FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Scientific Report

2017–2019

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2017 – 2019

Fritz-Haber-Institut der Max-Planck-Gesellschaft

Berlin, September 2019
www.fhi-berlin.mpg.de

General Aspects and Shared Facilities of the Institute

Report of the Executive Director
Prof. Dr. Robert Schlögl

Major developments

By far the most important development for the FHI was the double retirement of Hajo Freund (April 2019) and Matthias Scheffler (July 2019). These major changes in the Kollegium were of course foreseeable, and many considerations and preparatory actions led to a smooth transition into a new era that is, at the time of this report, not yet complete. The institute greatly welcomes the continuation of the scientific activity of both "emeriti" with research groups. Suitable locations that will not impede the activities of the new Departments and central support in the form of "emeritus funds" make this possible. Central to both groups are, however, external grants in the form of ERC advanced grants and of other coordinated funding actions.

The new ISC Department has now started its experimental activities. The relocation from Bochum was executed and some of the main infrastructure items together with new equipment have started productive operation. The whole process of setting up the Department was substantially impeded by delays in the necessary building actions. These delays also lead to the unfortunate situation that, despite his retirement, Hajo Freund's former buildings can only be used on a very provisional basis, as major renovation work was found to be necessary. This work is currently still in the planning stage. The planning and execution of the new chemistry building for the ISC Department is also not fast and will require several more years until the building can be used. The PC and AC Departments provided laboratory space to allow the ISC Department provisional operation of activities requiring chemistry infrastructure. The provisional and limited operation of this Department is thus a situation that will continue to exist for several years.

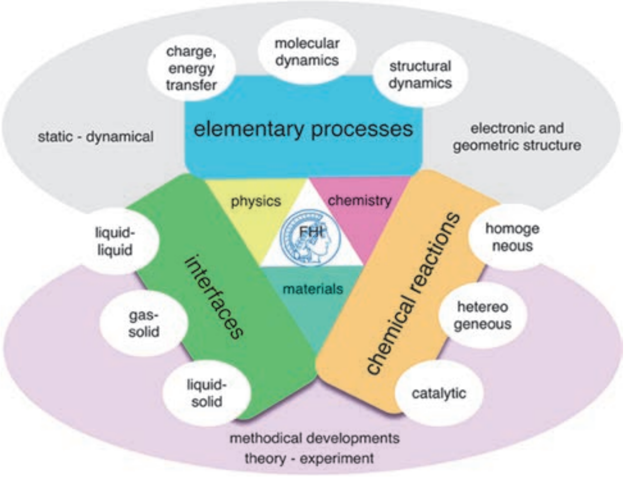
In the summer of 2019 the CPT section and senate of the MPG approved the appointment process of Karsten Reuter for the new TH Department (working title). We expect that the appointment negotiations will be completed by the time the Fachbeirat meets in Berlin. The FHI intends to locate the new Department in the renovated building A above the library. The building is now partly occupied by the ISC Department, which will remain there for some time. In addition, the Administration is located in the building. We expect to move the Administration into the former offices of the TH Department that will be free by the spring of 2020. This would allow that part of the new TH Department to move into its home in building A by 2021. In order to retain the continuity of the operation of several large projects in the TH Department the FHI was given the opportunity to allow Matthias Scheffler to continue the operation of his Department until the end of 2019. In January 2020 we expect that Karsten Reuter will take over the operation smoothly.

A masterplan for the operation of the Departments in transition will be presented at the meeting of the Fachbeirat. The Kollegium has transferred the responsibility for building and maintenance from Robert Schlögl to Gerard

Meijer who will oversee the execution of the building operations. The FHI was further given an adequate position for appointing a head of the building management team who will be instrumental for this plan. This addition followed a successful pilot phase in which the FHI tested the ability of an MPI to master its infrastructural maintenance in extended own responsibility yet under the final responsibility of the General Administration.

General Research Area

The Fritz Haber Institute (FHI) defined its research field in 2014. The appointment of three director positions in the then upcoming five years and the retirement of R. Schlögl in 2023 formed the framework for a discussion about the longer-term future of the institute approved by the Perspective Commission and the CPT section of the MPG. This plan guided all successive decisions and led to the appointments of Gerard Meijer, Beatriz Roldán Cuenya and most likely Karsten Reuter. The FHI has a traditional research focus in interface science and in the study of processes at interfaces. In a careful discussion including the Kollegium, the Fachbeirat and external members of the MPG and universities it was decided not to leave this general research field, but rather to evolve the activities in recognizing the insights achieved, the methods developed and the still unknown phenomena. By defining the status of understanding in several areas of interface science it was found that interfaces with liquids represent an area of enormous relevance in science and applications that is not reflected in the level of fundamental understanding. This sizeable "terra incognita" in interface science is largely due to a lack of suitable methodologies for studying liquid interfaces.



Scheme 1: The scheme locates the research area of the FHI as interdisciplinary operation between physics, chemistry and material science. It illustrates the fundamental nature of phenomena studied. The science base for these studies is the in-depth elucidation of geometric and electronic structures under working conditions which induce dynamic modifications of static structures. All this is only possible by a strong multi-disciplinary competence in developing novel methods in experimentation as well as in theory.

Theory and experimentation are likewise underdeveloped. The strong tradition of the FHI to develop methods in both areas is seen as a pre-requisite to take on the challenge of a substantial enlargement of our understanding of liquid interfaces. The scientific location of the institute is illustrated in scheme 1 which rationalizes its choice in finding the best persons as directors leading the institute into the future.

These considerations were also applied in defining future possible areas of research for the TH Department that required a new directorship in 2019. In 2018 the FHI conducted an extensive nomination process followed by an international symposium and a consultation process of MPG directors and external advisors. This process led to two candidates with equal quality. After intense discussions one of the candidates had to withdraw, and the FHI is now very happy to have found Karsten Reuter.

The Kollegium at the FHI

At the end of 2019 the Kollegium of the institute forms a "4+2" group with 4 regular Departments, the TH Department in intermediate operation and the research group of Hajo Freund.

Figure 2: The Kollegium of the FHI in July 2019: (right to left: Beatriz Roldán Cuenya, Matthias Scheffler, Martin Wolf, Hajo Freund, Robert Schlögl, Gerard Meijer)

The Departments are structured in groups with group leaders. The extent of internal structure varies between the Departments reflecting their individual organizational needs. The group leaders present their work conducted in the various Departments in the forthcoming sections of this report. The Kollegium highly values the extra responsibilities these scientists accept in the Departments in addition to their individual work. The following organigram of the institute reflects the internal organization. It further reflects the tradition that, at the FHI, there are no organizational units in science that are not formally attached to one of the Departments. The only exception are the two research groups headed by Hajo Freund and Matthias Scheffler. The responsible director represents the interests of the attached groups in the Kollegium meeting where the respective issues constitute a significant fraction of each meeting. In rare cases of discrepancies, the group leaders consult with the executive director.

Organigram

Free-Electron Laser	Joint Network Center (GNZ)	Computer Support Group (PP&B)	Electronics Lab	Mechanical Workshops
Wieland Schöllkopf	Gerd Schnapka	Heinz Junkes	Nicolai Große[b]	Franck Kubitz[c]
Responsible Director: Gerard Meijer	**Responsible Director:** Matthias Scheffler	**Responsible Director:** Beatriz Roldán Cuenya	**Responsible Director:** Gerard Meijer	**Responsible Director:** Martin Wolf

Central Services	Electron microscopy	Crystal Lab	Administration	Library
Sebastian Malotke	Thomas Lunkenbein	Beatriz Roldán Cuenya[a]	Gert von Helden / Axel Tscherniak	Uta Siebeky
Responsible Director: Executive Director	**Responsible Director:** Robert Schlögl	**Responsible Director:** Beatriz Roldán Cuenya	**Responsible Director:** Executive Director	**Responsible Director:** Robert Schlögl

[a] since April 2019
[b] since March 2019
[c] since May 2019

Inorganic Chemistry	Molecular Physics	Physical Chemistry	Interface Science[c]	Theory[e]	Chemical Physics[f]
Robert Schlögl	Gerard Meijer	Martin Wolf	Beatriz Roldán Cuenya	Matthias Scheffler	Hajo Freund
Hendrik Bluhm Axel Knop-Gericke Thomas Lunkenbein Katarzyna Skorupska Annette Trunschke	Sandra Eibenberger-Arias André Fielicke Bretislav Friedrich[b] Gert von Helden Jesús Pérez Rios Stefan Truppe Bernd Winter	Matthias Koch Takashi Kumagai Melanie Müller Alexander Paarmann Mohsen Sajadi Yujin Tong	See Wee Chee Markus Heyde[d] Christopher Kley Helmut Kuhlenbeck[d] Thomas Schmidt[d] Shamil Shaikhutdinov[d] Janis Timoshenko	Carsten Baldauf Christian Carbogno Luca M. Ghiringhelli Sergey V. Levchenko	Markus Heyde Helmut Kuhlenbeck Thomas Schmidt Shamil Shaikhutdinov
Theory Support Group Klaus Hermann **MPI CEC[a]** Mark Greiner Saskia Heumann Anna Mechler Holger Ruland	**Universität Leipzig** Knut Asmis **FU Berlin** Kevin Pagel	**ERC Group** Kramer Campen **ERC Group** Ralph Ernstorfer **ERC Group** Tobias Kampfrath **MPRG Group** Julia Stähler **MPRG Group** Michael Zürch **Emmy Noether Group** Laurenz Rettig		**Otto Hahn Group** Mariana Rossi **ERC Group** Matthias Scheffler **MP Partner Group** Xinguo Ren **MP Fellow Group** Claudia Draxl	**ERC Group** Hajo Freund

[a] MPI for Chemical Energy Conversion, Muelheim a.d. Ruhr
[b] until December 2018
[c] since October 2017
[d] since April 2019
[e] with Matthias Scheffler as acting director since July 2019
[f] until the end of March 2019

Figure 3: Organigram of the Fritz Haber Institute as of September 1, 2019.

The Institute could not function without the contributions from the science support groups. The Administration and the maintenance groups keep the operation going. The other groups form the invaluable technical science support. The Kollegium organizes the work such that the science support groups are associated with a Department and the respective director oversees the activities and reports to the Kollegium when necessary. In all these groups major changes of personnel was seen in the past two years, mostly owing to retirements of coworkers. The institute found many excellent new coworkers who bring new ideas and working concepts with them to the FHI. The unusual fluctuation in the groups and organizational overhauls in some groups led to a certain unrest in the institute that is expected to subside in the near future.

The FHI has adopted an approved formal managerial structure that essentially describes the past practice. The responsibility for day-to-day operations is organized between the executive director, the head of administration, the representative of the Kollegium (Bevollmächtigter der Geschäftsleitung) and the head of the maintenance group. The position of the representative of the Kollegium was made flexible in order to allow scientists who take this position to return to fulltime science work after some years. In this spirit, Gert von Helden will return to fulltime science in 2020 and Carsten Baldauf will resume the position of the representative of the Kollegium with the handover of the executive directorship from Robert Schlögl to Gerard Meijer in 2020.

The FHI decided that science communication to the outside, as well as to the inside, should be expanded and deepened in content. A relaunch of the institute website using the content management system offered by the General Administration was started as a critical instrument for modern communication. The FHI was further given part of an extra academic position to employ a scientific head of communication. This position was filled with Carsten Baldauf who will spend his other half position in the MP Department. The scientific content forming the basis of communication is collected by the Library of the FHI. The personnel there supported the creation and migration of the website intensely and professionally. It was thus decided to merge the activities of communication and of the Library and form a joint communication group. This is also adequate when considering that the Library is highly active in providing and securing access to the electronic scientific information media. The group retains their traditional activities of a Library, including their internal training function for using science information systems.

Equal opportunity actions

The FHI pro-actively supports equal opportunity activities in science. This is a continuous effort and thus requires continuous activity. In compliance with MPG rules the institute has equal opportunity officers. They are part of an MPG-wide network and work with the MPG equal opportunity officer. At the FHI they offer advice and consultation for all equal opportunity and family issues.

In 2019 the equal opportunity officers formed a committee for equal opportunity issues that prepares a written equal opportunity plan for the institute. This committee is formed from coworkers interested in the matter and has members from the Administration. The plan is also part of an MPG-wide activity. The plan documents the relevant activities and lists actions for improvement of the situation. It is expected that the plan will be put in action around the time of the visit of the Fachbeirat. These actions must comply to many rules narrowing the scope that are given by the funders of the MPG. The executive director had talks on these issues with the central equal opportunity officer and with the president of the MPG.

Practical activities of the local equal opportunity officers are giving advice on equal opportunity rights, in matters of possible discrimination, on solving issues with child care and on issues with organizing working conditions in compliance with family matters. They further broker child care and holiday activities for children.

The institute has created two special offices to help parents working with children. These offices are administrated by the equal opportunity officers and are in good use.

Figure 4: The parent-child rooms in the Haber Villa

Moreover, the equal opportunity officers are active in organizing the “Girls day” at the FHI aimed at increasing young women’s exposure to science. This is a highly successful activity in which all departments participate. Another practical activity is the organization of workshops in which female scientists receive special training for scientific presentations.

PhDnet at the Fritz Haber Institute

The Max Planck Society-wide and highly interdisciplinary PhDnet is also active at the Fritz Haber Institute. It's main purpose is to strengthen the exchange between the students employed at the institute, represent them officially in matters concerning the institute and – in general – to make their lives easier. The role of the PhD net is considered relevant among the students since power abuse and mental health issues are virulent in PhD students’ lives all over the world.

Each department at the FHI has at least two elected PhD representatives. Within the departments, the representatives organize regular meetings and activities. They are in contact with the head of the department and the administration.

The group of PhD representatives meets on a monthly basis to discuss current issues

In May 2019, the first Fritz Session took place at the Harnack House in Dahlem. Initiated by the board of directors and designed after previous institute-wide colloquia, the sessions were created by a group of PhD students. The goal is to invite internationally renowned speakers to talk about science relevant for the future and to address a general, scientifically interested audience. This gives PhD students the opportunity to organize a high-level event.

The theme of the first session on May 9th was "The future of our climate", with a lecture by Prof. Johan Rockström of the Potsdam Institute for Climate Impact Research, an internationally renowned expert for climate and sustainability who introduced the concept of "planetary boundaries". The event also featured an extraordinary art exhibition by the painter Agata Engelman and an interactive information fair by Erin and Aaron Redman from Leuphana University Lüneburg, in which everyone could estimate their personal carbon footprint. The 210 seats of the Hahn lecture hall in the Harnack House of the Max Planck Society were completely booked weeks ahead of the event, and the feedback was extremely positive. The event reached not only PhDs from the Fritz Haber Institute, but students from all over Berlin. The video-documentation of the event is being made available at fritz-sessions.org/climate. Upcoming events are in the planning phase. The organizing team has suggested three more topics and speakers for which the executive director has given consent and secured financial support to cover travel expenses of the speakers and a gathering with drinks and snacks after the event.

The bimonthly after work beer is the actual nucleus of the social activities. The PhD students, postdocs, technicians and undergraduate students at the FHI meet in the Richard Willstätter House and surrounding gardens to enjoy drinks, snacks, games, music and lively discussions. In this way, the students get to know each other, issues can be addressed, scientific exchange is fostered and international friendships are created.

When PhD students arrive at the institute for their first day, they often come from different cities, countries or even continents. Crucial for their success and well-being is that they know their way around at the institute and are introduced to the vibrant metropolis Berlin. Inside the departments the PhD representatives' approach new members, get them acquainted with the PhDnet and offer them help.

Figure 5:
Poster announcing the first edition of Fritz Sessions.

Honors and Awards

Over the past two years members of the FHI again received multiple honors and awards. An incomplete list of major honors given to FHI members reads as follows:

- Prof. Dr. Hans-Joachim Freund (CP)
  Lecture at the Hefei Forum of Great Minds (2017)
  Japan Society for the Promotion of Science Microbeam Analysis Committee Award (2017)
  CAS (Chinese Academy of Sciences) President's International Fellowship for Distinguished Scientists (2019)
  ACS Award in Surface Chemistry (2019)
- Dr. Francesca Mirabella (CP)
  Otto Hahn Medal (2018)
- Prof. Dr. Matthias Scheffler (TH)
  elected member of the German National Academy of Sciences Leopoldina (2017)
  Lecture at the Hefei Forum of Great Minds (2018)
- Dr. Mariana Rossi (TH)
  Elisabeth Schiemann Fellow (2018)
- Dr. Chris Nicholson (PC)
  Carl-Ramsauer-Award for excellent PhD thesis, Physical Society Berlin
- Prof. Dr. Robert Schlögl (AC)
  Ipatieff Lecture Northwestern University (2019)
  Eduard Rhein Award (science communication) (2019)
- Dr. Thomas Lunkenbein (AC)
  Lee Hsun Lecture (2018)
- Dr. Travis Jones (AC)
  HLRS Golden Spike Award (2019)
- Dr. Thomas Götsch (AC)
  Georg and Christine Sosnovsky-Award, Universität Innsbruck (2019)
- Dr. Eike Mucha (MP)
  Excellence in Glycoscience Award (2019)
- Prof. Dr. Gert von Helden (MP)
  "John B. Fenn Award for a Distinguished Contribution in Mass Spectrometry" by the American Society for Mass Spectrometry (2018)
- Dr. Johanna Hofmann (MP)
  Ernst Reuter Award of the Berlin Universities (2018)
  Wolfgang Paul Award of the German Society for Mass Spectrometry, (2018)
  Otto Hahn Medal of the Max Planck Society (2017)
- Dr. Sandra Eibenberger-Arias (MP)
  AScINA Young Scientist Award (2017)
  Elisabeth Schiemann Fellow (2019)

Major positions of co-workers from the FHI

As in previous years the FHI is happy to see that many of their co-workers found positions in academia documenting the excellent quality of the research in the institute. For this report the following names shall be listed:

- Dr. Xuefei Weng (CP), Associate Professor, Dalian University of Technology China, 2017
- Dr. Kramer Campen (PC), W3 professorship, University of Duisburg-Essen, Dep. of Physics, 2019
- Dr. Sarah King (PC), Assistant professorship with tenure track, University of Chicago, Dep. of Chemistry, 2018
- Dr. Julia Stähler (PC), Offer for W3 professorship, Humboldt University Berlin, Dep. of Chemistry, 2019
- Dr. Michael Zürch (PC), Max Planck Research Group (MPRG), assistant professorship with tenure track, University of California at Berkeley, College of Chemistry, 2018
- Dr. Dunfeng Gao (ISC), Associate Professor at State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics DICP, 2019
- Dr. Igor Ying Zhang (TH), Professor at Fudan University, 2018
- Dr. Yang-Gang Wang (TH), Associated Professor at the Southern University of Science and Technology of China, 2018
- Dr. Sergey V. Levchenko (TH), Assistant Professorship at the Skolkovo Institute of Science and Technology, 2018
- Dr. Mariana Rossi (TH), Head of a Lise Meitner Group at MPI for Structure and Dynamics of Matter, Hamburg, to start in 2020 (awarded in 2018)
- Dr. Honghui Shang (TH), Associate Professorship at the Institute of Computing Technology of the Chinese Academy of Sciences, 2018
- Dr. Runhai Ouyang (TH), Associate Professor of Materials at the Genome Institute of Shanghai University, 2019
- Dr. Jungho Shin (TH), Senior Researcher Position at the Korea Research Institute of Chemical Technology, 2019
- Dr. Amrita Bhattacharya (TH), Assistant Professor - IIT Bombay, 2018
- Dr. Mateusz Marianski (MP, TH), Assistant Professor, Hunter College, The City University of New York, 2018
- Dr. Jongcheol Seo (MP), Assistant Professor, Department of Chemistry, Pohang University of Science and Technology (POSTECH), 2018

Many other alumni of the Institute found positions as senior researchers in institutions all over the world or found positions in industry where many of them advanced to leading positions from where they are involved in contacts with the Departments of the FHI.

Publications of the FHI

The number of publications of the FHI in the past years was within the long-term average (274 papers in 2017, 261 papers in 2018, 193 papers until September 2019). The transitions in the department structure mentioned above did not impede the scientific productivity of the publications.

The distribution of the about 10400 publications (1953 - 2019) that appeared with an address of the FHI into different research fields (Fig. 6) reflects well the concept of research in the FHI as present in scheme 1. The following figure displays the distribution of the FHI papers to the research fields as defined by the web of science.

Figure 6: Distribution of all papers listed in web of science for the address "Fritz Haber Institute" to research fields as defined by web of science.

The scheme illustrates the interdisciplinary character of the research in the FHI averaged over several decades of activity. The diversity of the specialty fields besides the five big areas indicates on one side the methodical competence of the institute and reveals the activities to apply the conceptual insights to selected challenges in the broader research area.

Such a broad area of activity raises the question about the impact of the work in the community. One approach to answer this question is the analysis of how the work is cited in the literature. The following figure analyses the temporal evolution of the citations of the papers published over the last 10 years.

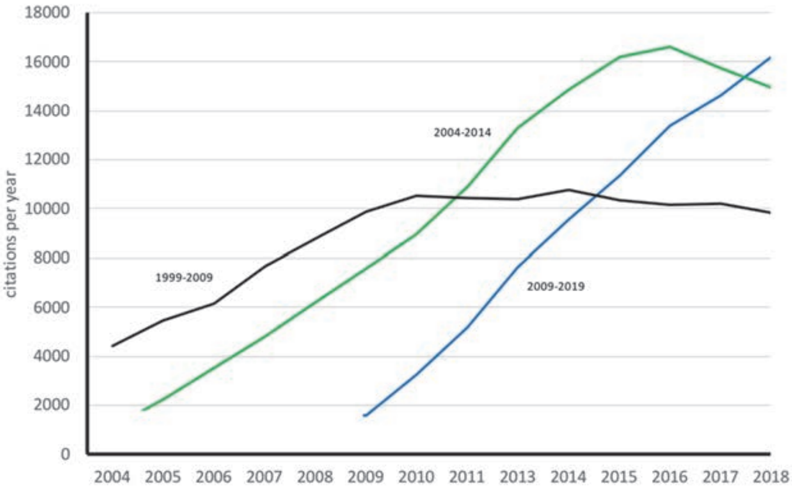


Figure 7: Evolution of the citations of all papers from the FHI in the time periods indicated.

The slope of the blue curve in the figure illustrates that the perception of the work takes time and is not immediate within the time interval of the visits of the Fachbeirat. If the citations of publications produced 5 (green) and 10 (black) years before the last decade are collected then one recognizes that a large fraction of papers have a constant impact even 10 and more years after their publication and that the number of papers with a lasting impact is substantially increasing over the last decade. Conditional to this analysis is the on average constant production rate (that had a maximum in 2012 that also recorded in the non-linear slope of the green curve). The fact that in all three curves one sees the bend for the incomplete 2019 data indicates that the citation activity affects both young and older publications. The data reveal that the work produced at the FHI has substantial long-term impact. It exhibits a significant induction period that may be typical for the field of physical chemistry where experimentation and theoretical work are painstaking and necessarily not fast. The work of the FHI is not driven by scientific hype. Care must be taken, however, to assign specific research fields to this trend as the mechanisms of impact are quite diverse between the different fields indicated in the previous scheme and between theory and experiment.

Acknowledgements

The Kollegium of the FHI wishes to thank all members of the Fachbeirat for spending their valuable time evaluating and advising the institute. Likewise, the Kollegium wishes to thank all co-workers for their dedication and creativity in creating all the results and insights on which the science production of the institute rests. This explicitly includes all support and administrative groups. Last but not least, the Kollegium wishes to thank all those involved in preparing the report and the visit of the Fachbeirat.

Head of the Joint Network Center (GNZ)
Dipl.-Ing. (FH) Gerd Schnapka

IT Community Award, InIT MPG (2019)
Appointment to BAR-Member (2014)
Head of the Joint Network Center (2009)
Graduate Engineer, TFH Berlin (1993)

Joint Network Center - GNZ

The Joint Network Center (Gemeinsames Netzwerkzentrum, GNZ) of the Berlin-Brandenburg Max Planck Institutions is a regional IT competence center, located and managed at the FHI. This group focuses on networking, backup, virtualization, IT-services and security services. At present, the center supports 15 Max Planck institutions including all 8 Max Planck Institutes.

We did a complete redesign of the active network (routing and switching) in 2018. After an extensive comparison of important network manufacturers (Cisco, Dell, Extreme, HPE/Aruba, Huawei etc.), we chose Dell Networks as new network supplier. A first successful project in 2019 (Institute extension at the Molecular Plant Physiology in Potsdam/Golm) confirmed this choice. Over the next two years all networks of the participating institutes in Berlin and Potsdam/Golm will be migrated. Figure 1 shows the new structural design of the interconnected network and the upcoming new active network at the FHI.

To increase the efficiency of the hardware used, we virtualized the IBM Spectrum Protect server backup software (formerly known as Tivoli Storage Manager). The software now runs within the VMware cluster and serves all clients from a common instance.

In 2018, the GNZ initiated a project for the Open Source Sync & Share alternative Nextcloud. More than 30 Max Planck Institutes and Institutions nationwide, including the FHI, participated in this project. A distributed system was created in this process. Together with the Max Planck Digital Library (MPDL), a central financing of this software was achieved in 2019. With this so-called Campus License, every institute in the Max Planck Society can now access the products support and a selection of office alternatives (LibreOffice or OnlyOffice) including license and support.

In 2018, we launched[1] the StorNext scale-out storage system (see Figure 2) in order to cover the storage requirements of the FHI and some other institutes and to consolidate disk space. This enables the participating institutions to access scalable and cost-efficient shared storage. Five institutions are already benefiting from this solution.

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[1] Case Study, https://datacenter.computerwoche.de/a/zukunftsfaehiges-storage-fuer-die-forschung,3570786, 29.05.2019

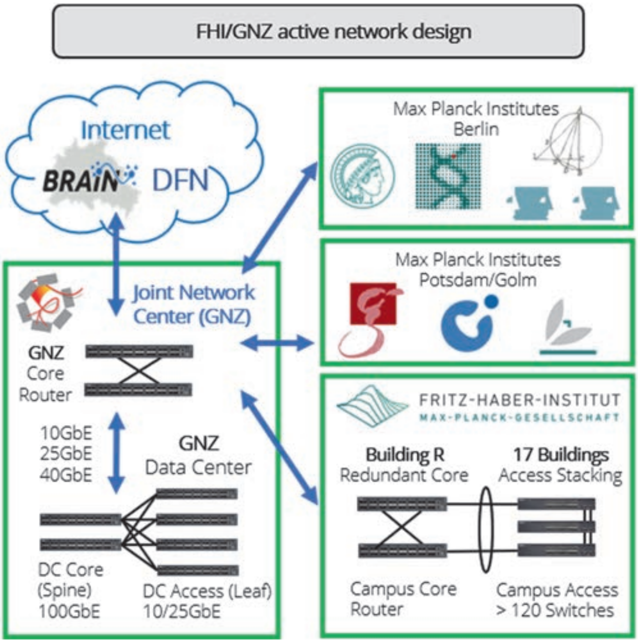

Figure 1: New FHI active Network design. The GNZ interconnects the FHI with regional Max Planck Institutes, the Internet and the German (DFN)/Berlin (BRAIN) research networks. The Data Center (DC) uses a modern Spine/Leaf architecture for high scalability and low latencies. In the FHI campus network design, stacking technology in the access and link aggregation technology in the backbone ensure a stable and economical network.

In 2018, the GNZ took over the IT service for the Archive of the Max Planck Society, the Harnack House (conference venue of the Max Planck Society) and the Berlin office of the Max Planck Society.

The group is committed to the KNITS (Competence Network IT Security) which takes care of the reorientation of IT security in the Max Planck Society. In cooperation with the GWDG (Gesellschaft für wissenschaftliche Datenverarbeitung mbH Göttingen) the GNZ designed the reporting and handling of IT security events and incidents. Two of the most important IT security concepts, network and backup, are also currently being developed with our cooperation.

In the years 2018 and 2019, the GNZ was also represented in the BAR-committee (with Gerd Schnapka as an appointed member). The committee advises the president, the institutes and the general administration on fundamental questions of IT deployment in the Max Planck Society and on specific IT procurement projects. The expertise of GNZ is particularly popular in questions of network, infrastructure, storage and security.

In addition to the firewall BAR-subcommittee, the GNZ was also involved in the BAR-subcommittee for server room planning in 2018/19. This permanent subcommittee supports the institutes especially in the initial phase of the

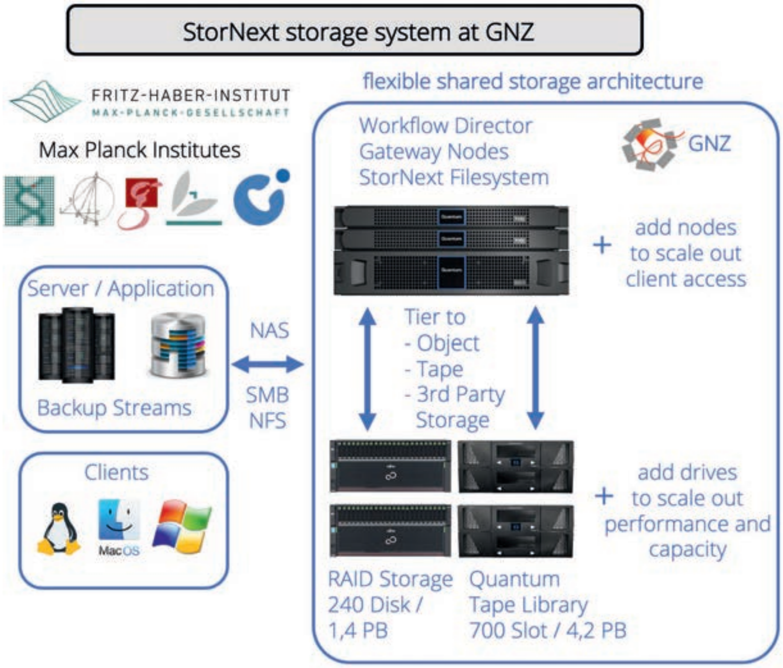

Figure 2: StorNext storage system at the GNZ. Although the new storage system in the GNZ is based on a complex technology, it provides clients with a simple interface for storing their data over the network (NAS, Network Attached Storage) using standard operating system protocols like NFS or SMB. The architecture of the storage system allows scaling according to the requirements of scientific projects by simple extension of gateway nodes or disk arrays.

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Head of IT (PP&B)
D. Ing.-grad Heinz Junkes

Group leader (since 1988)
MPG Communitas award (2019)
Guest lecturer Beuth-Hochschule, Berlin (since 2004)
Postgraduate studies (Diploma, 1988), Electrical Engineering, TU-Berlin
Ing. grad in Communications Engineering (1984), FH der Deutschen Bundespost

IT – Enabling Research

The IT support group PP&B at the FHI provides the typical IT services at the institute on the basis of the powerful network infrastructure provided by the GNZ. These services include user administration, the provision of mail, web and storage infrastructure as well as the installation and operation of desktop systems.

Many database applications support the organization at the FHI such as a document management system, inventory database, applicant portal and mailing-list server (mailman: http://fhi-lists.de). PP&B provides a cloud service (Powerfolder: https://cloud.fhi-berlin.mpg.de:8443) for sync&share but also collaboration platforms like Sandstorm and anyOffice. The latter is used by many other Max Planck Institutes as part of our Max Planck initiative. Furthermore, we operate a system for the organization of conferences and other events (indico: http://fhi.events) at the institute as well as a system that permits setting up electronic labjournals (elog: https://elog.fhi-berlin.mpg.de).

PP&B operates a computer cluster (HPC) at the institute, manages the telecommunications system and, in cooperation with the building services group, the building automation system (Webctrl: https://webctrl.rz-berlin.mpg.de), the access control system and a working time recording system.

PP&B is active in training and has started a project in which all FHI trainees work together (we are currently developing a new access control system). PP&B regularly offers training courses on IT-relevant topics at the institute. We are responsible for the procurement of software licenses at the institute and advise the staff and the directorate on data protection.

The services described above are normal IT services. However, our main focus is on scientific data processing to "enable science" and to ensure the quality of the obtained data. This is why all services we provide are science-oriented.

Implementing FAIR principles

In our measurement environment we already implemented principles that are known as the FAIR principles (Findable, Accessible, Interoperable, Reusable). E.g. we collect raw data and metadata to the experiments and keep them in our archiverAppliance[2] The metadata is kept in a well defined structure which makes them interoperable and reusable. Access to the data is guaranteed by a unique assignment (timestamp, name, version control). How this is to be organized in

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[2] ArchiverAppliance: https://slacmshankar.github.io/epicsarchiver_docs/index.html

the future is currently being discussed intensively within the framework of FAIRmat. See article by Claudia Draxl "Activities of the Max Planck Fellow Group". In a typical experiment, data and metadata are scattered. Some critical context for interpreting the data is stored only in people's memories. Metadata may be recorded cryptically in filenames or written in paper notes. Data may be encoded across a variety of formats – some proprietary – which can only be read by specialized software. This approach is manageable up to some few data sets but it does not scale well when the number of data sets rises, for example due to the use of faster detectors and higher repetition rates.

What are the specific limitations of the status quo in most experiments? The data is not machine-readable or searchable and the relationship between any two pieces of data is unclear. It is difficult to automate the routine steps of analysis, and code is difficult to generalize or reuse for future experiments. Multimodal analysis, involving connecting different techniques with different conventions, is labor-intensive. The traditional approach usually is also not streaming-friendly, which precludes exciting possibilities like observing partial results in real time or performing adaptive experiment steering.

To scale to modern data velocities and volumes, software must systematically track all of the data and metadata necessary for later analysis. This includes:

- Time stamps
- Secondary measurements (e.g. motor positions, sample temperature)
- “Fixed” experimental values (e.g. distance from sample to detector)
- Calibration data, Environmental data (incl. data from building control)
- Hardware settings (e.g. exposure time)
- Hardware diagnostics
- Physical details of the hardware (e.g. physical scale of a pixel)

It encompasses information about the sample and the purpose of the measurement including:

- Persistent identification of the sample
- Description of how it was prepared
- References/links to external databases (e.g. NOMAD)
- The intention of the measurement

Finally, it includes bureaucratic information about data management:

- Where are the data and how can they be accessed, both on/off-?
- Who collected the data?
- Who owns or can access the data?
- How long will the data be stored?
- Hardware settings (e.g. exposure time)
- Hardware diagnostics
- Physical details of the hardware (e.g. physical scale of a pixel)

A small variety of “records” represents data and metadata, key-value mappings that adhere to a minimal but formalized schema.

In our environment the scientist initiates data collection with an experimental procedure, a sequence of steps that may incorporate adaptive logic that depends on previous measurements. This can be realized with a Scanserver3. It was developed to allow the flexible assembly and execution of "recipes", that is a list of commands. All communication with the hardware occurs through an orchestration engine that captures readings and metadata and handles errors safely. Data flow from the control system (EPICS: https://epics-controls.org) through a hardware abstraction layer is organized in "records" (key-value mappings) that are dispatched to any number of consumers. The records are typically saved to the ArchiverAppliance and additionally exported to ordinary files (e.g. HDF5, CSV or TIFF) if desired. They are typically also sent directly to a live data processing and visualization pipeline. After the experiment, the data may be retrieved as standard data structures suitable for use with existing scientific Software (e.g. Matlab, Origin, Igor, python libs, etc.).

EPICS framework used at the FHI-FEL

Light source facilities are very complex machines that cannot be operated without the use of sophisticated systems executing tasks automatically, not manageable manually by physicists or operators.

Examples include automatization components that simply prevent maloperation or keep the required timings, such as, sequencer programs for energy ramping or beam switching between parts of the facility. Or there are optimization tools, ensuring the stability of critical parameters during operation (fill pattern, tune, path length), tune the machines, and improve their performance. For the FEL's specifically constant adjustment of bunch charge, compression, energy has to succeed on a shot-by-shot basis and involves accelerator units, timing devices, and detectors at the experiment.

Tuning and optimization techniques utilize feedback or feed-forward techniques. The ultimate goal, and thus of particular interest, are elements improved by artificial intelligence: human-like capabilities such as learning and adaption, which can make use of the acquired knowledge (data) and previously gained experience to understand and interpret behaviors and phenomena and help to solve complex problems.

Well-tuned, optimized, stable set-ups of the facility need to be re-achieved safely and fast. Thus a reliable snapshot channel save-restore-compare tool is an important component. It typically enables us to change operation modes, and recover from shutdown activities or power outages. Data gets tagged in the archiver and retrieved from there. Unintended data losses at the volatile front-end computers are prevented by Input-Output-Controller (IOC) autosave and recover procedures, either using a network drive or re-reading settings from the buffering hardware. The compare option allows one to identify deviations from the actual set points from the intended values. Precision setting of magnetic beam guiding elements requires additional reproducible cycling or degaussing procedures.

