientists, staying for at least six months, paid by FHI:**

|                        |                      |                     |                      |
|------------------------|----------------------|---------------------|----------------------|
| Sebastián A. Villaseca | <i>until 11/2016</i> | Susmita Basak       | <i>until 11/2016</i> |
| Amrita Bhattacharya    | <i>until 04/2016</i> | Fawzi R. Mohamed    |                      |
| Runhai Ouyang          |                      | Nathaniel Raimbault |                      |
| Honghui Shang          | <i>until 10/2017</i> | Tonghao Shen        |                      |
| Jungho Shin            |                      | Daria M. Tomecka    |                      |
| Haiyuan Wang           |                      |                     |                      |

**Guest scientists, staying for at least six months, paid from external funds:**

|                    |                                     |                    |                                         |
|--------------------|-------------------------------------|--------------------|-----------------------------------------|
| Björn Bieniek      | <i>NOMAD CoE<br/>until 05/2017</i>  | Mario Boley        | <i>NOMAD CoE<br/>until 01/2017</i>      |
| Wael Chibani       | <i>NOMAD CoE<br/>until 06/2016</i>  | Stefano Curtarolo  | <i>AvH Bessel Awardee</i>               |
| Bryan Goldsmith    | <i>AvH Fellow<br/>until 08/2017</i> | Svenja M. Janke    | <i>DFG (together with<br/>M. Rossi)</i> |
| Aliaksei Mazheika  | <i>DFG</i>                          | Ghanshyam Pilania  | <i>AvH Fellow</i>                       |
| Danilo S. Brambila | <i>BMBF</i>                         | Christopher Sutton | <i>AvH Fellow</i>                       |
| Maria E. Stournara | <i>DFG<br/>until 10/2016</i>        | Chenchen Wang      | <i>UCSB, US<br/>until 03/2016</i>       |
| Yanggang Wang      | <i>AvH Fellow</i>                   | Xunhua Zhao        | <i>DFG<br/>until 04/2016</i>            |
| Angelo Ziletti     | <i>NOMAD CoE</i>                    |                    |                                         |

**Graduate students:** 20 (4 from external funds, 2 IMPRS)**Joint Network Center (GNZ) of the Berlin-Brandenburg Max Planck Institutions****Head:** Gerd Schnapka**Staff members:** 10 (1 from external funds)

## Recent Developments in the *Theory Department*

Director: Matthias Scheffler

1. **General Remarks**
2. **Organizational**
3. **Personnel and Related Matters**
4. **New Concepts, Methods, and Techniques**
  - 4.1 *FHI-aims* Code
  - 4.2 The *NOMAD* (*Novel Materials Discovery*) CoE (*Center of Excellence*)
  - 4.3 Equality of the DFT Band Gaps When Read from the Kohn-Sham Band Structure or Calculated by Total-Energy Differences
  - 4.4 Advanced DFT and Quantum-Chemistry Methods for Molecules, Clusters, and Extended Solids
  - 4.5 Compressed-Sensing Approaches for Materials Science
  - 4.6 Phase Diagrams of Surfaces in Reactive Atmospheres: A Replica-Exchange Grand-Canonical Algorithm
  - 4.7 Efficient High-Throughput Calculations of Lattice Anharmonicities and Thermal Conductivity
  - 4.8 Insightful Classification of Crystal Structures by Deep Learning
  - 4.9 Unified Representation of Molecules and Crystals for Machine Learning
  - 4.10 Finding Interpretable Local Patterns in Big-Data of Materials by “Subgroup Discovery”
  - 4.11 Error Bars, Extrapolation Schemes, and Test Sets
5. **Applications to Timely Questions in Materials Science**
  - 5.1 Classification of Materials Properties with SISISO
  - 5.2 Predicting and Understanding Quantum Spin-Hall Insulators with SISISO
  - 5.3 Stabilities, Band Gaps, and Effective Masses of Polymorphs of Group-III Oxides
  - 5.4 Vibrational Effects on the Electronic Properties of Molecules and Solids
  - 5.5 Polarons in Different Polymorphs of  $\text{TiO}_2$  and  $\text{Ga}_2\text{O}_3$
  - 5.6 Adsorption and Disorder-Disorder Phase Transitions of H at ZnO (10-10) at Realistic ( $T$ ,  $p$ ) conditions
  - 5.7 Catalytic Conversion of  $\text{CO}_2$  at Metal-Oxide and Metal-Carbide Surfaces
  - 5.8 *Ab Initio* Biomolecular Simulations

6. **Otto Hahn Group Simulations from *Ab Initio* Approaches: Structure and Dynamics from Quantum Mechanics (Head: Mariana Rossi)**
7. **ERC Group on Organic Functional Materials and Intermolecular Interactions (Head: Alexandre Tkatchenko)**
8. **Publications of the *Theory Department***
9. **Invited Talks of Members of the *Theory Department***

## 1. General Remarks

Materials science is at present developing a new research paradigm: Parallel to (i) experimental or empirical studies, (ii) theoretical science (deriving laws and models) and (iii) computational materials science (performing simulations or computer experiments), we are now adding (iv) big data-driven materials science. Here, one starts from a large body of experimental or theoretical data, and by means of “big-data analytics”, which utilize methods from the signal-processing, image-recognition and machine-learning fields, one identifies patterns or structure in the data that would not be visible in a single study or even in several studies. In this way, we build maps that identify regions in the huge parameter space of compound materials, where different regions correspond to materials with different properties, such as, for example, electrical conductors, efficient catalysts for a certain chemical reaction, quantum-hall insulators, etc.

The challenge in building such a map is to find the appropriate descriptive parameters (called descriptors) that define these regions of interest. Importantly, inside these regions, interpolation between already known data enables an efficient identification of potentially interesting novel materials that have not been studied so far.

Up to now, scientific research is often characterized by a built-in bias deriving from the application of established criteria. For example, when looking for better catalytic materials, one studies substances from the same class of materials as those that have previously shown good catalytic properties. Obviously, this will hardly lead to revolutionary results. Moreover, the selection of materials that were studied in greater detail in the past is subjective, and this may imply that patterns in data just reflect the bias behind the selection, a phenomenon called the “Berkson paradox”. In general, it appears that from the about 240,000 inorganic materials that have been synthesized so far<sup>1</sup> (many more are possible), the properties mentioned in the first paragraph have been studied for less than 1% of them.

Developing this fourth research paradigm, but with the necessary caution, is becoming more and more the focus of the work of the *Theory Department*. For example, it was the motivation behind a paper that was published in March 2015 (L. M. Ghiringhelli, J. Vybiral, S. V. Levchenko, C. Draxl, and M. Scheffler, Phys. Rev. Lett. (2015): *Big data of materials science: Critical role of the descriptor*). That this was a rather new research field in 2014 is reflected in the initial editorial rejection of this paper, in which it was argued: “PRL has to decide how

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<sup>1</sup> <http://materials.springer.com/>



narrow it should be in the topics that it covers”. Interestingly, by September 1, 2017 this “narrow paper” had been cited 90 times!

Big data-driven materials science was also the main idea behind our proposal for a “*Centre of Excellence (CoE) for Computing Applications of the EC Horizon 2020 program: The Novel Materials Discovery Laboratory (NOMAD)*”, <https://nomad-coe.eu/>. The center, officially launched in November 2015, connects key scientists in many different institutions. At the FHI there are Claudia Draxl (Humboldt University Berlin, Max Planck Fellow at the FHI), Luca M. Ghiringhelli, Angelo Ziletti, and Christian Carbogno. More and more members are becoming involved (see section 4.2 below) also through international collaborators (e.g. Prof. Dr. Stefano Curtarolo, Duke University, now at FHI as AvH Bessel Awardee). A concise 3-minute introduction of the *NOMAD CoE* can be watched on YouTube:

<https://youtu.be/yawM2ThVIGw>.

While the last two years have witnessed substantial progress in the *NOMAD CoE* activities, other topics have also been highly successful. Four outstanding achievements of the *Department* are briefly described in the following:

- From *LASSO* (*least absolute shrinkage and selection operator*) to *SISSO* (*sure independence screening plus sparsifying operator*). Our initial work in data analytics started with the *LASSO* mathematical approach, originally developed for signal processing applications. *LASSO* can also be considered a forerunner of the field of *compressed sensing*. Unfortunately severe instabilities appear when the candidate descriptors are both highly correlated and in great number (e.g. more than 5,000 elements meant to describe 100 observables). These problems are solved by our *SISSO* approach, recently developed in the *Department*. *SISSO* does not suffer from the correlation problem. Instead, it can efficiently identify the best 2-3 descriptors out of the immensity of trillions candidates.
- An efficient, non-perturbative approach for determining the thermal conductivity of solids has been developed by Christian Carbogno. It was published in *Physical Review Letters* in April 2017. The preliminary work was already presented at the *Fachbeirat* meeting in 2015. The two most important aspects of this theory are: a) a first-principles formulation of the Green-Kubo method that allows the accurate assessment of the phonon-driven thermal conductivity of solid semiconductors and insulators by accounting for anharmonic effects to all orders via *ab initio* molecular dynamics calculations, and b) the achievement of size- and time convergence by a robust,

asymptotically exact extrapolation scheme. The technique was demonstrated for extremely-high and low heat conductors, namely Si and ZrO<sub>2</sub>. A systematic high-throughput study of many materials has just been started.

- *Van der Waals physics on the nano and mesoscopic scales.* Alexandre Tkatchenko's group has developed new methods for studying van der Waals (vdW) interactions in nano and mesoscopic systems, also in the presence of static and dynamic fields. This has led to the discovery of "dipole waves". In addition, a multiscale method was developed to compute the fully retarded vdW energy for an arbitrary arrangement of microscopic and macroscopic subsystems, leading to a unified treatment of vdW and Casimir interactions. Taken together, these new developments achieve control of mesoscale structures by tailoring matter and light waves.
- Last but not least, we mention the further development of our all-electron electronic-structure code FHI-aims. The code was released in 2009 and its functionality has been impressively extended due to contributions from an active worldwide community of FHI-aims users/developers. In brief, the code has been characterized to be "as accurate as WIEN2k and as fast as or faster than VASP". The key developer and coordinator is Volker Blum, now Associate Professor at Duke University. The "standard" publication [V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler: *Ab initio molecular simulations with numeric atom-centered orbitals*. Comp. Phys. Comm. (2009)] has been cited more than 800 times to date! Several specific aspects are described below and, of course, on an extensive poster.

The following Section describes organizational developments. Section 3 addresses personnel and related matters. Subsequently, a more complete discussion of the work of the *Department* can be found in Sections 4 and 5, as well as in the special sections on the Otto Hahn Group of Mariana Rossi (established in October 2016) and on the remaining FHI activities of Alexandre Tkatchenko. He holds a professorship at the University of Luxembourg since November 2015. A more in-depth presentation is provided by the posters displayed in the *Department* and in the selection of poster abstracts in the Yellow Book.

The account given here and the poster presentations focus on the developments in the last two years (since September 2015).

## 2. Organizational

As of September 1, 2017, the FHI *Theory Department* is structured into 9 research groups. Nevertheless, most of the work in the *Department* involves more than one of these groups. The groups and their leaders are:

- *Advanced First-Principle Methods for Materials Science and Engineering*, headed by **Igor Ying Zhang**
- *Unifying Concepts in Catalysis*, headed by **Sergey V. Levchenko**
- *Heat and Charge Transport*, headed by **Christian Carbogno**
- *Big-Data Analytics for Materials Science*, headed by **Luca M. Ghiringhelli**
- *Data Science for Similarity and Crystal-Structure Prediction in Materials*, headed by **Matthias Scheffler** (deputy: **Angelo Ziletti**)
- *Machine Learning for Materials*, headed by **Matthias Rupp**
- *Otto Hahn Group: Simulations from Ab Initio Approaches: Structure and Dynamics from Quantum Mechanics* headed by **Mariana Rossi**
- *Organic Functional Materials and Molecular Interactions* – FHI branch of **Alexandre Tkatchenko**
- *Ab Initio Biomolecular Simulations*, headed by **Carsten Baldauf**

In addition, we proudly host the *Max Planck Fellow Group* of **Claudia Draxl** and we support the *Max Planck Partner Group for Advanced Electronic-Structure Methods* of **Xinguo Ren** in Hefei/China. Emeritus **Alexander M. Bradshaw** has been a valued, stimulating member of the *Department* since January 2009. He works on photoionization in molecules and clusters as well as on questions of energy supply and resources in the context of the sustainability debate.