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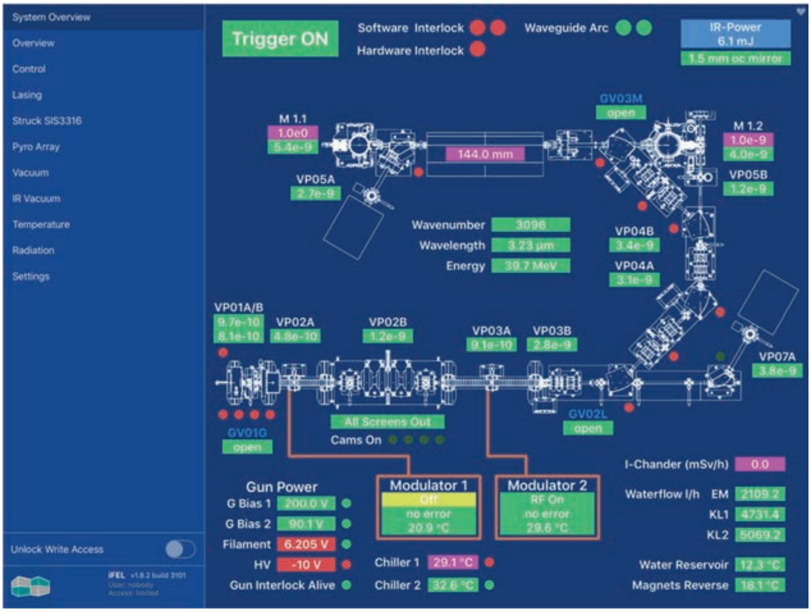
[3] EPICS Scanserver: http://controlsystemstudio.org/



IR-Power 6.1 mJ
1.5 mm oc mirror
GV03M open
M 1.1 1.0e0 5.4e-9
144.0 mm
M 1.2 1.0e-9 4.0e-9
VP05A 2.7e-9
VP05B 1.2e-9
Wavenumber 3096
Wavelength 3.23 µm
Energy 39.7 MeV
VP04B 3.4e-9
VP04A 3.1e-9
VP01A/B 9.7e-10 8.1e-10
VP02A 4.8e-10
VP02B 1.2e-9
VP03A 9.1e-10
VP03B 2.8e-9
VP07A 3.8e-9
GV01G open
GV02L open
I-Chander (mSv/h) 0.0
Gun Power
G Bias 1 200.0 V ●
G Bias 2 90.1 V ●
Filament 6.205 V ●
HV -10 V ●
Gun Interlock Alive ●
Modulator 1 Off no error 20.9 °C
Modulator 2 RF On no error 29.6 °C
Chiller 1 29.1 °C ●
Chiller 2 32.6 °C ●
Waterflow l/h EM 2109.2
KL1 4731.4
KL2 5069.2
Water Reservoir 12.3 °C
Magnets Reverse 18.1 °C

FEL Operation Overview, iPad App

E-logbook

Multiple e-logbook instances are in operation at the FHI (based on elog, developed by PSI) to make data even more FAIR compliant. It keeps track of the context in which data and metadata have been collected, thus enabling a better understanding of how data were gathered. This is essential for members of the experimental team and others to be able to reuse the data (the R in FAIR). The e-logbook contains a list of time-stamped events, which are either sent automatically from the experiment devices (errors, debug information, command lines) or written manually by the experimental team in the form of comments. In the FAIRmat project, Ralph Ernstorfer is responsible for coordinating the sensible use of e-logbooks in experiments. The FHI will actively support the implementation of the proposal developed there.

The project "EPICS für die Max-Planck-Gesellschaft" is funded by the Max Planck Software Commission with 1 FTE.

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Head of the Electronics Lab
Dr. Nicolai Grosse

Head of the Electronics Lab (since March 2019)
Staff member at the Fritz Haber Institute (2018)
Postdoc at the Technical University of Berlin (2009–2017)
PhD (physics) at the Australian National University (2003–2009)
Guest Scientist at the Max-Planck-Institute for Gravitational Physics (2003)
B. Sc. (physics) at the Australian National University (1999–2002)

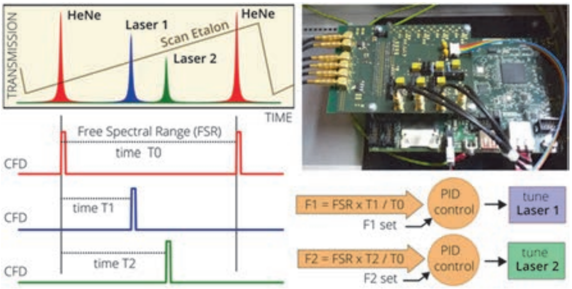
Overview of the Electronics Lab (E-Lab)

The E-Lab is a central facility that supports scientists with their needs concerning electronic instrumentation. Its key strength lies in developing and constructing specialized equipment for measurement and control that is not otherwise commercially available. The activities of the E-Lab are propelled by a well-integrated team of engineers (5), electronic technicians (9), apprentices (2) and students (1). The team is headed by Nicolai Grosse, who, having a background in experimental physics and electronics, now carries on the valuable legacy left by Georg Heyne who recently retired after 27 years of dedication to the E-Lab and its staff.

In addition to designing, developing, constructing, and programming customized electronic instrumentation in close cooperation with researchers, the E-Lab offers a much wider range of services. The rapid-repair service is particularly well-appreciated as it enables researchers to quickly continue with their experiments and gather data after an interruption caused by the unexpected failure of commercial equipment. Visits to the researchers' labs for consultation are also available. The need for small modifications to cables and connectors is met by the E-Lab with a fast turn-around time which is made possible by the well-organized inventory of spare components. This inventory, ranging from passive components to active modules, is also accessible to researchers throughout the institute.

By making use of the equipment on offer from the E-Lab's rental program researchers can realize pilot tests of new ideas at low cost and high speed. An important function of the E-Lab is its consulting service for researchers that is striving to push the experimental boundaries. The staff, as a whole, offers a wide knowledge base that includes high-bandwidth low-level signals, fast switching of high-voltages, field-programmable gate arrays (FPGA), precision temperature control and measurement-control systems that are commanded by LabView or custom software.

Safety and good documentation are important aspects of the E-Lab's operating principles. All equipment associated with high voltages that is built or modified at the E-Lab undergoes electrical safety tests and must be accompanied by a manual before being handed over to researchers. The E-Lab's comprehensive database stores all production and repair data and is intimately linked with the inventory of components and the tracking of finances. This system ensures transparency and reproducibility while also serving as great store of knowledge for future projects.



The inner-workings of the Laser-Frequency-Stabilizer designed, built and programmed by E-Lab staff to meet the requirements specified by researchers from the Molecular Physics department. An FPGA-board is coupled to an analog interface that processes signals via constant fraction detection (CFD) which are obtained from light transmitted by the reference etalon whose length is periodically scanned. The locations of 2 laser modes relative to the HeNe laser in the free spectral range are interpreted by the FPGA which sends feedback to control the laser frequencies.

Activities of the E-Lab

The main activities of the E-Lab over the two year period starting in September 2017 are summarized here. The E-Lab staff completed work on a total of 612 individual pieces of equipment. Surprisingly, as many as 220 of those projects were complete instruments of a complex nature. Shown in the figure above is an example of a particularly ambitious project that demonstrates excellent cooperation with the researchers. An impressive 87% of the 255 instruments brought in for repair were successfully repaired in-house. Good use of the rental program was made with 248 instrument rentals registered and handed-out for an average duration of 10 weeks. Thousands of electronic components from the inventory were passed on to the researchers directly in the 1000+ consultations made in person at the front desk. It should be noted that these figures fluctuate in general due to variable demand and the complexity of the tasks at hand but they are indeed consistent with the high level of activity and output of the E-Lab. Behind these figures there is a team of highly motivated people who take great care and pride in their work. The personal interaction between the E-Lab staff and the researchers of the institute is very positive.

Beyond its core activities, the E-Lab is committed to strengthening ties between the electronics groups of other Max Planck Institutes by sustaining the annual meetings and information network. With its apprenticeship program the E-Lab also strongly supports the next generation of electronic technicians for devices and systems as exemplified by one apprentice winning an MPG award (Azubi-Preis) in 2018. In addition, the E-Lab participates in the school work-experience program where students learn basic practical skills and gain insight into the profession. The E-Lab is engaged with public outreach, having co-hosted an event with the Mechanical Workshop, for members of the public to build their own electronic circuit that they could take home as part of the “Lange Nacht der Wissenschaften”.

Head of Precision Mechanical Workshop
Franck Kubitz

Head of the Precision Mechanical Workshop at the FHI since April 2019
Owner and manager of a metalworking company from 2003 to 2016 in Berlin
Technical business economist at the German chamber of industry and commerce (2002–2004)
Bachelor Professional and Instructor in precision mechanics (1997–2000)
Apprenticeship as an industrial mechanic at Osram (1980–1984)

Overview of the Precision Mechanical Workshop

The Precision Mechanical Workshop (Feinwerktechnik, FWT) is a central facility offering support to scientists to meet their needs in mechanical manufacturing. By working in close cooperation with the technical staff of the research departments and the E-Lab we construct specialized devices for scientific experiments that are not available on the world market. Given the demanding combination of geometry, tolerances and materials, the FWT often works at the limit of what is technically feasible. The scientists can, however, rely on the excellent expertise that is available at the FWT with its very experienced staff of craftsman who master the entire spectrum of precision mechanics. The FWT covers a large production depth with its good range of technical equipment. We manufacture parts in high-end quality ranging from millimeter-sized components up to the large stainless-steel chambers used for experiments in vacuum. In addition to the conventional machines and work done by hand that is still indispensable the workshop has two CNC 5-axis machining centers (see Fig. 1), one CNC turning cell, and three CNC-controlled EDM machines for component production. The use of CAM modules for CNC program development complete our production possibilities.

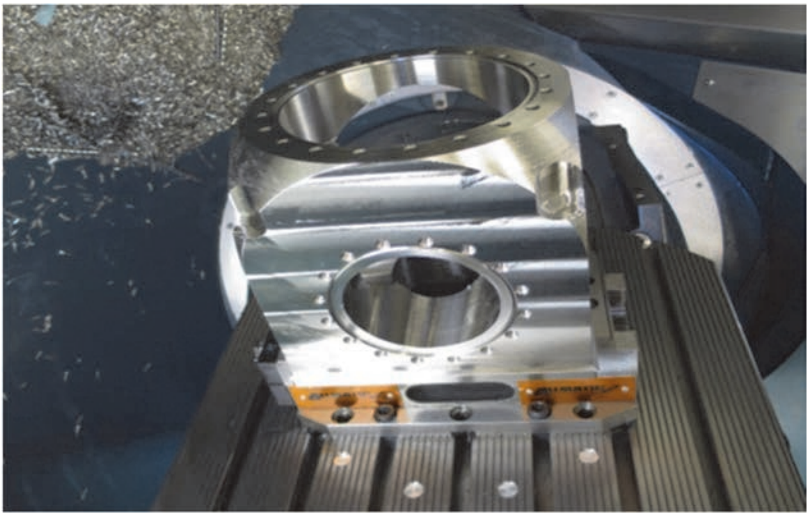


Figure 1: CNC 5 axis milling of an experimental chamber

The materials used at the institute range from rubbers to metals to technical ceramics. In order to meet these different material requirements the FWT plans to invest in a CNC micro-waterjet cutting machine. As a general principle, when processing orders, the FWT takes into account the critical timing of projects, for example, by meeting the deadlines for scientific experiments involving beam time. Although an economic analysis for projects is performed, successful scientific research always takes precedence.

Activities of the FWT

On average, approximately 450 orders per year are processed in the FWT, from small repairs to complete and fully-functioning complex projects. In addition to the sixteen skilled workers, there is an assistant to the management and two apprentices who are employed in the workshop. Constant developments and improvements for the staff and their work environment is encouraged, as in accordance with the Kaizen[4] philosophy. Modernization of the FWT is planned for the near future, where the use of the micro-waterjet cutting technology is currently being prepared. In autumn of 2019 the Crystal Laboratory and its two staff members will become integrated into the FWT. For the goal of public outreach, we work together with the E-Lab by promoting the different trades, and their relation to scientific research.

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[4] Kaizen = continuous improvement process from the Toyota Company

Operation Manager in the Division Central Services
Sebastian Malotke

Operation Manager and Construction Coordinator at FHI (since 2014)
Construction Coordinator at MPI for Biochemistry (2012–2014)
Manager for special-purpose projects in the district Oberhavel (2010–2012)
Dipl.-Ing. in Architecture, Technische Fachhochschule Berlin (2009)

Central Services, Facility Management, Construction and Engineering

Advanced science puts high demands on modern high-quality buildings as well as on reliable and stable technical infrastructure. For example, while decades ago, stable laboratory temperature, control of particles in the air, a steady flow of cooling water or the supply of various gases was a luxury, it is nowadays a requirement to operate state-of-the-art equipment. Our department supports science in the planning of facilities. We do our best to control the implementation by the various external companies and take care of the operations and maintenance. Further, we act as a bridge between the scientists at the FHI and the central construction department in Munich. A particular challenge lies in the history and diversity of the FHI campus which consists of buildings that are over 100 years old as well as new high-tech laboratory buildings.

The operation, maintenance and periodic modernization of advanced infrastructure also put high demands on the education and constant training of the employees. Over the years, we managed to assemble a highly motivated team team of skilled employees with four persons in the administrative and 14 persons in operational areas. The central services department at the FHI is divided into Technical Facilities Support and a Construction Division.

Construction division

In the construction division, we are involved in the construction of new buildings as well as the modernization and maintenance of existing ones. Large scale projects are handled by the central Max Planck construction division in Munich, together with architects and external technical planning companies. For those large-scale projects, we act as a bridge between Munich, the external companies and the scientists at the FHI. While it is not always easy to balance the interests of the different parties involved, our focus lies at the assessment and communication of the needs and wishes of scientists and further to oversee and control the planning and execution of the projects.

Smaller projects are handled inhouse. Those range from small repairs and maintenance to medium size modernizations. Again, the needs of the scientists are central. However, they also need to be balanced with rules and regulations as well as economic concerns. The rules and regulations are an important aspect and range from regulations concerning tendering processes to various safety rules that are always taken very seriously.

The FHI is in the fortunate situation to be an historic institute having a unique campus. We are especially proud of our outside gardens which provide a beautiful setting for the working environment at the FHI. They are as nice and as beautiful as they are because of the skilled and creative work of our team of gardeners.

Technical Facilities Support

The engineering division is responsible for the operation, maintenance as well as the periodic modernization of all technical facilities. The focus lies on creating a dependable infrastructure that allows scientists to run their state-of-the-art equipment. When infrastructure becomes ever more complex with complicated dependencies, an important aspect is then also the documentation of the installed soft- and hardware.

Most of the facilities are now integrated in the FHI data infrastructure network, which allows for monitoring the status and stability and the optimization of parameters. Further data is collected on, for example, energy consumption. Its reduction is important not only to minimise, not only costs, but also the institute's CO_2 footprint. As an example of the many other technical systems in the FHI we would like to briefly introduce the heating of building R.

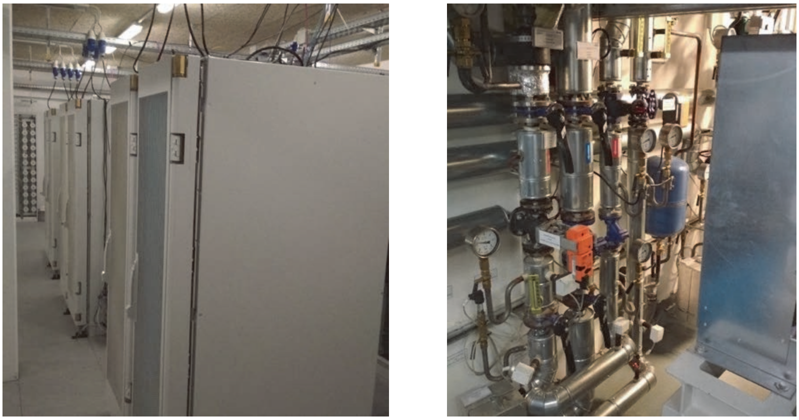


Figure 1: The server room (left). Heat recovering system (right). In the server room, a setpoint air temperature of 23 ° C is required. The flow temperature of the cold water must be 15 °C in the secondary circuit. The temperature of the re-cooling water is approx. 42 °C which exactly corresponds to the flow temperature for the underfloor heating. If this heat will not be used for heating, then it would be discharged via the re-cooler to the outside air

In addition to the workshops and the offices of the Central Services, building R contains the central server room of the Fritz Haber Institute, measuring approximately 100 m^2. This room is operated at a relatively high temperature level.

The waste heat resulting from the cooling of equipment is inducted directly to the underfloor heating system. This has made it possible to heat the entire building in an environmentally sustainable way for three years now without having to resort to other heating sources. Compared to conventionally heated buildings with similar energy requirements, this amounts to a savings of 35,000 kWh per year, and a corresponding reduction in CO_2 output amounting to approximately 4,76 tons per year.

Head of Library
M.A. Uta Siebeky

Head of Library of the Fritz Haber Institute (since 1993)
Magistra Artium, Humboldt-Universität zu Berlin (2008)

Library

A main focus of the library's work since autumn 2018 has been the renewal of the library's web pages and since the beginning of 2019 the collaboration in the creation of the new FHI web pages. The websites are developed with the content management system Fiona (Infopark) which is widely used in the MPG using responsive web design technology. The library has contributed to the menu navigation (flyout) of the new pages and helped to design the homepage.

During the last reporting period the library conceived and initiated the new event series 'Coffee Talk' at the FHI. The series includes short lectures from the FHI service groups. The target group is all FHI employees. The Coffee Talks stimulate internal communication about existing infrastructures and resources. As a result, this improves the efficiency of use for the future and thus creates a great benefit for the FHI. The Coffee Talks take place each first Thursday every two months. The first Coffee Talk took place in May 2018. Until now there have been seven contributions on the following topics:

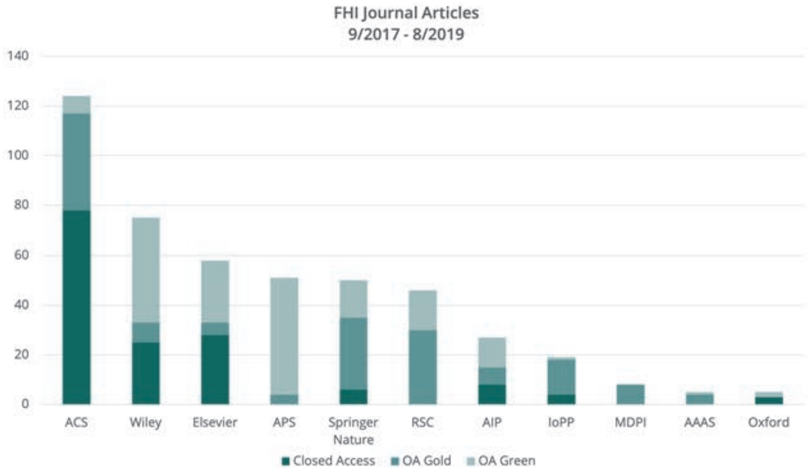
1. Read Newspapers Online (Library), May 2018
2. Nextcloud (GNZ), July 2018
3. Basic Data Protection Regulation (Administration), September 2018
4. Powerfolder (PP&B), November 2018
5. Electronics for Scientists (E-Lab), February 2019
6. Sub-threshold Allocation Ordinance (Administration), April 2019
7. Web Search Engines (Library), June 2019

The eighth Coffee Talk will take place after the summer break at the beginning of September 2019 on the topic 'EPICS in the MPG' (PP&B).

The project 'Correction of FHI Affiliation in the Web of Knowledge literature database' will be completed by the end of 2019. These corrected data will provide the scientific community with a high-quality database for research including historical publications.

In addition, the library supports the researchers in all questions of publication management and participates actively in the deposit of full texts according to the principles of the *Berlin Declaration on Open Access to the Knowledge in the Sciences and Humanities*. The articles are archived in MPG.PuRe – the institutional repository of the Max Planck Society. It supports the authors in the implementation of the Zweitveröffentlichungsrecht (right to secondary publication (§ 38 (4) UrhG)) and Open Access publication for ERC and HORIZON 2020 funded projects. The library maintains a fund for publications published in original Open Access journals. As a result of the FHI's continuous commitment to Open Access, it has a share of approximately 67%[5] of its journal articles (gold (32%) and green (35%)) for the reporting period 9/2017-8/2019. A total of 499 articles were published in peer reviewed journals during the period mentioned.

Most articles appear in high impact journals which are of great importance for the research orientation of the institute. These are mostly journals of the publishers ACS, Wiley, RSC etc.



FHI journal article 9/2017 – 8/2019, at least 5 articles per publisher, source MPG.PuRe

The library also 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 16,500 monographs in a reading room, which is designed as a common room for the whole institute. The library is 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.

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[5] The basis for the calculation is MPG.PuRe, the institutional repository of the Max Planck Society. The data is collected there by autopsy. A comparison with data from Web of Science is therefore not possible.

Head of Administration
Axel Tscherniak

Head of Administration (since 2018)
Managing Director, Onshore Wind Energy Agency, Berlin (2014–2017)
Head of Internal Management, German Commission for UNESCO, Bonn (2013)
Executive Director, Peterborough GreenUP, Canada (2010–2012)
Managing Director, Europarc Germany, Berlin (1998–2009)
MBA, Leuphana University, Lueneburg (2008)
Graduate Diploma Applied Geography, University Trier (1997)

The administration at a glance

The administration

Every Max Planck Institute, regardless of the research focus, has administrative duties that need to be handled with care in order for the organization to run smoothly. In the broadest sense, administrative tasks are the assignments and activities that secure the ongoing operation. These include staff administration, ordering goods, controlling the budget, correspondence, guest management - all of these tasks are the basis for a well-functioning and up-to-date research institute.

We are about 25 colleagues in the administration of the FHI, who - at the core of their job - work on administrative processes effectively, establish connections and initiate necessary improvements. Internally, we are organized in the classic areas of financial accounting, purchasing, personnel, travel agency, cash register and central services (see figure 1). The institute's driver is also part of the "team admin". The current tasks are performed by administrative assistants, receptionists, accountants and other specialists. In some areas where specific roles do not exist, staff works together to ensure that administrative tasks are carried out.

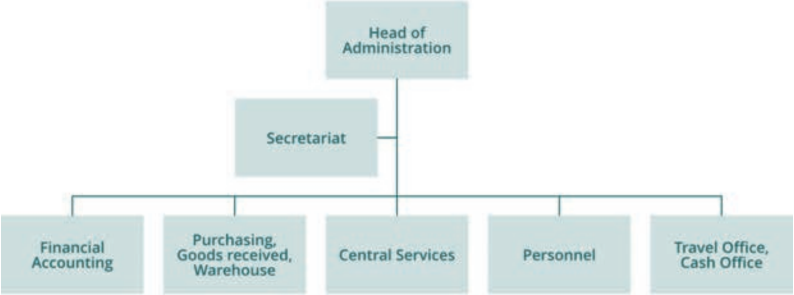


Figure 1: Organization chart

Knowledge and Competence

Without well-trained and motivated employees, even a technically well-equipped administration cannot be successful in the long run. Therefore, it is important to support the existing team and prepare it for new challenges. In

2018, our administration experienced something we often read about in newspapers: the retirement wave. We said goodbye to three highly esteemed and very experienced staff members who spent well over 75 years together at the FHI. Although this is an unfortunate loss, we have used the opportunity to hire competent new colleagues who question and improve our processes. However, it is a challenge to integrate new staff without interruption to the high volume of ongoing work and the unforeseen is in full swing all year round. Training courses and seminars are particularly useful, although they are often not offered on a needs-oriented and regular basis. Overall, the established, highly motivated existing team, together with the new colleagues, is open to prepare for the future with great commitment, able to learn and enjoys service. We are using change as an opportunity to optimize our cooperation and knowledge management within a unique MPG world.

Equal opportunities, health and diversity

These three terms have become indispensable in today's world of work. Against this backdrop, topics such as reconciling family and career, health management, attracting people with disabilities, leadership development, but also reduction of fears and prejudices gain fundamental importance. For the FHI, diversity means knowing the needs of a diverse workforce - people of different age groups, different genders, different sexual orientations as well as social, religious and cultural backgrounds with different abilities and experiences - and raising the potential associated with this diversity. In addition, immigration has made our society more diverse. There is a need for action with regard to the employment of people with a migration background, as the share of this group in the overall public administration has so far been low. Challenges also lie in better communicating the benefits of occupational health management. This includes both the strategic task of implementation by the executive leadership and the acceptance of prevention measures by the workforce.

Solution management

Technological and demographic changes, difficult budgetary situations, the juridification of almost all transactions and rigid external and internal regulations are all posing major challenges for the administration. Administrative tasks should continue to be performed efficiently, in a research-friendly manner and with high quality. This supports FHI’s competitive advantage in recruiting the best research minds. The more modern and competent our administration is, the more efficiently it can react to change and even actively shape it. As mentioned, the tasks of the future cannot be accomplished without well-trained and qualified employees. The basis for the attractiveness of the administration for new staff is therefore a flexible collective bargaining agreement and appropriate earning opportunities, which ensure a decent life for the employees at the respective location. If additional tasks arise at the institute or are transferred to the institutes, it is necessary for the MPG to provide funds for personnel growth. The administrative headquarter in Munich in particular has the task of ensuring the continuous development of the decentralized administrations. Only together can the challenges that arise be met appropriately.

It is in the DNA of the MPG that the individual institutes work in a self-organized way. The principle of subsidiarity applies here, although the institutes are not formally legally independent. It is therefore all the more important that the institutes and the administrative headquarter in Munich work hand in hand to support the scientists. All possible degrees of freedom must be used to improve the research environment and, where necessary, new ones created together. The administration of the FHI therefore cooperates proactively and transparently with the administration in Munich.

To conclude I would like to stress our ongoing dedication to supporting all researchers and other employees in the scientific departments as well as all colleagues in the service groups. To me administration means “engine room”, “glue” and “facilitation”. We work at the core of the institute and share a large piece of the responsibility of such a well-established and competitive facility. The “team admin” is a key component to the successful operation of the institute so that our researchers can focus on keeping the FHI among the leading research institutes in the world.

Geographers are aware of the old saying “without geography you’re nowhere”. In today's highly complex and regulated world, the analogy can be said: “Without administration you’re going nowhere“. Go find out if you don’t already know…

International Max Planck Research School: "Functional Interfaces in Physics and Chemistry"

Spokesperson: Prof. Dr. Martin Wolf
Coordinator: Dr. Alexander Paarmann
Secretary: Ines Bressel

General Remarks

The International Max Planck Research School (IMPRS) 'Functional interfaces in physics and chemistry' (http://www.imprs-cs.mpg.de), launched in 2002 by Prof. H.-J. Freund under the former name 'Complex Surfaces in Materials Sciences', is a structured PhD program that aims at attracting outstanding students from all over the world to the Fritz Haber Institute (FHI). It creates an interdisciplinary platform for PhD education that combines cutting-edge research with a thorough training of the students in the broad field of surface, interface, and material science. The school brings together interface science groups of all FHI departments and the Berlin and Potsdam universities, see Fig. 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.

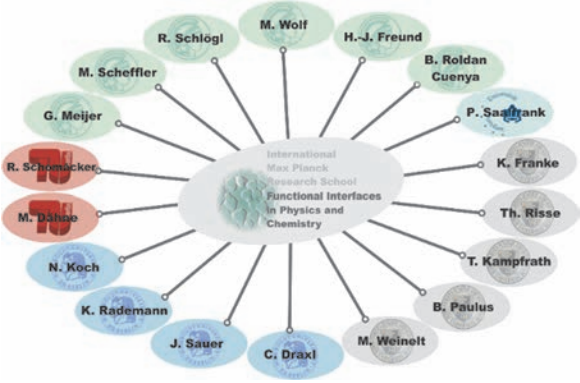


Figure 1: IMPRS Faculty members as of 2019. green: FHI, grey: FU Berlin, blue: HU Berlin, red: TU Berlin, light-blue: Uni Potsdam).

The budget of the school comprised ~400 T€/p.a. provided by the general administration of the Max Planck Society, complemented by an additional ~800 T€/p.a. that have complemented our budget in the form of salaries paid directly by the FHI and the partner universities. The majority of these funds (~ 90 %) was spent for the salaries of IMPRS students. The remaining budget was used to pay our secretary and to finance all school activities including guest speakers, seminars and workshops for the students.

We currently look at a total of 143 IMPRS students, counting the present (42) students as well as those (101) who graduated from 2005 to 2019. Notably, 4 new students joined the IMPRS in 2019 from the newly established interface science department. About 50 % of the students came from eighteen different foreign countries, for example Spain, Iran, Scotland, Greece, China, Madagascar, Argentina and India. The total published output amounts to an average of 4-6 papers per student. On a statistical average, 4 years were required to obtain a doctoral degree. Particularly positive events were the awards of distinguished prizes to seven of our students, the latest being the Carl-Ramsauer award 2018 which went to C. Nicholson. With their excellent education, the IMPRS students also had very good career perspectives after obtaining the Ph.D., both in academia and industry.

After successful evaluation in September 2014, the IMPRS is now reaching the end of its third funding period (10/2014-09/2020). Considering the recent new appointments of directors and the new research mission, the FHI will not apply for further extension of the existing school, but instead apply for a new IMPRS with new research focus and name to start in 01/2021. A continuous funding of running Ph.D. projects is warranted through the general administration of the Max Planck Society. The FHI internal discussion about the details of this new to-be-proposed school is ongoing, and the proposal will be submitted in the spring of 2020.

Student Training

A comprehensive education of our students, both in scientific 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.

Block Courses:

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 'Unifying Concepts in Spectroscopy'. The advanced courses (held in fall) address more specialized topics associated with surfaces and interfaces, such as 'Synthesis and Functional Characterization of Catalysts' and 'Surface Characterization by Atomic Force Microscopy'. 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 2017 and the fall of 2019. These featured a total of 7 external speakers. Additionally, the IMPRS featured two special block courses during that time: a) a student-organized workshop held at Schloß Ringberg in the spring of 2018 and b) a hands-on workshop in the spring of 2019.

The self-organized IMPRS block course was held in February 2018 at the Bavarian Castle Ringberg (https://indico.fhi-berlin.mpg.de/event/10/), see Fig. 2. The IMPRS students selected and invited 15 outstanding researchers from all over the world, as well as representatives from industry and scientific publishers. A special conference concept that 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.

Figure 2: IMPRS students and invited guests at the self-organized block course at castle Ringberg in Feb. 2019.

A special highlight was the hands-on block course held in March 2019, intended to provide practical experience in “real” experimental and theoretical laboratories throughout the involved groups. Each student participated in six 3.5h long labs out of 32 possible labs, which each of them could choose individually depending on their specific interests. This unique opportunity was highly recognized by the IMPRS students.

Discussion Meetings:

The discussion meetings (held every 2-3 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.

Soft-Skill Seminars:

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 two-day workshops in order to help students to optimize their research efficiency and prepare them for a possible academic or non-academic career. An overview of the seminars offered in 2019 is given in Table 1. Notably, a new soft-skill seminar entitled “Mental Health and Stress Management for Ph.D. Students” was offered for the first time, organized with the help of the Max-Planck-wide health partnership with the “Techniker” health insurance company. This "Pilot" was perceived extremely well by the IMPRS students. It is currently considered to offer similar courses also to all FHI employees.

Seminar	Lecturer	Time
Effective Presentations	F. Steven Weir	March
Academic Writing	Prof. Warren-Kretzschmar	March
Mental Health	Judith Bergner	March
Job Hunting	Rob Thompson	September
Project Management	Rob Thompson	September

Table 1: Soft-skill seminars offered to IMPRS students in 2019.

Research Achievements

The main task of the school is to provide a structured curriculum, covering the broad range of disciplines within the IMPRS. Therefore, the IMPRS students receive the benefit of a broad knowledge base they can then apply in their research. The success of that strategy is displayed in the high-quality research published by the IMPRS students. Beyond the mere statistics, the following example publications with IMPRS students as first author are representative of this success:

- C. W. Nicholson, et al., Beyond the molecular movie: Dynamics of bands and bonds during a photoinduced phase transition, Science 362, 821, (2018)
- S. Ketterl, et al., Origin of spin-polarized photocurrents in the topological surface states of Bi_2Se_3, Physical Review B 98 (15), 155406 (2018).
- E. Mucha, et al., Unravelling the structure of glycosyl cations via cold-ion infrared spectroscopy, Nature Communications 9, 4174 (2018)
- N. C. Passler, et al., Strong Coupling of Epsilon-Near-Zero Phonon Polaritons in Polar Dielectric Heterostructures, Nano Letters 18, 4285 (2018)
- G. Melani, et al., Vibrational spectra of dissociatively adsorbed D_2O on Al-terminated α-Al_2O_3 (0001) surfaces from *ab initio* molecular dynamics. The Journal of Chemical Physics 150, 244701 (2019)
- C. Feldt, et al., CO Adsorption on Au(332): Combined Infrared Spectroscopy and Density Functional Theory Study, J. Phys. Chem. C 123, 8187 (2018)
- L. Farinacci, et al., Tuning the Coupling of an Individual Magnetic Impurity to a Superconductor: Quantum Phase Transition and Transport, Physical Review Letters 121, 196803, (2018)
- C. Stemmle, et al., Analysis of electron-correlation effects in strongly correlated systems (N_2 and N_2^+) by applying the density-matrix renormalization-group method and quantum information theory, Phys. Rev. A 97, 022505 (2018)
- C. Vorwerk, et al., Addressing electron-hole correlation in core excitations of solids: An all-electron many-body approach from first principles, Physical Review B 95, 155121 (2017)
- K. Werner, et al., Toward an Understanding of Selective Alkyne Hydrogenation on Ceria: On the Impact of O Vacancies on H_2 Interaction with CeO_2 (111), Journal of the American Chemical Society 139, 17608 (2017)

FHI FEL Facility
Dr. Wieland Schöllkopf

Head of FHI FEL Facility (since 2009)
Work group leader FHI Dept. MP (since 2004)
Postdoc FOM Institute Rijnhuizen, NL (2003)
Postdoc Harvard University & Harvard-MIT Center for Ultracold Atoms, Cambridge, MA, USA (2000–2002)
Dr. rer. nat., Universität Göttingen (1998 with Prof. J.P. Toennies)

Introduction

The infrared free-electron laser at the Fritz Haber Institute (FHI FEL) provides intense, pulsed and widely tunable infrared radiation to FHI research groups and their collaboration partners. Since the start of user operation in November 2013 a wide variety of 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. This is reflected by a total of some 55 publications plus a large number of conference contributions by the FHI FEL user groups.
The FHI FEL generates ~10 μs long pulse trains (macro pulses) at 10 Hz repetition rate. Each macro pulse consists of several thousand short (~ps) micro pulses separated by 1 ns. The energy of ~10 μJ per micro pulse corresponds to ~100 mJ per macro pulse. The central wavelength can be set to any value between 2.9 and 60 micron, thereby covering the full mid infrared (MIR) regime. The spectral width of the radiation, and hence the micro-pulse length, can be varied by fine adjustment of the FEL cavity length. For most spectroscopic applications it is set to less than 0.5% (full width at half maximum) of the central wavelength, corresponding to a micro-pulse length of a few ps. Ultrashort pulses as short as 0.5 ps of high peak intensity, as needed in non-linear spectroscopy (second harmonic and sum frequency generation) and in time-resolved measurements, can also be generated at a correspondingly broader spectrum of several percent.

At the last Fachbeirat meeting we outlined an FHI FEL upgrade plan which was approved by the Max Planck Society in July 2018. The upgrade essentially includes four new components; an electron side-deflection (kicker) cavity, a second electron-beamline arc, a second undulator, and a second FEL cavity to generate far infrared (FIR) radiation at wavelengths up to ~160 micron. We have worked out a scheme allowing for parallel operation of both MIR and FIR branches by sending every 2nd electron bunch to the MIR and every other 2nd bunch to the FIR undulator. Based on this we plan to realize a 2-color IR FEL with independent wavelength adjustment by undulator gap change in each branch. Such a 2-color IR FEL will be a worldwide unique accelerator based 2-color radiation source, which will allow a variety of new spectroscopic experiments not possible with conventional radiation sources.