Together with Martin Vingron (director at the MPI for Molecular Genetics), Matthias Scheffler is responsible for the Joint Network Center (*Gemeinsames Netzwerkzentrum, GNZ*) for the Max Planck activities in Berlin and Brandenburg. 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 page 9, 10.

Members of the *Theory Department* take part in various national, European, and international research programs and initiatives. The following list of these activities is ordered alphabetically according to the funding agency:

- BMBF – Federal Ministry of Education and Research (Germany), *Berlin Big Data Center (BBDC) of Competence*, coordinator: V. Markl; project leader: M. Scheffler, since October 2014.
- BMBF – Federal Ministry of Education and Research (Germany), *Eigenwert-Löser für PetaFlop-Anwendungen: Algorithmische Erweiterungen und Optimierungen (ELPA - AEO)*, coordinator: H. Lederer; project leaders: M. Scheffler, C. Carbogno, since February 2016.
- DFG – German Research Foundation, Cluster of Excellence 314: *Unifying Concepts in Catalysis (UniCat)*, chair: M. Driess; project leader: M. Scheffler (S. V. Levchenko), 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)*, spokesperson: N. Koch; project leaders: P. Rinke, M. Scheffler (B4) and A. Tkatchenko, M. Scheffler (A10), second funding period: July 2015 - June 2019.
- DFG – German Research Foundation, FOR 1543: *Shear-flow Regulation of Hemostasis (SHENC)*, spokesperson: R. Schneppenheim; project leaders: F. Gräter, C. Baldauf (C1), second 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, April 2013 - March 2016.
- ERC – European Research Council, Advanced Grant: *Big-Data Analytics for the Thermal and Electrical Conductivity of Materials from First Principles*; M. Scheffler – starting October 2017.
- EU – European Commission, E-Infrastructures: *NOMAD (Novel Materials Discovery) Center of Excellence*, coordinator: M. Scheffler; work package leaders: L. M. Ghiringhelli and C. Draxl, since November 2015.
- Leibniz-Gemeinschaft – Leibniz-WissenschaftsCampus (LWC): *Growth and fundamentals of oxides for electronic applications (GraFOx)*, spokesperson: H. Riechert; project leaders: M. Scheffler, S. Levchenko, and C. Sutton, since July 2016.
- 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, A. Fontcuberta i Morral, A. Wodtke, M. Scheffler, since 2013. The *Theory Department* is currently involved in two projects: *Biomolecules on their*

*Way to Solvation*, C. Baldauf, G. von Helden, T. R. Rizzo (EPFL) and *Peptides at Surfaces: Simulating Organic-Inorganic Interface Systems*, C. Baldauf, M. Ceriotti (EPFL), M. Rossi.

- Max Planck Society - Central Funds – *MP Fellow Group* of C. Draxl, since July 2014.
- Max Planck Society - Central Funds – *MP Partner Group for Advanced Electronic-Structure Methods* by X. Ren at the University of Science and Technology of China (USTC) in Hefei, since December 2015.
- Max Planck Society - Central Funds – *BigMax, MaxNet on Big-Data-Driven Materials Science*, coordinator: P. Benner, M. Scheffler, since March 2017.
- 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; project leaders: S. V. Levchenko and M. Scheffler, 2012 - 2016.

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 governance institutions 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.

### 3. Personnel and Related Matters

Since the last visit of the *Fachbeirat* in November 2015 the following noteworthy developments have taken place:

- In October 2016, **Mariana Rossi** returned to the *Theory Department* as independent group leader of the Otto Hahn Group on *Simulations from Ab Initio Approaches: Structure and Dynamics from Quantum Mechanics* (see Section 6).
- **Christian Carbogno** was promoted to group leader in November 2015. His group is called *Heat and Charge Transport*.
- The Max Planck Partner Group on *Advanced Electronic-Structure Methods* at the University of Science and Technology of China (USTC) led by **Xinguo Ren** began its work in September 2015. 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 inauguration workshop on the *Frontiers of Advanced Electronic-Structure Methods* took place in Hefei in June 2016. The lineup of speakers was outstanding: V. Blum, K. Burke, Z. Fang, X.G. Gong, X. Gonze, E.K.U. Gross, L.X. He, W.X. Li, X.Z. Li, W. Liu, H. Jiang, S. Meng, I. Mertig, J. P. Perdew, P. Rinke, A. Ruzsinszky, M. Scheffler, G.E. Scuseria, E.G. Wang, H. Wu, X. Xu, Y. Xu, J.L. Yang, W.T. Yang, I.Y. Zhang, Z.Y. Zhang. The meeting was judged as highly successful.
- **Carsten Baldauf** completed his habilitation at the FU Berlin in 2017.
- In November 2015, **Alexandre Tkatchenko** became the Chair of Theoretical Condensed Matter Physics at the University of Luxemburg.
- **Bryan Goldsmith** has accepted a position as Assistant Professor of Chemical Engineering at the University of Michigan. He will start there in September 2017.
- **John P. Perdew** and **Gustavo Scuseria** were bestowed with Humboldt Research Awards and spent some time in the *Department*. **Andrew Rappe** received this award recently and will visit us next year.
- **Stefano Curtarolo** received the Friedrich Wilhelm Bessel Research Award of the Alexander von Humboldt Foundation for his pioneering work in computational materials science, in particular the development of data-mining and high-throughput

algorithms for computationally-assisted discovery of new materials. He is the initiator and director of the biggest repository for computational materials science data in the US, AFLOWlib. He is at present in Berlin and already involved in several joint research projects. It is also planned to establish close links between the AFLOW and NOMAD projects and coordinate future developments.

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 in 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, biophysics, and Big-Data science which have impacted upon the careers of very many students of theoretical materials science. Let us emphasize here in particular the 10-day hands-on schools which are organized by the *Theory Department* since 1994. They cover the whole field of DFT and all important methodologies (e.g. pseudo-potential plane wave, LAPW, numeric atomic orbital, Quantum Monte Carlo methods, etc.). And we invite top experts in these fields. The practical sessions take place in the afternoons and evenings, now using the FHI-aims code. Originally these schools were run every second year. However, the demand is significant and in the last few years we have organized these events yearly, alternating between Berlin and an international location. For example, this year we had more than 200 applicants but were only able to accept 70 participants (from 28 countries!). The workshop in Iran in 2016 was generously funded by the Alexander von Humboldt Foundation, and also the DAAD (German academic exchange program) contributed noticeably. The lack of official support from the Max-Planck Society was disappointing. The workshop 2016 in Esfahan and that in 2017 in Berlin-Adlershof (funded by Volkswagen Foundation) were great successes, and Carsten Baldauf, the main organizer, did a most impressive job. As always, the whole *Department* helped greatly.

Further activities in the last two years included:

- Workshop *Big Data of Materials Science - Critical Next Steps*, Lausanne, Switzerland, November 30 - December 4, 2015, organizers: L. M. Ghiringhelli, M. Scheffler, S. V. Levchenko
- Workshop *Towards a Common Format for Computational Materials Science Data*, Lausanne, Switzerland, January 25 - 27, 2016 (first part: discussion) and January 27 - February 4, 2016 (second part: implementation), organizers: D. Caliste (Alternative

- Energies and Atomic Energy Commission, France), C. Carbogno, L. M. Ghiringhelli, G. Huhs (Barcelona Supercomputing Center, Spain), M. Lueders (Daresbury Laboratory, UK), M. Oliveira (University of Liege, Belgium), R. Ramakrishnan, M. Scheffler
- *NOMAD*: first industrial meeting, Berlin, Germany, March 1 - 2, 2016, organizers: A. De Vita (King's College London, UK), A. Rubio (MPI Hamburg), M. Scheffler
  - Symposium on *Frontiers of Electronic-Structure Theory: Focus on Topology and Transport* at the DPG Spring Meeting in Regensburg, Germany, March 7 - 11, 2016, organizers: I. Mertig (Martin Luther University Halle), G. Vignale (University of Missouri-Columbia, USA), M. Scheffler
  - Workshop *Probing Potential-Energy Surfaces PPES IV 2016*, Zermatt, Switzerland, April 10 - 15, 2016, organizers: C. Baldauf, J. Pach, M. Scheffler
  - Hands-on workshop and Humboldt-Kolleg: *Density-Functional Theory and Beyond - Basic Principles and Modern Insights*, Isfahan, Iran, May 2 - 13, 2016, organizers: H. Akbarzadeh (Isfahan University of Technology, Iran), C. Baldauf, S. Javad Hashemifar (Isfahan University of Technology, Iran), M. Scheffler
  - Sino-German Workshop on *Biomolecular Simulations across Scales*, Shanghai, China, May 26 - 30, 2016, organizers: S. Xiao (Norwegian University of Science and Technology, Trondheim), X. Fei (East China Normal University) I. Y. Zhang, C. Baldauf
  - The 1st USTC-FHI Workshop on the *Frontiers of Advanced Electronic-Structure Methods*, Hefei, China, June 14 - June 18, 2016, organizers: X. Ren (USTC, China), M. Scheffler
  - FHI-aims Developers' and Users' Meeting on *Electronic-Structure Theory with Numeric Atom-Centered Basis Functions*, München, Germany, July 20 - 22, 2016, organizers: K. Reuter (TU München), C. Baldauf, V. Blum (Duke University, USA), M. Scheffler
  - Workshop on *Big-Data-Driven Materials Science*, Ringberg, Germany, July 27 - 30, 2016, organizer: M. Scheffler
  - *NOMAD* Analytics Hackathon, Berlin, Germany, January 18 - 20, 2017, organizers: L. M. Ghiringhelli, F. Mohamed, A. Ziletti, M. Scheffler
  - *NOMAD*: second industrial meeting, Hamburg, Germany, February 6 - 7, 2017, organizers: A. De Vita (King's College London, UK), Angel Rubio (MPI Hamburg), M. Scheffler
  - Symposium on *Frontiers of Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond* at the DPG Spring Meeting in Dresden, Germany, March 19 - 24, 2017, organizers: J. P. Perdew (Temple University, USA), A. Rubio (MPI Hamburg), M. Scheffler



- *NOMAD Analytics Hackathon*, Berlin, Germany, July 3 - 5, 2017, organizers: L. M. Ghiringhelli, F. Mohamed, A. Ziletti, M. Scheffler
- *NSF/CECAM School on Computational Materials Science: From Basics to Applications*, Lausanne, Switzerland, July 17 - 27, 2017, organizers: K. Fichthorn (PennState, USA), J. Sofo (PennState, USA), M. Scheffler
- Hands-on workshop on *Density-Functional Theory and Beyond - Accuracy, Efficiency and Reproducibility in Computational Materials Science*, Berlin, Germany, July 31 - August 11, 2017, organizers: C. Baldauf, I. Y. Zhang, P. Pavone (HU Berlin), V. Blum (Duke University, USA), M. Scheffler
- Workshop on *Big-Data Driven Materials Science*, Lausanne, Switzerland, September 11 - 13, 2017, organizers: L. M. Ghiringhelli, M. Scheffler
- *NOMAD SUMMER: A Hands-on Course on Tools for Novel-Materials Discovery*, Berlin, Germany, September 25 - 29, 2017, C. Draxl (HU Berlin), M. Rampp (MPCDF, Garching), S. Rigamonti (HU Berlin), A. Ziletti, G. Huhs (HU Berlin; Barcelona Supercomputing Center, Spain)
- Workshop on *Quantum-Chemistry Methods for Materials Science*, Lausanne, Switzerland, November 8 - 10, 2017, organizers: I. Y. Zhang, 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 the energy steering panel of the European Academies Science Advisory Council (EASAC).

#### 4. New Concepts, Methods, and Techniques

Since the last meeting of the *Fachbeirat*, two wider themes have dominated the work of the *Department*, namely, the continuing development of the *FHI-aims* code and the *NOMAD CoE* project. These themes will be discussed first, followed by 9 additional topics. ***As mentioned above, the work by Mariana Rossi and Alexandre Tkatchenko will not be described here, but in separate chapters.***

#### 4.1 *FHI-aims* Code

The FHI-aims code implements a unique set of features that distinguish it from other codes used in computational materials science. It combines (i) high-accuracy basis set (numerical atom-centered functions), suitable for efficient large-scale calculations, (ii) support for finite systems (molecules and clusters) as well as extended, periodic systems on equal footing and (iii) a broad spectrum of methods from ground-state DFT via several quantum-chemistry methods to excited states. Recent advances cover new exchange-correlation functionals (e.g. self-consistent SCAN), van der Waals interactions, spin-orbit coupling, GW, BSE, and more. A density-functional perturbation theory framework addresses phonons, electronic friction, and spectroscopic observables. Important further enhancements target high-throughput screening and embedding into statistical-mechanics tools that are dedicated to structure prediction as well as to cluster expansion (including Wang-Landau and nested-sampling approaches for the evaluation of the density of configurational states), molecular dynamics, and thermal conductivity calculations. (This work was performed by many colleagues and typically coordinated by Volker Blum and Matthias Scheffler jointly; see the poster abstract in the Yellow Book for the full list of authors.)