Design and performance of the FHI FEL

The relativistic electrons generating the IR radiation in the FHI FEL are supplied by a normal-conducting linear accelerator system that combines a thermionic electron gun, a sub-harmonic buncher cavity and two S-band (2.99 GHz) copper linacs. The linacs accelerate the electron bunches (200 pC bunch charge, 1 GHz repetition rate) to any final energy between 15 and ~50 MeV.

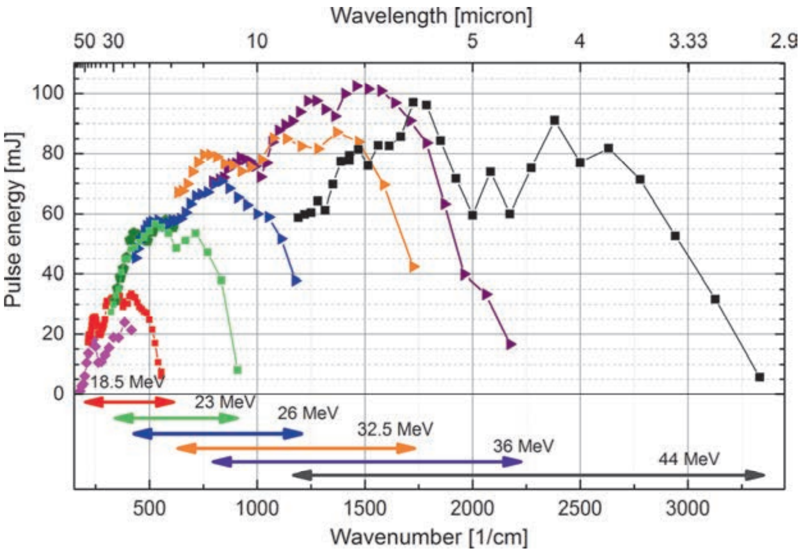


Figure 1: Macro-pulse energies measured at narrow bandwidth conditions for six usually used electron energies from 18.5 to 44 MeV. Different traces correspond to different electron energies and different settings of the FEL cavity. The arrows at the bottom indicate the wavelength ranges covered by the corresponding electron energies.

The MIR pulses are generated by the electrons passing through the planar hybrid-magnet undulator (2 m long, 50 periods) located within a 5.4 m long IR cavity. The IR pulses coupled out from the cavity pass through an evacuated, 18 m long IR beamline to the neighboring building (Building D), where the IR diagnostics and the user stations are located. Measurements of the FEL macro-pulse energy as a function of wavelength are shown in Fig. 1. Each trace in the figure corresponds to an individual accelerator tune-up at the indicated electron energy. All data shown in Fig. 1 correspond to narrow spectral widths (FWHM) of about 0.5% or less.

User projects at the FHI FEL

A total of 7 research projects are operational in the basement and ground floor of Building D. These include (i) vibrational spectroscopy of metal and metal-oxide clusters in the gas phase; (ii) vibrational spectroscopy of macro-molecules (e.g., peptides, small proteins or glycans) in the gas phase or embedded in helium nano-droplets at 0.4 K; (iii) nonlinear spectroscopy of solids based on second-harmonic or sum frequency generation; and (iv) surface sensitive vibrational spectroscopy of well-characterized surfaces or of metal clusters adsorbed on such surfaces.

User groups of the FHI FEL Facility as of summer 2019

1. Knut Asmis (Univ. Leipzig, Guest-group at MP)
   Vibrational spectroscopy of gas-phase cluster ions
2. André Fielicke (MP)
   Chemistry of transition metal clusters
3. Gert von Helden I (MP) and Kevin Pagel (FU Berlin, Guest-group at MP)
   Spectroscopy of bio-molecules combined with ion mobility mass spectrometry
4. Gert von Helden II (MP)
   Spectroscopy of molecular ions embedded in helium nano-droplets
5. Helmut Kuhlenbeck (bis 31.3.2019 CP, ab 1.4.2019 ISC)
   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

The FHI FEL Facility

The FHI FEL Facility is operated by Wieland Schöllkopf (scientist in charge), Sandy Gewinner (laser engineer), and Marco De Pas (RF engineer). They report directly to Gerard Meijer (director, Dept. MP). Additional support is provided by engineers and scientists of the FHI. For instance, development and administration of the FEL's complex control system is performed by Heinz Junkes from the computer support group PP&B.

Extensive renovation work of the lab space in Building D is ongoing in 2019 and scheduled to finish in 2020. As the ground floor of Building D will be completely refurbished, three FEL user experiments are going to be relocated from there to the basement to avoid having to stop experiments for several months. To this end, and to allow for additional user experiments in the future, the existing IR beamline system is extended. Next to the three existing user stations, the FEL radiation will be available at four more fields on either side of the aisle in the large basement hall. In addition, the IR beamline will be extended to two more labs in the ground floor. Thus, once renovation of Building D will be completed, the FEL radiation will be available at a total of 7 fields in the basement hall and in 5 ground-floor labs. This corresponds to twice as many user stations as there are today.

The 2-color upgrade: Scientific case

At the last Fachbeirat Meeting we described our motivation for IR pump-probe spectroscopy where two time-delayed pulses are applied to the sample. Observing the sample response as a function of time delay and its frequency or fluence dependence makes it possible to study the dynamics and interactions, 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. 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. 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. The synchronization of the FHI FEL pulses with femtosecond pulses at ~1 μm, generated by a table-top laser, allows for MIR-NIR 2-color spectroscopy at the FHI FEL Facility (see the group report of Alexander Paarmann, Dept. PC, in this booklet). The 2-color FEL setup will extend the scheme to a wide range of MIR and even FIR wavelengths.

To find out which MIR/FIR wavelengths and 2-color combinations are most relevant to the user community, we organized a workshop in 2018 attended by users from IR FEL facilities around the world, including FELIX (Nijmegen, NL), CLIO (Paris, F), FELiChEM (Hefei, China), and the FHI FEL. From the workshop we identified three essential user demands to be met by a 2-color IR FEL.

1. There is strong interest among the users to extend the FHI FEL's current wavelength range into the FIR regime. However, there is apparently little demand to go to wavelengths significantly longer than ~150 μm. The lower wavelength end of the second undulator lasing range shot be less than 5 μm.
2. The idea of a 2-color FEL is strongly embraced by the user community. It is agreed that a variety of novel spectroscopic investigations not possible with conventional radiation sources will become feasible; vibrational mode couplings and energy transfer can be investigated in detail.
3. Users will still need the option to measure spectra in the ordinary 1-color mode. This implies that the envisaged 2-color FHI FEL upgrade still allows operation of either FEL branch in the conventional mode of operation, where every electron bunch is sent to either the first or the second undulator.

The 2-color upgrade: Technical realization

The 2-color upgrade design plan including the second FEL branch in combination with a 500 MHz kicker cavity downstream of the electron accelerator is depicted in Fig. 2. In the kicker cavity a strong 500 MHz RF field will generate a peak electric field of 11.5 MV/m leading to transverse deflection of 50 MeV electrons by ± 2 degree. This will allow every second electron micro-bunch to be sent to the first and every other second bunch to the second FEL branch after a relatively short drift region behind the cavity. The kicker-cavity setup has been designed such that it will allow for 3 different modes of operation: (i) 100% of the electron beam goes to the MIR undulator; (ii) 100% of the beam goes to the FIR undulator; and (iii) the beam is split in two 500 MHz bunch-rate beams feeding both undulators, when the side deflecting cavity is energized (2-color mode).

The IR wavelength range of the second FEL, for the given range of accessible electron energies, depends on the choice of the 2nd undulator's period. We have selected 68 mm, because this will allow lasing from <5 μm to ~160 μm, compliant with the users' request.

As of August 2019, we have finalized the physics and engineering design. Long lead-time items such as the kicker cavity, the RF amplifier (65 kW, 500 MHz, pulsed) needed to power the cavity as well as the undulator magnets have been ordered. We have scheduled a 2-step installation process. In step 1, starting January 2019, we plan to retract the electron gun and accelerator system to its new position. In step 2, in the second half of 2020, we plan to install the new FEL branch including electron beamline, undulator, and FEL cavity.

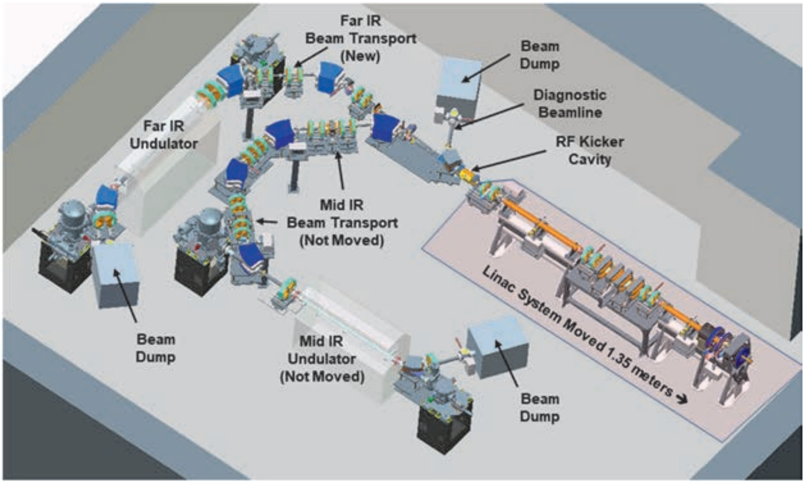


Figure 2: Schematic layout of the 2-color upgrade of the FHI FEL. The existing MIR FEL will stay as it is. A new FIR FEL branch will be installed. The accelerator system will be retracted to allow fo the insertion of the 500 MHz kicker cavity downstream of the second linac.

References

The research activities at the FEL resulted in a large number of publications. In the period of this report (late 2017 until September 2019), 30 publications appeared in peer reviewed journals, among them five in Angewandte Chemie, three in the Journal of the American Chemical Society, two in Nature journals and one in Physical Review Letters. Highlights of the scientific output can be found in the report of the research groups of A. Fielicke (MP), G. von Helden (MP), H. Kuhlenbeck (CP and ISC), A. Paarmann (PC) and K. Pagel (FU Berlin and guest at the MP dept.).

The complete list of publications can be found in a separate document which is associated to this report.

Inorganic Chemistry

Department of Inorganic Chemistry
Prof. Dr. Robert Schlögl

Director at FHI and Scientific Member of the Max Planck Society (since 1994)
Founding Director of Max Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr (since 2011)
Habilitation Fritz Haber Institute of the Max Planck Society, Berlin (1986–1989)
Dr. rer. nat. Ludwig-Maximilians-Universität München (1982)
Several Honorary Professorships
Eduard-Rhein-Culture Award (2019)
ENI Award Energy Transition (2017)
Alwin Mittasch-Award (2015)

General Developments

The Department has continued to maintain the Mülheim and Berlin locations. Despite the distance, operational efficiency has remained high, and connecting activities, such as those in the analysis of electrocatalysts[1], have proven extremely fruitful. It is expected that the duty of the founding director in Mülheim will be no longer necessary in the foreseeable future. The aim now is to concentrate the Department in Berlin and cease the activities that require the Mülheim branch. An exception will be involvement in the large-scale projects indicated below.

As announced in the last report, the Department terminated its activities in battery[2] science. The group leader (S. Cap) and the critical equipment were transferred to the HZB (Helmholtz Zentrum Berlin), and work will be continued there through a collaborative effort. The Department lost M. Willinger to a position at the ETH Zürich. We used this loss as an opportunity to alter the focus of the electron microscopy group. The operando activities[3] were consolidated which, coupled with hardware developments[4], has allowed the first observations wherein the morphological changes of catalysts[5] during operation have been quantified. Enlarged efforts in analysing the results from imaging and spectroscopy have also been initiated. The TITAN operando TEM is undergoing a major upgrade to greatly extend its life as an integral piece of core infrastructure. Collaboration with the ISC Department aimed at observing liquid-phase electrochemical processes has started.

The addition of a W2 position to the FHI permitted establishing the new group “Heterogeneous Chemistry at the Liquid-Vapour Interface” headed by H. Bluhm. He will contribute strongly to the liquid phase research focus of the FHI. Based on his pathfinding results he designed a novel experimentation strategy aimed at probing clean and well-defined static liquid surfaces and interfaces. The experimental flexibility of the concept will allow for participation of other Departments within the FHI with whom the strategy was discussed. The instrumentation, for which an application of a large-scale equipment grant was put in, will be installed in the collaborating PC Department. A suitable location was found to avoid the necessity of relocating the new instrument upon the closure of the AC Department in 2023.

Our successes in research on the catalytic applications of metal systems, conducted largely in the context of their electronic structure, increased demands for a more integrated treatment, including other analytical methodologies and catalytic testing. To meet this demand a new group, “metals”, was opened and is headed by K. Skorupska. The group, being still in its establishing phase, is headed by an experienced researcher[6] in operando photoelectron spectroscopy. In this way, a close collaboration between the emerging group and the “electronic structure” group is guaranteed, and the benefit of bundling the expertise in catalysis with metal systems is added to the evolution of the Department.

Collaborative activities

The Department involved itself in several new collaborative activities. In the National Excellence Initiative the Department is active with PI status in 3 clusters of excellence that are located in Berlin (UNisysCAT), Munich (e-conversion) and Aachen (Fuel Science Center). In a National Priority program (SPP2080) dealing with dynamic aspects of heterogeneous catalysts the Department is active mainly with its NAP XPS competence. In a Transregio SFB (TRR 247) linking the FHI with MPI CEC and the universities of Bochum and Essen the Department plays a coordinating role and organizes[7] the operando analysis of metal oxides in catalysis activated by different sources of energy (in collaboration with the ISC Department). Together with MPI CEC and KOFO, the Department won a Max-Planck International Research Centre with the UK (lead institution Cardiff university, G. Hutchings). The topic studied here, in collaboration with the TH Department, is the fundamental study of the interrelation[8] of selectivity and nano-structuring. A whole portfolio of collaborations is also operated by the electron spectroscopy group in the context of sharing the access to the NAP XPS infrastructure. Besides multiple user support activities, deep scientific collaborations with groups from Austria, France and Russia broadened the research portfolio.

A similar rich collaboration portfolio is operated by the electron microscopy group. A collaboration was started with Thermo-Fisher (former FEI) on the development of an electron microscope that can be used by non-expert chemists for rapid and synthesis-near sample characterisation. Through a web-based interactive guide the user is supported by adaptive instrument software. This was developed over the last 3 years and has now led to a commercial product. The microscope was bought for the MPI CEC/KOFO campus in Mülheim, where it will begin operation in 2020. One aspect of the new microscope is the capacity to study air-sensitive nanostructures directly from solution using a glove-box transfer.

From the local universities, we collaborate intensely with the TU Berlin. Besides the institutional activities mentioned above, a long-standing collaboration is active with P. Strasser[6a, 9] from the Department of Chemical Engineering at TU Berlin. We jointly study the evolution and material development of electrodes for the electrochemical oxygen evolution reaction. This collaboration forms a phenomenological basis for the more fundamental studies[1a, 1b, 10] on the nature of active electrocatalysts conduced as a major effort in the electron spectroscopy group.

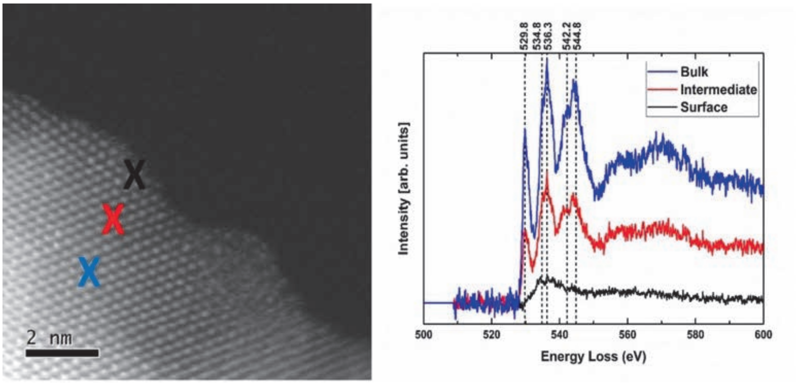
These collaborations augment the two large-scale external collaborations BASCAT and C2C (centred at MPI CEC). The BASCAT collaboration with BASF and the TU Berlin, which focusses on fundamental insights into the chemistry of C-H activation and selective oxidation, is anchored in the oxide catalysis group. Core questions[11] concern the dynamics of high-performance catalysts and the selective activation of oxygen. In the C2C collaboration[12] the first industrial implementation of the hydrogenation of tail gases from an industrial process (steel mill) is attempted in an effort to enable the design of a circular carbon economy. The Department is active in fundamental aspects of gas purification, dynamic operation of heterogeneous processes and in the verification of the performance of methanol synthesis[13] from a real-world CO_2 source.

Within the FHI, the AC Department continues to collaborate with all other Departments in efforts that have extended over the past several years. Examples include nanostructured STM tips with the PC department, using the FEL with the MP Department in the study of POM structures[14] and the nature of the active copper phase in the electroreduction[15] of CO_2 together with the ISC Department. And with this young Department the AC Department continues to expand its collaboration in several areas of common interest.

Clean data

In the TH Department the application of artificial-intelligence techniques in analysing theoretical and experimental data and the design of functional materials from structure-function relations became a research focus. All groups of the AC Department complement these activities with two projects. In one project a library of perovskites is synthesized and their surface electronic structure and catalytic activity are characterized. Perovskites were chosen due to their large variability in chemical composition within a common structural motif and because the large chemical contrast between the two constituting cation types allows us to expect substantial chemical effects from the composition of the termination layers. In the TH Department the corresponding high-level theory is conducted with the aim of finding a causal correlation between surface termination and reactivity.

In the other project involving all groups of the AC Department, and of BASCAT, a best practice procedure is aimed at establishing how to describe catalysis results and the corresponding meta data in such a way that they can be used for machine learning. Interoperability and re-usability for new unintended analyses are additional criteria for the development of a handbook of how to conduct such experiments ranging from synthesis to structural analysis and comparative functional analysis in several selective oxidation reactions. For this purpose, a set of 12 oxide systems was chosen to cover most structural variants of selective oxidation catalysts. Oxidation of ethane, propane and butane were chosen as the test reactions. The resulting matrix combines high-performing systems and poor catalysts. A large number of standard and operando characterization results form a catalogue of meta data. Research targets are the identification of experimental bottlenecks, the verification of the procedures of the handbook and the comparison of conventional structure-function relations with results from machine learning procedures. The Department conducts this large-scale experiment (ca. 20 FTE years) as input into activities in the National Research Data Infrastructure (NFDI). The Department participated significantly in generating a white book for DECHEMA ("The Digitalization of Catalysis-Related Science") and is active in the FAIR collaboration led by the TH Department. Past experience[16] in standardizing kinetic experiments and their analysis helped the Department in setting up the experimental campaigns.



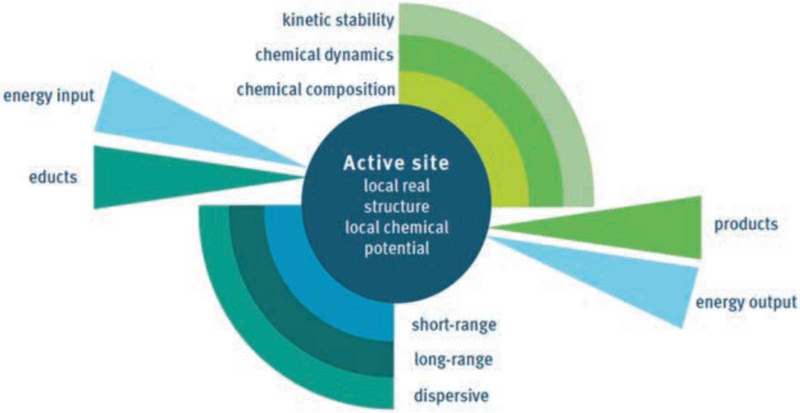
TEM of a La-based perovskite. Corresponding EELS of the oxygen K edge clearly shows that the "invisible" oxygen ions indicate the existence of a terminating layer that may not be obvious only from inspection of the cation disposition.

Dynamics of heterogeneous catalysts

The individual research projects in the Department are described in the contributions from the group leaders. Each of these projects was motivated by previous findings about the dynamical nature of the "catalyst" material. The traditional notion that catalytic mechanisms operate with a fixed number of active sites, the "*" in mechanistic descriptions, is valid in the limit of low performance reactions. Despite its apparent general validity in microkinetic models, the atomistic picture of active sites is much more involved. High performance catalysts need an activation period in the appropriate feed, during which time a termination layer constituting the active phase is formed. This active phase is metastable under reaction conditions; the stable phase to which it may transform represents the deactivated form of the catalyst. The active state is thus in a kinetically frustrated phase where its structure fluctuates between the precursor and the stable phase. This proximity to a phase transition allows for the temporal creation, destruction and re-creation of the local high energy sites that serve as the nucleation centers of the stable phase. These high energy sites are active in catalysis.

The way in which the active sites come into existence varies greatly from system to system. Sub-surface compound formation with reagents (oxygen in silver or copper, C in Ni, OH in iridium oxide, hydrogen in Pd,Pt hydrogenation-dehydrogenation catalysts), segregation and the formation of compounds different from the bulk structure (sulphur oxide in silver, Cu_xO over Cu, phosphoric acid in VPO catalysts, Te-Vanadate in the M1 structure, A cations in perovskites), surface melting (alkali vanadate) and overlayer formation (C over Pt, ZnO_{1-x} over Cu, TiO_{2-x} over Au, SrO or La_2O_3 over perovskites) are all examples of mechanisms of active phase formation from ongoing projects in the Department. The nanostructure of the catalyst material that is formed during synthesis or during activation controls the kinetic barrier of the phase transition. The example[17] of nano-Ag in EO formation reveals that strain induced by the size of the active phase may lead to such high barriers that the activation is inhibited and requires first re-sizing "calcination" before the system becomes active. The examples[18] of isolated single atoms (Ni in MgO, Cu in Ag) that cannot undergo a phase transition without destruction of the system highlight the limited chemical ability of single atom catalysts resulting in high selectivity.

The general consequence of these dynamics is that active sites need a kinetic description augmenting the static structural modelling attempted in conventional experimental and theoretical efforts. The dynamic nature of active sites requires a description of all influences from the local and non-local environments that affect the kinetics of the frustrated phase transition. A non-exhaustive list of descriptors is given in the following scheme.



Descriptors of active sites in the limit of a dynamical catalyst. The 4 arrows desig-nate macroscopic descriptors for a feedback between abundance of active sites and catalyst performance.

New to the description of the nature and abundance of active sites is the feedback regulation of this decisive quantity, which is controlled by the local chemical potential to which the active site is exposed at any moment in time. The 4 macroscopic variables indicated in the scheme by arrows are all needed to describe this influence. The "*" becomes a quantity depending on the activity of the catalyst. Its seemingly constant value in traditional concepts is understandable if the activity reaches limiting low values, or if the kinetics of site formation and their consumption by the reagents lead to a common steady state.

Synopsis: catalyst material science

The consolidated insight that performing catalysts undergo chemical transformations[11d] enabling frustrated phase transitions in the near-surface region of the material raises the question about consequences. This behavior explains the occurrence of "science gaps" in catalysis (pressure gap, material gap) as unified phenomenon. If the synthesized bulk crystal and its resulting termination is transformed into the active phase only under performance reaction conditions, then model studies based on the material analysis ex situ will only capture a small fraction of the catalytic behavior. Operando analysis then become a pre-requisite for characterization, not a "high-end" additive to ex-situ analysis. The current practice of characterizing catalysts would then have to be made surface-sensitive and operando in order to generate relevant (meta-)data about the catalyst material.

The existence of an active surface phase different from a termination variant of the catalyst[19] bulk hampers the application of theory and of digital catalysis. If the structure of the "bulk phase" is no longer sufficient for describing the active phase then the number of options for the nature of active sites and their exact function becomes too large to explore by brute force. Digital catalysis then needs the descriptor of the active phase, not its bulk precursor.

One experimental approach to address this critical issue emerging from the recognition of the dynamic nature of active catalysts is to synthesize the active phase as a thin layer that mimics the active phase of a bulk precursor. Such an approach facilitates a more accurate description and control of the active phase. There are, of course, several challenges with such an effort. The support of the thin layer should allow additional functionality, such as electrical or ionic conductivity, and enable the immediate energy transfer to the active phase, thereby minimizing the challenges of energy transport in conventional catalytic materials. As stated above, a core function of the support is to provide the long-range energetic landscape of the fluctuating active phase. Well-known are the influence of semiconducting properties[5, 11b] of oxides ("band engineering"), the effects of applied potentials[1a, 10, 20] and their gradients ("electrodes") and the consequence of spatial restriction ("confinement effects"). While the idea of minimizing the bulk of a catalyst is, of course, not new and has even been realized in grafted oxide catalysts[11d] (see selective oxidation project in the AC Department) and generally in supported metal nanoparticle catalysts (see activities in the metals project), the synthetic possibilities are limited and do not allow rapid prototyping of layer compositions and of lateral structures. The challenge of verifying the exact function of the active phase in conventional catalysts is substantial, as the nature of the support as a co-catalyst or an innocent carrier is unclear. The arsenal of support variations is rather limited and, due to the requirement of a large geometric surface area and the needs to provide anchoring sites for the active phase, its surface chemistry is critical. The AC Department has collected ample expertise in disentangling these functions and in analyzing active phase nanostructures. This capability was fueled by the critical role the "support" plays for all realizations of industrial catalysts, where even the slightest variations in support quality can have detrimental or beneficial effects on the technical performance. The role of "synergy" in the

Cu/ZnO system[12a, 13a, 21] is an excellent illustration for this critical issue in understanding the function of heterogeneous catalysts.

A step forward

The response to the shortcomings of conventional "powder" catalysts is a radical change in synthesis technology from chemical means to physical means. PVD-based catalysts have long existed as model systems in catalysis research. The extension of their synthesis concepts to performance reaction conditions and their scaling to technical relevance is, however, new territory. PVD synthesis with additional chemical modification and/or electrodeposition on conducting substrates are well-known large-scale technologies in many products outside the catalysis area (touchscreens, functional windows, solar cells, automotive). Consequently, all the required manufacturing technologies exist. Their application allows exact control of interface properties, a sheer endless combination of supports and active phases and a wide range of post-deposition modification strategies.

In this way novel combinations of functions of supports and of active phases can be realized. Besides electrocatalysis, the transport of reaction energy to the active phase by heating the active phase only, rather than the whole reactor, is an attractive option. Sensing reactivity by probing charge carrier dynamics of the support is also an option. The support can be chosen as a semiconductor or a metal. It may be shaped by additive manufacturing (3-D printing) or can be a metal foam or mesh. The support can also be a ceramic material (CERMET) with (ionic) conductivity. The active phase can be chosen from metallic elements or from oxides in very wide boundaries when combining evaporation, sputtering and electrodeposition. Post deposition modification by (reactive) annealing and the combination of deposition and annealing steps to complex multilayer structures offer enormous flexibility in generating films or nanostructured landscapes of active phases. A suitable chemical contrast (with buffer layers) between support and active phase can ensure the phase integrity of the active material in the sense that digital catalysis becomes applicable. True versions of atomic layer deposition can add to the arsenal of active phase formation.

This large option space carries the dual challenge of how to verify the product and how to choose the functional synthesis target. A further pre-requisite not existing today is a reactor concept that exploits the possibilities of such novel catalysts. The hitherto followed concept of micro-testing in probe reactions is not the aim. A set of reactor systems allowing testing of relevant surface areas (0.01-1 m^2) and providing options for unconventional energy input (cold wall reactors) needs to be designed and realized. The basic concept of slit reactors may serve as a blueprint for novel solutions.

Such a step forward is also timely. When the desire of chemical industry to work with non-fossil resources and green energy is taken seriously then novel concepts of reactors, catalysts and reactions need to be explored. Reaction targets for the present activity are the transition from oxidative dehydrogenation delivering energy and water to non-oxidative dehydrogenation delivering hydrogen and requiring energy. The Department has expertise in this area (ethylbenzene transformation) and has taken on research projects (metal group) building on this expertise. The control of selectivity towards carbon formation is a well-known issue in the Department that has recently been pursued with the synthesis of graphene. Now its inversion is needed. The concept to only feed energy to the active phase by heating the catalyst support electrically or inductively and to leave much of the reactor cold greatly reduces carbon deposition and also minimizes the need for energy recovery and reactor insulation. This in turn offers options for operando process control by probing the reactor internally with light (RAMAN, IR).

These opportunities require the restructuring of the work in the Department. The step forward is also risky because several areas in such an approach are novel to the Department. A strategy of mitigating measures addresses the risks. One element is the strict use of operando analysis in all steps of synthesis and functional verification of the novel catalysts. Here the Department has a full set of options and expertise at its disposal. Another element is the selection of reaction targets emerging from past experience of the Department. Central to this will be the comparative transition from oxidative dehydrogenation to dehydrogenation. This transition can be done gradually by changing reaction conditions and/or by pulsed operation schemes. The target is to perform selective dehydrogenation to molecular species (olefins) and hydrogen and prevent pyrolysis to hydrogen and carbon. The dehydrogenation of alcohols will be studied in a continuation of studies to synthesize formaldehyde from methanol without oxidative dehydrogenation. The third avenue is the concomitant dehydrogenation of reagents leading to coupling products and hydrogen. Here the benzene to aniline project is prototypical. The third element in risk mitigation is strong collaboration.

The CATLAB project

The AC Department of the FHI plans to merge with activities of the HZB Berlin (Helmholtz Zentrum) to form a new long-term project designated CATLAB. The MPG has a long-standing collaboration contract with HZB that started with the transfer of BESSY into the Helmholtz Association. At BESSY, the Department collaborates with HZB, inter alia, in the EMIL project. An extensive infrastructure to synthesize multi-element layer structures for solar cells was installed at EMIL by HZB, offering direct access to synchrotron radiation for operando analyses. The CATLAB project seeks to use this infrastructure after adaptation to catalyst synthesis (e.g. post deposition techniques and target geometries). It is located within the joint EMIL building and can, without problems, be combined with the NAP XPS module facility built at EMIL by the AC Department.

In order to extend the functional analysis, a joint project has already been started. It concerns the coupling of operando TEM with operando scanning transmission X-Ray microscopy. HZB is building such an instrument within the EMIL infrastructure. This new instrument is devoted to the study of layered structures. FHI-AC brings a new matching TEM (already financed to a large extent) and builds a sample environment compatible between the two instruments such that one and the same object can be studied with two complementary families of microscopy techniques by identical location techniques. It is intended to merge this project with the existing electron microscopy infrastructure in Berlin-Adlershof that belongs to the Humboldt University (Prof. Koch) and end up with a local multi-method center for electron microscopy. In these efforts a collaboration with the ISC Department, now operating the SMART project inherited from H. J. Freund, will be extremely valuable. The capacity of the SMART instrument to analyze the lateral nanostructure of thin film catalysts greatly enhances the TEM capabilities, including dedicated target preparation and high-pressure identical location TEM.

The Department will move its activities and infrastructure to Adlershof. It is intended to erect a dedicated building for CATLAB at the BESSY site. Until this building exists the Department will move into a suitable building belonging to the HU Berlin (IRIS) where multiple material science and thin film activities of the HUB are located. This building is in walking distance to BESSY and ensures an intense collaborative effort within the Department (the groups of electronic structure and metal/oxide catalysis) and between HZB and FHI with the thin film activities at EMIL. The operando electron microscopy of the Department will remain at FHI and will be further used. These facilities will be gradually transferred to the ISC Department. Prof. Roldán Cuenya will be the point of contact between the CATLAB and the FHI and MPG. The electrodeposition activities planned in CATLAB will be performed jointly. From the MPI CEC, that owns much of the spectroscopy infrastructure at BESSY (EMIL; BELCHEM), Prof. S. De Beer will form a second anchor point of CATLAB into the MPG. Several activities of the AC Department will remain in the FHI and either be terminated in 2023 with the retirement of R. Schlögl or will be continued with other departments. The most prominent case is the group of H. Bluhm, who will closely collaborate with the PC Department. Within the FHI the AC Department will continue its collaboration with the TH Department (M. Scheffler and K. Reuter) on Digital Catalysis science and specifically on defining procedures and standards of describing catalyst synthesis and testing. In addition, machine learning approaches towards understanding selective oxidation catalysts and, in the future, towards selecting target systems for dehydrogenation from theoretical data will be conducted.

The development of novel reactor concepts and the supporting enginering science will be performed in collaboration with BASCAT/BASF. To this end a project application in a joint program between BASF and the Helmholtz Association was sucessful. The project, also named CATLAB, is directed towards pathfinding reaction enigineering experiments in the area of dehydrogenation reactions and is financed for a 3 year period. With the TU Berlin and the Cluster of Excellence (COE) UNISYSCAT the reaction target of concomitant dehydrogenation with the synthesis of aniline from benzene will be jointly studied. This project is placed within the COE program and the TUB groups of A. Thomas and M. Driess collaborate with BASCAT and FHI.

In summary, CATLAB is the AC Department's response to the results of its own scientific results and to scientific requests coming from Digital Catalysis on one side and from applications minimzing the CO_2 footprint of chemical transformations on the other side. This project is only possible through a collaboration between institutions and universities. It is concentrated at one location in Adlershof where catalysis chemistry and synchrotron experimentation can be united. The university system of Berlin, being recently successful in the excellence initiative, underpins and supports the project in several critical elements. Its pre-competitve character with a strong fundamental component is adequately supportd by the collaboration between MPG and the Helmholtz Asoociation. Industrial partners, such as BASCAT/BASF, realize the enginnering aspects together with academic partners and give advice in selecting reaction targets and scale-up concepts. The support from Federal and Berlin funding instititutions provides a stable critical mass for the project. The character of a long-term project mitigates the risk in the project goals.

The project aims to find a novel catalyst technology. High densities of active sites will be generated by pre-empting the process of in-situ formation of an active phase on a conventional catalyst. From the beginning it uses a strong collaboration with theory, with the tools of Digital Catalysis, and makes effective use of operando micro-spectroscopic techniques to verify synthesis and function as a basis for feedback to theory. The project respects the unity of catalyst material, reaction conditions and reactor by co-developing suitable reactor and energy transfer concepts together with the material synthesis.

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Groupleader of the "Reactivity" Group (since 2004)
Dr. Annette Trunschke

Dr. rer. nat. Central Institute of Physical Chemistry, Berlin, Germany
Since 2004 group leader at the Department of Inorganic Chemistry, FHI, Berlin
Senior researcher, Institute of Applied Chemistry Berlin-Adlershof (1997–2003)
Alexander von Humboldt Postdoctoral Fellow with Prof. H. Közinger, Ludwig-Maximilians-Universität München (1991)
Dr. rer. nat. Central Institute of Physical Chemistry, Berlin (1990)

Catalysis on Oxides

Motivation

The chemical diversity of metal oxides accounts for the importance of this materials class in various functional applications. Oxides are used, for example, as chemical sensors, adsorbents, and catalysts in photo-, electro-, and thermal catalysis. The current challenges in the energy and chemistry sector require new, more stable and effective catalysts to reduce or replace fossil fuels by closing the carbon cycle. In addition, the improvement of existing technologies in heterogeneous catalysis, for example the production of chemical intermediates and consumer products, is of vital importance in terms of sustainable utilization of resources and CO_2 mitigation considering the dimension of these applications.

Research areas

Our work is devoted to the investigation of metal oxides for activation of C-H, O-O, and C-O bonds. The oxidation of short-chain alkanes and oxygenates on the surface of bulk and supported V-based mixed oxides, perovskites, and alkaline earth metal oxides is investigated with the aim of identifying descriptors to predict selectivity.[1-3] In the field of CO and CO_2 activation, the influence of transition metal oxide promoters on the reactivity of metal nano-particles is investigated.[4, 5]

Scientific challenges in catalysis with oxides

The materials chemistry of high-performance metal-oxide catalysts is particularly intricate, because, according to the present empirical knowledge, superior selectivity to the desired reaction product at acceptable conversion of the reacting molecules requires a certain level of catalyst complexity. Catalysis, in general, inherently involves dynamic interactions between the catalyst and reaction medium. These interactions are modulated by transport phenomena at various length and time scales. The materials chemistry of bulk oxides, as well as supports, needs to counterbalance structural and electronic surface changes to enable stable operation. In addition, physical and textural properties of the oxide catalyst need to be adapted to ensure heat and mass transport in an optimal way.