#### 4.2 The *NOMAD (Novel Materials Discovery) CoE (Center of Excellence)*

The *NOMAD CoE* maintains the largest *Repository* for input and output files of all important computational materials science codes worldwide (more than 32 codes). Using its open-access data *NOMAD* forms the basis for several *Big-Data Services* which in turn help to advance materials science and engineering.

Before 2015, it was very unusual in materials science to provide access to, and share fully research data (other disciplines were not any different!). This was also noted in a recent *nature editorial*<sup>2</sup>, entitled: Empty rhetoric over data sharing slows science -- not-so-open data. Since end of 2014, this issue has been successfully addressed by the *NOMAD Repository*. Our work emphasizes that ***data is a crucial raw material of the 21st century***, from which valuable knowledge can be extracted using novel data-mining tools.<sup>3</sup>

In fact, the *NOMAD*<sup>4</sup> project has fostered a cultural shift in attitudes towards open data in the

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<sup>2</sup> Nature **546**, 327 (2017), <https://www.nature.com/news/empty-rhetoric-over-data-sharing-slows-science-1.22133>

<sup>3</sup> The *NOMAD* Center of Excellence <https://nomad-coe.eu>

materials science community. The *NOMAD Repository* now provides open access to input and output files of computational materials science from all<sup>4</sup> major data collections in the field, together with those of many individual researchers and research groups. In this role, the *NOMAD Repository* is also listed among the recommended repositories of *Nature Scientific Data*, where it is the only one for materials science. The *Repository* currently contains more than 40 million total-energy calculations, corresponding to billions of CPU-core hours used at high-performance computers worldwide.

*NOMAD* hosts the data for at least 10 years (for free), it offers DOIs (digital object identifiers) to make data citable, and it provides several services. For example, it supports all important electronic-structure codes used in the community (more than 32 codes). Moreover, it converts this very heterogeneous data and stores it in a **code-independent archive**. We offer an *encyclopedia* to access all this data, numerous **big-data analytics tools**, and **advanced graphics**. (The PIs of the *NOMAD CoE* are: Jose Maria Cela (Barcelona Supercomputing Centre (BSC)), Ciaran Clissmann (Pintail Ltd), Alessandro De Vita (King’s College London), Claudia Draxl (Humboldt-Universität zu Berlin), Daan Frenkel (University of Cambridge), Stefan Heinzel (Max Planck Computing and Data Facility, Garching), Francesc Illas (University of Barcelona), Kimmo Koski (CSC – IT Center for Science, Espoo), Dieter Kranzlmüller (Leibniz Supercomputing Centre (LRZ), Garching), Risto Nieminen (Aalto University), Angel Rubio (Max Planck Institute for the Structure of Dynamics of Matter, Hamburg), Kristian S. Thygesen (Technical University of Denmark, Lyngby), and Matthias Scheffler (coordinator).)

### 4.3 Equality of the DFT Band Gaps When Read from the Kohn-Sham Band Structure or Calculated by Total-Energy Differences

During a visit of John P. Perdew to the *Theory Department* we realized that an elementary misunderstanding persists in many publications with respect to the discussion of *band gaps of solids in generalized Kohn-Sham theory* (GKS). This was addressed by giving a simple proof of a theorem<sup>5</sup>: In GKS, the band gap of an extended system equals the fundamental gap for the

<sup>4</sup> The biggest “single” repository is AFLOWlib (<http://aflowlib.org>) which provides numerous results as well as the input and output files of the underlying calculations. OQMD (<http://oqmd.org>) and Materials Project (<https://materialsproject.org>) offer numerous results but the underlying input and output files can be only obtained from *NOMAD*.

<sup>5</sup> J.P. Perdew, W. Yang, K. Burke, Z. Yang, E.K.U. Gross, M. Scheffler, G.E. Scuseria, T.M. Henderson, I.Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Görling, *Understanding Band Gaps of Solids in Generalized Kohn-Sham Theory*. Published in PNAS (March 6, 2017).

approximate functional, if the GKS potential operator is continuous and the density change is delocalized when an electron or hole is added. This work explains how GKS band gaps from meta-generalized gradient approximations (meta-GGAs) and hybrid functionals can be more realistic than those from GGAs or even from the exact KS potential. The band edges in the GKS one-electron spectrum are also related to measurable energies. (J.P. Perdew, W. Yang, K. Burke, Z. Yang, E.K.U. Gross, G.E. Scuseria, T.M. Henderson, I.Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Görling)

#### 4.4 Advanced DFT and Quantum-Chemistry Methods for Molecules, Clusters, and Extended Solids

While the connection from the ground-state electron density to the total energy of the many-electron system is clear in principle<sup>6</sup>, it is also plausible that any exchange-correlation (xc) functional, that can be written in a closed mathematical form, will be an approximation.

A significant amount of work in the *Theory Department* has therefore been devoted to implementing quantum-chemistry methods into the FHI-aims code for molecules and clusters as well as for extended, periodic systems. This concerns, in particular, coupled-cluster theory with single, double and perturbative triple excitations (CCSD(T)) as well as standard and reduced-scaling MP2. Obviously, CCSD(T) is restricted to closed shell systems or insulators, and it is expensive. However, it is very important for benchmark studies. (Tonghao Shen, Arvid C. Ihrig, and Igor Y. Zhang)

We have also developed and analyzed an improved orbital-dependent correlation functional that explicitly includes two-electron correlations. The functional is called sBGE2 (screened Bethe-Goldstone equation to second order). We then took the sBGE2 functional as a building block for an orbital-dependent xc functional, termed ZRPS (the authors' initials), which is a natural extension of the PBE0 hybrid functional. ZRPS delivers an overall mean absolute deviation of less than 70 meV in an extensive list of benchmarks. (Igor Y. Zhang, Patrick Rinke, and John P. Perdew)

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<sup>6</sup> The exact route from the density to the total energy goes as follows: The ground-state electron density determines the many-body hamiltonian. Subsequently, solving the many-electron Schrödinger equation gives the total energy. In this sense  $n(\mathbf{r})$  also determines not just the ground state but also all excited states and any observable.

#### 4.5 Compressed-Sensing Approaches for Materials Science

In various (big-) data analytics studies we have developed and employed tools that build on compressed sensing (CS), a recent signal-processing concept that has revolutionized the recovery of signals by efficiently identifying their underlying sparsity patterns. One application direction aims to improve the quality and size of basis sets, as they crucially control the accuracy and CPU and memory requirements. Two complementary schemes are compared, where each identifies the basis functions that carry the most relevant information of the system. (Ingo Roth, Adrian Steffens, Christian Krumnow, Jens Eisert, Niklas Menzel, and Luca M. Ghiringhelli)

A very different application of CS addresses materials properties and building “a map of materials”. Our previous “LASSO plus  $\ell_0$  sparsification” approach is limited to modest pool sizes and descriptor candidates with low mutual correlation. The newly developed CS scheme replaces LASSO by Sure Independence Screening (SIS). It overcomes the above-mentioned problems. In most cases we find that the  $\ell_0$ -norm regularization provides the best solution. The method has been carefully tested and applied to various timely systems, some will be discussed in Section 5 below. (Runhai Ouyang and Luca M. Ghiringhelli)

#### 4.6 Phase Diagrams of Surfaces in Reactive Atmospheres: A Replica-Exchange Grand-Canonical Algorithm

Our *ab initio* atomistic thermodynamics approach has been very successful in predicting phase diagrams for surfaces and gas-phase clusters in contact with a realistic environment at realistic  $(T, p)$  conditions. The surface structures considered in such studies may be plausible, but, in general, the selection process is subjective, and it may miss the relevant structure. Indeed, in several situations, relevant to catalysis and corrosion, the surface composition and structure may be hard to guess. We have therefore developed a replica-exchange grand-canonical Monte-Carlo/molecular-dynamics algorithm that enables the unbiased, efficient calculation of these phase diagrams. We specifically target open systems (surfaces and free clusters in a reactive atmosphere) in the grand-canonical ensemble. Test-case applications demonstrate the potential of the approach. (Yuan Yuan Zhou and Luca M. Ghiringhelli)

#### 4.7 Efficient High-Throughput Calculations of Lattice Anharmonicities and Thermal Conductivity

Anharmonic effects of solids are typically treated perturbatively by solely accounting for the third-order term in a Taylor expansion of the potential-energy surface. To overcome this approximation, we are presently developing a high-throughput framework that is specifically targeted at the automatized calculation of fully anharmonic thermodynamic equilibrium (phonons, Grüneisen parameters, thermal expansion, specific heat, etc.) and non-equilibrium properties (thermal conductivity). Planning calculations for 1,000 specific systems, we began by looking at representative examples with increasing anharmonicity (e.g. Si, Mg<sub>2</sub>Si, Ga<sub>2</sub>O<sub>3</sub>, CuCl, ZrO<sub>2</sub>) and calculating their properties both perturbatively and with our recently developed *ab initio* Green-Kubo molecular-dynamics approach. For strongly anharmonic systems such as CuCl and ZrO<sub>2</sub> the higher-order anharmonicity drastically alters the equilibrium properties, e.g., the phonon band structure. We are presently analyzing strategies to reduce the numerical cost by using higher-order, temperature-dependent Taylor expansions of the PES. (Hagen-Henrik Kowalski, Florian Knoop, Maja-Olivia Lenz, and Christian Carbogno)

#### 4.8 Insightful Classification of Crystal Structures by Deep Learning

Computational methods that automatically extract knowledge from data are critical for enabling data-driven materials science. Identification of lattice symmetry is crucial for materials characterization and analytics. Current methods require a user-specified threshold, and are unable to detect “average symmetries” for defective structures. Here, we propose a machine learning-based approach to automatically classify structures by crystal symmetry. First, we represent crystals by a diffraction image, and then construct a deep-learning model for classification. Our approach is able to correctly classify a dataset comprising more than 80,000 structures, including heavily defective ones, belonging to the cubic crystal system. The internal operations of the neural network are unraveled through attentive response maps, demonstrating that it uses the same landmarks a materials scientist would use, although never explicitly instructed to do so. (Angelo Ziletti, Devinder Kumara, and Luca M. Ghiringhelli)

#### 4.9 Unified Representation of Molecules and Crystals for Machine Learning

Machine learning can accurately interpolate between reference calculations given a sufficiently

high volume of data. For this, an invariant, unique, differentiable, fast numerical representation that supports interpolation is essential. We developed and tested a many-body tensor representation (MBTR). Numerical results are presented for 7,000 organic molecules as well as 7 *ab initio* molecular dynamics trajectories (energy prediction errors are below 1 kcal/mol) and for 11,000 elpasolite crystals (energy prediction errors are below 3 meV/atom). Applicability is demonstrated for phase diagrams of Pt-group/transition-metal binary systems, where convex hulls are correctly identified for AgPt, IrZn, CdPt, AgPt, and IrPt. (Haoyan Huo and Matthias Rupp)

#### **4.10 Finding Interpretable Local Patterns in Big-Data of Materials by “Subgroup Discovery”**

Data-analytics tools applied to materials-science data often focus on the inference of a global prediction model for some property of interest. However, the underlying mechanism for some target property could differ even qualitatively for different materials. As a physical example, the transition metals of the periodic table are a subgroup, and the actinides and halogens are other subgroups.