Approach

Structurally well-defined metal oxides are prepared by applying various techniques of synthetic inorganic chemistry with a focus on hydrothermal synthesis. Automated synthesis reactors (Figure 1) have been developed and equipped with analytic tools to detect key synthesis parameters that control the functionality. Raman and UV/Vis spectroscopy are the relevant spectroscopic techniques that provide information concerning the speciation under synthesis conditions.[7] Mass spectrometry, in combination with electrospray ionisation (ESI) ion mobility spectrometry–mass spectrometry (IMS–MS), infrared multiple photon dissociation (IRMPD) spectroscopy, and infrared action spectroscopy in helium nano-droplets, has been used ex-situ in collaboration with the MP Department.[8]

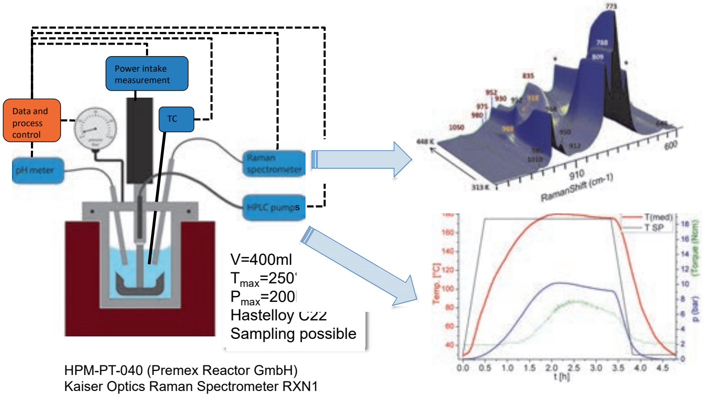
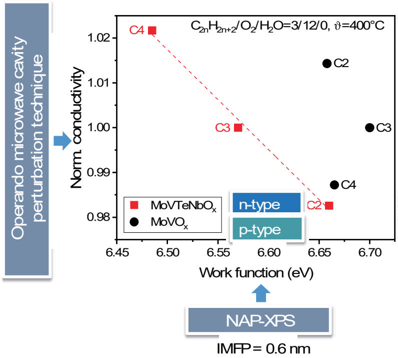


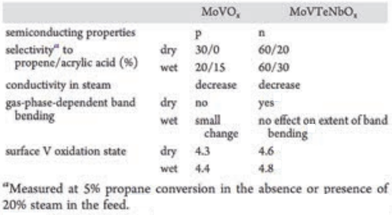
Figure 1: Schematic layout of an automated hydrothermal reactor equipped with a Raman probe.[6] The synthesis is controlled by the computer. Temperature, pressure, power intake of the stirrer and Raman spectra are recorded. Sampling and dosing at high pressure are possible.

The nano and atomic structures of the oxide catalysts are analysed by electron microscopy.[9] Interactions of substrate and probe molecules with the catalyst surface are studied by infrared spectroscopy and microcalorimetry.[4, 5, 10-13] Various spectroscopic techniques are applied in operando to monitor the catalysts under working conditions.[1-3, 14] The interpretation of spectroscopic data is assisted by close collaboration with theory.[15] Reaction networks in oxidation reactions have been analysed by the variation of operation parameters over a wide range.[13, 16, 17] Selected research highlights are summarized below.

Design concepts in oxidation catalysis

Monolayers of vanadium and molybdenum oxide supported on meso-porous silica SBA-15 were investigated to simulate the surface of mixed oxide catalysts.[18] The work shows that the catalytic properties, as a consequence of the local electronic structure, are by no means proportional to the loading or the dilution factor. Semiconductor oxides including n-type MoVTeNb-oxide, p-type MoV-oxide, n-type V_2O_{5-x}, and p-type vanadyl pyrophosphate (VPP) were investigated by operando conductivity and permittivity measurements complemented by NAP XPS.[1, 2] The results indicate that catalysts, which exhibit a high selectivity to the desired oxidation product at high alkane conversions, reveal the property of a "buffer" for charge carriers in their bulk that can be transported to the active sites when the delivery of redox equivalents between adsorbed molecules is too slow. Likewise, the surface layer containing the active sites is robust against chemical changes induced by the lack of redox equivalents leading to chemical oxidation or reduction of the sites. The "buffer" function change is reflected in band bending, i.e., the formation of a dynamic (gas-phase-dependent) surface potential barrier that controls oxygen activation (Figure 2). In accordance with these results, concepts solely based on ideal crystal structure motifs as functional active ensembles in oxidation catalysis are questioned by the investigation of a series of manganese tungstate catalysts that differ only in their particle morphology.[3]





		MoVO$_x$	MoVTeNbO$_x$
semiconducting properties		p	n
selectivity[a] to propene/acrylic acid (%)	dry	30/0	60/20
	wet	20/15	60/30
conductivity in steam		decrease	decrease
gas-phase-dependent band bending	dry	no	yes
	wet	small change	no effect on extent of band bending
surface V oxidation state	dry	4.3	4.6
	wet	4.4	4.8

[a] Measured at 5% propane conversion in the absence or presence of 20% steam in the feed.

Figure 2: Comparison of two oxidation catalysts with the same crystal structure by operando microwave cavity pertubation technique and NAP XPS in the oxidation of ethane, propane, and n-butane.[1] Differences in band bending for the less selective MoVO$_x$ catalyst in the different reaction atmospheres become only detectable in wet feed when the catalyst shows improved selectivity to acrylic acid.

The governing function of oxygen activation has also been observed in the oxidative coupling of methane (OCM) over alkaline earth oxides. Even though the bond dissociation energy of methane is large, 423 kJ/mol, the activation of oxygen is much more important to direct the selectivity towards the desired products.[19] The strong basicity, which is needed for the reaction, is also a major weakness of those materials, forming stable hydroxides and carbonates. The latter are incapable of activating oxygen even at high temperatures.

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Groupleader of the "Electronic Structure" Group (since 1998)
Dr. Axel Knop-Gericke

Postdoc at Fritz-Haber-Institut (1996–1998)
Scientific Assistant at the Freie Universität Berlin (1993–1995)
Scientific Assistant at Siemens (1983–1993)
Dr. rer. nat., Technische Universität Berlin (1995)

Main research fields:

We focus our research on the investigation of the electronic structure of catalysts and electrode surfaces used in heterogeneous catalytic reactions and electrochemical processes like propylene epoxidation over Ag, the oxygen evolution reaction (OER) and the CO_2 reduction reaction (CO_2RR). The development of electrochemical cells enabling operando X-ray absorption spectroscopy and X-ray photoelectron spectroscopy in the soft X-ray range is an essential part of our work.[1-4]

IrO_x in the OER

In the case of Ir anodes in the OER a strong hybridization between iridium and oxygen leads to holes shared between the two; the further the material is charged, the more charge transfer from iridium to the oxygen ligand is expected.[2] Depending on its coordination, oxygen can ultimately end up as a radical oxyl species, μ_1-O. Such a species was proposed to be highly active in O-O bond formation.[5] We were able to find such a species under wet conditions via its O K-edge absorption signal. A small amount appeared at the onset of the OER. Calculations and experiments are in good agreement about the deprotonation potentials and the O K-edge absorption energies of the considered surface oxygen species.

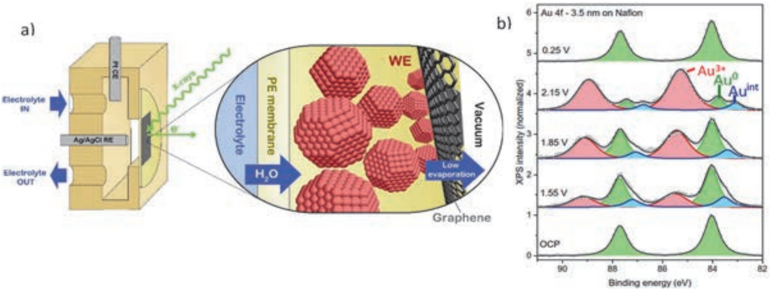

Figure 1: a) Cell design. b) In situ XPS spectra recorded with 0.1 M H_2SO_4 electrolyte.

To probe active electrocatalyst surfaces in a liquid environment, we have developed an XPS/XAS cell in which the catalyst is confined between a proton exchange membrane and graphene. While the proton exchange membrane supplies a steady flow of electrolyte to the electrode, the X-ray and electron-transparent graphene layer greatly reduces the evaporation of water into the NAP-XPS chamber. Using O K-edge spectra, we confirmed that this can lead to the formation of a thin layer of liquid electrolyte between the graphene and the membrane. Thus, electrocatalysts can be studied under operating conditions using surface sensitive soft X-ray XPS and XAS.[3,4]

With this methodology, we have studied the potential-driven restructuring of Ru, Pt and Au oxides in 0.1 M H_2SO_4 during the oxygen evolution reaction. Using Ru 3d/M-edge, Pt 4f and Au 4f spectra, we identified the distribution of cationic oxidation states as a function of potential (e.g. Figure 1b). For Au oxide, which is strongly covalent, only Au^{3+} is found, whereas the more oxophilic Pt displays a gradual transition from Pt^0 to $Pt^{\delta+}/Pt^{2+}/Pt^{4+}$ and further to Pt^{4+}.[4] For the yet more oxophyllic RuO_x, we find a gradual oxidation to primarily Ru^{4+} under OER conditions, with some minor contributions of higher oxidation states.

O K-edge spectra, complemented by theory, indicate that the final stages of oxidation of the catalysts occur through deprotonation, even in the bulk of the materials. The deprotonation proceeds through multiple stages: hydroxyl groups with higher coordination deprotonate at lower potential. Interestingly, we find that deprotonation is not complete during the oxygen evolution reaction on Ru oxide, in contrast to ab initio thermodynamic predictions.[6]

Several studies have identified that the degree of crystallinity of OER electrodes influence their activity and stability.[7] Our in situ studies suggest that the reactive (deprotonated) oxygen species that dominate the surface of amorphous and crystalline Ru oxides under OER conditions are similar in nature. Rather, we explain the correlation between crystallinity and activity/stability by the larger number of reactive species on amorphous electrodes.

CuO_x in CO_2RR

Copper is unique due to its ability to electro-reduce CO_2 to hydrocarbons and alcohols in aqueous electrolytes, as was probed by Hori et al..[8] Nevertheless, the selective electroreduction of CO_2 into fuels is challenging due to the multiple complex proton-coupled electron transfer steps that must occur.[9] This complex network makes the cathodic CO_2 reduction reaction (CO_2RR) run with relative low current density and high overpotential and in addition electrode deactivation may occure over time. By tracking the electronic structure of the Cu catalysts, using in situ X-ray spectroscopies, we have tuned and precisely set the initial Cu redox state, such as Cu^0, Cu^+ and Cu^{2+}, by controlled applied potential protocols.[10] It was shown that the magnitude of the CO_2 dissociation barrier depends on the degree of surface oxidation and on the nature of surface defects. Therefore, we calculated the barrier associated with dissociative CO_2 adsorption on several copper catalysts, indicating that the dissociation barrier is lowered in the presence of missing oxygen on the surface and enhanced in presence of extra oxygen on the surface.

Propylene epoxidation over Ag

We used NAP XPS to study the Ag surface under propylene epoxidation conditions. As opposed to ethylene epoxidation, $SO_{4,ads}$ is not present under steady state propylene oxidation conditions. $SO_{4,ads}$ can, however, be formed by introducing an SO_2 pulse to the reaction feed, resulting in an increase in selectivity to PO. Though, $SO_{4,ads}$ is rapidly titrated under reaction conditions and PO selectivity decreases with time following the decrease in $SO_{4,ads}$ coverage.

During this process we observe the formation of $SO_{3,ads}$. As in the case of ethylene epoxidation, it seems that $SO_{4,ads}$ is also responsible for propylene epoxidation and $SO_{3,ads}$ is seen as a titration product. However, NAP XPS demonstrates atomic O has a low coverage under propylene epoxidation conditions, as compared to those for ethylene epoxidation. As a consequence, $SO_{3,ads}$ is not reoxidized to $SO_{4,ads}$ and is instead continuously titrated under propylene epoxidation conditions, resulting in a low steady state coverage. In addition, the low coverage of adsorbed atomic O precludes the formation of oxygen induced surface reconstructions, necessary to partially lift the Ag/SO_4 reconstruction and make the active species $SO_{4,ads}$.[11,12]

Instrumentation

Figure 2 compares the experimentally determined photon flux of three beamlines operated by the FHI: ISISS (under operation since 2007) BElChem beamline (under commissioning since 2018) at comparable spectral resolution under standard AP-XPS working conditions and sample position, along with CAT@EMIL. It becomes apparent that the beamline characteristics of BElChem and ISISS nicely complement each other. The photon flux of the soft X-ray branch of EMIL (Energy Materials In-Situ Laboratory Berlin) served by the UE48 undulator at the focus position in the CAT laboratory (red line) is shown in Figure 1 as well. It is obvious that the soft EMIL beamline provides a broad photon energy range with a high photon number in the whole energy range.

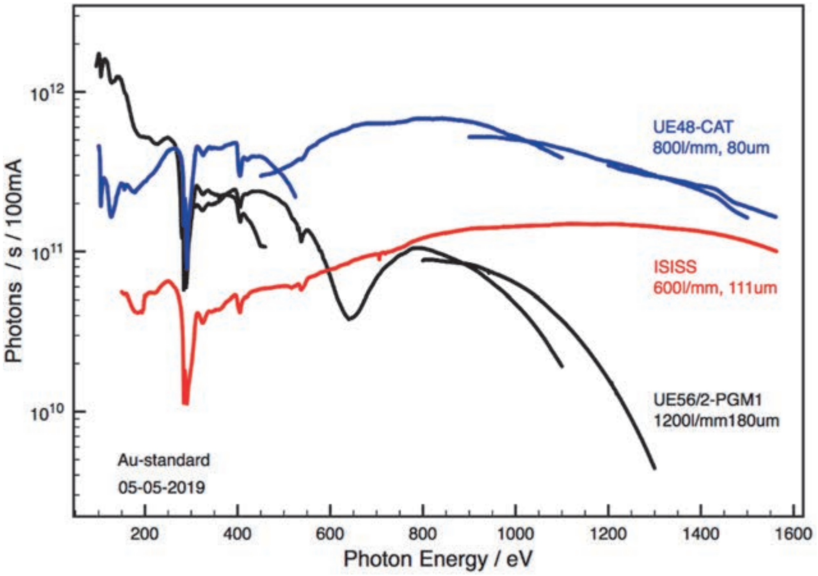

Figure 2: Comparison of the photon flux at sample position of the soft X-ray beamlines ISISS, BElChem (UE56/2-PGM1), and CAT@EMIL at BESSY dedicated to AP-XPS spectroscopy.

A strategy of commissioning phases combined with user experiments (e.g. within the CRC project cobalt based catalysts in isopropanol oxidation) is applied to put the CAT@EMIL facility into operation. This station combines an AP-XPS spectrometer equipped with a wide acceptance lens and high kinetic energy capabilities (up to E_{kin}=7000eV) with a sophisticated laboratory infrastructure optimized for in-situ XPS experiments with a chemical background. The photon energy range will be extended to the tender X-ray regime up to 8000eV by exploiting the radiation of the cryogenic in-vacuum undulator U17 in a second installation phase of this project[13,14] in the end of 2019/beginning of 2020, hence providing a perfect match with the spectrometer specification with its broad kinetic energy range.

In summary, while the permanent user operation of the workhorse ISISS is ensured, the new AP-XPS facilities BElChem and CAT@EMIL have been put into operation step by step within the last year. All set-ups are equipped with the modular endstation/reaction cell concept developed at the FHI to optimize flexibility and possibility to adapt the instrumentation to the user needs.

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Groupleader of the “Electron Microscopy” Group (since 2018)
Dr. Thomas Lunkenbein

Postdoctoral Fellow of the Electron Microscopy Group of the Department of Inorganic Chemistry at FHI (2012–2018)
Dr. rer. nat., University of Bayreuth (2012)
Education in Chemistry, University of Bayreuth (2004–2009)
Lee Hsun Young Scientist Lecture Award (2018)
Election to the 30 most promising young chemists under 30 (2013)
Cultural Award of Bavaria (2013)

Untangling Structural Complexity by Chemical Electron Microscopy

Since the last visit of the Fachbeirat the Electron Microscopy Group has been restructured and is under new guidance.

From the atomic to the macroscopic scale, heterogeneous catalysts are complex materials. Their constitutional complexity is able to influence their catalytic performance and can be expressed by the presence of different kinds of defects, particle shapes or microstructures. In addition, chemical potential induced changes of the catalyst during operation may add complexity to the system. During the last two years we have focused our research activities on exploring the different facets of structural complexity and their evolution under catalytically relevant reaction conditions using different techniques of electron microscopy and related analytics, including electron energy loss spectroscopy (EELS).

This approach has led to two main research directions within the Electron Microscopy Group:

- Local insights into the structural complexity of heterogeneous catalysts
- Development of multi-modal operando electron microscopy to track the evolution of structural complexity under relevant reaction conditions

Local insights into the structural complexity of heterogeneous catalysts

Local structures beyond translational symmetry are difficult to capture by integral and averaging techniques that are commonly applied. Defects on the atomic scale can locally alter the composition of any material, which can lead to reactivity gradients within the material. We have therefore complemented our recent catalogue of local structures for orthorhombic $(Mo,V)O_x$ that was obtained by scanning transmission electron microscopy (STEM)[1] by adding compositional information. The compositional information was obtained by an in-depth evaluation of spatially-resolved EELS spectra recorded at different parts of the catalysts. We concluded, for instance, that the surface is preferentially enriched in one of the cations, but the local Mo/V surface ratio can vary depending on the exposed facet. This local investigation was backed up by complementary information obtained by integral XPS and elemental analysis, which suggested the same trends.

Development of multi-modal operando electron microscopy to track the evolution of structural complexity under relevant reaction conditions

Heterogeneous catalysis is a multi-scale phenomenon and catalysis related processes can be observed from the atomic to the macroscopic scale. We have developed an operando electron microscopy analysis strategy that allows for bridging this scaling gap. Hereby, our strategy is based on three techniques:

- Quasi in situ TEM
- Operando TEM
- Environmental scanning electron microscopy (ESEM)

1. Quasi in situ TEM

Quasi in situ TEM allows us to track the evolution of local structures on the atomic scale by decoupling the catalytic reaction from local structural and compositional analysis. This ability comes at the expense of real time information, but minimizes the impact of the electron beam on the sample. Changes of identical particles can then be studied by comparing images taken before and after the reaction.[2]

In a first attempt, defective orthorhombic $(Mo,V)O_x$ has been used as a model. This open structured oxide is active and selective in the oxidative dehydrogenation of ethane (ODE) to ethylene. For this reaction, the catalytic function for TEM amounts of sample could be proven by coupling the quasi in situ TEM grid reactor to an ultra-sensitive proton-transfer reaction mass spectrometer (PTR-MS).

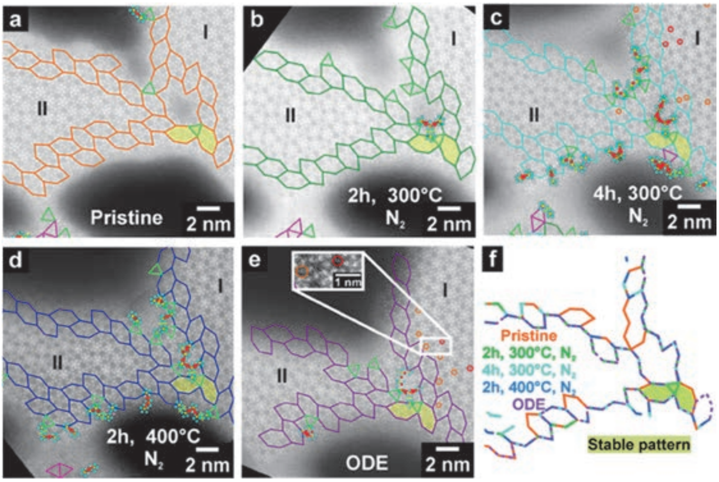

Figure 1: High resolution identical location ADF-STEM images of two two different $(Mo,V)O_x$ grains: grain I and grain II. a) pristine, b) after thermal activation in N_2 atmosphere at 300°C for 2h, c) after thermal activation in N_2 atmosphere at 300°C for 4h, d) after thermal activation in N_2 atmosphere at 400°C for 2h, e) after ODE and f) schematic overlay of the M1 surface contours after each heating step. Hexagons: M1 phase; green and magenta triangles: triangular motifs; red arrows: translated motifs; yellow lines mirrored motifs; red circles: shared motifs; green circles: twinned motifs, orange circles: filled hexagonal channels, red circles: filled heptagonal channels.

Identical location imaging of the open oxide after thermal activation in an N_2 atmosphere and after conditions relevant for ODE, reveal the occurrence of mass transport phenomena, surface smoothing, changes of the connectivity of pentagonal building blocks at the surface, the appearance of matter inside the structural channels and grain reorientation around the interphase. The observed phenomena are either partially reversible or irreversible and can depend on the redox potential of the gaseous environment. Our results further highlight that cations can migrate through structural channels of open structured materials in order to supply the active surface. This migration is possible as charges between bulk and surface can be compensated by an adaption of the connectivity of the pentagonal building blocks at the surface. Examples of the observed changes during heat treatments in different atmospheres at an identical location are shown in Figure 1. In addition, these heat treatments of the sample induce a reversible restructuring of the internal structure of the pseudo-trigonal intergrowth that is, for instance, independent of the gaseous environment.

2. Operando TEM

Heterogeneous catalysts are metastable compounds that dynamically adapt to the chemical potential of the environment. The shapes and phases that are generated under operation conditions are only stable in a narrow parameter range (pressure, gas composition, temperature). In addition, in order to judge the relevance of the observed changes during the reaction, the conversion has to be detected. When this criterion is met, the investigation is called operando. To meet the criterion of conversion detection, we have modified an existing gas feeding and analysis setup for in situ TEM investigation using commercially available gas cell TEM holders. After modification the setup now allows operando TEM investigation of heterogeneous catalysts to be conducted under relevant reaction conditions (Figure 2a).[3, 4]

To prove the functionality of the setup, we studied CO oxidation over Pt nanoparticles. This local operando analysis highlighted the possibility of disentangling different characters of chemical dynamics. As long as the CO partial pressure changes, i.e. during the activation period of the catalysts, morphological transformations occur (Figure 2b). These morphological transformations tend to form equilibrated surface facets and are detrimental to the catalytic performance. At constant chemical potential and high conversion, structural dynamics occur that affect the crystalline bulk of the Pt nanoparticles (Figure 2c). The changes in the crystallinity of Pt can be induced by the diffusion of reactants through the ordered bulk. These structural changes are triggered by frustrated phase transitions. In brief, the system aims to undergo a phase transition due to energy minimization. This phase transition is hindered by a relatively high energy barrier and can cause strain in the bulk structure. Strain and stress can then be relieved by atomic scale roughening of flat surfaces (Figure 2d). Thus, frustrated phase transitions seem to be beneficial for maintaining a high catalytic activity.

3. Environmental scanning electron microscopy (ESEM)

In order to investigate catalysts on a more global scale we have improved the functionality of an existing ESEM. The advancements feature a contamination free stabilization of oxophilic metal surfaces. A new tubular reactor was introduced to further reduce the concentration of oxidants remaining in the chamber.

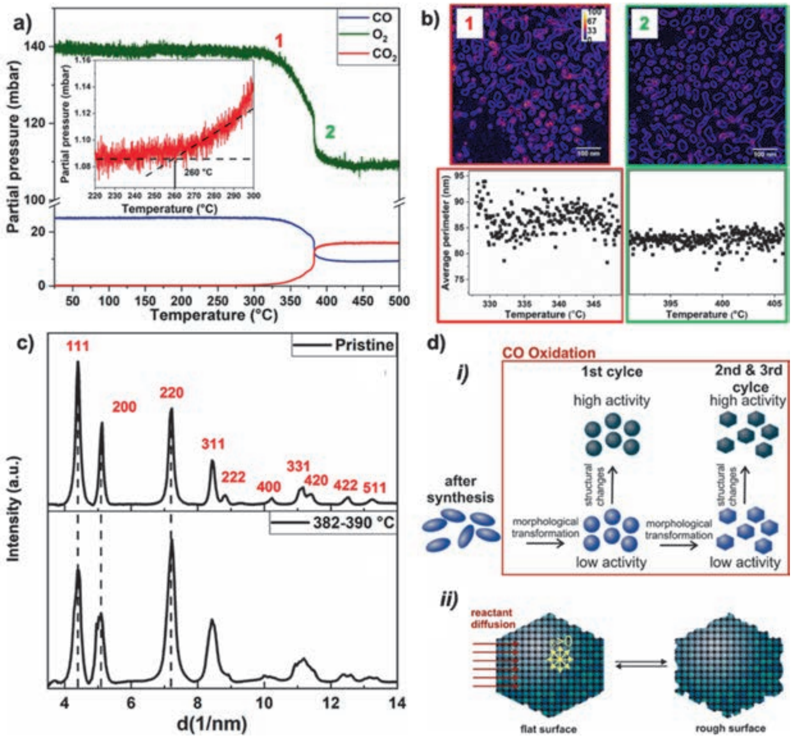

Figure 2: a) MS data for CO oxidation over Pt NPs heated to 500 °C as obtained from operando TEM. Experiment. The inset in a) shows the onset of CO_2 production. b) Particle shape analysis with corresponding average perimeter distribution of NPs at different temperature regimes: 1) 328 – 348 °C, 2) 391-406 °C. white/yellow/red: greater shape changes; purple/blue/black: small to no changes. c) Radial profiles obtained from selected electron diffraction data. Changes in shape and position of reflections that correspond to (111), (200) and (220) lattice planes are marked with dashed lines. d) Schematic representation of the operando TEM results: i) morphological transformations and structural dynamics occur at different reactivity regimes. ii) Reactant diffusion through the Pt NPs induces a frustrated phase transition which leads to strain ($\varepsilon > 0$) inside the particle that is relieved by atomic surface reconstruction.

Dry reforming of methane (DRM) over Ni surfaces was tested as a model reaction (Figure 3). The simultaneous acquisition of visual information and mass spectrometry (MS) data revealed the presence of surface oxides in the low activity state. These surface oxides were deplete during reaction. Labeling experiments with $C^{18}O_2$ proved that CO_2 is the cause for the formation of surface NiO. In addition, oscillatory behavior was observed in the oxide traces, which was correlated to the transition of oxide and metallic surfaces. The importance of this phase transition can also be highlighted by calculating the 1st derivative of the trace with respect to time. Thus, conditions, at which pronounced changes occur can be highlighted. Our results revealed the importance of oxide-metal phase transitions in catalytic processes as they can be responsible for their initiation.

We have developed new routines to obtain insights into the structural complexity of heterogeneous catalysts. Furthermore, we established different operando techniques (quasi in situ TEM, operando TEM, ESEM) for the investigation of such materials. This multi-modal approach can be used in a complementary fashion to visualize chemical potential induced changes in the structure and morphology of heterogeneous catalysts over different length scales. The local and global scale analysis of catalysts under static and operando conditions with different techniques of electron microscopy shows that structural complexity is a general phenomenon in heterogeneous catalysis. This complexity can be further increased during the reaction. Using the outlined operando approach, we are now able to convert local observables into more detailed understanding of how a catalyst works.

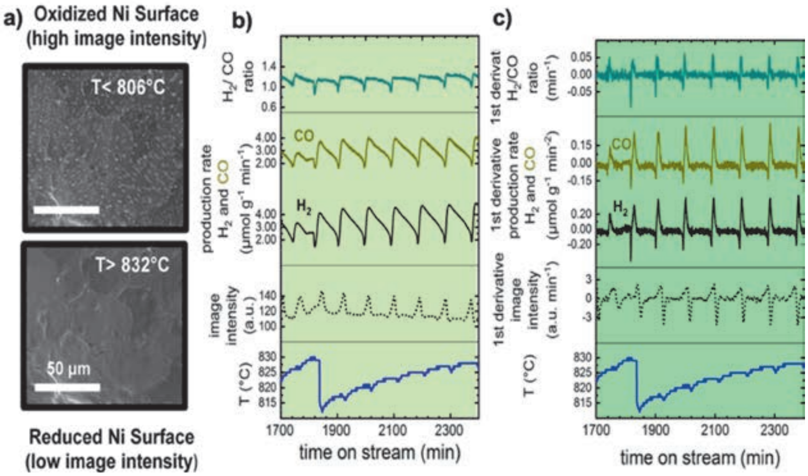

Figure 3: Environmental SEM investigation of syngas production over metallic Ni catalyst during thermal cycling between 770 °C and 890 °C under DRM conditions. a) SEM images recorded under reaction conditions. b) and c) Self-sustained catalytic oscillations observed during DRM over Ni catalysts. b) Compilation of simultaneously recorded temperature, image intensities, production rates, and H_2/CO ratio. c) 1st derivatives of time of the operando data presented in b).

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Group leader of the "Liquid/vapor Interfaces" Group (since 2018)
Dr. Hendrik Bluhm

Dr. rer. nat., Universität Hamburg (1996)
Postdoc at Lawrence Berkeley National Laboratory (1996–2000)
Staff Scientist at Fritz-Haber-Institut der Max-Planck-Gesellschaft (2001–2004)
Staff/Senior Scientist at Lawrence Berkeley National Laboratory (2004–2018)
Friedrich Wilhelm Bessel Research Award, Alexander von Humboldt Foundation (2013)
Fellow, American Association for the Advancement of Science

Heterogeneous Chemistry of Liquid/Vapor Interfaces

The research of the "Liquid/Vapor Interfaces" group in the AC Department of the FHI focuses on the elucidation of heterogeneous chemical reactions at aqueous solution/air interfaces under realistic conditions present in the environment and the atmosphere. The properties of liquid/vapor interfaces play a major role in natural processes. For example, they strongly influence the abundance and reactivity of trace gas molecules that are major drivers in heterogeneous processes in atmospheric and environmental chemistry.[1] In particular, aqueous aerosols catalyze heterogeneous reactions in the troposphere and can act as both sinks for (e.g., HNO_3, HCl, N_2O_5) and sources of (e.g., halogen radicals) atmospheric trace gases. To date, little is known about the concentration of a wide range of solution phase species at the liquid/vapor interface, which can significantly differ from that in the bulk.

Even less is known about the fundamental pathways in heterogeneous reactions of gas phase species at liquid/vapor interfaces and the role of surfactants in these reactions. Surfactant layers can affect the interface properties through direct chemical interaction with the constituents of the solution. The presence of a surfactant may, for instance, change the propensity of certain ions for the interface[2], which in turn can lead to changes in the reaction rates between trace gas molecules and solvated ions. Recent experiments on the influence of long-chained alcohol surfactant layers on the evaporation coefficient of neat water have shown that an increase in the carbon chain length by four carbons can decrease the evaporation coefficient by several orders of magnitude.[3] Similar effects are also expected in the opposite gas diffusion direction, i.e., for the migration of vapor-borne molecules through a surfactant layer towards the liquid interface.

Another possible influence of surfactants concerns their direct reaction with trace gases, such as a reaction between carbonaceous surfactants and strong oxidizers (O_3, OH*) which can lead to a partial or complete removal of the surfactant layer and consequently to an increase in the transport of molecules from or to the liquid/vapor interface. These and other processes at, and properties of, the liquid/vapor interface are potentially influenced by the presence and the specific chemical nature of surfactants. For a basic understanding of these phenomena, interface-sensitive studies of model systems with a well-controlled chemistry and surfactant coverage are important.

While there is a wealth of reactor studies that monitor changes in the gas phase composition to conclude upon reactions at the liquid/vapor interface, these methods do not provide direct information about the reaction products and other properties of the liquid/vapor interface during heterogeneous chemical reactions. Over the years a number of surface sensitive optical spectroscopies, such as sum frequency generation (SFG) and reflection-absorption infrared spectroscopy (RAIRS), as well as X-ray based methods, such as grazing incidence small angle X-ray scattering (GISAXS) have been developed to investigate liquid/vapor interfaces under realistic conditions. AP XPS has also been used to determine the concentration of ions near aqueous solution/vapor interfaces in the presence of the equilibrium vapor pressure. AP XPS offers the exciting opportunity to investigate these interfaces under relevant pressures for all important environmental trace gases, such as CO_2, NO_x and O_3, including the reaction of these gases with surfactants at the interface.

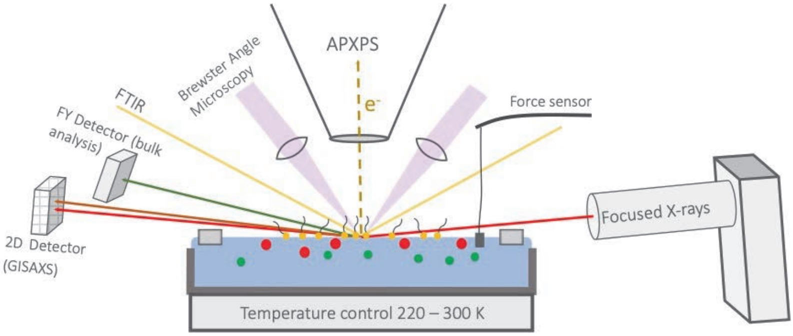

Figure 1: Schematic layout of the new instrument for the investigation of liquid/vapor interfaces. It combines microscopy, scattering and spectroscopy methods that can be carried out simultaneously under realistic conditions of temperature, trace gas composition, pH, bulk solution and surfactant concentration.

We are currently planning and designing a new experimental setup for a more comprehensive investigation of liquid/vapor interfaces. Its principal layout is shown schematically in the Figure 1. The instrument will combine AP XPS, RAIRS, GISAXS and Brewster Angle Microscopy, which deliver complementary information on the composition, chemical nature and structure of the interfacial region. Since diffusion rates are high in liquids it is also important to monitor the bulk of the solution which will be accomplished by X-ray fluorescence measurements. Liquid/vapor interfaces will be prepared using a Langmuir trough setup which allows dynamic control over the surfactants density at the interface. The instrument will use a laboratory X-ray source so that systematic, long term studies of the correct methodology of preparing liquid/vapor interfaces with high control over their chemical purity can be performed. This also requires the design of a vacuum-compatible Langmuir trough and force sensor for the surface pressure measurements.

Langmuir troughs are an excellent method to prepare liquid/vapor interfaces with adjustable surfactant coverage and chemistry. Changes in the packing and the structure of the surfactant layer are traditionally monitored through measurements of the surface pressure as a function of the mean molecular area (MMA). The relatively straightforward nature of a Langmuir trough setup lends itself for a combination with other surface sensitive methods, such as infrared spectroscopy and grazing-incidence small-angle X-ray scattering. AP XPS allows us to observe changes directly in the surfactant chemistry, as well as all the other constituents of the solution, with high interface sensitivity. In a proof-of-principle experiment we have combined a Langmuir trough setup with an AP XPS experiment to monitor the density and orientation of a stearic acid ($C_{17}H_{34}COOH$) surfactant layer on neat water.[4] These experiments were carried out at the Advanced Light Source in Berkeley, CA.

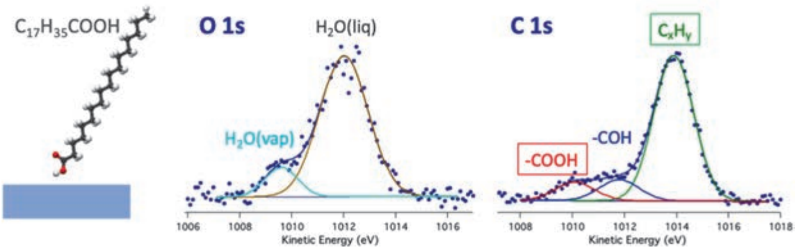

Figure 2: O 1s and C 1s spectra of a compressed stearic acid layer on neat water taken with APXPS at room temperature.[4]

From the measured C 1s and O 1s peak areas (see Figure 2) one can quantify the coverage of water by stearic acid as a function of compression, and in addition also determine changes in the orientation of the stearic acid molecules at the surface. For low coverages of stearic acid on water, i.e. at low compression, the O 1s signal from water is expected to be less attenuated by stearic acid and there are less stearic acid molecules per unit area at the water surface, resulting in a low C 1s/O 1s peak area ratio. This ratio will increase as the stearic acid layer is compressed. Changes in the orientation of the stearic acid molecule with respect to the water surface can be detected through changes in the C 1s signal of the CHx chain (I_{CHx}) with respect to that originating from the acid group (I_{COOH}), where it is expected that this ratio will increase with increasing upward tilt of the hydrophobic CHx chains. Our measurements do indeed show these trends and correlate well with off-line compression curves from surface pressure measurements. These measurements also show that, even with careful preparation, the surface of neat water is always at least partially covered by a carbon contamination layer, which demonstrates that better methods for the controlled preparation of static liquid/vapor interfaces need to be developed. The results of these proof-of-concept experiments provide important information for the correct design of the experimental cell and the preparation of water surfaces with a high degree of cleanliness in our new setup (see Figure 1).