Thus, identification of subgroups helps to understand similarities and differences between materials. In this spirit we developed subgroup discovery (SGD) for materials-science data by characterizing physical properties in terms of Boolean conditions. In contrast to global modelling algorithms, SGD finds interpretable descriptions of subpopulations in which, locally, the target property takes on an interesting distribution. The approach is demonstrated for several examples. (Bryan R. Goldsmith, Mario Boley, Jilles Vreeken, and Luca M. Ghiringhelli)

#### **4.11 Error Bars, Extrapolation Schemes, and Test Sets**

Significant work in the *Department* is devoted to determine numerical error bars associated to DFT calculations in diverse Kohn-Sham implementations, specifically, plane-wave pseudopotentials (and PAWs), LAPWs, and numerical, atom-centered basis sets. With all these implementations, extended convergence studies were performed for elemental and binary solids with respect to the numerical parameters up to full numerical convergence. On the basis of the error bars identified in this way, schemes are proposed to estimate reliably the numerical error bars associated with the incompleteness of the basis set and not fully converged k-meshes for arbitrary systems: <https://analytics-toolkit.nomad-coe.eu>. These schemes are validated for

randomly chosen ternary systems obtained from the *NOMAD Repository*. (Christian Carbogno, Oliver Hofmann, Claudia Draxl, Kristian S. Thygesen, *et al.*)

We have also been strongly involved in benchmarking different codes for PBE calculations of perfect solids<sup>7</sup> and for *GW* calculations for 100 molecules<sup>8</sup>. This work has had significant impact, and is presently being continued for more advanced functionals as well as for solids with surfaces and defects. (Xinguo Ren, Christian Carbogno, Claudia Draxl, *et al.*)

The work for creating a *test set for materials science and engineering (MSE)* continues. This project considers cohesive energies, lattice constants, and bulk moduli for representative materials. Specifically, we consider (as the first step) first- and second-row elements and their binaries with cubic crystal structures and various bonding characters. So far we studied several different density functionals as well as MP2 and RPA. Over the next few months it is planned to include also CCSD(T). (Igor Y. Zhang, Andrew J. Logsdail, Norina A. Richter, Toktam Morshedloo, Xinguo Ren, Sergey V. Levchenko, and Luca M. Ghiringhelli)

## 5. Applications to Timely Questions in Materials Science

### 5.1 Classification of Materials Properties with SISO

As a first application of our SISO approach, we addressed the challenge to represent the vast amount of materials in terms of a map that assigns different regions to electrical conductors and semiconductors/insulators. Because of the size of available experimental data we restricted our study to  $A_xB_y$  binary compounds and certain structure prototypes. As primary features for our machine-learning strategy we used properties of neutral atoms, interatomic distances and the unit-cell volume of the considered materials. From these primary features more than a billion candidate descriptors were created; SISO then determines the best two-dimensional descriptor. This defines the wanted two-dimensional map as well as the equation of the line dividing the two regions, which contains the key physical factors that determine the metallic vs. nonmetallic character of the material. The model achieves perfect (100%) classification of the training data. Interestingly, though the learning did not include information on the pressure

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<sup>7</sup> K. Lejaeghere, *et al.*, Reproducibility in density functional theory calculations of solids. *Science* **351**, aad3000 (2016).

<sup>8</sup> M.J. van Setten, *et al.*, *GW 100: Benchmarking  $G_0W_0$  for molecular systems*. *J. Chem. Theory Comput.* **11**, 5665 (2015).



dependence, the resulting equation also describes pressure-induced insulator  $\rightarrow$  metal transitions. (Runhai Ouyang, Emre Ahmetcik, Stefano Curtarolo, and Luca M. Ghiringhelli)

## 5.2 Predicting and Understanding Quantum Spin-Hall Insulators with SISSO

Quantum spin-hall insulators (QSHIs) are two-dimensional topological insulators (TIs). They have attracted considerable interest in recent years for spintronic applications, since backscattering is forbidden in their edge states due to the topological band inversion. We have computed the topological  $Z_2$  invariant of 220 two-dimensional, functionalized honeycomb-lattice materials  $ABC_2$  ( $AB$  are IV-IV, III-V, II-VI materials, and  $C$  is from group VII) using FHI-aims (DFT-PBE). Their classification into metals, insulators, and QSHIs can be described and understood using a two-dimensional descriptor identified via SISSO. Since this descriptor is physically meaningful and only depends on the properties of the isolated constituent atoms, it is highly transferable. This was demonstrated by using it to predict and subsequently validate over 50 additional 2D honeycomb QSHIs that consist of elements not included in our original machine-learning study. (Carlos Mera Acosta, Runhai Ouyang, Adalberto Fazzio, Luca M. Ghiringhelli, and Christian Carbogno)

## 5.3 Stabilities, Band Gaps, and Effective Masses of Polymorphs of Group-III Oxides

Despite the strong interest in transparent, conducting oxides, the fundamental properties of the various polymorphs of group-III sesquioxides ( $Ga_xAl_yIn_zO_3$ , with  $x+y+z=2$ ) are still poorly understood. In fact, reliable experimental data are rare. We have therefore performed a high-throughput screening of these materials, focusing on the stability and electronic properties of various phases for the alloy as a function of composition and temperature. The results are obtained by sp-HSE06@PBEsol, i.e. single-point HSE06 calculations at the PBEsol-optimized ground-state and wavefunctions. This gives bandgap energies that are in good agreement with experimental values (13% error). To efficiently search (meta)stable configurations for many lattice types, we use a combination of DFT-based cluster-expansion models and fast stochastic optimization techniques. (Christopher Sutton and Luca M. Ghiringhelli)

## 5.4 Vibrational Effects on the Electronic Properties of Molecules and Solids

Our recent real-space implementation of density-functional perturbation theory (DFPT) was applied to compute the phonon-induced renormalization of the electronic band structure of 82 octet binaries (zincblende and rock salt structure) for both zero-point vibrations and finite temperatures. The SISSO approach is then used to identify physically meaningful descriptors for these effects, which allows the several exceptions observed with respect to established scaling rules, e.g., for the mass, to be rationalized.

Furthermore, we computed fully anharmonic Raman spectra for both molecular and crystalline polymorphs of paracetamol and aspirin. These spectra are obtained by evaluating the DFPT polarizability tensors along equilibrium *ab initio* molecular-dynamics trajectories. Besides being in quantitative agreement with experimental data, these results reveal strong anharmonic effects on some localized (NH bending) and some delocalized (lattice phonon) modes. (Honghui Shang, Nathaniel Raimbault, Carlos M. Acosta, Patrick Rinke, Mariana Rossi, and Christian Carbogno)

## 5.5 Polarons in Different Polymorphs of $\text{TiO}_2$ and $\text{Ga}_2\text{O}_3$

An important factor limiting the electrical conductivity in solids is the interaction of the charge carriers with phonon modes and polaron formation. We studied oxides of Ti and Ga where it is expected that the electron-phonon coupling is large and polarons are strongly localized.

In order to address uncertainties caused by the exchange-correlation approximation, we used the hybrid HSE functional and took into account the whole range  $0 \leq \alpha \leq 1$  of exact exchange. Furthermore, in order to obtain the polaron properties in the dilute limit, we consider elastic long-range distortions and finite-size corrections in a supercell approach. The approach is applied to rutile and anatase  $\text{TiO}_2$ , and monoclinic  $\beta$ - and orthorhombic  $\varepsilon$ - $\text{Ga}_2\text{O}_3$ . Unexpectedly, we find that in rutile  $\text{TiO}_2$  only small, i.e., strongly localized, *electron* polarons are stable, whereas only small *hole* polarons are found in anatase. On the other hand, for  $\text{Ga}_2\text{O}_3$  we predict the existence of small hole polarons for both polymorphs. Their binding energies are, however, significantly different. (Sebastian Kokott, Sergey V. Levchenko, and Patrick Rinke)

## 5.6 Adsorption and Disorder-Disorder Phase Transitions of H at ZnO (10-10) at Realistic ( $T$ , $p$ ) conditions

Following earlier work in the *Department*<sup>9</sup>, we combined a DFT-based cluster-expansion model with the Wang-Landau algorithm to describe the thermodynamics of atomic H adsorbed at ZnO (10-10), including the configurational entropy of the adsorbate. Our study reveals that at coverages below 6%, H atoms adsorb exclusively on surface O atoms. At higher coverages, H adsorbs also on Zn. Neighboring O-H/Zn-H pairs form chains along surface -O-Zn- rows, always ending by O-H. The interaction between chains is dominated by the repulsion between the O-H ends, and ordering of the chains is destroyed for  $T > 60$  K. Interestingly, there are different disordered phases of adsorbed H that are characterized by their quantitative O-H excess over Zn-H. The calculated work function (as function of coverage) is in good agreement with recent experimental results by Julia Stähler *et al.* (PC Department). (Maria E. Stournara, Sergey V. Levchenko, Santiago Rigamonti, Maria Troppenz, Oliver T. Hofmann, Patrick Rinke, and Claudia Draxl)

## 5.7 Catalytic Conversion of CO<sub>2</sub> at Metal-Oxide and Metal-Carbide Surfaces

The catalytic conversion of the greenhouse gas CO<sub>2</sub> to fuels or to other useful chemicals is highly desired, and thus there is a need for finding new, more efficient catalysts. The O-C-O bending angle of an adsorbed CO<sub>2</sub> is an indicator of the activation of the molecule, while the adsorption energy is an indicator of the stability of the system with respect to carbonate formation. Using DFT with a carefully validated xc approximation, we calculated the properties of the molecule adsorbed on various cuts of about 14 binary carbides and 72 binary and ternary oxides (over 200 different surfaces overall). SISO is then used to identify physically meaningful descriptors for the CO<sub>2</sub> activation. (Aliaksei Mazheika, Yanggang Wang, Runhai Ouyang, Rosendo Valero, Christian Kunkel, Helena Muñoz Galan, Luca M. Ghiringhelli, Francesc Illas, and Sergey V. Levchenko)

In a co-operation with colleagues from the AC Department we have also studied Ni<sub>x</sub>Mg<sub>y</sub>O for dry reforming of CH<sub>4</sub> and for CO<sub>2</sub> hydrogenation. Poly-crystalline samples with low concentrations (3-10%) of Ni in MgO were successfully synthesized for the first time,. The homogeneous distribution of Ni in MgO allowed a clear comparison of theory and experiment.

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<sup>9</sup> M. Borg, C. Stampfl, A. Mikkelsen, J. Gustafson, E. Lundgren, M. Scheffler, and J.N. Andersen, “Density of configurational states from first-principles: The phase diagram of Al-Na surface alloys”. *ChemPhysChem* **6**, 1923 (2005).

The calculations reveal that Ni doping and CO<sub>2</sub> adsorption stabilize low-coordinated sites (corners and steps) and promote the formation of stepped (110) and reconstructed (111) MgO surfaces. The experimental differential heat of adsorption values of these samples are perfectly explained by the occupation of CO<sub>2</sub> vacancies in the surface carbonate at steps, as well as adsorption at the reconstructed (111) surface with Ni<sub>Mg</sub> defects. (Aliaksei Mazheika, Marie M. Millet, Sabine Wrabetz, Andrey Tarasov, Elias Frei, Sergey V. Levchenko, and Robert Schlögl)

## 5.8 *Ab Initio* Biomolecular Simulations

The *Ab Initio Biomolecular Simulations* group aims at laying a solid foundation for the description of the energetics and dynamics of biomolecules by simulation. They develop structure search techniques and test across-the-scale energy functions. The group works closely with Mariana Rossi. One topic concerns hybrid inorganic-organic materials. Modeling their electronic structure is challenging, since xc approximations are often not working reliably. We have studied organic systems ranging from rigid aromatic molecules to flexible biomolecules adsorbed on semiconductor [H-Si(111)] and metallic [Cu(111)] surfaces. The peptide HisProPheH<sup>+</sup> and the amino acid ArgH<sup>+</sup>, for example, are known from experiment to form distinct structures on metal surfaces like Cu(111). To predict such structures, our first-principles structure search package *Fafoom* was extended to include the position and orientation of molecules with respect to the surface. (Carsten Baldauf, Volker Blum, Svenja Janke, Sergey V. Levchenko, Dmitrii Maksimov, Haiyuan Wang, and Mariana Rossi)

Furthermore, peptide-cation systems were studied to understand how metal cations shape the structure of proteins. Specifically, we investigated a model system for helix formation in the gas phase by a combination of first-principles molecular simulations with cold conformer-selective vibrational spectroscopy experiments in the gas phase that allow for detailed structure elucidation. (Markus Schneider, Chiara Masellis, Tom Rizzo, and Carsten Baldauf)

**6. Otto Hahn Group Simulations from *Ab Initio* Approaches: Structure and Dynamics from Quantum Mechanics**      **Head: Mariana Rossi**

**Guest scientists, staying for at least six months, paid by FHI:**

Nathaniel Raimbault  
Haiyuan Wang

*Otto Hahn*  
*Otto Hahn*

**Guest scientists, staying for at least six months, paid from external funds:**

Svenja Janke

*DFG (together with M. Scheffler)*

**Graduate students:** 2 (1 from FHI, 1 from MP-EPFL center)

**General Remarks**

The Otto Hahn Group led by Mariana Rossi was established in October 2016. In the Max Planck Society, a very small number of recipients of the Otto Hahn Medal are selected for the Otto Hahn Award. This distinction gives them the opportunity to choose a Max Planck Institute of their choice in order to head a small group, independently funded by the MPS, for a period of 3 years (plus 2, after evaluation), after doing a post-doc abroad. In Mariana Rossi's group H-bonded systems composed of biomolecules, organic molecules, and their interfaces with inorganic systems are studied. In particular, the focus lies on the influence of temperature, anharmonic effects, and nuclear quantum phenomena, studied using first-principles quantum mechanical simulations. The two members of the group funded directly from the Otto Hahn Award started in November 2016, and, between February and March 2017, three more members have joined the group. There are active collaborations with experimental groups in the Fritz Haber Institute and other Max Planck Institutes, as well as co-operations with other group leaders in the *Theory Department* and theoretical scientists in other institutions, such as Prof. Michele Ceriotti (EPFL), Prof. Jeremy Richardson (ETH-Zürich), Prof. Davide Donadio (UC Davis), and Prof. Volker Blum (Duke University).