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Group Leader of the "Metal" Group (since 2019)
Dr. Katarzyna Skorupska

Electronic Structure group at the AC FHI (2015–2019)
Centre for Photoconversion and Catalysis at the University of Wyoming, Laramie, USA (2013–2015)
Max Planck Institute of Colloids and Interfaces Potsdam-Golm, Germany, group of Prof. Dr. M. Antonietti (2010–2012)
Hahn-Meitner-Institute (from 2008 Helmholtz-Zentrum Berlin), group of Prof. Dr. H.J. Lewerenz (2002-2012) comprising invited guest researcher appointments at the University of Warsaw, Poland, and the University of Portsmouth, UK
Dr. rer. nat., Poznań University of Technology, Poland (2001)
Master of Chemistry, Adam Mickiewicz University (Poznań), Poland, (1997)

OER on Manganese Oxides

Manganese oxides attract considerable attention as anode material candidates for water oxidation. The inspiration comes from the manganese rich metaloenzyme, the core of the oxygen evolving complex (OE) in photosystem II (PS2) which is the integral part of photosynthesis.[1] Considering the different complex goals of nature and despite of the functionality there it seems that manganese oxides may not be advantageous as oxygen evolution catalysts for large-scale technical applications. Nevertheless, the variability of existing MnOx makes them very interesting systems to study. A major challenge in the exploration of manganese oxides is the understanding of the behavior of such catalysts during the oxygen evolution reaction (OER). The standard manganese oxides before and after oxygen evolution reaction (OER) were investigated. Different membrane based techniques were adapted for in-situ measurements of MnOx wherein electrochemical and spectroscopic experiments were performed simultaneously. In both cases depth profiling of the catalyst has been obtained by combining surface and bulk sensitive detection methods. For the ex-situ approach as synthesized powders of Birnessite, Bixbyite, Hausmannite and Manganosite, respective pristine electrodes of these on FTO pyrolysed in air under 450ºC and finally the same electrodes after the OER in phosphate buffer of pH7 were tested. It was found that the studied manganese oxides could be divided into two groups (i) where the surface and the bulk (whole electrode) actively contribute to the electrochemical process and (ii) where the surface contributes to electrochemistry while the bulk acts as a charge carrier conductor. K-Birnessite (δ-MnO_2) and Manganosite (MnO) belong to the first, electrochemically better performing, group where their dynamic structures can more easily respond to applied external potentials. Hausmannite (Mn_3O_4) and Bixbyite (Mn_2O_3) can be assigned to the second group with only changes at the surface: incomplete surface oxidation (Mn_3O_4 to Mn^{4+}) and hydroxide layer formation (few nm on Mn_2O_3) were found after OER. The conductivity properties of the bulk material makes Bixbyite a better performing electrode than Hausmannite.

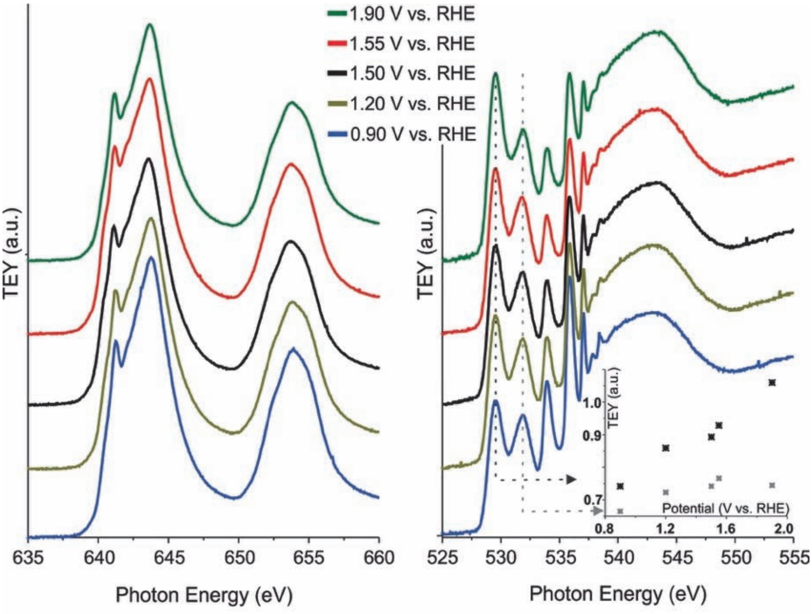

Figure 1: From the left Mn L- and O K-edge XA spectra registered in the in-situ experiment under external applied potentials in 0.1M Phosphate buffer, pH7.

In the in-situ studies during electrochemistry the Mn L- and O K- absorption edges were recorded. This approach gives the opportunity to monitor changes (under applied potential) in the oxidation state of Mn and the Mn 3d / O 2p hybridization. Because of operation at the apparatus' detection limit with respect to the species created under the OER, the architecture of manganese oxide containing the highest interface with the electrolyte was experimentally required. Based on the results from the ex-situ part of the project the Birnessite related manganese oxides were selected to meet this requirement.

The measurements were performed with total electron yield (TEY, 10 nm information depth), fluorescence yield (FY, 30 μm information depth) and transmission (information across the entire electrolyte - catalyst). From all techniques, the Mn L-edges show a majority of Mn^{4+} during the OER. At the same time, an increase in covalent character of the manganese oxides leads to an increase in the O K-edge white line (Fig.1).[2] The activity of the catalysts was confirmed by detection of the product oxygen. These phenomena were observed in 0.1M phosphate buffer at pH=7 and 0.1M KOH at pH=13 solutions.

Propane dehydrogenation

Propylene and hydrogen are two valuable products of non-oxidative propane dehydrogenation (PDH) via heterogeneous catalysis. Therefore, the production of these materials from cost-effective sources, such as propane, has attracted significant interest, such that PDH has already been established for commercial production at industrial scale.[3] Among the catalysts used for PDH, Pt-based catalysts offer remarkable propane conversion and propene yields, as well as relatively low coke formation properties compared to some other commonly used catalysts. Nevertheless, Pt catalysts still suffer from substantial deactivation as a result of coking. In addition, changes to the catalyst particles themselves, such as sintering or other morphological changes, are thought to potentially increase rates of deactivation. However, factors influencing coking, the composition of the coke, as well as the possible changes to the Pt particles and their relation to deactivation, remain poorly understood. Furthermore, successful regeneration - a recipe to remove coke and at the same time retain activity of the catalyst - also remains challenging in PDH.

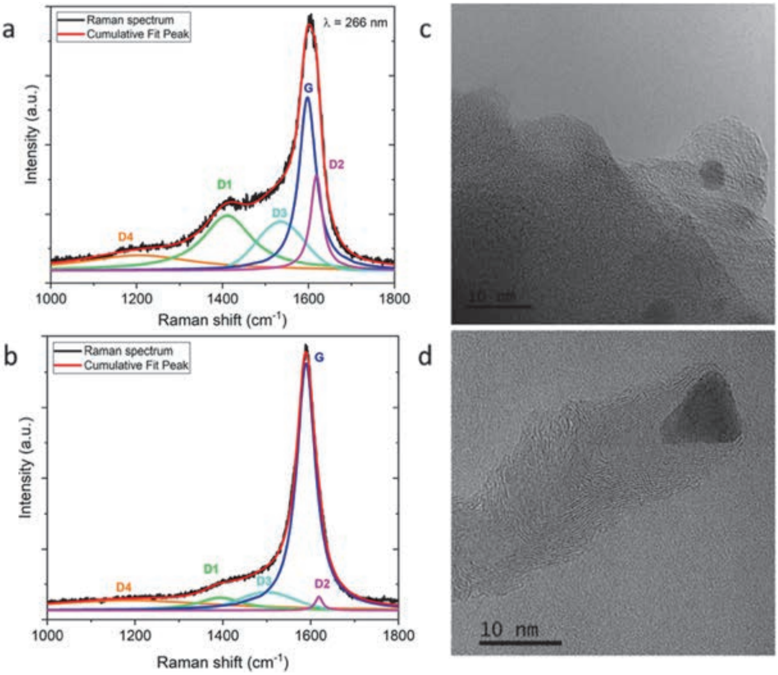

Figure 2: Raman and transmission electron microscopy (TEM) analysis of coke formed after 1st cycle and after regeneration followed by 2nd cycle: a) Raman spectrum of coke in first activity cycle and (b) after first regeneration cycle. The bands were labeled according to the nomenclature suggested by Sadezky et al.[4] c) Bright Field (BF) TEM image of the coke formed during PDH after >200h. d) BF TEM image of carbon nanotube formed after first regeneration cycle.

In this project, we are studying the amounts and nature of the coke formed during PDH, as well as the effects of the coke on activity. The general mechanisms of deactivation are also investigated and, subsequently, possible effective regeneration recipes developed. We address these challenges by meticulously examining fresh, coked and regenerated industrial Pt-catalysts using various complementary, multi-scalar techniques, for both in-situ and ex-situ analysis and imaging. In an effort to develop an efficient regeneration protocol, the kinetics of coke burning at different oxygen concentrations was also investigated.

After the first regeneration cycle, using both Raman and TEM, it was found that the coke formed on the catalyst had a more graphite-like character (Fig. 2a-c), which was consistent with the measured decrease in activity of the catalyst. In addition, TEM revealed the formation of carbon nanotubes initiated at the Pt particles (as shown in Fig. 2d). These results suggested that coke formation was a major factor in the catalyst deactivation but that the coking itself could never be totally avoided.

An investigation of the catalytic effect of minerals on the formation of ethanol from syngas

The most promising catalysts for ethanol synthesis using syngas are Rh-based. In the search for alternatives to this high cost and low abundance material, the manganese nodules known for their catalytic activity seem to be promising candidates.[5] The present work aims to explore the catalytic behavior of manganese nodules under CO conversion to ethanol.

The studied manganese nodule, collected from the eastern Pacific Ocean, was provided by the Federal Institute for Geosciences and Natural Resources (BGR). The structural and elemental analysis by means of TEM and XRD was combined with the catalytic activity tests. The hydrogenation of carbon monoxide on the manganese nodule is not as efficient as the most promising catalyst for ethanol synthesis (Rh-Mn-Fe@SiO_2). The product detection shows mainly methane, followed by ethane, ethanol, methanol, propane and smaller amounts of acetone and alkenes.

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Theory Support
Prof. Dr. Klaus Hermann

Visiting Scientist (AC) (since 2011), Scientific Group Leader (C3, TH) (1990–2011),
Head Network Center (GNZ) (1990–2008), Fritz Haber Institute (since 1990)
Staff member Physics Department, Free University Berlin (since 1989)
Assoc. Prof. (C2), Technical University Clausthal (1982)
Habilitation, Technical University Clausthal (1977)
Dr. rer. nat., Technical University Clausthal (1974)

Theory support by K. Hermann has continued to provide insight and offer interpretation to theoretical issues connected with experimental results obtained by the experimental groups of the department. Recently the activities have focused mainly on bulk and surface crystallography. The results of collaborations with all groups of the department have proven to be valuable. Here we mention only support for the

- *Electron Microscopy group* (T. Lunkenbein) in the evaluation of crystallographic shapes of metal and oxide particles in connection with corresponding electron microscopic images.[1] Two-dimensional tiling has shown to provide a convincing classification of local structure perturbations at complex oxide particles.[2]

In addition, various subjects not immediately connected with experimental work in the department, but also in collaboration with external groups, have been studied. This includes work on

- *Electronic and geometric structure of nanomachines*. Interlocking molecular gear chains built at surfaces[3,4] have been examined by DFT calculations to find out about details of energy transfer induced by rotational motion (with M.A. Van Hove et al., Hong Kong Baptist University and City University Hong Kong).
- *Analyses of rotational and translational motion in large molecular machines*. A formalism has been developed to analyze internal rotation and translation characterizing motion in molecular machines[5] based on quasiclassical concepts (collaborative research grant (CRG) project involving experimental and theoretical groups of the six leading Hong Kong universities).
- *Metal particle transport by dendridic molecules*. Detailed DFT calculations on a G3-n dendron molecules enclosing a Au_{78} cluster together with synthetic preparation and analysis can shed light on the “grabbing” of small metal nanoparticles by dendrites which may facilitate particle transport[6] (with K. Leung et al. at the Chemistry Dept., Baptist University, Hong Kong).

Finally, crystallographic code development has been continued with bug fixes and upgrades, as well as implementations of advanced features which proved to be necessary for specific applications.

- *The Balsac package* (Build and Analyze Lattices, Surfaces, and Clusters)[7] has been adapted to run on Windows 10 PCs. Further, options to build and analyze surfaces with interference lattices (forming moiré patterns), as well as predefined regular cubic and icosahedral nanoparticles, have been included in version 4.3. This package is used quite frequently for the design and analysis of complex crystal bulk and surface structures. It is also distributed commercially outside the institute by the MPG.
- *The Surface Explorer*,[8] a web application to visualize surface structures of common crystals has been further upgraded. The interactive application (based on an early Unix version of Balsac) is accessible from the internet and has been running successfully already for 22 years with 1.56 Mio. visits in total (corresponding to about 200 visits daily since 1997).

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Interface Science

Department of Interface Science
Prof. Dr. Beatriz Roldán Cuenya

Director at FHI and Scientific Member of the Max Planck Society (since 2017)
Honorary Professor Freie Universität Berlin (2019), Technische Universität Berlin (2018), and Ruhr-Universität Bochum (2017)
Full Professor at the Ruhr-Universität Bochum (2013–2017)
Distinguished Research Professor University of Central Florida (2013)
Full Professor at the University of Central Florida (2012–2013)
Associate/Assistant Professor at the University of Central Florida (2004–2012)
Postdoc at University of California at Santa Barbara (2001–2003)
Dr. rer. nat. at the University of Duisburg-Essen (2001)

Department of Interface Science

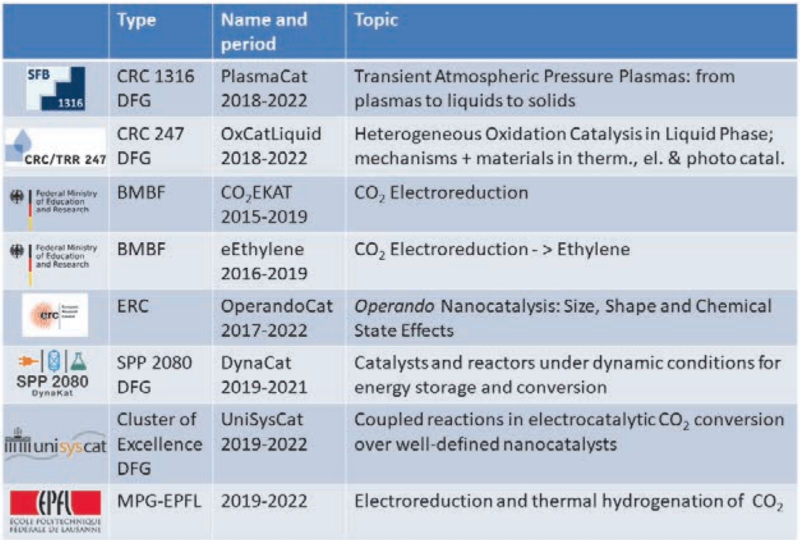
The Department of Interface Science (ISC) was established at the FHI in October 2017 with the appointment of Prof. Beatriz Roldán Cuenya. The ISC research program focuses on the investigation of structural, electronic, vibrational and chemical properties of size- and shape-controlled nanostructures and thin films and their interfaces with gas and liquid environments for applications in thermal catalysis and electrochemistry. Advanced synthesis methods and state-of-the-art *in situ* and *operando* characterization techniques are systematically employed to gain in depth mechanistic understanding into catalytic processes.

In the last two years, significant effort has been dedicated to the planning of new laboratory space and the renovation of existing one, including implementing temporary solutions within the FHI till the construction of a new building dedicated to thermal catalysis and electrochemistry is completed (currently projected for 2022). My group remained in Bochum during the first year of my MPG appointment until provisional laboratory space was available at the FHI. From October 2018 until May 2019, most of the scientists, four large ultrahigh vacuum (UHV) systems, a complete chemistry lab, all electrochemical setups and high pressure reactors were moved from Bochum to Berlin. On April 1st 2019, all employees with permanent positions of the former Department of Chemical Physics (CP) were integrated into the new ISC Department and the corresponding laboratory space was made available. Due to diverse reasons outside my control, the renovation projects have been drastically delayed, which has seriously affected the progress of my research program. At the moment the renovation of the former CP building is scheduled to begin at the end of 2020. Meanwhile, the focus of four groups of the former CP Department was re-directed while taking advantage of their expertise and integrated into the new research areas of the ISC Department.

The ISC Department group leaders (transferred from CP) are Markus Heyde (Scanning Probe Microscopy), Helmut Kuhlenbeck (Thin Films), Thomas Schmidt (Spectro-Microscopy), and Shamil Shaikhutdinov (Structure and Reactivity). In addition, three new group leaders recently joined: Janis Timoshenko (*Operando* hard X-ray spectroscopy), Christopher Kley (Photo-Electrochemical Scanning Probe Microscopy, funded by the Helmholtz Society but with workplace at the FHI), and See Wee Chee (Liquid Phase Electron Microscopy).

A major task during the last 2 years has been the acquisition of new equipment and refurbishment/re-design of existing ones, including adaptations for their use in electrochemical applications and thermal catalysis investigations under realistic reactions conditions, including high pressures. For instance, a new scanning electron microscope with gas-dosing/heating environmental capabilities has been secured and upgraded for its use in a liquid environment in combination with an electrochemical (EC) holder. In parallel, another EC-holder has been purchased and is already in operation in an existent FHI environmental transmission electron microscope. A new X-ray diffractometer has been acquired including a reactor cell designed for thermal catalysis experiments, and several UHV systems from the former CP Department, including the LEEM/XPEEM set-up at BESSY have been restructured in order to enable quasi *in situ* electrochemical experiments.

The Department is engaged in several third party funding projects at the national and international level from the German National Science Foundation, the Federal Ministry of Education and Research, and the European Research Council, Figure 1.



	Type	Name and period	Topic
SFB 1316	CRC 1316 DFG	PlasmaCat 2018-2022	Transient Atmospheric Pressure Plasmas: from plasmas to liquids to solids
CRC/TRR 247	CRC 247 DFG	OxCatLiquid 2018-2022	Heterogeneous Oxidation Catalysis in Liquid Phase; mechanisms + materials in therm., el. & photo catal.
Federal Ministry of Education and Research	BMBF	CO_2EKAT 2015-2019	CO_2 Electroreduction
Federal Ministry of Education and Research	BMBF	eEthylene 2016-2019	CO_2 Electroreduction - > Ethylene
erc	ERC	OperandoCat 2017-2022	*Operando* Nanocatalysis: Size, Shape and Chemical State Effects
SPP 2080 DynaKat	SPP 2080 DFG	DynaCat 2019-2021	Catalysts and reactors under dynamic conditions for energy storage and conversion
unisyscat	Cluster of Excellence DFG	UniSysCat 2019-2022	Coupled reactions in electrocatalytic CO_2 conversion over well-defined nanocatalysts
EPFL ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE	MPG-EPFL	2019-2022	Electroreduction and thermal hydrogenation of CO_2

Figure 1: Third party funding projects of the Department of Interface Science.

Finally, Prof. Roldán Cuenya is serving in a number of national and international scientific advisory committees including the advisory committee of the Office of Basic Energy Sciences of the US Department of Energy (2011-present), the advisory committee of the Synchrotron Facility ALBA in Spain (2019 – present), the Scientific Council of DESY - Deutsches Elektronen-Synchrotron in Hamburg (2019-present), and the executive board of the Cluster of Excellence UniSysCat, in Berlin (2019-present). She is also an associate editor of the international journal ACS Catalysis (2018-present) and a member of the advisory editorial board of the Journal of Catalysis (2018-present).

Electrocatalysis

The research focuses on the fundamental understanding and further development of high-performance, stable catalysts for reactions of technological interest, such as the CO_2 reduction reaction (CO_2RR), alcohol oxidation, oxygen evolution and reduction reactions (OER, ORR), hydrogen evolution reaction (HER) and nitrogen reduction reaction (N_2RR).

Our goal is to improve the mechanistic knowledge of electrocatalytic reactions taking place over nanostructured materials. For this purpose, we are developing synthesis routes leading to well-defined electrocatalysts by systemically varying their morphology (size, shape, defects), electronic, and chemical properties (multimetallic systems and NP/support interactions). The synthesis routes commonly used include colloidal chemistry approaches, solvothermal and electrochemical synthesis.

Insights into the parameters affecting the activity and selectivity of electrochemical processes are being gained by using advanced *in situ* and *operando* laboratory surface science and synchrotron-based techniques, such as X-ray photoelectron (XPS) and X-ray absorption spectroscopy (XAS), nuclear resonant inelastic X-ray scattering (NRIXS), electrochemical atomic force microscopy (EC-AFM) and transmission electron microscopy (EC-TEM), differential electrochemical mass spectrometry (DEMS), Fourier-transform infrared (FTIR), Raman and UV-Vis spectroscopy.

In addition, the influence of the electrochemical treatment and conditions on the activity/selectivity and re-structuring of model electrocatalysts such as single crystal surfaces, is being explored by applying potential pulses. The role of the electrolyte is also studied in terms of pH effects, electrolyte-induced surface reconstructions, or electronic changes on the electrode surface. Some examples of the work we have conducted in the last two years are shown below.

Electrochemical Reduction of CO_2

The electrochemical conversion of CO_2 to chemicals and fuels powered by electricity derived from renewable energy sources is a promising strategy towards sustainable energy generation. Among the metals studied for CO_2RR, copper is the only one that can reduce CO_2 to hydrocarbons and fuels with a significant yield due to its optimum binding of adsorbed CO and H_2.[1,2] Unfortunately, the selective CO_2RR to multicarbon products (C_{2+}) on Cu is still characterized by low current densities even at high overpotentials, and is hindered by the competitive HER. Therefore, highly active and selective electrocatalysts for C_{2+} products are urgently needed to improve the energy efficiency of the CO_2RR, Fig. 2.

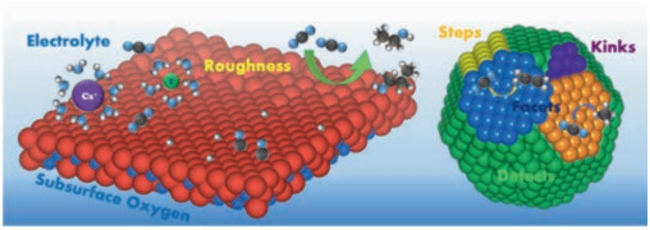


Figure 2: Parameters influencing CO_2 electroreduction.[2]

Single crystal surfaces

Single crystal electrodes are important model systems to study the effect of the surface atomic arrangement on a given electrocatalytic reaction. We have used Cu single crystals in order to distinguish the influences that the Cu surface structure and chemical state play in CO_2RR selectivity. Previous contributions have suggested that Cu(111) and Cu(100) surfaces boost the formation of CH_4 and C_2H_4, respectively. In recent years, the possible catalytic role of Cu(I) species and sub-surface oxygen for the C-C coupling enhancement and alcohol production has also been discussed. Nonetheless, the lifetime of the Cu(I) species under CO_2RR conditions is expected to be very short. In order to overcome this issue, we used oxidizing pulses to continuously regenerate Cu(I) species during CO_2RR. As shown in Fig. 3, the Cu surfaces measured under pulsed CO_2RR conditions displayed a distinct selectivity, favoring C_{2+} products. In particular, a significant enhancement in ethanol production was obtained and a decrease in hydrogen. We applied *quasi in situ* Cu LMM Auger spectroscopy, Fig. 3(a), to identify the species generated by the anodic pulses, while the surface structure of the electrodes was monitored by cyclic voltammetry and AFM, Fig. 3(b). Our results point out that the coexistence of (100) sites (favoring C_2H_4) and Cu(I) surface species (favoring ethanol), is the best combination towards reactions pathways that favor C_{2+} products, Fig. 3(c). However, the pulses also resulted in drastic morphological transformations of the Cu(100) surface that are expected to affect the reaction selectivity, Fig. 3(b). Thus, by using a pulsed potential technique, simultaneous control over the surface structure and the oxidation state of Cu surfaces could be achieved.

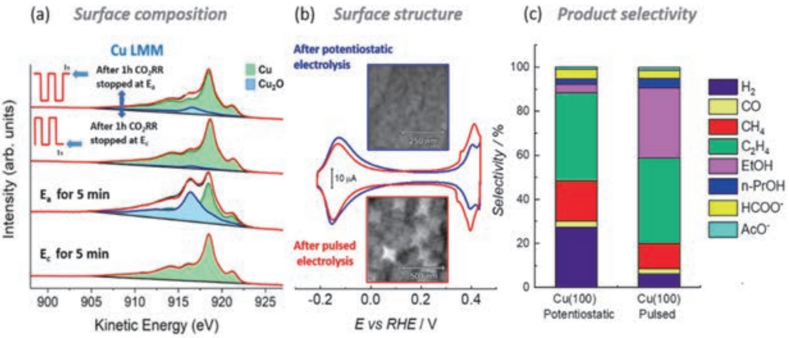


Figure 3: Pulsed CO_2 electrolysis. (a) Quasi *in situ* Cu LMM Auger spectra of Cu(100) after pulsed electrolysis, stopping the potential at either the anodic (Ea) or cathodic (Ec) pulse for 1s or 5 min. (b) Surface structure characterization by *ex situ* AFM and cyclic voltammetry after CO_2RR under potentiostatic or pulsed conditions. (c) Product selectivity during CO_2RR at constant -1.0 V and pulsed conditions (+0.6 V for 1s/-1.0 V for 1s during 1 hour) in 0.1M $KHCO_3$.

Despite significant recent advances, rational design of CO_2 electrocatalysts having enhanced selectivity and efficiency is still strongly limited by the lack of high spatial resolution insight into the dynamic material properties and structure-property relations under reaction conditions (i.e., in an electrolyte and under applied potential). Within our department, **Kley's group** addresses this challenge by EC-AFM. Fig. 4 shows a potentiodynamic AFM series of Cu(111) measured in 0.1 M $KHCO_3$ and plotted above its corresponding cyclic voltammogram. Upon exposure to the electrolyte and subsequent electrochemical reduction, a mesa and pit morphology with flat terraces is observed. Morphological changes upon anodic and cathodic potential cycling were also observed. Current work aims to advance imaging at highly gas-evolving potentials, discriminate between conducting and non-conducting phases, and to correlate *in situ* morphology and electrocatalytic product distribution.

As illustrated above, the characterization and modification of well-defined single-crystal metal electrodes is a promising way to gain mechanistic insight into CO_2RR. The implementation of electrode preparations using UHV facilities in combination with traditional surface science characterization can overcome uncontrolled pretreatments of electrode materials under changing ambient conditions. This approach is now being employed in the **Heyde group** to evaluate differently pre-treated Cu electrodes. Since both, surface reconstruction and oxidation state of copper are expected to play a role in CO_2RR, a low-temperature UHV scanning tunneling microscope (STM) has been upgraded with an *in situ* O_2-plasma source to carry out and monitor the controlled oxidation of surfaces. In addition, sample transfer capabilities under controlled atmosphere have been designed to evaluate the electrochemical properties of the UHV-prepared surfaces.

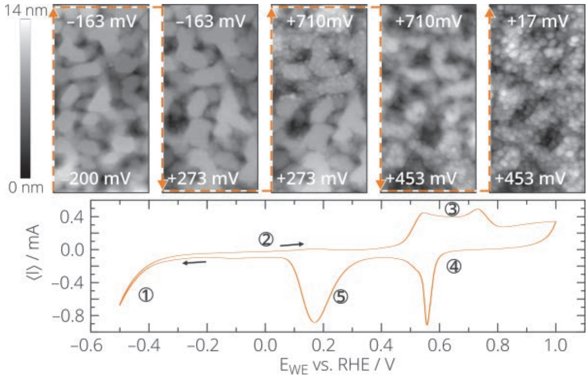


Figure 4: EC-AFM of UHV-prepared Cu(111). Top: Potentiodynamic series in 0.1 M $KHCO_3$. (500 nm × 250 nm). Bottom: cyclic voltammogram of such a system. Numbers indicate the potential ranges of the images from left to right.

As demonstrated in Fig. 3, the stabilization of the surface structure and oxidation state of copper is highly desirable for CO_2RR applications. A promising strategy consists in using permeable two-dimensional materials as an encapsulating system. In this context, 2D silica is of interest for the modification of electrocatalysts, and could likewise provide chemical selectivity through confinement effects. Taking these ideas into account, the growth of silica thin films on metallic as well as on O_2-plasma treated Cu single-crystals has been initiated. The structural and electronic properties of such systems are being investigated via low energy electron diffraction (LEED) and scanning tunneling microscopy and spectroscopy (STM/STS). The structural stability of these samples has already been tested *ex situ* towards ambient conditions and different solvent solutions. The properties of silica films as an encapsulating layer for electrochemical applications are promising. STM images suggest the preservation of the underlying copper oxide structure up to 1000 K.

A complementary approach is being adopted in the SMART microscope (**Schmidt group**) operating at the synchrotron light source BESSY-II. The strength of this instrument is the possibility of following chemical reactions and morphological changes in model catalysts in real time under reactive conditions, with comprehensive characterization of local structural and chemical properties based on a variety of surface science techniques such as µ-LEED, µ-XPS, µ-NEXAFS (near-edge X-ray absorption fine structure), low energy electron microscopy (LEEM) and X-ray photoemission electron microscopy (XPEEM). Surface reactions on model systems can be studied in real time, focusing on finding structure/reactivity relationships that could lead to improvements on catalysts performance. A recent instrumental upgrade has made possible performing quasi *in situ* electrochemical experiments with the sample transfer taking place under a controlled environment. In this way, spatially-resolved information on chemical and structural changes taking place during electrochemical reactions such as CO_2RR can be obtained. This includes the recent identification of distinct chemical species (Cu^0 and Cu(I)) present on different regions of the same Cu(100) surface after pulsed CO_2RR electrolysis.

Nanostructures

Based on previous insight into the importance of Cu(100) surfaces for enhanced C_2H_4 selectivity, we developed and patented (DE-10 2017 011 341.6) the electrochemical synthesis of Cu nanocubes (NCs) on different supports through Cl stabilization, Fig. 5. Cu NCs grown on a Cu foil showed superior selectivity towards C_2-C_3 products when compared to the underlying Cu substrate. In order to understand the role of the support, the same NCs were also grown on carbon. Dynamic changes in the morphology and composition of the Cu NCs supported on carbon were monitored under potential control during CO_2RR via EC-AFM and XAS, and after reaction via *quasi in situ* XPS. Under reaction conditions, roughening of the NC surface, partial disappearance of the well-defined (100) facets, formation of pores, loss of Cu and reduction of CuO_x species were observed for the Cu NC/C system.[3] They led to a suppression of the selectivity for C_2H_4 versus CH_4, Fig. 5(a). The analogously synthesized Cu NCs/Cu foil revealed an enhanced morphological stability and persistence of Cu(I) species under CO_2RR in comparison.

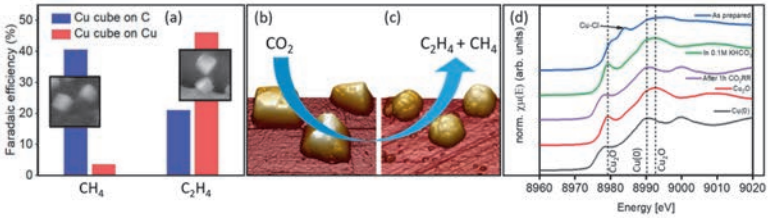


Figure 5: Electrochemically-grown Cu NCs under CO_2RR. Panel (a) shows the differences in C_1/C_2 Faradaic efficiency at -1.1 V in 0.1M $KHCO_3$ depending on the substrate. Panel (b) and (c) show EC-AFM data from the morphological transformation of Cu NCs/HOPG during 3h of CO_2RR under the same conditions as in (a). Panel (d) shows the *operando* XANES of the Cu NCs and respective references.[3]

Both factors contributed to the higher C_2/C_1 product ratio observed for Cu NCs/Cu versus Cu NCs/C. Our findings highlight the importance of the active nanocatalyst structure and its interaction with the underlying substrate for CO_2RR selectivity.

As discussed above, the direct visualization of electrochemical processes is highly challenging. Ideally, one would like to monitor *in situ* first the electrochemical growth of the catalysts, and subsequently their evolution under electrochemical reaction conditions. These aspects are being studied within the ISC Department via electrochemical TEM by the **Chee group**. Here, we targeted Cu NCs as the first model system to explore the capabilities of the EC-TEM for tracking the electrochemical formation of the NCs within the *in situ* cell, Fig. 6. The first experiments were conducted at the FHI in collaboration with the Electron Microscopy Group (Lunkenbein) from the Department of Inorganic Chemistry. A Cu salt solution was flowed into the microfluidic cell and the potential at the working electrode was cycled. The formation of Cu NCs was achieved after optimizing the cycling parameters (scan rate, potential range etc.). As can be seen, no Cu is deposited on the working electrode at open circuit potential (OCP), while ramping the potential to negative values leads to nucleation and growth of Cu NPs. At these potentials, the size and shape distribution of the electrochemically-deposited Cu NPs was not homogeneous. However, after ramping the potential to positive values, the non-cubic nanostructures dissolved and only the cubic Cu NPs remained on the working electrode. This reveals the higher stability of the cubic Cu structure against electrochemical dissolution. In future experiments, we will employ this technique to study dynamic microstructural changes that take place during CO_2RR on these Cu NCs.

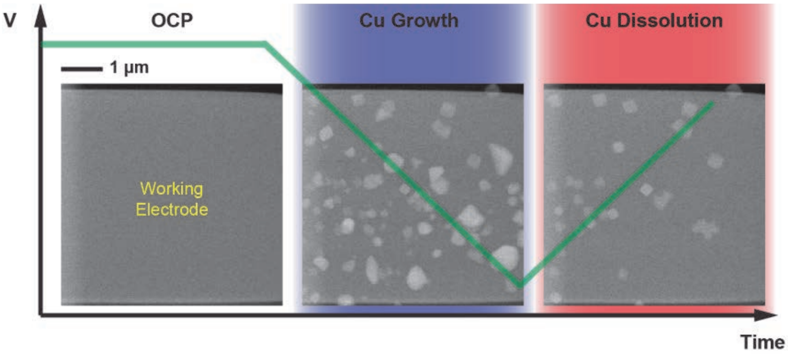


Figure 6: EC-TEM images displaying the morphological evolution of electrodeposited Cu NPs as the working electrode (Pt) potential is cycled towards reducing and then towards oxidizing potentials. A solution of 5 mM $CuSO_4$ was used. The (100) facets are stabilized by the addition of 5 mM KCl.

Continuing with the CO_2RR work, we have expanded our materials library by investigating Cu-free and binary CuM NPs. Zinc is one of the most promising materials for selective CO production because it is a cost-effective alternative to noble metals such as Au and Ag. Here, we have explored the size-dependent activity and selectivity of Zn NPs synthesized by inverse micelle encapsulation.[4] As shown in Fig. 7, Zn NPs ranging in size from 3 to 5 nm showed high activity and >70% CO selectivity, while those above 5 nm exhibited bulk catalytic properties. In addition, a drastic increase in H_2 production was observed for Zn NPs below 3 nm, which is associated with the enhanced content of low-coordinated sites on these small NPs. Moreover, the stability of oxides/hydroxides in these catalysts was observed during CO_2RR via *operando* XAS, Fig. 7(c).

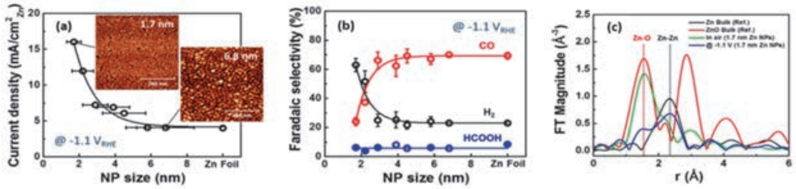


Figure 7: Activity and selectivity measurements of CO_2RR over Zn NPs. Current densities (a) and Faradaic selectivities (b) at -1.1 V vs. RHE in 0.1 M $KHCO_3$ as a function of Zn NP size. (c) k^2-weighted EXAFS spectra of 1.7 nm Zn NPs in air and under *operando* CO_2RR.[4]

The influence of the composition of size-selected NP for the CO_2RR was studied for CuZn NPs prepared by inverse micelle encapsulation. The fraction of the secondary metal was varied at a constant NP size (~5 nm). In the case of $Cu_{100-x}Zn_x$ NPs, a drastic increase of CH_4 selectivity (~70% F.E.) for x ≈ 10 - 50 was observed after 1h of reaction, while H_2 production was suppressed, Fig. 8(b). For higher Zn contents, mainly CO was produced. *Operando* time-dependent XAS measurements revealed that when CH_4 was produced, reduced Cu was present within the pre-oxidized NPs and Cu segregated from Zn. With increasing reaction time, cationic Zn species also become reduced, which leads to stronger Cu-Zn interaction, brass formation and a change in the selectivity to exclusively CO and H_2 production, Fig. 8(c,d).