**Scientific Scope**

The research in our group focuses on including temperature and nuclear quantum effects in electronic structure calculations for systems where these effects are particularly important. Most of our research involves bio-organic materials and bio-organic/inorganic interfaces. In general, matter is not static, and for non-covalently bonded systems the fluctuations induced by temperature can completely change the structure, the thermodynamic equilibrium, and also the

properties of the electronic structure. If the materials involved are organic or biological, the ubiquitous presence of hydrogen atoms makes approximations like the treatment of nuclei as classical particles unsuitable. The interplay of temperature and nuclear quantum effects can give rise to several important effects such as the displacement of thermodynamic equilibria in reactions and the changing of the pH and pKa of substances. Moreover it is responsible for band gap renormalization in water and other materials; it can induce changes in charge transfer behavior, and also induce work function changes. In particular, we are focusing on bio-organic/inorganic interfaces, where new technological developments can stem from the combination of the robust properties of inorganic materials and the flexibility and modularity of bio-organic components. We develop structure searches tailored for flexible molecules, acceleration techniques and new methods to treat dynamical properties including nuclear quantum effects, and frameworks to calculate anharmonic vibrational properties of materials. Our group can study these effects with speed and accuracy, thus bringing the electronic-structure calculations closer to actual experiments.

## **Research Highlights and Recent Developments**

### ***Hydrogen Transfer Reactions on Surfaces Down the Deep Tunneling Regime***

Surface-mediated hydrogen transfer reactions can be particularly impacted by nuclear quantum effects, but these can either be dominated by zero-point energy (ZPE) or tunneling. For example, we have studied the impact of nuclear quantum effects (NQE) on the dissociation of water wires on stepped Pt(221) surfaces at finite temperatures. Some interesting findings of our study are that (i) several competing minima co-exist at finite temperatures, (ii) temperature and anharmonicities make NQE contributions to the free energies 20% larger per dissociated dimer, (iii) the magnitude of NQE contributions is comparable to the free energy differences themselves at finite temperatures, and (iv) temperature and NQE impact particularly work-function changes on these stepped surfaces, changing their average value by 0.2 to 0.4 eV. We find that the dissociation process is dominated by ZPE, which can enhance the rate of dissociation by three orders of magnitude. In collaboration with Takashi Kumagai in the PC department, we are also studying hydrogen transfer reactions in molecular switches like porphycenes adsorbed on metallic surfaces. In this case the reactions are dominated by tunneling at low temperatures, and the surface changes the potential energy landscape of the reaction. In order to perform our simulations we have proposed and implemented in the i-PI code an acceleration scheme that makes a spatial partition in the system where a ring polymer contraction can be performed, resulting in considerable computational savings for this class of

systems. In collaboration with Jeremy Richardson (ETH Zürich), we have also implemented the ring polymer instanton method in i-PI, thus giving access to calculations of reaction rates in the deep tunneling regime and tunneling splittings, which, through the interface with FHI-aims, can now be used also for *ab initio* calculations on surfaces. (Yair Litman)

### ***Anharmonic Vibrational Spectra: IR, Raman, and Sum Frequency Generation***

Vibrational Raman spectroscopy is important for the structural characterization of many systems. Through the optimization and extension of the DFPT framework for electric field responses in the FHI-aims code, we could obtain polarizability tensors for isolated and periodic systems. Joining this framework with molecular dynamics gives access to different vibrational spectra where temperature and anharmonicities are automatically accounted for. We take as an example molecular crystals, where we calculate anharmonic Raman spectra from the Fourier transform of the polarizability autocorrelation functions. We also treat lattice expansion in a quasi-harmonic framework that gives direct access to the anisotropic expansion of different lattice components. By studying paradigmatic molecular crystals like aspirin and paracetamol, and performing simulations including many body dispersion interactions, we find an extremely good agreement with published data for the far infrared region, which is known to be quite anharmonic and very sensitive to the crystal structure. Our implementation can also give access to vibrational sum frequency generation spectra, which is sensitive to interfaces. It can also be coupled to recently developed methods like thermostatted ring polymer molecular dynamics to account for nuclear quantum effects in vibrational spectra. We are currently exploring ways, based on kernel ridge regression techniques, to make the calculation of the polarizability tensors cheaper in these simulations. (Nathaniel Raimbault)

### ***Organic molecules adsorbed on H-Si(111)***

Hybrid inorganic-organic systems (HIOS) are promising materials especially for optoelectronic devices such as light-emitting diodes, solar cells, or sensors. When the interface between the organic layer and the semiconductor is formed, measurable work function changes take place that one would ideally like to control. In our group we study highly efficient dopants (F4-TCNQ and F6-TCNNQ) as well as renowned singlet fission materials (tetracene and pentacene) adsorbed on hydrogen-passivated Si(111) [H-Si(111)]. A key difficulty in describing quantitatively the electronic structure of organic molecules at surfaces is to determine the adsorption geometry of the organic layer at the surface. To tackle this problem, we develop structure search strategies that allow us to determine the adsorption geometry for different

coverages on H-Si(111). Through the calculation of core-level shifts, consideration of the space-charge layer, and comparison to X-ray photoelectron spectroscopy data from the group of Prof. Norbert Koch (HU-Berlin), we are able to disentangle different contributions to the work function change (band bending and surface dipole) and to provide physical insight into this process. (Svenja Janke, Haiyuan Wang, Sergey V. Levchenko, Volker Blum, and Matthias Scheffler)

### ***Conformational Search of Biomolecules on Inorganic Surfaces***

For the structure search of flexible bio-organic molecules in contact with inorganic surfaces, where properly accounting for the internal degrees of freedom is a challenge, we have extended the *Fafoom* code (a genetic algorithm code that works on internal degrees of freedom) to include orientations and translations of flexible molecules with respect to one another and to fixed frames, such as surfaces. This work is performed jointly with the group of Carsten Baldauf in the *Theory Department*. We obtained results from density-functional theory for the case of the arginine amino-acid in different protonation states. From our data we can show how the conformational space of the molecule is changed upon adsorption and can consider how to obtain simpler energy functions and entropy estimations for an initial structural pre-screening of these systems. When  $\text{ArgH}^+$  adsorbs on metallic surfaces, we find that the positive charge is efficiently screened by concentration of electrons from the surface close to the charged group and the conformational space is expanded with respect to the gas-phase picture. This efficient screening of the charge on a peptide is likely to play a role in the 2D self-assembly observed for these same systems in the group of Klaus Kern and Stephan Rauschenbach (MPI FKF Stuttgart), with whom we actively collaborate in this project. (Dmitrii Maksimov and Carsten Baldauf)

### **External funding**

- CSCS - Swiss National Supercomputing Centre, 450'000 node hours over 1 year on the Cray XC30, Piz Daint, since October 1st 2016.
- MP-EPFL Center for Molecular Nanoscience and Technology, Project *Peptides at Surfaces: Simulating Organic-Inorganic Interface Systems*, 1 Ph.D. student.



## 7. ERC Group on Organic Functional Materials and Intermolecular Interactions

Head: Alexandre Tkatchenko

### Guest scientists, staying for at least six months, paid from external funds:

|                        |               |                           |
|------------------------|---------------|---------------------------|
| Mausumi Chattopadhyaya | until 05/2017 | AvH Fellow                |
| Fairoja C. Kabeer      | until 07/2017 | DFG                       |
| Andrii Kleshchonok     |               | DFG                       |
| Gionni Marchetti       | until 08/2016 | DFG                       |
| Majid Mortazavi        |               | DFG                       |
| Huziel E. Sauceda      | until 12/2017 | DFG                       |
| Limin Zheng            | until 03/2016 | China Scholarship Council |

**Graduate students:** 3 (2 from DFG, 1 FHI)

### General Remarks

The ERC (European Research Council) Research Group *Organic Functional Materials and Intermolecular Interactions*, led by Alexandre Tkatchenko, was established in May 2010 and is hosted by the *Theory Department*. In November 2015, A. Tkatchenko became a full professor at the University of Luxembourg, where he holds a chair in theoretical chemical physics and also has an ERC Consolidator grant. There is a strong connection between his group in Luxembourg and FHI; part of his group is hosted by the FHI. To strengthen the collaboration between the two groups, A. Tkatchenko visits Berlin once every two months. In addition, the FHI members of the group visit Luxembourg at least twice a year.

The ERC Group has recently been responsible for fundamental developments in efficient first-principles methods for the accurate modeling of non-covalent interactions in molecules, solids, and interfaces. The methods developed are applied to a wide range of fundamental complex materials, with the aim of understanding their qualitative and quantitative structural, cohesive, and electronic properties at the atomic scale. The group at FHI currently consists of three postdoctoral researchers, and two PhD students, together with the Principal Investigator (PI). Since the last meeting of the *Fachbeirat*, several postdoctoral researchers and PhD students have left for academic and industry positions elsewhere. Since February 2017, Anthony Reilly is an assistant professor in computational chemistry in the School of Chemical Sciences at Dublin City University. In total, three PhD students have defended during the last two years (Vivekanand V. Gobre, Victor G. Ruiz, and Nicola Ferri). All of them are pursuing academic careers: Vivekanand Gobre has become a research associate at the Interdisciplinary School of Scientific Computing in Pune, India; Victor Ruiz is a postdoctoral fellow at the Helmholtz-

Zentrum in Berlin; and Nicola Ferri is considering several postdoctoral opportunities after his contract at FHI expires. These successful career moves 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. They make possible the existence of molecular liquids and solids, control protein-protein and drug-protein binding inside our cells, and give geckos the ability to “defy gravity” by climbing 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 from 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.

In addition to non-covalent interactions, the group has recently expanded its interests towards developing efficient methods for modeling the coupling between electronic correlations and nuclear dynamics, and employing data-driven machine learning techniques to construct accurate representations of molecular properties in chemical space and next-generation interatomic potentials.

### **Research Highlights**

#### ***New van der Waals Physics at the Nano and Mesoscopic Scale***

With a strong focus on the accurate description of interactions that define the functionality of materials at the nano and mesoscopic scales, it becomes crucial to develop increasingly reliable methods for the description of vdW interactions in materials of increasing complexity and size (systems under confinement, subject to heterogeneous electromagnetic and optical fields, as well as nano/bio heterostructures and engineering materials). In addition, new physical

phenomena often emerge when coupling external fields to electronic fluctuations inherent to a material of interest. In this context, several major advances have been accomplished by the ERC Group during the last two years, including:

(1) We have demonstrated that in large molecular 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 arguments. Further application to carbon-based supramolecular complexes demonstrates that omitting wave-like 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 (*Science* 2016; *Chem. Mater.* 2016; *Nature Commun.* 2017; *Chem. Rev.* 2017; *J. Chem. Phys.* 2017).

(2) In collaboration with P. Venkataram and A. W. Rodriguez (Princeton University), we have developed a method that unifies calculation of van der Waals interactions with Maxwell-based solvers for Casimir interactions. Specifically, we developed an approach for computing long-range van der Waals (vdW) interactions between complex molecular systems and arbitrarily shaped macroscopic bodies, melding atomistic treatments of electronic fluctuations based on density functional theory in the former with continuum descriptions of strongly shape dependent electromagnetic fields in the latter, thus capturing many-body and multiple scattering effects to all orders. Such a theory is especially important when considering vdW interactions at mesoscopic scales, i.e., between molecules and structured surfaces with features on the scale of molecular sizes, in which case the finite sizes, complex shapes, and resulting non-local electronic excitations of molecules are strongly influenced by electromagnetic retardation and

wave effects that depend crucially on the shapes of surrounding macroscopic bodies. We show that these effects together can modify vdW interaction energies and forces, as well as molecular shapes deformed by vdW interactions, by orders of magnitude compared to previous treatments based on Casimir-Polder, non-retarded, or pairwise approximations. The latter are valid only at macroscopically large or atomic-scale separations or in dilute insulating media (*Phys. Rev. Lett.* 2017; *Rev. Mod. Phys.* 2016).

### ***Quantitative Prediction of Molecular Crystal Polymorphs***

Molecular crystals are versatile materials that find applications as pharmaceuticals, explosives, organic semiconductors, in solid-state reactions, and plastic materials. A molecular crystal composed of the same moieties can have several different crystal-packing motifs or polymorphs. This has far-reaching consequences, since polymorphs can exhibit completely different physical and chemical properties. Therefore, accurately predicting the relative energies of all thermally accessible polymorphs of a given molecule is a difficult fundamental problem, which also plays a crucial role in the pharmaceutical industry.

In order to demonstrate the capabilities of our methods in the study of polymorphism, our group participated in the 6<sup>th</sup> blind test of organic crystal structure prediction, organized by the Cambridge Crystallographic Data Centre (CCDC). Remarkably, our submission achieved the best energetic ranking for eight molecular crystal polymorphs among the 25 research groups and companies who participated in the blind test (*Acta Cryst. B.* 2016).

Following on this success, we have established collaborations with several leading research groups and pharmaceutical companies to further develop and apply our methods to increasingly challenging polymorphic systems (*Chem. Sci.* 2017; *WIREs: Comput. Mol. Sci.* 2017; *Phys. Rev. Lett.* 2015, 2017).

### ***Towards Machine Learning of Chemical Space and Interatomic Potentials***

Learning from data has led to paradigm shifts in a multitude of disciplines, including web, text and image search, speech recognition, as well as bioinformatics. Can machine learning enable similar breakthroughs in understanding quantum chemistry? The main challenge is the disproportionately large size of chemical space, estimated to contain  $10^{60}$  molecules even when only counting small organic drug-like candidates.

With the aim of applying machine learning to quantum chemical space, we have developed an efficient deep learning approach that enables spatially and chemically resolved insights into

quantum-mechanical observables of molecular systems. This is done by unifying concepts from many-body Hamiltonians with purpose-designed deep tensor neural networks, which in turn leads to size-extensive and uniformly accurate (1 kcal/mol) predictions in compositional and configurational chemical space for molecules of intermediate size. As an example of chemical relevance, the machine learning model reveals a classification of aromatic rings with respect to their stability. Further applications for predicting atomic energies and local chemical potentials in molecules, reliable isomer energies, and molecules with peculiar electronic structure demonstrate the potential of machine learning for revealing insights into complex quantum-chemical systems (*Nature Commun.* 2017).

For constructing next-generation machine-learned force fields, we have used conservation of energy to develop an efficient gradient-domain machine learning (GDML) approach to construct accurate molecular force fields using a restricted number of samples from *ab initio* molecular dynamics (aiMD) trajectories. The GDML implementation is able to reproduce global potential energy surfaces of intermediate-sized molecules with an accuracy of 0.3 kcal/mol for energies and 1 kcal/mol/Å for atomic forces using only 1000 conformational geometries for training. We demonstrate this accuracy for aiMD trajectories of molecules, including benzene, toluene, naphthalene, ethanol, uracil, and aspirin. The challenge of constructing conservative force fields is accomplished in our work by learning in a Hilbert space of vector-valued functions that obey the law of energy conservation. The GDML approach enables quantitative molecular dynamics simulations for molecules at a fraction of cost of explicit aiMD calculations, thereby allowing the construction of efficient force fields with the accuracy and transferability of high-level *ab initio* methods (*Science Adv.* 2017).

### **Third-Party Funded Projects**

- ERC – European Research Council, Starting Grant: Van der Waals Interactions in Complex Materials; A. Tkatchenko – Sept. 2011 – Aug. 2016.
- 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 – August 2014 – Oct. 2016.
- DFG – German Research Foundation, SFB 951, Hybrid Inorganic/Organic Systems (HIOS), spokesperson: Norbert Koch; A. Tkatchenko, M. Scheffler – since 2015.

## 8. Publications of the Theory Department

### 2015 (late publications)

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Barberis, M., T.D.G.A. Mondeel, C. Linke, A. Supady, A. Chasapi, W. Liebermeister, M. Loog, I. Xenarios and H. Kitano: Deciphering the design principles of dynamic cell cycle control. *Yeast* **32** (Suppl. 1), W3-1 (2015).

Bhattacharya, A. and S. Bhattacharya: Exploring N-Rich Phases in  $\text{Li}_x\text{N}_y$  Clusters for Hydrogen Storage at Nanoscale. *The Journal of Physical Chemistry Letters* **6** (18), 3726–3730 (2015).

Brehm, M., S. Lippok, K. Kolšek, D. Eggert, T. Obser, R. Schneppenheim, F. Gaeter, C. Baldauf and J. Rädler: Role of protein disulfide isomerase pdi in von Willebrand factor dimerization. *Journal of Thrombosis and Haemostasis* **13** (S2), 223 (2015).

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Säkkinen, N., Y. Peng, H. Appel and R. van Leeuwen: Many-body Green's function theory for electron-phonon interactions: Ground state properties of the Holstein dimer. *The Journal of Chemical Physics* **143** (23), 234101 (2015).

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## Doctoral Thesis

*Chibani, W.*: Self-Consistent Green's Function Embedding for Advanced Electronic Structure Calculations based on a Dynamical Mean-Field Concept. Technische Universität Berlin 2015.



*Knuth, F.*: Strain and Stress: Derivation, Implementation, and Application to Organic Crystals. Freie Universität Berlin 2015.

*Zhao, X.*: Adsorbate-adsorbate interactions on metal and metal oxide surfaces: critical role in surface structures and reactions. Technische Universität Berlin 2015. 

## 2016

*Alarcón Villaseca, S., S.V. Levchenko and M. Armbrüster*: CO adsorption on the GaPd(TTl) surface: a comparative DFT study using different functionals. *Physical Chemistry Chemical Physics* **18** (21), 14390–14400 (2016). 

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### Habilitation

Baldauf, C.: Biomolecular Simulations - From mechanics of a blood protein to peptides in isolation to molecular structure sampling. Freie Universität Berlin 2016.

### Doctoral Thesis

Bieniek, B.: Ultra thin ZnO on metal substrates: An ab initio study. Technische Universität Berlin 2016. 

Flick, J.: Exact Nonadiabatic Many-Body Dynamics: Electron-Phonon Coupling in Photoelectron Spectroscopy and Light-Matter Interactions in Quantum Electrodynamical Density-Functional Theory. Humboldt-Universität zu Berlin 2016. 

Gobre, V.: Efficient modelling of linear electronic polarization in materials using atomic response functions. Technische Universität Berlin 2016. 

Ruiz Lopez, V.G.: Adsorption of Atoms and Molecules on Surfaces: Density-Functional Theory with Screened van der Waals Interactions. Technische Universität Berlin 2016. 

Supady, A.: Exploring Molecular Conformational Space. Freie Universität Berlin 2016.

### Master's Thesis

Ahmetcik, E.: Machine Learning of the Stability of Octet Binaries. Technische Universität Berlin 2016.

Buchholz, F.: Exact Solutions in Lattice QED. Technische Universität Berlin 2016.

Hoffmann, N.: Response formalism in density-functional theory for quantum electrodynamics. Technische Universität Berlin 2016.

Kowalski, H.-H.: First-principles Study of Thermoelectric Magnesium Silicides with High-Throughput Techniques. Technische Universität Berlin 2016.

## 2017

Al-Hamdani, Y.S., M. Rossi, D. Alfè, T. Tsatsoulis, B. Ramberger, J.G. Brandenburg, A. Zen, G. Kresse, A. Grüneis, A. Tkatchenko and A. Michaelides: Properties of the water to boron nitride interaction: From zero to two dimensions with benchmark accuracy. *The Journal of Chemical Physics* **147** (4), 044710 (2017).

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*Troppenz, M., S. Rigamonti and C. Draxl*: Predicting Ground-State Configurations and Electronic Properties of the Thermoelectric Clathrates  $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$  and  $\text{Sr}_8\text{Al}_x\text{Si}_{46-x}$ . *Chemistry of Materials* **29** (6), 2414–2424 (2017).

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### Doctoral Thesis

*Dimitrov, T.*: Exact Maps in Density-Functional Theory. Technische Universität Berlin 2017.



*Ferri, N.*: The Role of van der Waals Interactions on the Electronic Properties of Molecules and Materials. Technische Universität Berlin 2017.



## 9. Invited Talks of the Members of Theory Department

- Baldauf, Carsten: Potential-Energy Surfaces of Biomolecules in Isolation. (Sino-German Workshop on Biomolecular Simulations Across Scales, Shanghai, China, May 2016).
- Baldauf, Carsten: Sampling and Searching the Conformational Space of Molecules. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Baldauf, Carsten: First-Principles Simulation of Cation-Peptide Interaction and Carbohydrate Structure and Dynamics. (Seminar, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, Jun 2016).
- Baldauf, Carsten: Chemische Evolution und der Ursprung des Lebens. (Seminar, Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany, Dec 2016).
- Baldauf, Carsten: Biomolecules in Thin Air – First-Principles Studies of Peptides and Cation-Peptide Interactions in the Gas Phase. (The 22nd Biophysics Conference, Kaohsiung, Taiwan, May 2017).
- Baldauf, Carsten: First-Principles Based Simulations of Carbohydrates and Chemical Reactions. (Seminar, Institute of Biomedical Sciences, Academia Sinica, Taipei, Taiwan, May 2017).
- Baldauf, Carsten: Sampling and Searching the Conformational Space of Molecules. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Bhattacharya, Amrita: Stability and Properties of Intermetallic Clathrates from First Principles: The Challenges of Designing High Performance Thermoelectrics. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Bieniek, Björn: Numerical Quality Control in Computational Materials Databases. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Carbogno, Christian: Data Veracity and Error Bars. (Kickoff Meeting, The NOMAD Laboratory, A European Centre of Excellence, Berlin, Germany, Oct 2015).
- Carbogno, Christian: Towards the First-Principles Discovery of (Novel) Thermoelectric Materials. (4th Science Day of the Max Planck-EPFL Center for Molecular Nanoscience & Technology, Lausanne, Switzerland, Oct 2015).
- Carbogno, Christian: Electron-Phonon Coupling: Fundamental Concepts & Heat-Transport Calculations. (18th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany, Nov 2015).
- Carbogno, Christian: Thermodynamic Equilibrium and Non-Equilibrium Properties from First Principles. (CECAM/Psi-k/HERALD Workshop, Simulation of chemistry-driven growth phenomena for metastable materials, Marburg, Germany, Nov 2015).
- Carbogno, Christian: Numerical Quality Control in Computational Materials' Databases. (CECAM/Psi-k/NOMAD Workshop, Towards a Common Format for Computational Materials Science Datas, Lausanne, Switzerland, Jan 2016).

- Carbogno, Christian: Accurate Thermal Conductivities from First Principles. (Miniworkshop on simulations of thermoelectric materials (Part I), Helmholtz-Zentrum, Dresden-Rossendorf, Germany, Feb 2016).
- Carbogno, Christian: Novel Theoretical Approaches to Electron-Phonon and Phonon-Phonon Coupling. (Seminar, Department of Physical Chemistry, Fritz Haber Institute, Berlin, Germany, Feb 2016).
- Carbogno, Christian: Vorstellung des Projektpartners Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Theorie. (Kickoff-Meeting, BMBF Projekt ELPA-AEO, Munich, Germany, Mar 2016).
- Carbogno, Christian: Phonons and Heat Transport. (Seminar, Department of Materials Science, University of Milano-Bicocca, Milan, Italy, Apr 2016).
- Carbogno, Christian: Thermal Conductivities in Solids from First Principles: Accurate Computations and Qualitative Insights. (ASTS Seminar, Videostream, BIOVIA, Cambridge, England, Apr 2016).
- Carbogno, Christian: Phonons, Electron-Phonon Coupling, and Transport in Solids. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Carbogno, Christian: Novel Real-Space Approaches to Harmonic Phonons, Anharmonicity, and Electron-Phonon Coupling. (Electronic Structure Theory with Numeric Atom-Centered Basis Functions, FHI-aims Developers' and Users' Meeting, Munich, Germany, Jul 2016).
- Carbogno, Christian: First-Principles High-Throughput Design and Discovery of Novel Materials, and Its Application to Thermoelectrics. (5th Science Day of the Max Planck-EPFL Center for Molecular Nanoscience & Technology, Stuttgart, Germany, Oct 2016).
- Carbogno, Christian: Introduction to Ab Initio Theory of Heat Transport in the Bulk and at Surfaces. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Carbogno, Christian: Thermal Conductivities in Solids from First Principles: Accurate Computations and Rapid Estimates. (Group Seminar, Theoretical Chemistry (AG Peter Saalfrank and AG Thomas Körzdorfer), University of Potsdam, Potsdam, Germany, Nov 2016).
- Carbogno, Christian: Ab Initio Molecular Dynamics Simulations for the Thermal Conductivity of Solids. (MPCDF Workshop, High-performance computing and data-intensive applications in the Max-Planck Society, Kreuth, Germany, Dec 2016).
- Carbogno, Christian: NOMAD: Novel Material Discovery. (MPCDF Workshop, High-performance computing and data-intensive applications in the Max-Planck Society, Kreuth, Germany, Dec 2016).
- Carbogno, Christian: NOMAD: Novel Material Discovery. (3. Sitzung des wissenschaftlichen Beirats zum Themenfeld „Material“ der BAM, Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany, Apr 2017).