In addition to the strong structure-sensitivity of the CO_2RR described above, we have also explored the influence of the electrolyte composition on the activity and selectivity for C_{2+} hydrocarbon and alcohol products over rough, plasma pre-oxidized Cu catalysts. By varying the cations, including halides in our aqueous electrolytes, and working on highly defective Cu surfaces, we were able to achieve up to ~69 % faradaic efficiency (F.E.) for C_{2+} products for 0.1M $CsHCO_3$ + 0.1M CsI. Increasing the size of the alkali metal cations in the electrolyte improved significantly the C_{2+} product yield. Interestingly, we found a stronger interaction of the cations with the pre-oxidized Cu surface as compared to metallic Cu and a significant surface reconstruction. A theoretical collaboration with the Janik group (Penn State Univ.) revealed that if sub-surface oxygen is present, the adsorption of cations is favored, which leads to the stabilization of key reaction intermediates for C-C coupling pathways involved in the generation of C_{2+} products.

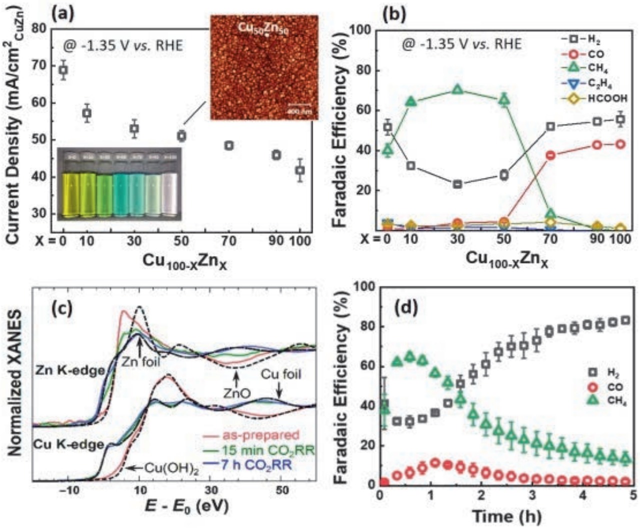


Figure 8: CO_2RR activity and selectivity over 5 nm $Cu_{100-x}Zn_x$ NPs. Current densities (a) and Faradaic efficiencies (b) acquired at −1.35 V vs. RHE in 0.1 M $KHCO_3$ as a function of the composition. (c) *Operando* Zn and Cu K-edge XANES spectra for $Cu_{50}Zn_{50}$ NPs showing complete reduction of Cu and incomplete reduction of Zn after 15 min CO_2RR. The corresponding time-dependent selectivity is shown in (d).

Electrochemical Oxidation Reactions

We are also investigating reactions relevant for electrochemical energy conversion such as ethanol oxidation reaction (EOR) and oxygen evolution reaction (OER) for fuel cells and electrolyzers, respectively.

Direct ethanol fuel cells (DEFC) are attractive alternatives to technologies based on fossil fuels. Ethanol is a non-toxic, renewable and eco-friendly fuel and its complete oxidation to CO_2 and H_2O leads to high energy densities. For EOR, affordable and more efficient catalysts are essential. While Pt has been proven to be the most suitable metal catalyst for this reaction, its high cost and scarcity limits its use in DEFC. Catalysts with lower Pt loading and where only the most active facets are exposed are needed, Fig. 9(a).[5] We have synthesized ~9 nm Pt-Sn-Co nanocubes with predominantly (100) facets for EOR. The as-prepared NCs exhibit a core-shell structure with Sn mostly in the shell and Co in the core, Fig. 9(b). After EOR, the NCs remained well-dispersed and cubic, but Sn is partially leached from the shell, leading to a thin-Pt skin, Fig. 9(c). The leaching of Sn from the NC shell was confirmed by *quasi in situ* XPS, Fig. 9(d,e). The EOR activity of the Pt-Sn-Co NCs was higher than that of Pt-Sn NCs and Pt NCs, and DEMS measurements revealed an increased formation of CO_2 and acetaldehyde by adding Co, Fig. 9(f). These results demonstrate how activity and selectivity may be tuned by rational catalysts design.

The OER is an important reaction since it constitutes the anodic counter reaction for the HER and CO_2RR. The goal of our OER projects is to understand size effects and the role of trace metal ions in oxide electrocatalysis for Co-, Fe-, and Ni-based NPs. By using *operando* XAS, the chemical state and local atomic structure of the catalysts are being determined at different stages of the OER and compared to the pre-catalysts in order to gain insight into the formation of the active state (site).

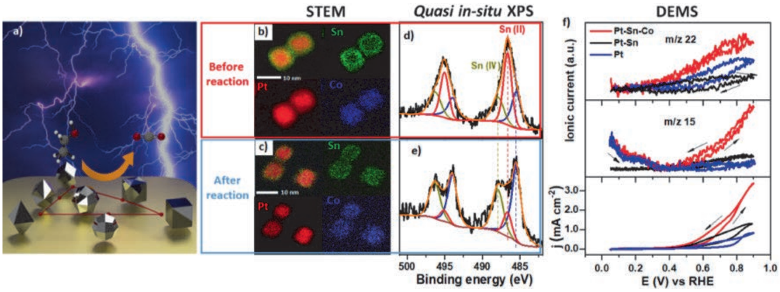


Figure 9: (a) Stereographic triangle illustrating polyhedral nanocrystals bounded by different planes.[5] EDX composition maps of 9 nm PtSnCo NCs as-prepared (b) and after 1h EOR at 0.5 V in 0.5 M H_2SO_4 + 1M EtOH (c). Quasi *in situ* Sn 3d XPS data of the Pt-Sn-Co NCs before (d) and after reaction (e). (f) DEMS data from EOR over Pt, Pt–Sn and Pt-Sn-Co NCs in the same electrolyte. CVs (bottom) and mass spectrometry data for m/z = 22 (CO_2) and m/z = 15 from CH_4 (E<0.35 V) and acetaldehyde (E>0.35 V).

Thermal Catalysis

The performance of metallic NP catalysts for heterogeneously catalyzed reactions depends sensitively on the particle size, shape, chemical state, and underlying support. These parameters can change significantly as a function of temperature, pressure, and reactant flow during the catalytic reaction. Our Department has specialized in the use of a variety of *in situ*/*operando* microscopy, spectroscopy and diffraction techniques for the investigation of nanoscale thermal catalysts under dynamic environmental conditions. These methods include near ambient pressure NAP-AFM/STM, E-TEM, temperature-programed desorption (TPD), FTIR, NAP-XPS, XAS and XRD. At present, we are targeting the hydrogenation of CO_2 to methanol and hydrocarbons (**Shaikhutdinov group**).

These activities are supported by studies of ordered thin films and single crystal surfaces with different orientations. These samples are characterized down to the atomic scale and provide information on the effect of surface structure on catalytic properties, which is useful for an improved understanding of NP reactivity and the effect of substrate orientation. Defined introduction of defects and stoichiometry deviations permits to study their impact on the catalytic performance. At present, $CoFe_2O_4$ surfaces are being investigated with respect to methane conversion and alkane, alkene and alcohol oxidation reactions (**Kuhlenbeck group**).

Heterogeneous catalysis systems based on bimetallic NPs often exhibit superior catalytic properties compared to their monometallic counterparts due to synergetic geometric and electronic effects between the constituent metals. Knowledge of the elemental composition of the surface, which changes during the reaction as a result of alloying and segregation phenomena, is necessary to disentangle the contributions of the factors that are responsible for the improved catalytic performance. Some examples of ongoing research activities in this field follow.

CO_2 Hydrogenation to Methanol

CO_2 hydrogenation to methanol is a promising process to convert CO_2 into a more valuable chemical. It is an industrially mature reaction and uses a $Cu/ZnO/Al_2O_3$ catalyst with a $CO/CO_2/H_2$ gas mixture at high pressures and moderate temperatures. However, even though this process has been known for a long time, it is not yet fully understood. Several factors like the synergetic effect of Cu and Zn, the role of other promoters or the nature of the active site are still under discussion.

Several studies have shown that doping of Cu catalysts with Ni drastically increases the rate of methanol production from CO_2 and H_2, but only when CO is also present in the reactant mixture. It was suggested that CO in the reactant mixture induces surface segregation of Ni, to which CO can then bind, but direct experimental evidence was missing. NAP-XPS is ideally suited for these studies, since it allows element-specific and chemical-state-sensitive probing of the surface properties under reaction-relevant environmental conditions.

In order to gain insight into the reaction mechanism, size-selected (5 nm) micellar $Cu_{0.5}Ni_{0.5}$ NPs were deposited on either SiO_2/Si(111) or SiO_2 powder and studied by NAP-XPS, AFM, STEM, and gas chromatography (GC, fixed-bed flow reactor). The morphology of the model NPs remained unchanged after the NAP-XPS measurements, and lack of agglomeration was also observed on the powder samples after the reaction at 20 bar. NAP-XPS spectra acquired at two different photon energies, Fig. 10, revealed moderate Ni surface segregation in O_2, stronger Ni surface segregation in H_2 or in the $CO+H_2$ reaction mixture, and even stronger Ni segregation in CO. A remarkable inversion of this trend is observed in CO_2+CO+H_2, which drives Cu to the surface.[6]

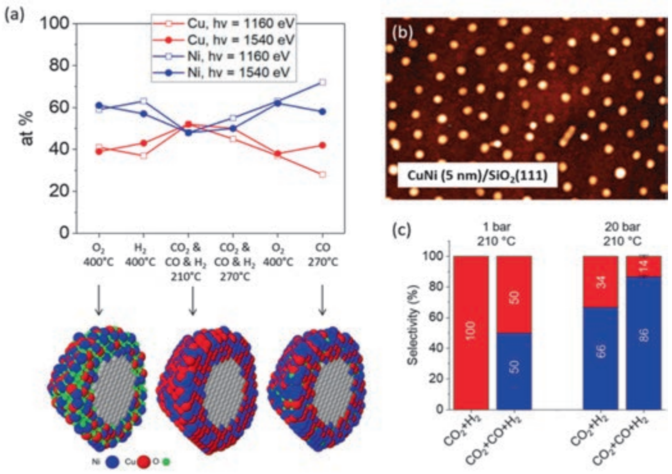


Figure 10: (a) Cu (red) and Ni (blue) atomic percentages extracted from NAP-XPS measurements in the presence of various gases at the temperatures indicated. The inset shows atomic models of the variation of the elemental surface composition. (b) AFM image of CuNi NPs on SiO_2/Si(111). (c) Selectivity towards methanol (blue) and methane (red) during CO_2 hydrogenation over the $CuNi/SiO_2$ catalyst in a fixed-bed flow reactor. [6]

This experimental finding can only be explained by taking into consideration the influence of the products and reaction intermediates. DFT calculations from our

collaborator (Beien Zhu, Shanghai Institute of Applied Physics) showed that in the three gas mixture methoxy species (CH_3O) are the most stable and that they are responsible for the change of the Ni surface segregation energy. When CO is not present among the reactants, the most stable species is HCOO, which barely affects the segregation trend. The promoting role of CO in the reactant mixture was confirmed with catalytic characterization measurements of CuNi NP/SiO_2 powder. Even at atmospheric pressure, 50% methanol selectivity is achieved at 210°C in CO_2+CO+H_2, whereas only CH_4 is produced in CO_2 + H_2. We also started to explore the role of the NP support and Cu-Zn interaction in this reaction using size-controlled (<8 nm) micellar Cu NPs impregnated on nanocrystalline ZnOAl and Cu-Zn NPs on SiO_2 and Al_2O_3, Fig. 11. Synchrotron XAS was used to follow the structural and chemical transformation of the NPs under *operando* reaction conditions, i.e., at pressures up to 40 bar.
Regardless of the support, Cu was always fully reduced under CO_2 hydrogenation reaction conditions in CO_2+CO+H_2, while Zn remained mostly oxidized. For the CuZn NP/SiO_2 system, a feature was seen in the extended X-ray absorption fine-structure (EXAFS) spectra (black arrow) linked to a Zn-metal bond, Fig. 11. Because Cu and Zn are neighbors in the Periodic Table, one cannot distinguish between Zn-Zn and Zn-Cu bonds (brass formation). The reactivity experiments showed clear differences between similarly sized (3 nm) NP catalysts on different supports. In particular, more methanol was produced with the CuZn NPs/Al_2O_3 compared to those on SiO_2, although the selectivity was worse.

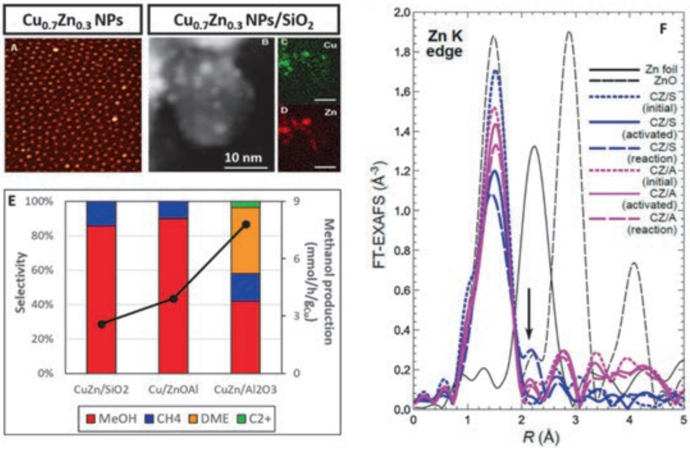


Figure 11: (A) AFM image of CuZn NPS on SiO_2/Si(111). (B) TEM image of the NPs on SiO_2 powder with the EDX maps for Cu (C) and Zn (D). (E) Selectivity and methanol production of different catalysts at 20 bar and 280°C. (F) *Operando* Zn K-edge spectra of 3nm CuZn NPs on SiO_2 (CZ/S) and Al_2O_3 (CZ/A) for various conditions: as prepared (initial), after reduction in H_2 at 245°C (activated), and during reaction in CO_2+CO+H_2 at 40 bar and 320°C. Spectra from bulk ZnO and Zn references are also shown.

Another aspect that we are investigating is the role of NP shape, i.e., how specific crystal facets affect the activity and selectivity of Cu NPs/ZnO. In the first stage of this project, we created, using colloidal chemistry and solvothermal synthesis routes, shape-controlled cubic Cu catalysts impregnated on nanocrystalline

ZnO, Fig. 12(a,b), as well as Cu cubes with a thin ZnO shell deposited on ZrO_2, Fig. 12(e).

We are now exploring the morphological stability of the cubes under high pressure CO_2+H_2 in order to establish links with their catalytic performance. A rounding during the pre-reduction activation treatment was observed (TEM), but a preferential (100) orientation remained. Furthermore, selectivity data revealed that the Cu/ZnO catalysts derived from cubes have a higher methanol/CO product ratio compared to non-size-/shape-controlled catalysts under similar conditions, i.e., the competing reverse-water-gas-shift reaction is suppressed in favor of CO_2 hydrogenation.

Interestingly, when Cu NCs on ZnO were compared with Cu NCs coated by a thin (<5 nm) ZnO shell and deposited on ZrO_2, even better selectivity was obtained for the latter, highlighting the importance of the intimate contact between the Cu and Zn component of these catalysts.

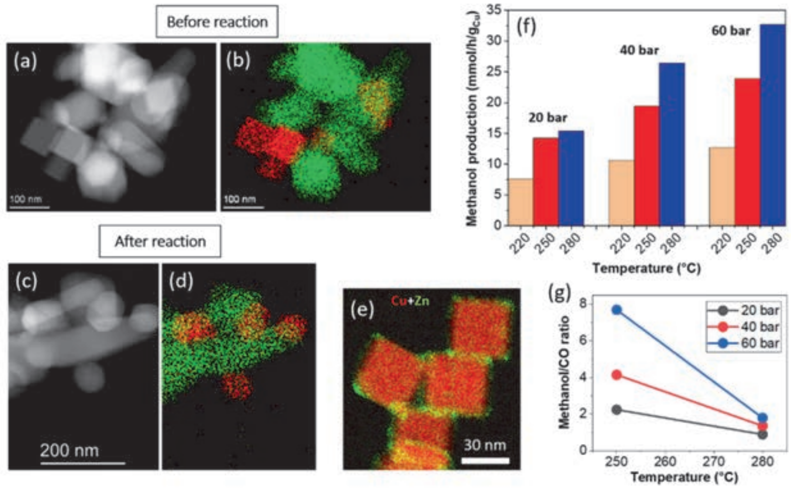


Figure 12: Microscopy (a)-(e) and reactivity data (f),(g) of Cu NCs. STEM data of Cu NCs on ZnO before (a,b) and after (c,d) reaction with EDX maps. (e) EDX map of Cu cubes with a thin Zn shell. Methanol production (f) and methanol to CO ratio (g) for the Cu NCs/ZnO under reaction conditions.

Advanced Spectroscopy and Data Analysis Methods Applied to Catalysis

As illustrated earlier in the electrochemistry and thermal catalysis sections, XAS is a premier method for revealing structural transformations in catalysts. Unfortunately, deciphering XAS data for such disordered, heterogeneous materials under *in situ* and *operando* conditions is not straightforward. Within our Department, the **Timoshenko group** is addressing this problem by using machine learning approaches, such as artificial neural networks (NNs).

First, NNs are trained to recognize the relationship between spectral features and structural motifs using large sets of *ab initio* calculated XAS spectra for NP models with different sizes and shapes. The trained NN can then be applied to the interpretation of experimental data. Using this approach, temperature-dependent EXAFS data for size-selected Pt NPs on different supports and in different environments were interpreted, providing for the first time insight into the non-Gaussian shapes of bond-length distributions in small (< 3nm) supported Pt NPs, Fig. 13. This new data analysis allowed us to solve a long-standing controversy regarding anomalies in their thermal properties such as reduced thermal expansion and enhanced Debye temperature. In particular, we concluded that the negative thermal expansion previously reported for supported NPs is not intrinsic to the metal NPs, but is a result of either a temperature-dependent change in adsorbate coverage during the experiments, or a strong metal NP/oxide support interaction.

Ongoing work deals with the generalization of the NN-based approach for non-metallic multi-element NPs for studies of catalysts changing oxidation state under reaction conditions. Another important advantage of the NN method is that it is suitable for high-throughput (on-line) analysis of changes in the catalyst structure. Therefore, we are working to couple the NN-XAS analysis method with advanced time-resolved QEXAFS measurements for the detection of fast changes in the catalyst structure under dynamically changing reaction conditions. These approaches are currently being used to study pre-oxidized bimetallic systems acting within our group as CO_2 electroreduction and hydrogenation catalysts.

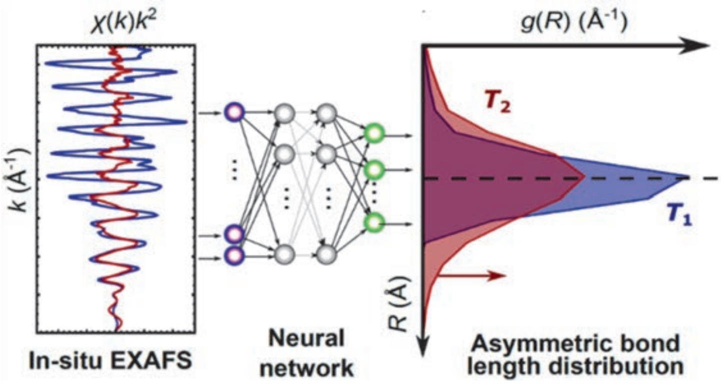


Figure 13: Neural-network based analysis of temperature-dependent EXAFS data for size-selected Pt NPs allows one to probe the non-Gaussian shape of Pt-Pt bond length distributions, and to follow temperature-induced changes in its asymmetry.

We are also exploring the possibility of generating 3D structural models from *in situ* X-ray absorption data for morphologically well-defined supported NPs. Such information is very valuable for very small non-flat NPs (<3 nm), where tip-convolution effects will obscure the determination of their shape via scanning probe microscopy, or when they have to be measured under catalytic reaction conditions in harsh environments (e.g., high pressures or high temperatures) not accessible to common microscopy methods.

To single out and understand the effect of particle-support interactions in detail, studies of size- and shape-selected NPs deposited on single crystals measured in the absence of adsorbates (vacuum) must be conducted. However, such XAS studies are challenging due to low metal loading in the sub-monolayer NP coverages. On the other hand, one can benefit from the fact that the bonds with different orientation with respect to the X-ray polarization contribute differently to the measured XAS spectrum, providing the possibility to probe directly the anisotropy in the NP structure as well as NP dynamics. Interpretation of the obtained experimental data in terms of a 3D structure model, nevertheless, is non-trivial. We addressed this problem by using reverse Monte Carlo (RMC) simulations to interpret, for the first time, polarization-dependent XAS data. Here, a 3D structure model of a Pt NP was constructed and refined in an iterative stochastic process, until it agreed with all experimental EXAFS data available, Fig. 14. Our initial model of the small Pt NPs was constructed based on experimental AFM and STM data, conventional EXAFS data fitting and a NN-based interpretation of XANES data. Only through combination of our colloidal NP synthesis methods (which ensured narrow NPs shape- and size-distributions), characterization by microscopy and spectroscopy methods and the RMC-based modeling we could construct unambiguous structural models of Pt NPs on different supports, obtaining important clues about the differences in particle-support interactions for Pt NPs deposited on TiO_2(110) and SiO_2/Si(111) from the polarization-dependent UHV-measured XAFS data.[7]

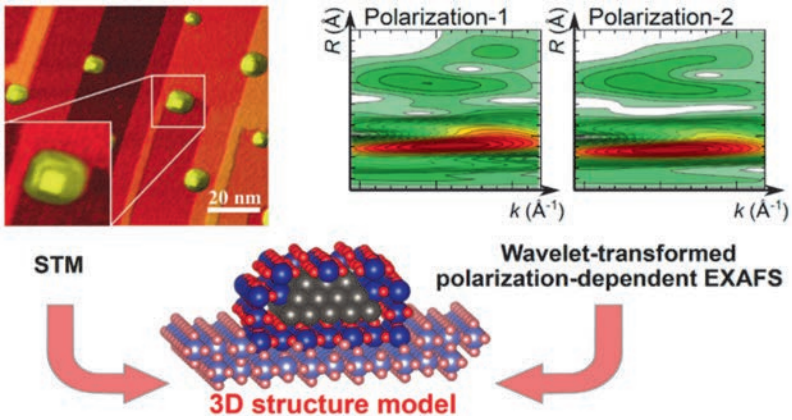


Figure 14: Morphological insight from STM measurements of Pt NPs on TiO2(110) is combined with information from polarization-dependent EXAFS data through RMC simulations to construct a 3D structure model of a supported Pt NP as well as to gain insight into the NP/support interaction.[7]

Summary and Outlook

In conclusion, the newly created ISC Department at the FHI has experienced in the last two years an extraordinary growth, reaching now a size of about 50 co-workers. We have moved all relevant instrumentation from my former institution in Bochum and have started to develop the required research infrastructure at the FHI. Despite significant delays in the construction and renovation projects, and thanks to the help from other Departments at the FHI, we have been able to re-start our research activities in Berlin, as illustrated by the recent and mostly yet unpublished examples featured here. Since April 2019, we have also welcome the four group leaders from the former CP Department and have worked towards their integration in the new research activities. As demonstrated in their own contributions to the ISC Fachbeirat report, and despite the short time available, this important aspect is on the right track. I have also added to my team three new group leaders. Since the last Fachbeirat, two PhD students have graduated and one of my postdocs (Dr. Dunfeng Gao) has obtained a faculty position at the Dalian Institute of Catalysis. In terms of the scientific direction of my department, in the years to come I plan to build up on our strengths related to the synergistic use of surface science tools and synchrotron-based radiation for the understanding of thermal and electrocatalytic processes at the atomic level. *In situ* and *operando* microscopy and spectroscopy methods will be employed to shed light into the dynamic nature of nanostructured surfaces and nanoparticle catalysts while operating under industrially-relevant non-static conditions (i.e., variable electrochemical potentials, reactant flux, temperature, pressure, etc). For this purpose, we will make extensive use of the MPG facilities currently available at the BESSY synchrotron in Berlin (e.g., EMIL, BELChem) for soft X-ray materials characterization. In addition, I have recently presented a proposal to the MPG (co-PI DeBeer, Chemical Energy Conversion Institute) for the construction of a new hard X-ray beamline at the DESY synchrotron in Hamburg that would be dedicated to *operando* catalysis studies via X-ray absorption spectroscopy and X-ray diffraction. We plan to continue exploring different thermal and electrocatalytic routes for the efficient and selective conversion of carbon dioxide to valuable chemicals and fuels, the ultimate goal being a rational design of the catalyst, reaction environment and conditions.

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Dr. Markus Heyde

Research Group Leader, Department of Interface Science (since April 2019)
Research Group Leader, Department of Chemical Physics (2007–2019)
Habilitation Humboldt-University in Berlin (2015)
Postdoctoral Scholar, Lawrence Berkeley National Laboratory (2001–2003)
Fritz-Haber-Institute (2003–2007)
Dr. rer. nat. Humboldt-University in Berlin (2001)

Scanning Probe Microscopy

Introduction

The research group "scanning probe microscopy" has been established with a focus on high-resolution local structure measurements on model systems for heterogeneous catalysis. Well defined crystalline and amorphous thin oxide film systems have been developed and characterized by atomic resolution scanning probe microscopy and spectroscopy to gain insight into local structural environments for chemical reactions taking place at these surfaces. The previous activities are reported in a separate section of the department of chemical physics.

New concepts and ideas towards applied projects within the department of interface science are currently tested in my group. In the field of electrocatalysis the degradation and erosion of noble metal electrodes is an unsolved problem. A detailed understanding is only slowly emerging compared to the current global energy transition needs. Modification of metal single crystal electrodes with a two-dimensional barrier layer is proposed as a model system to address alterations at electrode surfaces under electrochemical reactions that might lead to changes in their activity and selectivity. Chemical and structural effects created by two-dimensional overlayers have been reported by Yasuda et al. [1]. Therein, graphene on Au(111) electrodes has been studied under potential cycling with electrochemical scanning tunneling microscopy (STM).

Thin Film Systems for Tuning Electrode Materials

Here we plan to benefit from our expertise in synthesizing two-dimensional thin silica films on metal single crystals. They could be used as an alternative barrier layer for modification of various metallic electrode materials. Thin silica films have already been grown on several different metal substrates [2]. Depending on the underlying metal support, different oxygen affinity and lattice constants are provided, and thus allow for tuning the growth behavior of the thin films from monolayer to bilayer structures as well as from crystalline to amorphous network structures.

Atomic and Molecular Selectivity by Defined Network Structures

It has also been shown that these films can act as an atomic sieve together with specific site-selectivity [3]. The network structure of silica thin films allows small species to penetrate through the layer system. The impact of different network ring sizes on the adsorption of single metal atoms in silica films has been investigated in previous studies [4]. These first experimental verifications have been followed by detailed density functional theory studies and provide promising insights for further potential applications.

Furthermore, chemical reactants can be trapped inside of the film or between the substrate and the film [5]. Chemical reactions have also been shown to proceed under silica films in a confined space [6]. Another interesting point is the physical and chemical stability of silica films under ambient conditions as well as in polar liquids or diluted electrolytes [7].

Two-dimensional Materials in Electrochemistry

This study aims to complement recent efforts to elucidate the electrochemistry of two-dimensional materials, where wide band gap materials have so far not been addressed in great detail [8]. Two-dimensional silica is somewhat complementary to the prominent graphene. The bilayer silica film is a wide band gap material (E_g = 6.5 eV). Its insulating properties and larger pore size compared to graphene suggest different alteration of the surface electrochemistry by electron transfer, mass transfer and confinement effects.

We expect that the ultrathin SiO_2 films could become prominent test systems in the field of electrochemistry for water splitting and CO_2 electroreduction (CO_2RR) applications [9-10]. Platinum and copper single crystals are reasonable samples as electrode materials. While the silica bilayer film has been successfully prepared on Pt(111) surfaces, the group is currently testing possible preparations for silica films on clean Cu(111) as well as on pre-oxidized Cu samples. Cu is the only metal known to electrocatalyze the reduction of CO_2 to hydrocarbons and alcohols. Nevertheless, there are still stability problems unsolved for this system related to the loss of specific morphological motives as well as the reduction of Cu_2O species under reaction conditions.

Comparison to Encapsulated Core-Shell Particles

Recently, the deposition of ultrathin microporous silica membranes on Pt nanoparticles has been shown to alter undesired recombination reactions in water splitting [10]. The membranes can selectively restrict passage of molecular oxygen and larger hydrated ions, while allowing penetration of protons, water, and molecular hydrogen. Such experiments could be transferred to atomically defined and controlled thin film preparations on metal single crystals. Comparative studies between bare single crystal electrodes and those coated by two-dimensional ultrathin oxide barriers are expected to yield differences in reaction parameters such as activity or selectivity by a modification of surface processes. These parameters usually are correlated to surface chemistry and morphology effects, which might be drastically altered by two-dimensional barrier layers. Additionally, a defined surface modification can be further supplemented with analog experiments on vicinal surfaces, alloyed, argon-sputtered and plasma-oxidized surfaces.

Electrochemistry on Thin Silica Electrode Overlayers

Cyclic voltammograms and *ex situ* surface science methods will be combined to evaluate the potential structure sensitivity of the reaction. Changes in the surface structure before and after electrochemical treatment can be tested by low energy electron diffraction and scanning tunneling microscopy measurements. Care needs to be taken to distinguish between differences in the pristine surfaces (bare, treated, or two-dimensional barrier covered) and possible structure and morphology changes under reaction conditions. Morphology, structure, accessibility and dynamics all affect the behavior of electrodes in electrochemical reactions like water splitting and CO_2 electroreduction. For instance, it is known that smooth, low Miller index single crystal electrodes may show decreased reactivity compared to stepped surfaces and small particles with diverse surface structure.

The recent study of silica-covered Pt core-shell particles [9] demonstrated that overlayer effects on electrode surfaces might serve to tune the catalyst performance for reactions such as water splitting. Clearly, it is known that ultrathin surface layers develop under changing reaction conditions locally or globally. Such overlayers may profoundly alter the surface morphology by modification of adsorption, blocking of terrace dynamics, or even microfacetting of the surface like in the oxidation of CO on platinum.

Current Progress

In first attempts we have grown defined copper oxide layers referenced as the well-known “44” and “29” structure on Cu(111) and compared the results to previously reported measurements from the literature. The STM images have been complemented by scanning tunneling spectroscopy and field emission resonances, low energy electron diffraction and Auger electron spectroscopy. The clean crystal and the copper oxide structures on Cu(111) have been used as a platform for the growth of thin silica films. The relative high affinity of copper to oxygen together with the first characterizations revealed the successful preparation of a monolayer SiO_2 film structure. The silica films on the Cu(111) are mostly closed, flat, and exhibit six-membered network elements.

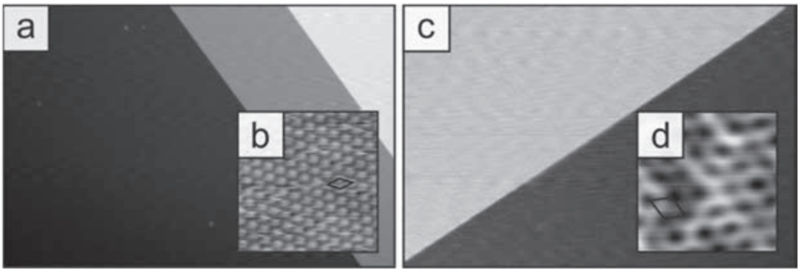

Figure 1: STM images of a clean Cu(111) surface (a): 150 nm × 100 nm, (b): 3 nm × 3 nm, compared to silica film grown on Cu(111) (c): 150 nm × 100 nm, (d): 3 nm × 3 nm).

The detailed surface science analysis is now followed by a stability study of these samples. They are transferred from ultra-high vacuum into ambient conditions towards applied environments and back again. The resulting surface structures have been characterized in ultra-high vacuum for each individual step. From the first results the stabilizing effect of the silica films on Cu(111) seems to be verified. The new experiments proceed towards electrochemical test measurements. These measurements will be performed in close cooperation with Dr. Rosa M. Arán-Ais.

The second most reasonable sample system for electrochemical experiments is Pt(111) with the capability of supporting nicely formed bilayer film structures. The preparation conditions are currently being revisited and tuned. Pt is not used as CO_2RR electrocatalyst, since only hydrogen is produced. However, it is the reference material for other important electrochemical reactions such as hydrogen evolution (HER) and oxidation (HOR) as well as various alcohol oxidation reactions. In the former examples, an overlayer-induced modification of the electronic structure of the Pt surface is expected to help tune its electrocatalytic performance.

Concluding

It is planned to compare single crystal electrode surfaces to structurally modified ones (plasma treated to controllably create defects and induce surface oxidation, sputtered, vicinal surfaces, or nanoparticles) as well as to corresponding surfaces overgrown by two-dimensional barrier layers in a comprehensive and fundamental study. While structural and chemical properties of the electrode are tuned by the various pretreatments, the surface stability is addressed by two-dimensional barrier layers which, in addition, are known to allow intercalation of adsorbates into the space between the two-dimensional barrier and the substrate.

Current Group Members

Jens Hartmann, Sebastian Kunze, Dr. Juan Jesus Navarro, Gero Thielsch

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Dr. Christopher Seiji Kley

Helmholtz Young Investigator Group Leader (since Feb. 2019)
Postdoctoral Researcher, UC Berkeley (2014–2018)
Postdoctoral Researcher, MPI Solid State Research (2014)
Dr. sc., EPF Lausanne, MPI Solid State Research (2013)
Dipl. Phys., Karlsruhe Institute of Technology (2009)
Diploma thesis, MPI Chemical Energy Conversion (2008–2009)

Photo-electrochemical atomic force microscopy

Introduction

The Helmholtz young investigator research group *Nanoscale Operando CO_2 Photo-Electrocatalysis* has been established in February 2019 jointly at the Helmholtz Center Berlin for Materials and Energy and the Interface Science Department at the Fritz Haber Institute of the Max Planck Society. We focus on nanoscale understanding of solid / liquid interfaces for applications in catalysis and energy conversion combined with material synthesis.

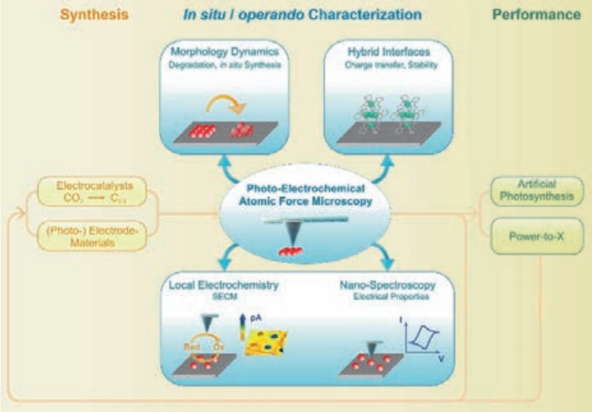

Figure 1: Research overview. (1) Synthesis of electro- and photoelectrocatalytic materials for CO2 conversion. (2) High-resolution *in situ* AFM methods for characterizing the morphology dynamics of heterogeneous catalysts and hybrid interfaces under reaction conditions, as well as the local electronic and electrochemical properties. (3) Material performance tests.

To date, progress toward rational design of catalysts and photo-materials is hampered by deficient knowledge of nanoscale dynamic materials properties and structure-property relationships under reaction conditions. Multi-electron and proton-coupled catalytic reactions including CO_2 conversion are particularly challenged by material transformations and degradation under operating conditions as well as performance-limiting inefficiencies at catalyst-electrode interfaces. Intrinsic reaction kinetics are further augmented by the log-linear relationship between reaction rate and applied potential. Our group addresses selected challenges in catalysis by employing scanning probe microscopy including atomic force microscopy (AFM) in liquid phase[1,2] to decipher *in situ / operando* the local structural, electronic, and catalytic properties of key materials under external stimuli. These studies are combined with catalytic reactivity and spectro-electrochemical characterization to elucidate structure-property relationships and charge-transport phenomena at solid-liquid interfaces. In a synergistic manner, strategies for synthesizing novel functional materials are also being developed.