- Carbogno, Christian: Novel Theoretical Approaches to Electron-Phonon and Phonon-Phonon Coupling. (Group Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria, May 2017).
- Carbogno, Christian: Phonons and Electron-Phonon Coupling: Limits in Theoretical Approaches and How to Overcome Them. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Carbogno, Christian: Phonons, Electron-Phonon Coupling, and Transport in Solids. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Carbogno, Christian: Phonons and Electron-Phonon Coupling: Limits in Theoretical Approaches and How to Overcome Them. (International Workshop, Thermoelectric Materials: From Theoretical Design to Industrial Application, Tyndall National Institute, Cork, Ireland, Jul 2017).
- Ghiringhelli, Luca M.: Compressed Sensing for Optimal Basis Sets Identification. (CECAM Workshop, Big Data of Materials Science - Critical Next Steps, Lausanne, Switzerland, Nov 2015).
- Ghiringhelli, Luca M.: Towards Ab Initio Modelling of Heterogeneous Catalysis: Beyond the Static, Monostructure Description. (Seminar, NYU-ECNU Center for Computational Chemistry, Shanghai, China, Nov 2015).
- Ghiringhelli, Luca M.: A Common Energy Zero for Total Energies. (CECAM/Psirk/NOMAD Workshop, Towards a Common Format for Computational Materials Science Datas, Lausanne, Switzerland, Jan 2016).
- Ghiringhelli, Luca M.: Causal Models in Big-Data Analytics for Novel Materials Discovery. (2016 MRS Spring Meeting and Exhibit, Phoenix, AZ, USA, Mar 2016).
- Ghiringhelli, Luca M.: Learning Descriptors from Materials Science (Big) Data. (Seminar, Department of Chemistry, University of California, Davis, CA, USA, Mar 2016).
- Ghiringhelli, Luca M.: Learning Descriptors from Materials Science Big Data. (Seminar, Department of Condensed Matter Theory, The Czech Academy of Sciences, Prague, Czech Republic, Mar 2016).
- Ghiringhelli, Luca M.: Big-Data Analytics in Materials Science. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Ghiringhelli, Luca M.: From Ab Initio Molecular Dynamics to Statistical Mechanics. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Ghiringhelli, Luca M.: Finding Descriptors for (Predicting the Plasticity of) Real Materials. (Workshop on Big-Data-Driven Materials Science, Kreuth, Germany, Jul 2016).
- Ghiringhelli, Luca M.: Machine Learning for Fast Property Predictions. (Electronic Structure Theory with Numeric Atom-Centered Basis Functions, FHI-aims Developers' and Users' Meeting, Munich, Germany, Jul 2016).

- Ghiringhelli, Luca M.: Big Data of Materials Science: The Critical Role of the Descriptor. (Meeting, Berlin International Graduate School of Natural Sciences and Engineering (BIG-NSE), Berlin, Germany, Nov 2016).
- Ghiringhelli, Luca M.: Learning Descriptors from Materials-Science (Big) Data. (Workshop, Beyond! Materials Design and Discovery, Kreuth, Germany, Dec 2016).
- Ghiringhelli, Luca M.: Big Data of Materials Science: Critical Role of the Descriptor. (Conference on Molecular Nanostructures 2017, Ascona, Switzerland, Mar 2017).
- Ghiringhelli, Luca M.: Big-Data Driven Materials Science. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Ghiringhelli, Luca M.: Materials Informatics Towards Open Science - NOMAD. (Science and Technology of Advanced Materials (STAM) workshop @ E-MRS 2017 Spring Meeting, Strasbourg, France, May 2017).
- Ghiringhelli, Luca M.: Big-Data of Materials Science: The Critical Role of the Descriptor. (Platform for Advanced Scientific Computing (PASC17) Conference, Lugano, Switzerland, Jun 2017).
- Ghiringhelli, Luca M.: Learning Descriptors from Materials-Science (Big) Data. (CECAM Workshop, Interface Morphology Prediction with Robust and Efficient Structure Search (IMPRESS), Helsinki, Finland, Jun 2017).
- Ghiringhelli, Luca M.: The NOMAD Laboratory: Interactive Big-Data Driven Materials Science. (International Workshop on Materials Genome Infrastructure and Materials Design, Beijing, China, Jun 2017).
- Ghiringhelli, Luca M.: The NOMAD Laboratory: Interactive Big-Data Driven Materials Science. (Seminar, Computer Network Information Center, Chinese Academy of Sciences, Beijing, China, Jun 2017).
- Ghiringhelli, Luca M.: Ab Initio Statistical Mechanics. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Ghiringhelli, Luca M.: (Big-)Data Driven Materials Science. (Lecture Series, Fundamental Research in Energy and Sustainability Hour Minisymposium (FRESH Lecture), Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands, Jul 2017).
- Ghiringhelli, Luca M.: (Big-)Data Driven Materials Science. (NSF/CECAM School on Computational Materials Science: From Basics to Applications, Lausanne, Switzerland, Jul 2017).
- Ghiringhelli, Luca M.: Compressed Sensing and Screening for Properties. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Ghiringhelli, Luca M.: Computational Modeling of Energy Materials from First-Principles II: From the Atomic Scale to the “Real World”. (Lecture, Energy & Sustainability Summer School 2017, Leiden University, Leiden, The Netherlands, Jul 2017).

- Ghiringhelli, Luca M.: Configurational Sampling. (NSF/CECAM School on Computational Materials Science: From Basics to Applications, Lausanne, Switzerland, Jul 2017).
- Ghiringhelli, Luca M.: Interactive, Big-Data Driven Materials Science over the Web. (CECAM Workshop, Synergy between quantum computing and high-performance computing, Zurich, Switzerland, Aug 2017).
- Goldsmith, Bryan: Systematic Framework for Modeling Isolated Catalyst Sites on Amorphous Supports. (251st ACS National Meeting & Exposition, Division of Catalysis Science and Technology: Surface Chemistry & Catalysis of Metal Oxides, San Diego, CA, USA, Mar 2016).
- Goldsmith, Bryan: Role of van der Waals and Entropy on Nanocluster (Meta)Stability. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Goldsmith, Bryan: Influence of van der Waals and Entropy on Cluster (Meta)Stability. (Workshop, Bio-inspired nanosystems for energy conversion, Berlin, Germany, Jul 2016).
- Goldsmith, Bryan: Introduction to First-Principles Modeling of Catalysis at Surfaces. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).
- Goldsmith, Bryan: Patterns, Correlations, and Discovery of Descriptors in Big Data of Materials. (NOMAD Year 1 Meeting, Novel Materials Discovery Laboratory, Barcelona, Spain, Oct 2016).
- Levchenko, Sergey V.: Accurate and Efficient Calculation of Electron-Repulsion Integrals. (CECAM Workshop, Big Data of Materials Science - Critical Next Steps, Lausanne, Switzerland, Nov 2015).
- Levchenko, Sergey V.: Compact Representation of Scalar Fields: Density, Wavefunction, xc Potentials, etc. (CECAM/Psi-k/NOMAD Workshop, Towards a Common Format for Computational Materials Science Datas, Lausanne, Switzerland, Jan 2016).
- Levchenko, Sergey V.: Ab Initio Modelling of Charge Carriers and Defects in the Bulk and at Surfaces of Doped MgO: Polarons, Charge Compensation, and Activation of Small Molecules. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Levchenko, Sergey V.: Ab Initio Thermodynamics and Cluster Expansion. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Levchenko, Sergey V.: DFT in Practice. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Levchenko, Sergey V.: Periodic Structures. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).

- Levchenko, Sergey V.: Big Data Analytics for Heterogeneous Catalysis Design. (The 2nd Hokkaido University-RIKEN - AIST Joint Symposium “Catalyst Informatics for Sustainable Society”, Sapporo, Japan, Oct 2016).
- Levchenko, Sergey V.: First-Principles Modelling of Surfaces at Realistic Temperature, Pressure, and Doping Conditions. (Colloquium, Department of Chemistry, Bar Ilan University, Ramat Gan, Israel, Nov 2016).
- Levchenko, Sergey V.: Search for Alternative Catalytic Materials. Example: CO<sub>2</sub> Activation. (Second NOMAD Industry Meeting, Hamburg, Germany, Feb 2017).
- Levchenko, Sergey V.: Effects of Temperature, Pressure, and Charge-Carrier Doping on Surface Properties from First Principles. (Colloquium, Kyoto University, Kyoto, Japan, Mar 2017).
- Levchenko, Sergey V.: Finding Physically Meaningful Descriptors for High-Throughput Computational Materials Design: Methods and Applications. (Colloquium, National Institute for Materials Science (NIMS), Tsukubar, Japan, Mar 2017).
- Levchenko, Sergey V.: A Compressive-Sensing Approach to Finding Physically Meaningful Descriptors from Materials Data. (International Workshop of Materials Informatics and Materials Data, National Institute for Materials Science (NIMS), Tsukubar, Japan, Apr 2017).
- Levchenko, Sergey V.: Ab Initio Studies of the Effects of Doping on Surface Properties at Realistic Temperatures and Pressures. (Colloquium, Skolkovo Institute of Science and Technology, Moscow, Russia, May 2017).
- Levchenko, Sergey V.: CO<sub>2</sub> Activation at Complex Oxide and Carbide Surfaces. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Levchenko, Sergey V.: First-Principles Modelling of Defects and Interfaces at Realistic Temperatures and Pressures. (Colloquium, All-Russia Research Institute of Automatics (VNIIA), Moscow, Russia, May 2017).
- Levchenko, Sergey V.: Combining Ab Initio Calculations with Electrostatic Models to Describe Defects at Surfaces at Realistic Temperature, Pressure, and Doping Conditions. (Platform for Advanced Scientific Computing (PASC17) Conference, Lugano, Switzerland, Jun 2017).
- Levchenko, Sergey V.: Ab Initio Atomistic Thermodynamics. (Lecture, Hokkaido Summer Institute 2017, Hokkaido University, Sapporo, Japan, Jul 2017).
- Levchenko, Sergey V.: Ab Initio Thermodynamics. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Levchenko, Sergey V.: Density-Functional Theory and Ab Initio Atomistic Thermodynamics for Bulk Materials and Interfaces. (Lecture, Energy & Sustainability Summer School 2017, Leiden University, Leiden, The Netherlands, Jul 2017).
- Levchenko, Sergey V.: Density-Functional Theory for Materials. (Lecture, Hokkaido Summer Institute 2017, Hokkaido University, Sapporo, Japan, Jul 2017).

- Levchenko, Sergey V.: Periodic Systems: Concepts and Numeric Atom-Centered Orbitals. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Rossi, Mariana: Anharmonic and Nuclear Quantum Effects in H-Bonded Systems from Ab Initio Methods. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Rossi, Mariana: Ab Initio (Path Integral) Molecular Dynamics for H-Bonded Systems: Dynamical Properties. (Summer School Solvation Science, Bochum, Germany, Jun 2017).
- Rossi, Mariana: Colored Noise Thermostats for Path Integral Approximations to Dynamical Observables. (CECAM Workshop, Practical problems with dynamical nuclear quantum effects through semi-classical methods, Paris, France, Jun 2017).
- Rossi, Mariana: Evaluating Anharmonic and Nuclear Quantum Effects in Bio-Organic Systems. (Seminar, Physics and Materials Science Research Unit, University of Luxembourg, Esch-sur-Alzette, Luxembourg, Jun 2017).
- Rossi, Mariana: Ab Initio Molecular Dynamics. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Rossi, Mariana: Ab Initio (Path Integral) Molecular Dynamics for H-Bonded Systems: Interplay with Anharmonicities. (Workshop on Understanding Quantum Phenomena with Path Integrals: From Chemical Systems to Quantum fluids and Solids, Trieste, Italy, Jul 2017).
- Rupp, Matthias: Challenges in Development of Accurate and Efficient Atomistic Machine Learning Models. (CECAM Workshop, Big Data of Materials Science - Critical Next Steps, Lausanne, Switzerland, Nov 2015).
- Rupp, Matthias: Machine Learning Models for Materials Science at the Atomic Scale. (Seminar, National Institute for Materials Science (NIMS), Tsukuba, Japan, Nov 2015).
- Rupp, Matthias: Predicting Results of Quantum Mechanical Calculations: Challenges for Machine Learning. (Workshop, Frontiers in Data-Driven Science and Technology: Recent Advances in Machine Learning and Applications, Nagoya, Japan, Nov 2015).
- Rupp, Matthias: New Data, Validation, Code and Representation for Interpolation Across Chemical Compound Space. (IPAM Workshop on Machine Learning Meets Many-Particle Problems, Los Angeles, CA, USA, Sep 2016).
- Rupp, Matthias: Practical Tutorial on Machine Learning for Electronic Structure Calculations. (IPAM Workshop on Understanding Many-Particle Systems with Machine Learning, Los Angeles, CA, USA, Sep 2016).
- Rupp, Matthias: Understanding Many-Particle Systems with Machine Learning. (Workshop, Institute for Pure and Applied Mathematics (IPAM), Lake Arrowhead, CA, USA, Dec 2016).
- Rupp, Matthias: Many-Body Tensor Representation for Machine Learning of Solids. (57th Sanibel Symposium, St. Simons Island, GA, USA, Feb 2017).

- Rupp, Matthias: Accurate Machine Learning Predictions for Materials Properties. (Workshop on Machine Learning Strategies for Materials Science, Aalto, Finland, Mar 2017).
- Rupp, Matthias: Many-Body Tensor Representation. (Working Conference on Materials and Data Analysis, CMSA Harvard University, Cambridge, MA, USA, Mar 2017).
- Rupp, Matthias: Many-Body Tensor Representation for Machine Learning of Materials. (APS March Meeting 2017, New Orleans, LA, USA, Mar 2017).
- Rupp, Matthias: Unified Representation for Machine Learning of Molecules and Crystals. (Workshop on Machine Learning and Many-Body Physics, Beijing, China, Jun 2017).
- Rupp, Matthias: Machine Learning for Quantum Mechanics. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (Lecture, Peking University, Beijing, China, Oct 2015).
- Scheffler, Matthias: Causal Models in Big-Data Analytics for Novel Materials Discovery. (Colloquium, Nanjing University of Science and Technology, Nanjing, China, Oct 2015).
- Scheffler, Matthias: Causal Models in Big-Data Analytics for Novel Materials Discovery. (6th Exploratory Round Table Conference, Big Data in the Natural Sciences and Humanities, Shanghai, China, Nov 2015).
- Scheffler, Matthias: The NoMaD (Novel Materials Discovery) Center of Excellence: Challenges and Solutions to Build a Code-Independent Data Base for Computational Materials Science and to Identify Causal Models in Machine Learning. (2015 MRS Fall Meeting, Boston, MA, USA, Nov 2015).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (Symposium on Surface and Nano Science 2016 (SSNS'16), Furano, Japan, Jan 2016).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (Colloquium, University of Southern California, Los Angeles, CA, USA, Feb 2016).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (Colloquium, Department of Chemistry, University of California, Santa Barbara, CA, USA, Feb 2016).
- Scheffler, Matthias: Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype. (Chemistry Colloquium, University College London, London, UK, Mar 2016).
- Scheffler, Matthias: Novel Materials Discovery (NOMAD) a European Center of Excellence. (MI2I Symposium, Division of Physics, University of Tsukuba, Ibaraki, Japan, Apr 2016).

- Scheffler, Matthias: Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discover. (Colloquium, University of Tokyo, Tokyo, Japan, Apr 2016).
- Scheffler, Matthias: Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discovery. (Colloquium, National Institute for Materials Science (NIMS), Kashiwa, Japan, Apr 2016).
- Scheffler, Matthias: Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discovery. (Colloquium, Hokkaido University, Sapporo, Japan, Apr 2016).
- Scheffler, Matthias: Electronic Structure Theory Overview. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Scheffler, Matthias: High-Level Calculations and Benchmark Datasets for Materials. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Scheffler, Matthias: Van der Waals Interactions. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).
- Scheffler, Matthias: Fundamental Concepts of Electron-Phonon Coupling and Heat-Transport Calculations. (IPAM Reunion Conference on Materials for a Sustainable Energy Future, Lake Arrowhead, CA, USA, Jun 2016).
- Scheffler, Matthias: Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discovery. (Workshop on Theoretical Challenges: Simulating Materials out of Equilibrium, Hamburg, Germany, Jun 2016).
- Scheffler, Matthias: Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discovery. (The 1st USTC-FHI Workshop, On the Frontiers of Advanced Electronic Structure Methods, Hefei, China, Jun 2016).
- Scheffler, Matthias: Causal Models in Big-Data Analytics for Novel Materials Discovery. (International Conference on Electron Materials, IUMRS-ICEM2016, Singapore, Jul 2016).
- Scheffler, Matthias: Test Set for Materials Science and Engineering. (Electronic Structure Theory with Numeric Atom-Centered Basis Functions, FHI-aims Developers' and Users' Meeting, Munich, Germany, Jul 2016).
- Scheffler, Matthias: Computational Materials Science and the Future. (CAMD Summer School on Electronic Structure Theory and Materials Design, Copenhagen, Denmark, Aug 2016).
- Scheffler, Matthias: First-Principles Methods in Materials Science, High-Throughput Calculations. (Summer School on Interfaces and Energy, Göttingen, Germany, Sep 2016).
- Scheffler, Matthias: Learning Descriptors from Materials-Science (Big) Data. (IPAM Workshop on Understanding Many-Particle Systems with Machine Learning, Los Angeles, CA, USA, Sep 2016).

- Scheffler, Matthias: Strong Electron-Vibrational Coupling and Ab Initio Theory of Heat Transport. (Colloquium, Pennsylvania State University, State College, PA, USA, Sep 2016).
- Scheffler, Matthias: Strong Electron-Vibrational Coupling and Ab Initio Theory of Heat Transport. (Symposium on Modern Simulation Approaches to Soft Matter, Max Planck Institute for Polymer Research, Mainz, Germany, Oct 2016).
- Scheffler, Matthias: Strong Electron-Vibrational Coupling and Ab Initio Theory of Heat Transport. (2nd International Symposium on Energy Chemistry and Materials, Hefei, China, Oct 2016).
- Scheffler, Matthias: Neue Datenräume kreativ nutzen – Bessere Verzahnung von Wissenschaft, Informationsinfrastrukturen und Wirtschaft. (Nationaler IT-Gipfel 2016, Saarbrücken, Germany, Nov 2016).
- Scheffler, Matthias: Strong Electron-Phonon Coupling and Ab Initio Theory of Heat Transport - Concepts and Calculations. (2016 MRS Fall Meeting, Boston, MA, USA, Nov 2016).
- Scheffler, Matthias: Thermal Transport from First Principles. (Symposium on Surface and Nano Science 2017 (SSNS'17), Furano, Japan, Jan 2017).
- Scheffler, Matthias: Advanced Properties and Methods, Big Data and Complex Materials. (NSF-MolSSI Workshop on Materials Software, Berkeley, CA, USA, Feb 2017).
- Scheffler, Matthias: DFT, Its Impact on Condensed Matter and on “Materials-Genome” Research. (APS March Meeting 2017, New Orleans, LA, USA, Mar 2017).
- Scheffler, Matthias: Strong Electron-Phonon Coupling and Ab Initio Theory of Heat Transport - Concepts and Calculations. (Colloquium, Materials Science and Engineering, University of California, Berkeley, CA, USA, Mar 2017).
- Scheffler, Matthias: Discovering Interpretable Patterns, Correlations, and Causality in Big Data of Materials. (Chinese Materials Conference 2017, Yinchuan, China, Jul 2017).
- Scheffler, Matthias: Discovering Interpretable Patterns, Correlations, and Causality in Big Data of Materials. (The 15th International Nanotech Symposium & Nano-Convergence Expo (NANO KOREA 2017), Goyang, South Korea, Jul 2017).
- Scheffler, Matthias: Electronic-Structure Theory (Introduction). (NSF/CECAM School on Computational Materials Science: From Basics to Applications, Lausanne, Switzerland, Jul 2017).
- Scheffler, Matthias: Materials Discovery from Electronic Structure. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Scheffler, Matthias: Novel Materials Discovery by DFT and Compressed Sensing. (NSF/CECAM School on Computational Materials Science: From Basics to Applications, Lausanne, Switzerland, Jul 2017).
- Schneider, Markus: Wavefunction Methods and Benchmark Data Sets for Molecules. (Hands-on workshop and Humboldt-Kolleg: Density-Functional Theory and Beyond - Basic Principles and Modern Insights, Isfahan, Iran, May 2016).



- Sutton, Christopher A.: High-Throughput Screening and Guided Design of Transparent Conducting Oxides. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Tkatchenko, Alexandre: Modeling Energetics and Dynamics of Molecules at Surfaces: Recent Advances and Remaining Challenges. (Electronic Structure and Processes at Molecular-Based Interfaces (ESPMI VIII), Tucson, AZ, USA, Oct 2015).
- Tkatchenko, Alexandre: Electronic Properties of Molecules and Materials with a Self-Consistent Interatomic van der Waals Density Functional. (Total Energy and Force Methods 2016, University of Luxembourg, Luxembourg, Jan 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, Technische Universität München, Munich, Germany, Jan 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, Leiden University, Leiden, The Netherlands, Feb 2016).
- Tkatchenko, Alexandre: Modeling Energy Efficient Catalysts from First Principles: Non-Covalent van der Waals Interactions. (251st ACS National Meeting & Exposition, Computers in Chemistry, San Diego, CA, Mar 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, Luxembourg Institute of Science and Technology (LIST), Luxembourg, Mar 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland, Apr 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, Universidad Autonoma de Madrid (UAM), Madrid, Spain, Apr 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (Seminar, Princeton University, Princeton, NJ, USA, May 2016).
- Tkatchenko, Alexandre: Many-Body Dispersion: Dipole Limit and Beyond. (CECAM Workshop, Density- and response density-based models for Intermolecular Interactions in Molecular Assemblies and in Solids, Nancy, France, Jun 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (11th USPEX workshop, Villa Monastero, Varenna, Italy, Jun 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem? (BIOVIA Forum 2016, Noordwijk aan Zee, The Netherlands, Jun 2016).
- Tkatchenko, Alexandre: Non-Covalent van der Waals Interactions in Molecular Materials: A Solved Problem? (Computational Chemistry, Gordon Research Conference, Girona, Spain, Jul 2016).

- Tkatchenko, Alexandre: Seamless Dispersion Interactions for Molecules and Solids. (Electronic Structure Theory with Numeric Atom-Centered Basis Functions, FHI-aims Developers' and Users' Meeting, Munich, Germany, Jul 2016).
- Tkatchenko, Alexandre: Accurate and Affordable Lattice Energy Calculations: A Solved Problem? (30th Meeting of the European Crystallographic Association, Basel, Switzerland, Aug 2016).
- Tkatchenko, Alexandre: A Primer on van der Waals Interactions and Quantum Fluctuations. (IPAM Workshop on Understanding Many-Particle Systems with Machine Learning, Los Angeles, CA, USA, Nov 2016).
- Tkatchenko, Alexandre: Electronic and Nuclear Quantum Fluctuations at the Nanoscale. (10th International Conference on Computational Physics (ICCP10), Macao, China, Jan 2017).
- Tkatchenko, Alexandre: Approaches to van der Waals Interactions. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).
- Zhang, Igor Ying: Reaching a Uniform Accuracy for Complex Systems. (SINO-GERMAN Workshop on Biomolecular Simulations Across Scales, Shanghai, China, May 2016).
- Zhang, Igor Ying: Advanced Quantum-Chemistry Methods for Solids in the Numeric Atom-Centered Orbital Framework. (The 1st USTC-FHI workshop on the Frontiers of Advanced Electronic Structure Methods, Hefei, China, Jun 2016).
- Zhang, Igor Ying: Periodic MP2 and Coupled Cluster Theory for Numeric Atom-Centered Orbitals. (Electronic Structure Theory with Numeric Atom-Centered Basis Functions, FHI-aims Developers' and Users' Meeting, Munich, Germany, Jul 2016).
- Zhang, Igor Ying: Basics and State of the Art of Quantum-Chemistry Methods for Molecules, Clusters, and Materials. (Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, Berlin, Germany, Jul 2017).