Nanoscale studies of catalysts under reaction conditions in the liquid phase

In heterogeneous catalysis, non-uniformly distributed active sites on surfaces are triggered for instance by the surface nanostructure, degree of restructuring, and oxidation state. These remain key challenges to tune catalytic selectivity and activity, which are inherently linked to the ability of resolving the catalyst morphology under reaction conditions. We aim at establishing structure-property relations and advance mechanistic understanding by resolving the morphology of electrode materials strictly under reaction conditions on nanometer length scales.

In a first project, we investigate copper surfaces relevant for CO_2 electroreduction.[3] So far, results were obtained from three types of copper surfaces, including electropolished, single crystal Cu(100) surfaces as well as ultrahigh vacuum (UHV) prepared Cu(100) and Cu(111) surfaces, Figure 2. UHV-prepared surfaces feature steps of single atomic layer height. AFM images in air show granular structures to cover the flat terraces which likely originate from the heterogeneous nucleation already during initial oxidation steps at low coverage and O_2 partial pressure.

Upon contact with the electrolyte, all prepared Cu surfaces underwent substantial morphological changes, with the step morphology being largely or completely lost. Instead, a rough surface emerges under open circuit (OCV) conditions, which is riddled with several nanometer deep pits and shows barely any crystalline structure. Only the hexagonal pit shape measured points to the crystal symmetry. Such morphologies change upon application of negative electrochemical potentials. Upon entering a reducing regime, smooth clean terraces may be obtained[4], which, however, are different in size and shape from the original UHV prepared or electropolished step morphology. Removal of the oxide at negative potential and re-oxidation at more positive potentials proceed at vastly different rates during potentiostatic series or anodic and cathodic sweeps.

Currently we are working towards an identification of surface structures and phases under reducing conditions, studying the origin of the peculiar pits and a normalization of our results with respect to electrochemical parameters such as total conducted charge. Furthermore, we are working on improving the sample transfer into the electrolyte under utmost clean conditions. To this end, a UHV suitcase and glovebox transfer has been developed. Capabilities to use perfusion and CO_2 saturation during imaging are continuously extended. This will be vital for measuring electrodes under highly gas evolving reaction conditions. Tracing surface morphology changes from clean UHV prepared and electrochemically *in situ* reduced metallic crystals through as large as possible potential ranges will allow to gain an understanding of electrode surfaces observed in electrochemical and physical averaging techniques during electrocatalytic reactions. To reach this goal, the above results have to be carefully correlated to electrochemical measurements and eventually connected to detailed chemical analysis of gaseous and liquid reaction products. Work to reach this goal is in progress.

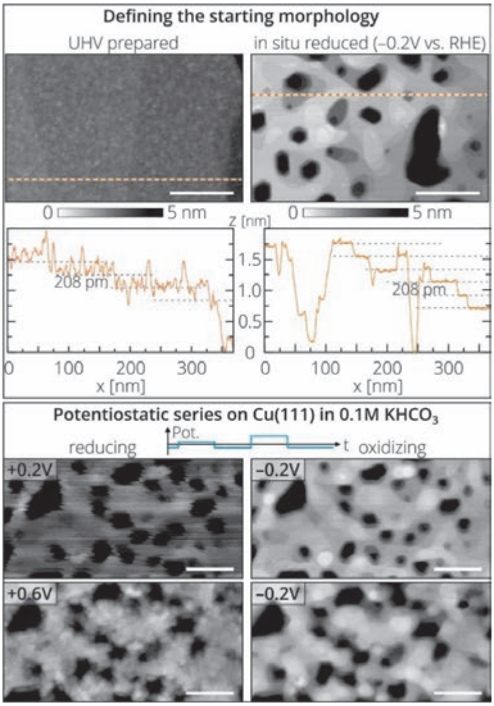

Figure 2: EC-AFM topographies of UHV-prepared Cu(111). Top: imaged in air (left) and in 0.1 M KHCO3 under reducing conditions. Bottom: Imaged at a sequence of fixed electrochemical potential steps. All potentials are given versus the reversible hydrogen electrode (RHE). All scale bars: 100 nm.

In situ nanoscale electrical characterization of photo-electrocatalytic materials

Photoelectrochemical performance of recently developed semiconductor materials for artificial photosynthesis is largely limited by poor charge separation and transport in the bulk of the materials as well as photocorrosion in aqueous solutions. It remains a central challenge to develop semiconductors that not only feature solar-spectrum matched bandgaps, but also are photochemically robust to withstand continuous operation while driving fuel forming reactions. To ultimately develop materials with enhanced durability and efficiency, *in situ / operando* identification and understanding of the morphological, compositional and electronic factors that contribute to material corrosion is urgently required.

However, structural changes at photoactive surfaces often appear only when accumulated stress caused by degradation / corrosion processes reaches a certain level. Real-time changes in corrosion sites cannot necessarily be visualized by AFM or STM. To overcome this challenge, we work on employing potential sensing AFM to monitor in real space the potential distribution in electrolytic solutions and provide insights into local defect and corrosion domain formation. State-of-the-art photocathode and photoanode materials will be synthesized in close collaboration with the Helmholtz Center Berlin for Materials and Energy. We will map electrode morphologies as well as the heterogeneous electrical and photoelectrical response at the nanoscale to decipher prevailing photo-degradation processes under reaction conditions. Key insights will guide the synthesis of structurally robust photo-absorbers with tailored compositions and geometries.

Resolving catalytic activity at the nanoscale

Chemical and biological processes that occur at solid-liquid and liquid-liquid interfaces typically involve charge transport or storage. The nanoscale electrochemical reactivities at underlying surfaces govern a system's macroscale performance, function, and lifetime. While understanding the complex and heterogeneous electrochemical dynamics is crucial for various applications in catalysis, energy storage, corrosion and sensing, few techniques are capable of directly measuring local reaction rates or currents generated at an interface with nanoscale precision.

The group plans to establish scanning electrochemical microscopy using an AFM (AFM-SECM) to enable mapping of chemical surface activity with correlated structural information at nanometer length scales. For reliable low-noise electrochemical measurements that are localized at the region of interest, we will employ AFM probes with only their tip apex being electroactive and the remainder of the probe being insulated to prevent delocalization of the electric field in polar solvents. Overall, we aim at pushing the limits of nanoscale electrochemistry by deconvoluted topography and current maps based on AFM-SECM.

Translating fundamental findings into novel synthetic design strategies

Our group combines previously described nanoscale *in situ* scanning probe microscopy studies with the characterization of the materials' catalytic selectivity and reactivity. Synthetic protocols will be derived to develop electrocatalysts and photo-electrocatalysts featuring enhanced structural robustness, selectivity and activity.

Current Group Members

Dr. Georg Hermann Simon

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Dr. Helmut Kuhlenbeck

Research Group Leader
Department of Interface Science (since April 2019)
Chemical Physics Department (1996–2019)
Academic councilor, Ruhr-Universität Bochum (1994–1996)
Research associate, Ruhr-Universität Bochum (1988–1994)
Research stay at the University of Sherbrooke (1993)
Dr. rer. nat., Universität Osnabrück (1988)

Current and Future Activities of the Thin Films Workgroup

Thin Film Catalyst Models

There is a long-standing experience within my group concerning the preparation and characterization of thin films on an atomic scale, and the investigation of their catalytic properties in diverse environments. Typical questions are related to the effect of surface structure, defects and dopants on catalytic processes, aiming at a microscopic understanding of the reaction mechanisms and possible reaction intermediates. Usually, the morphology of a catalyst changes under reaction conditions, depending on the type of reaction, gas pressure, gas composition, temperature and time, and therefore, the structure of the catalyst before reaction just defines the starting condition of the pre-catalyst. Thus, the systematic study of surface modifications by chemical reactions and their role in the catalytic performance of a given material system is the main focus of our work.

At present, we are part of a German collaborative research program (SFB) focusing on the investigation of oxidative catalytic reactions taking place at gas/solid and liquid/solid interfaces using cobalt ferrite-based catalysts. Our part deals with the synthesis, structural, electronic and chemical characterization of oxidic model catalyst layers [crystalline $CoFe_2O_4$]. Since my group's incorporation into the ISC department in April 2019, we have synthesized first $CoFe_2O_4$(100)/Pt(100) layers with a reasonable crystalline quality and have characterized them with STM, XPS and LEED. Figure 1 shows STM images of one of these films.

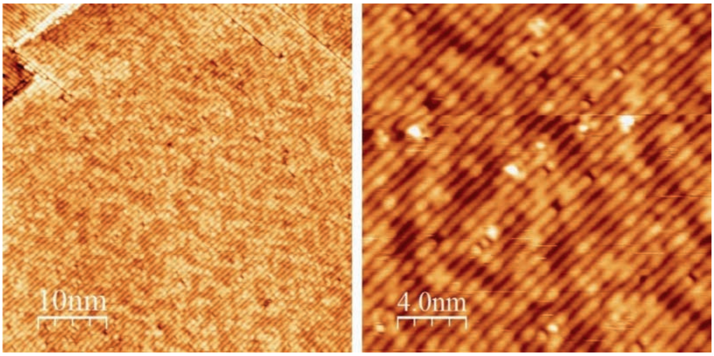

Figure 1: STM images of $CoFe_2O_4$(100)/Pt(100). The STM image areas with different brightness are assumed to result from different iron/cobalt concentration ratios.

In order to test structure-reactivity correlations, we plan to prepare also $CoFe_2O_4$(111) layers on Pt(111). My group plans to test these materials for thermal catalysis processes such as alkane, alkene and alcohol oxidation reactions (e.g. 2-propanol oxidation, cyclohexane, and cyclo-hexene oxidation) applying *in situ/operando* methods. In parallel, the same films will be provided to our electrochemistry group to be used as oxygen evolution reaction (OER) and 2-propanol electro-oxidation catalysts. Surface analysis studies will also be performed after reaction to further reveal irreversible changes of the surface properties induced by the reaction.

Future plans also involve the study of iron sulfide thin film catalysts. We have some experience with the preparation of well-ordered iron sulfide layers (NiAs type structure) on Au(111). For the planned experiments, a different substrate will be used to prepare a sulfide with a higher iron content than what was possible on Au(111), where iron had the tendency to diffuse into the substrate. The layered iron sulfide mackinawite would be an interesting candidate since it has attracted significant interest for its role in environmental remediation chemistry, its catalytic properties [1], and its possible implications in the origin-of-life chemistry.

Surface Action Spectroscopy

Surface Action Spectroscopy (SAS) is a surface vibrational spectroscopy method developed at the FHI in recent years. It is similar to the action spectroscopy method used to measure vibrational spectra of gas phase aggregates with the help of infrared radiation from a free electron laser. [2] In the Surface Action Spectroscopy variant, a sample is covered with a weakly bound adsorbate layer, the messengers, and irradiated with infrared radiation from a free electron laser at the FHI (see Fig. 2). When the IR radiation is in resonance with a surface vibration, then the absorbed energy may induce desorption out of the messenger layer, which can be measured with a mass spectrometer. A plot of the desorption rate versus the photon energy is a vibrational spectrum of the surface. [3,4].

Obtaining a spectrum of a sample's surface vibrational modes with the SAS method is rather straight forward for dielectric samples. Such a spectrum is a fingerprint of the surface structure and therefore, one application of SAS is surface structure determination. This requires the calculation of surface vibrational modes which necessitates cooperation with theory groups.

Figure 2: Working scheme of the surface action spectroscopy experiment.

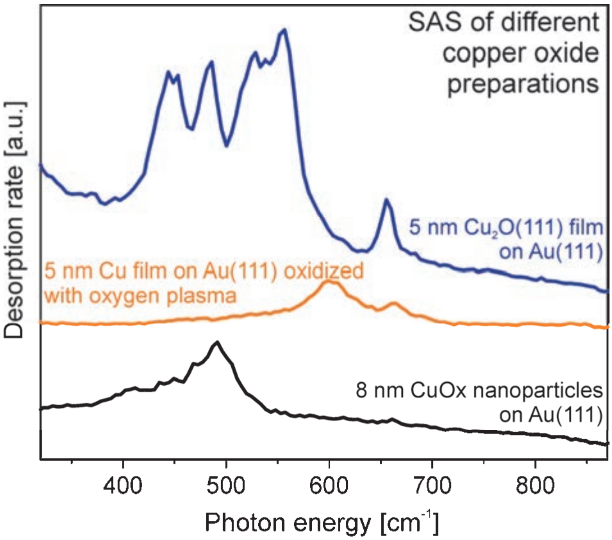

Figure 3: SAS spectra of different copper oxide preparations recorded with HD messenger molecules.

We have successfully applied this approach to $Fe_3O_4(111)$ layers on Pt(111) [see report of the Chemical Physics Department] and intend to apply it also to thin film systems presently under investigation (cobalt ferrites, copper oxide films, sulfides, ect.). Spectra of some copper oxide preparations from the ISC Department are shown in Fig. 3. We note that SAS is better suited than IRAS for such an application since reference spectra, as required for IRAS, are not required for SAS. This method has also advantages with respect to HREELS, where in spectra of dielectric surfaces much is hidden by intense Fuchs-Kliewer polariton losses and combination losses, which is not the case for SAS.

There are some yet untested application areas of this method. Checking the feasibility of these approaches will be one of the group's future activities. The SAS method can also be applied to non-crystalline samples like amorphous layers or inhomogeneous surfaces. In this case the spectra rather consist of wide structures with a certain shape than of well-defined peaks and the obtained information will be less detail-rich. Nevertheless, if dielectric function data are available for model systems, then some information about the bulk properties might be derived from a comparison of calculated absorption data with experimental SAS data. Another, yet untested area of applications of the SAS method is the vibrational spectroscopy of rough samples including powder samples. Rather complex spectra are to be expected also in these cases. Sometimes selective decoration of surface features with messenger gas may help to reduce the spectral complexity, since the spectral information stems only from areas covered with the messenger gas. If the messenger coverage is small, then areas where the interaction with the messenger gas is stronger will have a higher messenger coverage, and that area will contribute accordingly more to the SAS spectrum. Such an approach may also help to extract detailed spectroscopic information from deposited clusters, since it might be possible to strongly damp the substrate signal in this way.

Finally, some work has already been invested into the use of helium as a messenger gas. Rather low sample temperatures of less than 3 K are required, and these temperatures have not yet been reached at the sample in our current configuration (so far ~1.5 K were reached at the sample holder). However, further improvements of the sample setup and the heat shield are possible, which may permit to reach the required temperatures also at the sample. The use of helium as messenger gas will probably lead to a higher sensitivity and extend the usable energy range to lower energies, since only very little energy is required to desorb helium.

At present we use mostly molecular hydrogen messengers, which have a higher sensitivity than neon messengers, although the substrate-messenger binding energies are similar. We attribute this to the larger number of vibrational coupling channels for an energy transfer from the excited surface vibration into the bond between the hydrogen messenger and the surface.

Current Group Members

Dr. Earl Davis, Dr. Yun Liu, Matthias Naschitzki, Walter Wachsmann

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Dr. Thomas Schmidt

Research Group Leader, Dept. of Interface Science (since April 2019)
Research Group Leader, Dept. of Chemical Physics (2009–2019)
Senior Scientist, University of Würzburg (1999–2008)
Postdoctoral Fellow, ELETTRA, Trieste (1996–1999)
Postdoctoral Fellow, University of Würzburg (1996)
Postdoctoral Fellow, Technical University of Clausthal (1994–1996)
Dr. rer. nat., University of Hannover (1994)

Spectromicroscopy as a tool for fundamental questions in catalysis

The group activities focus on the preparation and modification of catalytically active systems, like thin oxide films on metal supports or metal nanoparticles, and on the investigation of their structural, electronic and chemical properties. In particular, we aim at gaining a better understanding of the correlation between structure, chemical composition and shape of these objects and their reactivity and selectivity. Also we are involved in the project "Coupled Chemocatalytic Reactions" of the UniSysCat Cluster of Excellence in Berlin. The investigations are carried out with a spectromicroscope which allows *in situ* observation of dynamic processes like chemical reactions on surfaces.

Spectromicroscopy

The experiments are performed with the high resolution spectro-microscope SMART (Spectro-Microscope with Aberration Correction for many relevant Techniques) operating at a high flux undulator beamline at the BESSY II electron storage ring of the Helmholtz Center Berlin (HZB). This aberration corrected and energy filtered Low Energy Electron Microscopy (LEEM)/X-ray induced Photo-Emission Electron Microscopy (XPEEM) instrument combines microscopy, spectroscopy and diffraction of photo-emitted and reflected electrons and has demonstrated an outstanding lateral resolution of 2.6 nm (LEEM) and 18 nm (XPEEM) at a spectral resolution of 180 meV. The instrument excels as a probing tool with many advantages. First of all it allows a comprehensive characterization of complex systems by the combination of a multitude of surface science techniques such as LEEM, Hg-PEEM, energy filtered XPEEM, NEXAFS-PEEM, XPS, UPS, NEXAFS, LEED, XPD (photoelectron diffraction), and valence band mapping. Secondly, it has excellent surface sensitivity due to the low kinetic energy of the utilized electrons (typically between 0 and 200 eV); therefore, the main information steams from the atomic layers relevant for the chemical reactivity. Third, it permits fast direct (i.e. non-scanning) imaging that allows real-time and *in situ* observations of surface processes like film growth, oxidation, structure formation or chemical reactions. Fourth, it can operate in a wide pressure range between UHV and 10^{-5} mbar, which in principle can be extended to the mbar range. Such capabilities allow *operando* catalysis experiments that are at the core of our new research department. A few of the ongoing and planned projects are briefly discussed in the following.

In order to open the instrumental possibilities for the new scientific questions of the ISC department, the microscope set-up has been extended. A commercial plasma source for non-thermal oxidation or hydrogenation was integrated in the preparation chamber. Secondly, an electrochemical cell (EC) was attached to the UHV system of the microscope. A special transfer system allows to transfer the EC-treated sample without exposing to air or other reactive gases to the imaging chamber. This *in situ* spectromicroscopic investigation of electrochemically-treated samples enables the application of well-known and highly precise surface science probing tools to fundamental questions in electrochemistry, characterizing e.g. the morphology, atomic surface structure, local chemical composition and electronic structure quasi *in situ* after each stage of the electrochemical treatment. This unique set-up is the first synchrotron based spectromicroscope with an *in situ* integrated EC cell.

Addressing effects of confinement on chemical reactions

The physical confinement, as observed in Zeolites, has general effects on chemical reactions, such as (i) changes of adsorption sites and energy, (ii) stabilization of alternative transition states, (iii) changes in selectivity in multiple path reactions (size effect vs. transition state), (iv) acting as a molecular sieve (size selection for the reactants/products migrating into and out of the confined space) and (v) introduction of diffusion steps which are not present without confinement. A model system for two-dimensional confinement is a silica bilayer physisorbed on a Ru(0001) surface. The group has a long time experience in the preparation of this film, which under certain conditions exhibits a hexagonal crystalline structure, a vitreous structure, and also a chemisorbed rectangular zigzag-like structure. The SiO_2 bilayer has been used to study reactions in confined space. As part of the previous CP department we studied the water formation reaction in the confined space between the bilayer and the transition metal single crystal surface. Now in the new department we will investigate more complex systems and will start with the intercalation of CO and CO_2. Beside these *operando* experiments in the gas phase, we will also utilize the newly installed EC cell to study the CO (CORR) and CO_2 reduction reaction (CO_2RR) at the silica/Ru(0001) system.

So far, the silica bilayer has been used for chemical reactions only on the Ru(0001) surface. However, this can be extended to other transition metal (TM) supports. The most obvious candidate would be Cu(111) and also Cu(100) to study CO_2RR. Here, the effect of the confinement and mainly the influence of silica as a molecular sieve are the focus of our interest. The hexagonal structure might affect the selectivity of the reaction, because only small molecules can permeate the silica bilayer, and therefore, silica acts as a molecular sieve for C_1 vs. C_2 and C_3 products. Another option is to alloy the substrate with materials that are relevant for electro-catalysis (Pt-Ru, Pt-Sn, Cu-Ru, Cu-Au, Cu-Ag, Cu-Zn, etc.). Other possible reactions that could be studied in the confined system are: (a) the ammonia synthesis under silica on partially Ba-covered Ru(0001), (b) methane oxidation on Ru based catalysts modified with ZrO_2 or CeO_2, and (c) NO oxidation. Finally, apart from confinement there is the option of using the silica bilayer as a support for catalytically active nanoparticles or three dimensional islands. Because the silica bilayer has no open bonding and is chemically inert, the deposited material is not expected to wet the silica layer, but will grow as clusters (Vollmer-Weber growth). Size and distance of these NPs could be tuned by the growth temperature, deposition rate, and the deposited amount. As a next step, one might combine the catalytic activities of both, the metal islands on top and the TM support under the silica bilayer, for consecutive reactions. In this model system for coupled catalysts, the silica bilayer would act as a membrane separating or controlling what products can permeate and interact with the other side. Thermal catalysis with reactions in gas phase would allow a real time observation and are therefore the first choice. But also electrochemical reactions with this coupled catalyst system would give new insights.

Carbon dioxide reduction reaction (CO_2RR) by electrochemistry using plasma activated copper

Among all studied catalysts for CO_2 electroreduction, copper is unique due to its ability to produce hydrocarbons and alcohols with a significant yield. CO is an important key intermediate across the reaction pathway and known to bind on certain facets with different strength, making the surface structure an important parameter. Recent studies also revealed that using oxidized copper surfaces as starting material enhances the catalytic activity and selectivity towards C_2 and C_3 products such as ethylene, ethanol and propanol [1]. It is still under debate whether oxides involved in the reaction are important to facilitate a different reaction pathway or if the nano-structuring evoked by the catalyst pre-oxidation and consequent reduction during the reaction is more important for the process. Also, it remains unclear if oxides that might be present during reaction favor specific active sites which are known to enhance the ethylene selectivity i.e. (100) facets. Since April 2019 the group had two weeks of beamtime to test the new extensions of the microscope, the UHV plasma source and the *in situ* EC cell, and to apply them to investigate the catalytic behavior of copper surfaces.

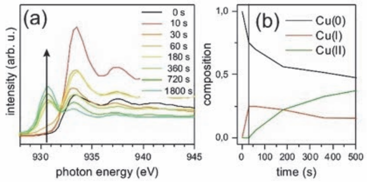

Figure 1: Oxygen plasma treatment of Cu(100). (a) NEXAFS data at different doses. (b) The analysis displays the composition of metallic Cu, Cu(I) and Cu(II) versus time.

In the first beamtime we studied the effect of the oxygen plasma treatment over time on two crystalline orientations of copper: Cu(100) and Cu(111). The Cu L-edge NEXAFS spectra showed significant differences for Cu, Cu_2O and CuO and therefore allow a quantitative estimation of the oxide species. We found that on the more active (100) surface, first solely Cu_2O is formed, and afterwards CuO on top. However, on the (111) surface, both oxide structures are formed from the beginning, but dominated by CuO at the end. This confirms results previously obtained in the ISC department with other methods. Furthermore, our LEED system revealed the atomic surface structure during the plasma treatment. Whereas on Cu(100) the order of the topmost two to three surface layers disappeared immediately, the Cu(111) exhibited a weak order even after 30 min of plasma treatment. In both cases the surface was rough with a distance between the objects of about 30 nm as seen in LEEM and chemically homogenous as proven in XPEEM. In the second beamtime, we used copper (100) crystals as electrodes for *in situ* electrochemistry. We applied pulsed voltages (+0.6 V and -1.0 V vs. RHE) and interrupted the process at certain stages (OCP, after positive and negative pulse), and investigated the chemical composition, structure and lateral inhomogeneities. After 15 min of pulsed treatment, interrupted at the negative potential, metallic copper particles were formed, surrounded by the Cu substrate containing Cu(I). Local XPS analysis proofs K to be on the particles, but not on the surrounding, and an inverted behavior was observed for carbon.

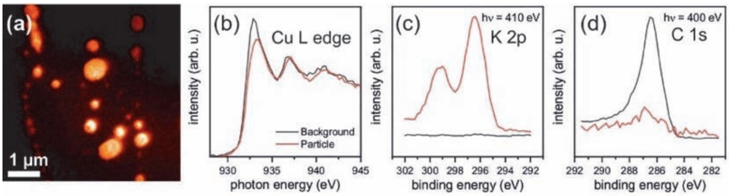

Figure 2: Quasi *in situ* CO_2 electroreduction using Cu(100) electrode with 1 s pulses of +0.6 V and -1.0 V vs. RHE, stopped at -1.0 V, 0.1 M of $KHCO_3$. (a) XPEEM shows particles, (b) µ-NEXAFS exhibits the local oxidation states, (c-d) µ-XPS reveals the local distribution of potassium and carbon.

Coupled catalysts model systems

The coupling of different catalysts is commonly used in thermal catalysis to increase the activity and selectivity of chemocatalytic reactions, while displaying significant synergetic effects. The general concept includes different active sites which can catalyze individual steps within the complete reaction. Bimetallic, metal-metal oxide and metal oxide-zeolites are major types of materials being used as multi-functional catalysts. For instance, for the CO_2 methanation catalyzed by ZrO_2-supported Ni, the metal sites were responsible to dissociate H_2 and further spillover [2], whereas the oxide stabilizes and activates CO_2 in the form of bicarbonate and carbonate species. In our project we will explore different routes to synthetize and characterize coupled catalysts. Fabrication methods will range from chemical routes, such as wet chemical and reverse micelle encapsulation synthesis, to evaporation and lithography. The second stage involves analyzing reactions *in situ* and in real time, taking advantage of the local structural and chemical characterization the SMART provides. The distance between active sites, their size and composition will be studied, aiming to understand the role of each component in the overall reaction, and therefore enabling the rational design of long-lasting catalysts with enhanced activity and selectivity.

Current Group Members

Dr. Mauricio J. Prieto, Dr. Liviu C. Tănase, Lucas de Souza Caldas, Marcel Springer, Stephan Pohl.

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Dr. Shamil Shaikhutdinov

Group Leader Department of Interface Science, FHI (since April 2019) and Department of Chemical Physics, FHI (2004–2019)
Postdoctoral Fellow, FHI (1998–2004), University Hannover (1996), University Ulm (1994)
Research Associate, Boreskov Institute of Catalysis, Novosibirsk (1987–1998)
PhD at Moscow Institute of Physics and Technology (1986)

"Structure and Reactivity" Group

The research activity of the group focuses on fundamental understanding of surface chemistry of metal and transition metal oxide nanoparticles (NPs) and thin films in reactions including CO_2 hydrogenation to alcohols and olefins and chemical transformations of methane. In particular, our studies address the effects of particle size, shape, and the nature of the (oxide) support on reactivity (both activity and selectivity).

Chemical conversion of CO_2 into value-added products is one of the most promising technologies to reduce CO_2 emissions to the atmosphere. In order to elucidate the reaction mechanisms and establish structure-reactivity relationships for such reactions, we follow the "surface science" approach based on using well-defined planar model systems, which are structurally characterized by a number of surface sensitive techniques and then tested in catalytic reactions. The mono- and multi-component (e.g., bimetallic, alloy) NPs with a narrow particle size distribution are primarily prepared by colloidal chemistry and solvothermal synthesis (Figure 1). In our laboratories, several UHV setups are equipped with low energy electron diffraction (LEED), scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), temperature programmed desorption (TPD), infrared reflection-absorption spectroscopy (IRAS), and X-ray photoelectron spectroscopy (XPS). In addition, the elementary steps of reactions can be studied by molecular beam (MB) techniques in combination with IRAS and mass-spectrometry. To address the catalyst structure at more realistic conditions, we employ state-of-the-art apparatuses to perform measurements at near atmospheric pressures (NAP) such as NAP-XPS and NAP STM/AFM as well as a Raman spectroscopy and X-ray diffraction (XRD), the latter showing new capabilities for the *operando* characterization of both, planar model systems and powder samples, also investigated in our group for comparison.

Methanol synthesis via CO_2 hydrogenation is commercially realized on $Cu/ZnO/Al_2O_3$ catalysts. Although the reaction is widely studied in the catalytic community, we addressed the structure sensitivity of the Cu-based catalysts by preparing cube-shaped Cu particles primarily exposing (001) facets (Figure 1b). Size-selected Cu-oxide nanocubes were synthesized using NaOH, ascorbic acid and $CuCl_2$ or $CuSO_4$ as precursors. The recipe was additionally modified to have the cubes decorated by Zn. The cubes (bare or encapsulated by Zn) were then supported onto ZnO or ZrO_2.

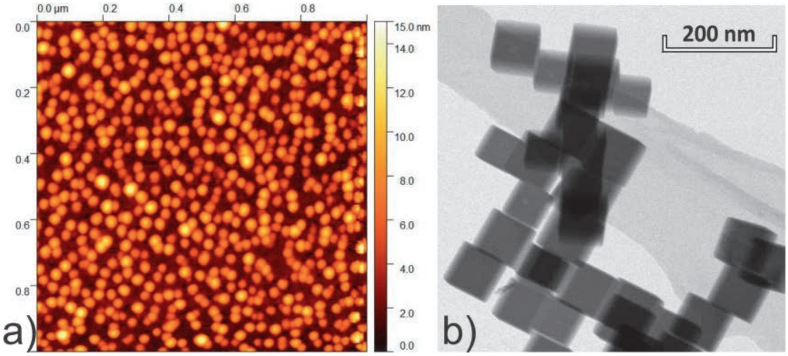

Figure 1: (a) AFM image of CuZn NPs dip coated on SiO_2/Si(001) and subsequently treated with oxygen plasma to remove the polymer ligand. (b) TEM image of Cu_2O cubes.

Structure and chemical state of the catalysts before and after reaction were characterized by STEM, XPS and XRD. The catalysts showed good activity for the CO_2 hydrogenation to methanol, as tested in a fixed-bed flow reactor in the CO_2 and H_2 (1:3) mixture, while suppressing the reverse water gas shift (r-WGS) reaction (*i.e.*, $CO_2 + H_2 \rightarrow CO + H_2O$) as compared to "conventional" catalysts exposing rather poorly-shaped NPs. Nevertheless, drastic transformations in the NP shape were observed under reaction conditions. While Cu cubes supported on ZnO showed higher activity than those supported on ZrO_2, the formation of a thin Zn shell on ZrO_2-supported Cu cubes considerably improved the selectivity and activity. Future studies are aimed at a direct comparison of the Cu cubes with other particle shapes, e.g. octahedrons. In addition, the role of the oxide support in the shape-selected catalysts as well as the effects of partial decoration *versus* full encapsulation by Zn will also be addressed.

These results highlight that the intimate interaction of Cu and Zn (ZnO) phases constitutes the key factor for the superior catalytic performance of the Cu/ZnO catalysts. To shed more light on this, we carried out NAP XPS measurements (using both conventional X-ray sources and synchrotron light) of the Cu-Zn NPs (Figure 1a) to monitor *in situ* the chemical composition and electronic state of the model catalysts during calcination/reduction treatments as well as in CO_2 hydrogenation reaction conditions in the mbar pressure range, Fig. 2. In addition, photon energy dependence allowed to analyze the elemental depth profile of the NPs studied. Note, however, that the study revealed considerable X-ray beam damage effects which have to be thoroughly controlled in such experiments, for example, by regularly changing the irradiated spot position. The results showed that "as deposited" NPs, after removing the polymer shell by oxygen plasma and further oxidized at 400°C are slightly enriched with Cu oxide species at the surface. The measured Cu/Zn ratio is close to that expected from the elemental composition of the synthesized particles. Reduction in H_2 at 350°C, however, leads to strong Zn segregation to the surface. Furthermore, the Cu/Zn surface ratio in reduced NPs does not change in the $CO_2 + H_2$ (1:3) reaction mixture at 350°C at these pressures. Comparative *ex situ* XPS measurements on the samples treated in O_2 and H_2 at 1 bar revealed the same trend, albeit the Zn segregation was not as strong as observed at low pressures in the NAP-XPS experiments. Complementary IRAS studies of the particle surface via adsorption of CO and CO_2 as probe molecules are under way which will shed light on the surface structure of the prepared NP_S as well as surface species formed under reaction conditions.

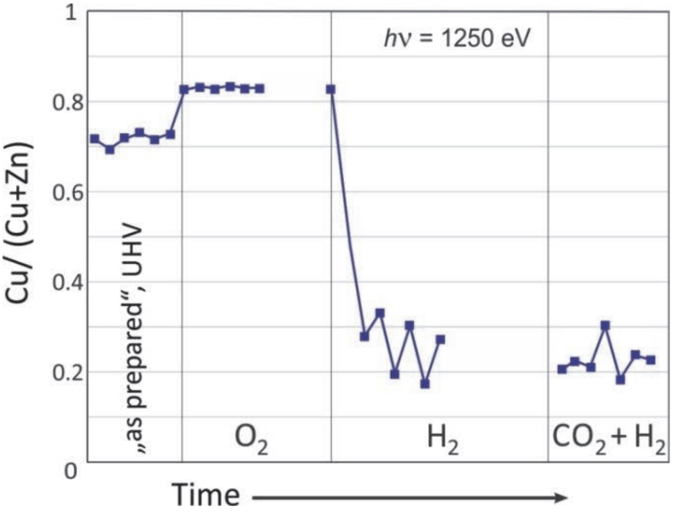

Figure 2: Surface concentration of Cu in Cu70Zn30 NPs/ SiO_2/Si(001) measured by NAP-XPS for the samples: “as deposited” and treated with O_2-plasma, then exposed to 0.6 mbar O_2 at 400°C, then 1 mbar of H_2 at 350°C, and finally to the 1.5 mbar CO_2 + H_2 (1:3) mixture at 250°C. To minimize beam induced effects, the spectra were measured in different spots in alternative sequence for the Cu 2p and Zn 2p regions in every new spot, which most likely resulted in the small oscillations observed in H_2 atmosphere.

Among CO_2 hydrogenation catalysts based on highly dispersed 3d metals, Fe catalysts have recently received considerable attention due to their high selectivity towards C_{2+} hydrocarbons. Since Fe- and Co-based catalysts are well-known for the Fischer-Tropsch (FT) and r-WGS reactions, the process, often referred to as modified FT (or CO_2-FT) route, may also proceed via sequential r-WGS (to form CO from CO_2) and FT reactions. Also, it has been proposed that the active phase is an iron carbide layer formed during the reaction. However, full understanding of the reaction mechanism, in particular, the role of particle size and of promoters on the catalytic performance, is still missing. In our approach, we synthesized Fe and Fe-Co NPs by inverse micelle encapsulation and deposited them onto both, planar and powder oxide supports. The catalytic tests on Fe NPs deposited onto γ-Al_2O_3 showed some activity to the C_2-C_3 products (which remains to be identified precisely). Chemical state and surface transformations of the model catalysts deposited onto SiO_2/Si and α-Al_2O_3 (sapphire) substrates were monitored by XPS. Our preliminary results suggested a considerable resistance of the iron oxide NPs towards reduction even in 1 bar of H_2 at temperatures as high 600°C. In addition, the particles showed no carbide formation under the reaction conditions used ($CO_2/H_2 = 1/3$, 10 bar, 350°C), thus indicating that the reduction step may be crucial for the primary reaction pathway.

Many heterogeneous reactions exhibit particle size effects for supported metal catalysts which are often linked to the abundance of low-coordinated atoms present on the nano-particulate systems. Recently, there were reports in the literature claiming that the particle size in powder catalysts can be reduced down to a single atom. Albeit the fact that it is not trivial to prove its presence or absence at the catalyst surface, such "single atom" sites are believed to be responsible for the superior activity as observed, for instance, in CO oxidation. Extrapolating this approach to our target reactions involving CO_2, we address the question, whether atomically dispersed noble metals like Pt supported on transition metal oxides (TiO_2 and CeO_2) can be used for CO_2 hydrogenation or other related reactions. If this is proven true, we plan to investigate in detail the reaction mechanism. In our approach, we use TiO_2(110) single crystal surface as the support for Pt deposited via physical vapor deposition. We are studying electronic state, surface morphology and the adsorption behavior of such surfaces using XPS, STM and TPD, respectively. In particular, thermal and environmental stability of "single atom" is examined by characterizing the catalysts used under high pressures (up to 20 bar) conditions.

Within the "surface science" approach, it is common to link the results of structural characterization of the well-defined planar model systems, performed under controlled UHV compatible conditions, to the reactivity of relatively ill-defined powder catalysts. This is because measuring catalytic activity of the planar catalysts, having both very low surface area (~1 cm^2) and low active phase loading, under realistic high pressure and temperature conditions, is often difficult and remains challenging. Meanwhile, powder catalysts possess high surface area and can be more easily measured, using routine techniques such as on line-gas chromatography. In order to examine, at least quantitatively, the catalytic performance of our model catalysts, we put much effort into gas analysis of products in high-pressure reactors operating at pressures up to 20 bar, which is often required to achieve reasonable conversion in reactions like CO_2 hydrogenation to methanol. Our setup using silica capillary and mass–spectroscopy analysis was successfully tested on the above-mentioned Cu(cube)+ZnO powder catalysts and even Cu NPs deposited onto a ZnO single crystal surface by dip coating. The results make us quite confident that catalytic performance of the model NP catalysts on planar supports can, indeed, be examined, albeit the activity remains difficult to quantify. Nonetheless, it will allow establishing structure-activity relationship in more definite manner as compared to the situation when structural characterization of the model catalysts is linked to the reactivity measurements performed on powder catalysts.

Group Members

Uwe Härtel, Dr. Osman Karslioglu, Burkhard Kell, David Kordus, Mauricio Lopez Luna, Dr. Weiming Wan, Dr. Jian Qiang Zhong

Dr. Janis Timoshenko

Group leader in the Interface Science Department at the FHI of the Max Planck Society (since October 2018)
Postdoctoral scholar, Stony Brook University, USA (2016–2018)
Postdoctoral scholar, Yeshiva University, USA (2015–2016)
PhD, University of Latvia (2015)

Operando Hard X-ray spectroscopy

To understand the reaction mechanism and to single out the active species in heterogeneous catalysts, detailed knowledge of their atomistic and electronic structure is necessary. Both, however, respond to changes in the environment, and are under reaction conditions likely different from those of the pre-catalyst material.
X-ray absorption spectroscopy (XAS) is a premier method for understanding the relation between catalyst structure and its properties due to its element-specificity, sensitivity to the details of local electronic and atomistic structure, applicability to a broad range of materials, and to the fact that it allows studies under harsh reaction conditions. Application of XAS (in combination with complementary synchrotron- and lab-based techniques) to reveal the key structural motifs in heterogeneous catalysts and their transformations is the main objective of the research group “Operando Hard X-ray Spectroscopy”. We focus on *in situ* studies of catalysts in reactive atmospheres, at high temperatures, high pressures, or under applied potential. To track the fast changes in catalyst structure, we rely on recent progress in X-ray sources that now allows one to collect good quality data with sub-second time resolution. Note, however, that deciphering the intriguing details included in the XAS data of such disordered, heterogeneous catalyst systems under working conditions is not straightforward. Therefore, an important component of our research is the development of advanced data analysis approaches.

3D structure models of nanoparticles from *in situ* XAS

To understand the effect of particle-support interactions, UHV studies of size- and shape-selected nanoparticles (NPs) deposited on single crystals are helpful. For such oriented samples one can benefit from the fact that the bonds with different orientation with the respect to the X-ray polarization contribute differently to the measured XAS spectrum. Thus, the anisotropy of the NP structure can be probed. Data interpretation in terms of a 3D structure model, nevertheless, is non-trivial. We approach it by using reverse Monte Carlo (RMC) simulations. Here, a NP structure model (constructed based on the insights from AFM and STM data, conventional extended X-ray absorption fine structure (EXAFS) spectroscopy data fitting and X-ray absorption near-edge structure (XANES) analysis), is refined in an iterative process, until it agrees with all experimental EXAFS data. Through a synergistic combination of our synthesis method (which ensures narrow NP shape- and size- distribution), characterization by microscopy and XAS and the RMC-based modeling we construct unambiguous structural models of NPs on different supports. For instance, we have recently studied the differences in NP shape and NP/support interaction for Pt NPs deposited on $TiO_2(110)$ and $SiO_2/Si(111)$ single crystals, Fig. 1(a-c), and could gain insight into the role of the support in the anisotropy of bond-length distributions within the NP.[1]

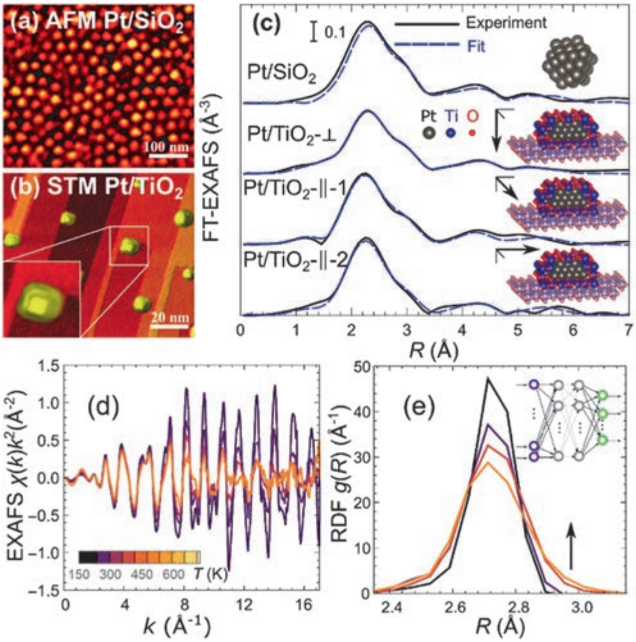

Figure 1: (a) AFM and (b) STM image of Pt NPs. (c) Fourier-transformed (FT) experimental EXAFS data for Pt NPs acquired with different X-ray polarizations (indicated by the arrows). Fits for the RMC model are shown in the insets. Temperature-dependent EXAFS for Pt NPs (0.8 nm) on Al_2O_3 (d) are processed by neural network (inset in (e)). (e) Resulting shape of the 1st RDF peak.

Deciphering structural/chemical information from XAS by machine learning

Machine learning (ML) methods, such as neural networks (NNs), provide new opportunities for extracting structural information from XAS data. In our approach, NNs are trained to recognize the relationship between spectral features and structural motifs using large sets of *ab initio* calculated XAS spectra for NP models. The trained NN can then be applied to the quantitative interpretation of experimental XANES and EXAFS data. Note here that XANES is more robust towards disorder, hence can be more reliable for studies under harsh experimental conditions. XANES-based approach, enabled by ML, is also better suited for lab-based XAS experiments, capabilities that we plan to develop at the ISC department in the near future. EXAFS, in turn, is more sensitive to the details of bond length distributions. For example, we have recently interpreted temperature-dependent EXAFS data from size-selected Pt NPs on different supports and in different environments using the NN-EXAFS method, providing the insights into the non-Gaussian shapes of the radial distribution functions (RDFs) of small (< 3nm) supported Pt NPs (Fig. 1(d-e)). By following the changes in the shapes of RDFs, we could extract accurate information about the thermal expansion and Debye temperature of Pt NPs.[2] Our results clarified the long-standing controversy of the intrinsic thermal properties of small metallic NPs. In particular, the negative thermal expansion previously reported was found to be determined by the presence of adsorbates on the NP surface as well as a strong NP/support interaction.

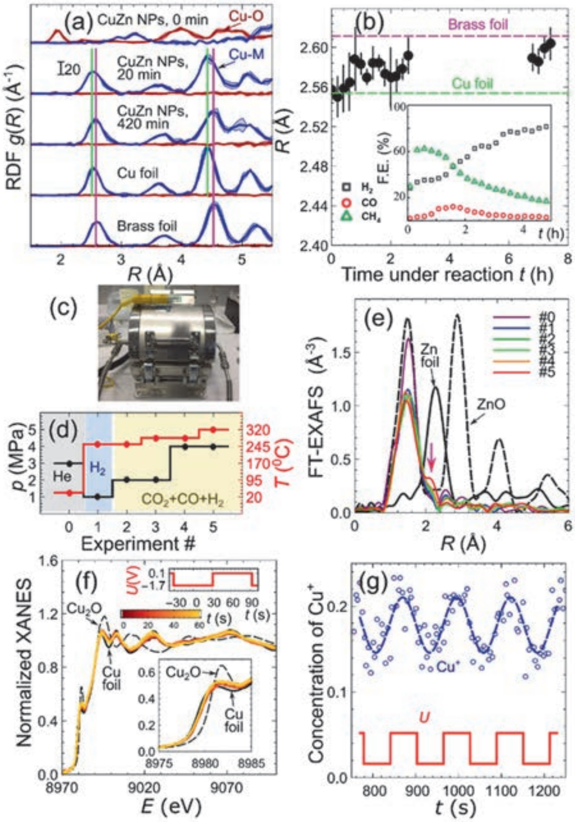

Figure 2: (a) RDFs for Cu-O and Cu-M (M = Cu or Zn) bonds, obtained by NN from time-dependent Cu EXAFS for CuZn NPs under CO_2RR. (b) Changes in the nearest-neighbor distance, and Faradaic efficiencies for CO_2RR (inset). (c) Sample chamber with Be reactor for high pressure XAS measurements. (d) Experimental conditions applied during CO_2 hydrogenation with CuZn NPs. (e) Zn FT-EXAFS data showing the formation of Zn-M bonds (indicated by a vertical arrow) under reaction conditions. (f) Time-resolved Cu XANES for Pd-decorated Cu nanocubes under pulsed CO_2RR conditions. (g) Corresponding evolution of Cu^+ species concentration, as obtained from XANES analysis.

Our current ongoing work is the generalization of the NN approach for non-metallic NPs. In Fig. 2(a-b) we apply it for the interpretation of time-dependent Cu K-edge EXAFS data in $Cu_{50}Zn_{50}$ NPs, collected under CO_2 electrochemical reduction reaction (CO_2RR) conditions (collaboration with Dr. Jeon, ISC). The obtained RDFs demonstrate that Cu is oxidized in the as-prepared samples. After potential application, Cu is quickly reduced. However, the structure continues evolving, and we observe a gradual increase in the interatomic distances around Cu from 2.55 Å (characteristic of pure Cu) to 2.61 Å (characteristic of CuZn brass), which we interpret as an evidence of gradual Cu alloying with Zn. The observed changes in structure can be correlated with the time-dependent change in product selectivity and will lead to the understanding of the role of different species in this catalyst.

Catalysts at extreme conditions

For understanding the role of the catalysts structure on the reaction mechanism, structure studies should be carried out in an environment matching the actual reaction conditions. For industrially relevant catalysts (e.g., for CO_2 hydrogenation to methanol) this often means working under moderate temperatures but high pressures (several MPa). Our beryllium tube-based reactor for *in situ* XAS studies gives us the unique ability to probe the catalyst structure at these extreme conditions. By performing *operando* XAS studies of CuZn-based catalysts for CO_2 hydrogenation (in collaboration with Dr. Divins and David Kordus, ISC), we were able to detect a partial reduction of Zn and formation of metallic Zn species under reaction conditions (Fig. 2(c-e)), which may be an important step towards understanding the still controversial role of Zn in Cu-based catalysts for CO_2 conversion.

Catalyst structure under dynamically changing conditions

Control of catalyst oxidation state is one of the possibilities to tailor its activity. Under CO_2RR conditions, Cu species are quickly (within minutes) reduced (Fig. 2(a)). At the same time, our studies suggest that cationic species can be recovered by applying a short pulse of positive potential, providing the possibility to control the catalyst oxidation state on demand. To monitor and understand these changes, *in situ* studies with time-resolution of several seconds or better are needed. Quick-XAFS mode (QXAFS), available now at several synchrotron radiation beamlines worldwide, provides such possibilities. In collaboration with Dr. Aran-Arais and Clara Rettenmaier, ISC, we carried out one of the first QXAFS experiments at PETRA-III facility in Hamburg, where XAS data collection was done in fluorescence mode (as required by the electrochemical experiments). The analysis of the collected data (Fig. 2(f-g)), demonstrates our ability to track the fast transformations in the catalyst structure and oxidation state under dynamically changing reaction conditions, and, in particular, the periodic reduction and re-oxidation of Cu-based catalysts for CO_2RR. The fast processing of large data sets, enabled by machine learning methods, will be indispensable for the on-line analysis of QXAFS data.

Collaborations within ISC department

Dr. Hyo Sang Jeon, Dr. Rosa Aran-Arais, Clara Rettenmaier, Felix Haase, David Kordus

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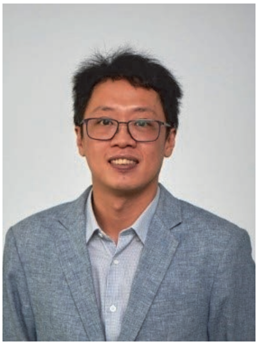

Dr. See Wee Chee

Group Leader, Fritz Haber Institute (since Aug 2019)
Senior Research Fellow, National University of Singapore, (2014–2019)
Visiting Scholar, Rensselaer Polytechnic Institute (2014)
Applications Scientist, Hummingbird Scientific (2013)
Postdoctoral Scholar, Rensselaer Polytechnic Institute (2010–2012)
Postdoctoral Scholar, Arizona State University (2008–2010)
PhD, University of Illinois at Urbana-Champaign (2008)

Understanding the Structural Evolution of Nanoscale Electrocatalysts in Liquid and under Reaction Conditions

The economic viability of several prospective sustainable energy technologies depends critically on the discovery of improved catalysts. In general, new catalyst development is a complicated and time-consuming process, often requiring years of trial and error. Rational design is an important way by which we can accelerate the creation of such catalysts. However, we still have limited understanding of a catalyst's working state because the catalyst structure captured under the typical high vacuum conditions of various surface characterization techniques can be vastly different from that found under reaction conditions, especially in electrochemical systems. This need to clarify a catalyst's structure during reaction has spurred the adaption of several techniques towards probing catalyst materials under conditions where there is, for example, an electrified liquid-solid interface.

Introduction to Liquid-Cell Transmission Electron Microscopy

Liquid cell transmission electron microscopy (LC-TEM) is an emerging technique that can be used to study the behavior of nanoscale electrocatalysts at high spatial resolution and under electrified conditions. Unlike conventional TEM studies where the catalysts are compared before and after reaction, LC-TEM permits the direct, real-time imaging of these structures within the electrolyte and at the liquid-solid interface. A modern LC-TEM set-up is described in Figu. 1. Current commercial holders also incorporate tubing for fluid flow and electrical connections to thin electrodes inside these cells, allowing electrochemical studies (EC-TEM) to be performed. So far, EC-TEM has been used to look at the electrodeposition of metals, lithiation processes and metallic corrosion. Comparatively, there is relatively little work in the study of electrocatalysts, despite the significant opportunities for scientific breakthrough.

The liquid-phase electron microscopy group was established in Aug 2019 in the Department of Interfacial Science to pioneer research involving the study of nanoscale electrocatalysts using EC-TEM. I bring to the FHI my prior experience using LC-TEM to study the aqueous corrosion of metals as well as nanoparticle dynamics in liquids.

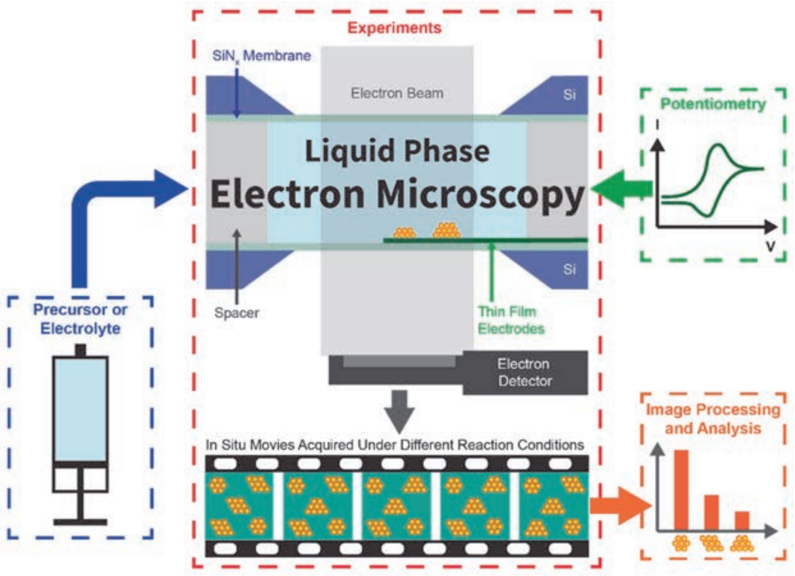

Figure 1: Schematic representation of a liquid cell TEM setup. The reactant solution or electrolyte is injected from outside of the TEM into a microfluidic cell consisting of two chips with silicon nitride membrane windows that are sandwiched together and separated by spacers. Integrated film electrodes that are connected to an external potentiostat allow for biasing of the specimens.

Structural Transformations in Cu Electrocatalysts for the CO_2 Reduction Reaction

Our initial work uses this approach to monitor the electrochemical synthesis of Cu nanocubes. In particular, we seek to understand the key parameters responsible for a narrow particle size and shape distribution. Preliminary results acquired in collaboration with electrochemists in our department and the microscopy group in the Department of Inorganic Chemistry are presented in Figure 2. Here we performed voltammetric cycling experiments in order to grow Cu nanoparticles with cubic shapes from a 5 mM $CuSO_4$ + 5 mM KCl solution. The EC-TEM images show that during cycling, when Cu is first deposited and then dissolved, cubic-shaped nanoparticles can be synthesized under certain potentials in the presence of Cl. Interestingly, the cubic structures are the last ones to dissolve during cycling.

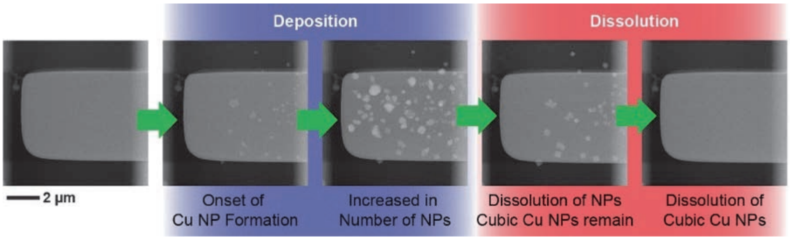

Figure 2: Morphological evolution of electrodeposited Cu nanoparticles (NPs) as the working electrode (Pt) potential is cycled towards reducing potentials and then towards oxidizing potentials. A solution of 5 mM $CuSO_4$ was used. The (100) facets are stabilized by the addition of 5 mM KCl to the solution.

At present, we are looking to extend this system towards probing the dynamic morphological changes that occur during the electrochemical reduction of CO_2 on these as-deposited Cu nanocubes. We also expect to capture the associated dynamics at much higher temporal resolution with a new camera that has been recently installed on the Titan TEM and to perform further chemical mapping of these nanostructures in solution with the new energy dispersive X-ray spectrometer.

In the coming years, we will use this method to explore the electrochemical synthesis of nanostructures with controlled morphology and to follow changes in the size, shape and composition of electrocatalysts that are being used for structure-sensitive chemical reactions. These studies include the electroreduction of CO and CO_2, as well as the electrooxidation of alcohols and the oxygen reduction reaction taking place over multi-metallic nanostructured catalysts.

Current Group Members
Dr. Stefanie Kühl

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Molecular Physics

Department of Molecular Physics
Prof. Dr. Gerard Meijer

Director at FHI and Scientific Member of the Max Planck Society
(2002–2012, and since 2017)
President of the Executive Board, Radboud University Nijmegen,
Nijmegen, The Netherlands (2012–2016)
Director FOM-Institute for Plasmaphysics, Nieuwegein,
The Netherlands (2000–2003)
Honorary Professor Freie Universität Berlin, Berlin (since 2004)
Professor in Experimental Physics, Radboud University Nijmegen,
Nijmegen, The Netherlands (since 1995)
Ph.D. in Physics, Radboud University Nijmegen,
Nijmegen, The Netherlands (1988)

Recent Developments in the Department

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. Supported by the last two reports of the Fachbeirat, investments funds have been secured for an upgrade of our IR-FEL facility, *i.e.* to set up a second undulator and optical cavity. This will extend the spectral range covered by the FEL to longer wavelengths and, in particular, will enable two-colour operation. An international team of electron accelerator and FEL specialists has been brought together to design and construct the various components needed for the upgrade, which is planned to be completed by the end of next year. The upgrade of the FEL facility coincides with the renovation of the laboratories in the adjacent building (Bldg. D), where several new user stations will be made available.

Since the last meeting of the Fachbeirat in November 2017, two new research group leaders have been appointed in the MP department on six-year, temporary positions – Sandra Eibenberger-Arias (per January 2018) and Jesús Pérez Ríos (per July 2019) – whereas Bretislav Friedrich has formally retired. Sandra Eibenberger-Arias has been involved in molecule interferometry experiments during her PhD research (in the group of Markus Arndt in Vienna) and in proof-of-principle enantiomer-selective state-transfer (ESST) experiments during her post-doctoral stay at Harvard University (in the group of John Doyle). At the FHI, she is setting up a chirped-pulse Fourier transform microwave spectrometer to perform broadband, high-resolution microwave spectroscopy on chiral molecules and to test original and more sensitive schemes to exploit the ESST method that she co-developed. Jesús Pérez Ríos has a theoretical background in quantum scattering, and started in January of this year as a post-doctoral co-worker in the MP department, theoretically supporting the ongoing experiments aimed at laser-cooling and trapping of diatomic halides. He is internationally well-connected to various leading theoretical and experimental groups, and he has developed interest and expertise in diverse subjects, *e.g.* the possibility to use molecules like CO as detectors for dark matter. In collaboration with co-workers from the Theory department at the FHI he will explore the possibility to use machine learning on existing molecule databases to identify candidate molecules that are optimally suited for laser manipulation and control. He has been given the opportunity to establish his own research group in the MP department per July of this year.

Since January of this year, Bretislav Friedrich has formally retired. In April, we have organized a Symposium for him, to celebrate his contributions to the wider area of molecular physics and to the history of science. Bretislav will keep his office in the MP department and is expected to stay as active as ever for the coming years. He will be the managing editor of the soon-to-be-launched Wiley journal *Natural Sciences* – planned as a fully Open Access revival and rejuvenation of the original (then German-language) journal *Naturwissenschaften*.

The research in the MP department can broadly be divided in three themes. A large experimental effort is devoted to research under the theme of "Molecular physics studies with infrared radiation". In these studies, the IR optical properties and dynamics of molecules, clusters and cluster-adsorbate complexes are investigated in the gas-phase. The second theme is on "Controlled molecules" and 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. The third theme centres around the study of "Gas-liquid interfaces", making use of liquid microjets. In the following, a high-level general overview of these three themes is given. More detailed information on the various research projects is to be found in the individual sections of the research group leaders.

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 μm, 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 will "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 μs 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 cm^{-1} for a central frequency of 1000 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").

The research group on *Infrared excitation of gas-phase molecules and clusters* of Gert von Helden, the research group on *Spectroscopy and Chemistry of Metal Clusters and Cluster Complexes* of André Fielicke, as well as the guest-groups of Knut Asmis and Kevin Pagel, have successfully made use of the unique capabilities of the IR-FEL facility in a variety of studies.

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. Over 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 decade, it has been demonstrated that laser cooling – the workhorse to control atoms – can also be used for a subset of molecules, that have a specific electronic and ro-vibrational energy level structure. In this research theme, we explore the possibilities that the combined manipulation with optical fields and with electric and magnetic fields holds to achieve ultimate control over molecules.

Stefan Truppe started per May of 2017 on a six-year, temporary position and he has set up a research group on *Cold and Controlled Molecules*. He brought hands-on experience with laser cooling and trapping of molecules with him, 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. The diatomic molecule aluminium monofluoride (AlF) has been identified as an ideal candidate molecule for these studies, and the basic properties of this molecules in the most relevant electronic states have been accurately determined.

The experimental research of Sandra Eibenberger-Arias, the analytical modelling of Bretislav Friedrich and the theoretical research of Jesús Pérez Ríos all fit under this theme, as do the matter-wave diffraction experiments of Wieland Schöllkopf.

Gas-liquid interfaces

In the MP department we have set up a new research line, aimed at improving our understanding of gas-liquid interfaces. We 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.

Bernd Winter joined the MP department per January 2017 as a permanent staff member and he leads the research activity on *Liquid Microjets*. Bernd 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. A newly designed experimental setup for photo- and Auger-electron spectroscopy from vacuum liquid microjets has become operational in the MP department. With this setup, valence and core-level electronic structure as well as electronic relaxation (autoionization) processes can be accessed. Combining 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 will enable us to obtain a more complete picture of the gas-liquid interface. Some of the topics we plan to investigate are the solutions' work functions, the interactions of a molecular beam with an aqueous-solution surface and the forward-backward asymmetry in the photoelectron angular distribution from chiral molecules dissolved in water, when using circularly polarized light, *i.e.* PECD from liquid jets. A vacuum liquid-ammonia microjet has been developed with which high concentrations of solvated electrons in solution can be achieved, enabling us to experimentally study the liquid-to-metal transition. We have also designed our own flat jets, resulting from the crossing of two circular liquid microjets under the right angle, and we have studied their mixing behaviour. These flat jets will be used to explore how well-characterized cold molecular beams interact with an aqueous surface in vacuum, to advance our understanding of the occurring chemical and physical processes.

The DEAL negotiations

Since my return to Germany in the beginning of 2017, I have been actively involved in Project DEAL, as Max-Planck representative in the DEAL negotiation team, led by Prof. Hippler, the former president of the German rector's conference. DEAL is the abbreviation for *DEutsche Allianz Lizenzen*, referring to national licenses from major academic publishers for all institutes belonging to the Alliance of Research Organizations in Germany (Alexander von Humboldt-Stiftung, Nationale Akademie der Wissenschaften Leopoldina, Deutsche Akademische Austauschdienst, Deutsche Forschungsgemeinschaft, Fraunhofer-Gesellschaft, Helmholtz-Gemeinschaft, Hochschulrektorenkonferenz, Leibniz-Gemeinschaft, Max-Planck-Gesellschaft, Wissenschaftsrat). The goal of Project DEAL is to conclude nationwide licensing agreements (reading access) for the entire portfolio of electronic journals from major academic publishers in general and from Wiley, SpringerNature and Elsevier in particular. The intention is also to bring about significant change in the status quo in relation to negotiations, content, pricing and the transparency thereof, in the process. The Alliance requests from the publishers that all articles that have a corresponding author who is affiliated with one of the institutes of the Alliance partners, are immediately published Open Access, free to read for everybody, everywhere. The copyrights of the article should stay where they belong, namely with the authors, under an author's-choice Creative Commons license, with CC-BY as default. The costs for publishing the article will be covered by the institution of the corresponding author or, more generally, by the research funding body and the cost per article should be transparent. At the institutional level, a reallocation of library budgets and research budgets might be required but the overall costs for publishing and reading scientific articles for Germany will be lower in the future than it was up to now. Non-disclosure agreements will no longer be signed, and the final contracts will be made public.

Within the MPG, the licenses with the academic publishers for all the Max Planck Institutes (over 80 in total) are already for many years organized and centrally financed by the Max Planck Digital Library (MPDL), located in Munich. To handle a national license for all the institutes that belong to the Alliance of Research Organizations in Germany (over 700 in total), the MPG stepped forward and set up a daughter company, the MPDL Services GmbH. With the MPG taking this prominent role for all academic institutions in Germany upon them, I *de facto* had to take the lead in the negotiations with the publishers. In January of this year we signed a first national contract with Wiley and in August we announced that from January 2020 on a similar contract with SpringerNature will be in place. The mere scale of these contracts (with an annual volume of about 30 M€ each) as well as their structure and transparency are a breakthrough for Open Access of scientific publications worldwide, and will be highly beneficial for the visibility and impact of German academic research output.

Dr. André Fielicke

Group Leader at FHI (2004–2012, since 2017)
Heisenberg fellowship of the DFG (2016–2017)
Visiting professor, Technische Universität Berlin (2015–2016)
Research group leader, Technische Universität Berlin (2013–2017)
Postdoc, FOM Institute for Plasmaphysics, Nieuwegein, The Netherlands (2001–2004)
Dr. rer. nat., Humboldt-Universität zu Berlin (2001)

Spectroscopy and chemistry of metal clusters and cluster complexes

The main topic of the group is the investigation of strongly bound clusters in the gas phase to elucidate their geometric and electronic structures. The central goal thereby is to obtain a fundamental understanding of the (often) unusual chemical properties of nano-scale materials and, more specifically, of the role of nano-particles in catalysis [1]. As an important tool, the FHI infrared free electron laser serves as unique light source to obtain cluster-size specific infrared spectra that are fingerprints of the clusters' structure. Complimentary information, that is more directly sensitive to the electronic structure, is obtained using anion photoelectron spectroscopy. Here, in addition to the more classical application of probing the valence orbital structure, we have started the investigation of the photoelectron circular dichroism in the photo-detachment from chiral anions.

Infrared spectroscopy of gas-phase clusters

Neutral clusters

Using IR-UV two color ionization, size-selective IR spectra of neutral clusters can be obtained without the need to form messenger complexes. This technique exploits the fact that close to the ionization threshold, the ionization efficiency usually increases with internal energy. Resonant excitation of vibrational modes via absorption of IR photons can therefore raise the efficiency of the ionization process and the mass-selective measurement of ion-signal vs. IR frequency allows cluster-size specific infrared spectra to be obtained. However, as the UV photon energy needs to be close to the threshold energy for ionization and as the ionization energy of a cluster depends on its size, this requires a tunable (V)UV laser to be able to characterize a wider range of cluster sizes.

Motivated by predictions of stable fullerene-like structures for neutral boron clusters containing ~40 B atoms, we set up a tunable VUV laser system based on 4-wave mixing in Xenon to cover the 6.5-8.2 eV photon energy range. In the past, we already characterized smaller boron clusters (with L.-S. Wang, Brown University, Providence, USA) that have their ionization threshold near the photon energy of a commercial F_2 laser (7.9 eV) [2]. In initial test measurements, in which we recorded the IR-UV spectra using 7.9 eV photons generated by 4-wave mixing, we have been able to reproduce our earlier results.

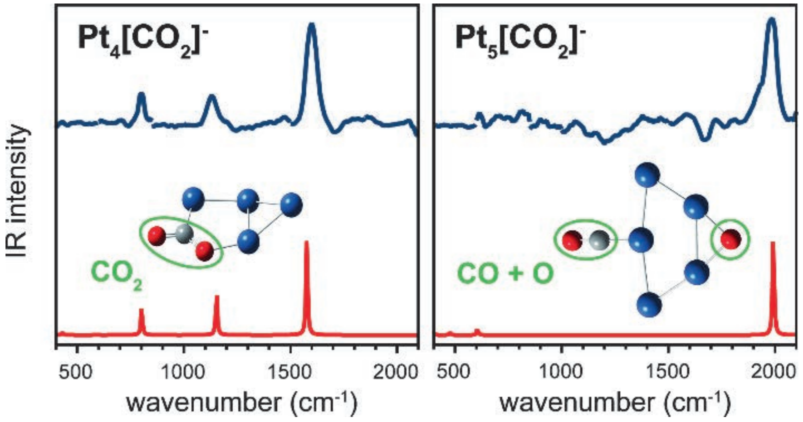

Figure 1: Two different binding modes observed for CO_2 activated by small platinum cluster anions.

Gas-phase chemistry of metal clusters

In various ongoing collaborations, we have studied the activation of small molecules like H_2, N_2O, CO_2, CO by metal clusters using IR multiple photon dissociation spectroscopy. One intriguing result of the study of CO_2 binding to anionic platinum clusters is a size-specific reactivity: in most cases, dissociation of the CO_2 to CO and O is observed on the cluster's surface, while for Pt_4^-, for example, only formation of an (probably kinetically trapped) activated CO_2^- complex is detected (with S. Mackenzie, University of Oxford, UK) [3]. We have also studied cluster models for possible H_2 storage systems (with E. Janssens, KU Leuven, Belgium). For V and Rh doped aluminum clusters the transition metal dopant has clearly been identified as center for the H_2 activation and splitting. In certain cases, molecular H_2 complexes have been found. The stability of these complexes can be explained by the shape of the frontier orbitals of the clusters and their interaction with H_2; H_2 can only be split when an effective donation of electron density into the σ^* orbital of the H_2 ligand can occur [4,5].

Anion photoelectron spectroscopy

Electronic structure and isomerism of platinum clusters

High resolution anion photoelectron spectroscopy using velocity map imaging (VMI) allows to obtain a wealth of experimental information on the anionic and neutral species involved in the detachment process. In detail, for a mass-selected anion and as a function of photon energy, information on the photoelectrons' kinetic energy, spatial distribution and detachment efficiency can be analyzed to obtain, e.g., electron binding and electronic excitation energies, vibrational frequencies, structural changes (via Franck-Condon profiles) and the angular momentum of the electrons' initial state.

As an example we have applied this technique to Pt_3^- and resolved a multitude of earlier undetected vibronic transitions giving, in combination with density functional theory calculations (with J. Jellinek, Argonne National Lab, USA), Franck-Condon (FC) simulations and anisotropy parameter analysis, insights into the structures of the anionic and neutral states. We have assigned the linear, $^4\Sigma_g^-$, and triangular, $^3A_2''$ structures, as ground state isomers for the anionic and neutral clusters, respectively. A second anionic isomer with triangular geometry ($^2A_2'$), has been theoretically predicted 0.637 eV higher than the ground state. It appears to be non-Boltzmann populated in the experiment as the decay to the anionic linear ground state is spin-forbidden and it is characterized by prominent features in the photoelectron spectrum. Its vibrational temperature, obtained through FC simulations, is estimated to be ~100 K. By assignment of the experimental spectrum an adiabatic electron affinity of 1.857 ± 0.001 eV is determined for the triangular isomer. Furthermore, the lowest energy band is shown to be composed of overlapping transitions from the $^2A_2'$ anionic state to two very close-lying neutral electronic states, $^1A_1'$ and $^3A_2''$.

A third neutral state reached by a vertical transition from the anion having D_{3h} symmetry to a corresponding $^3E''$ state is predicted to undergo stabilization to a C_{2v} symmetric $^3A_2$ state due to the Jahn-Teller effect with a stabilization energy of 96 cm^{-1}. FC simulations for these transitions could not give satisfactory agreement with the experiment but did raise questions, however, on the relevance of spin orbit (SO) vs. Jahn-Teller (JT) effects in this heavy atom system.

Photoelectron circular dichroism of chiral anions[6]

Photoelectron circular dichroism (PECD) is an enantiomer discriminating effect like the more common circular dichroism (CD) in the absorption of photons. However, instead of measuring the subtle difference of the absorption cross-section of left- and right-handed circularly polarized light by a specific enantiomer like it is done in CD, in PECD the light is used to ionize a chiral molecule in the gas phase followed by analyzing the spatial distribution of the photoelectrons. Since the emission of the electron is governed by electric dipole effects and does not just depend on weak magnetic dipole interactions like in CD, typical signal strengths can be orders of magnitude larger. Measuring the intensity difference between electrons emitted in forward and backward direction relative to the direction of the ionization laser beam, the PECD effect has been found to reach more than 10%. While until now this effect has been demonstrated only in the photoionization of neutral molecules, here, the aim is to study its occurrence in the photodetachment from chiral anions.

Initially, complexes between atomic gold anions and several chiral molecules (alaninol, fenchone, menthone, 3-hydroxy-tetrahydrofuran) have been studied. For these complexes the classical photoelectron spectra revealed a weak interaction between the closed shell metal anion and the chiral molecule, and within our measurement uncertainty of about 1% no PECD signal has been detected. Recently, we installed a photoelastic modulator that allows reversing the orientation of light polarization shot-by-shot, i.e., for alternating cycles of the experiment that runs at 10 Hz. In comparison to the former manual polarization change, a significant improvement of sensitivity for PECD is expected.

[6] This project has been funded by the DFG (Fi 893/6)

As PECD has been shown to be rather sensitive to vibrational states [6] we built a new anion source where the chiral anions are formed by deprotonation using, e.g., OH^- or in a plasma discharge. The anions are then entrained in a supersonic Ar expansion to obtain anions with low internal energies (design is following ref. [7]). Preliminary studies of deprotonated chiral molecules, for instance $[\text{alaninol-H}]^-$, did not reveal a detectable PECD signal yet either, although it needs to be said that these anions where probably not cold yet.

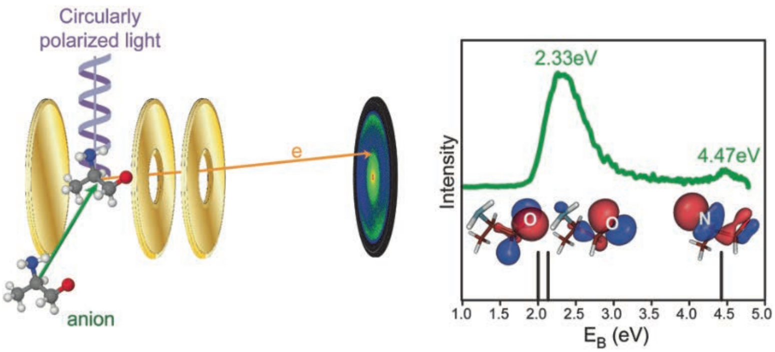

Figure 2: Left: Scheme of the PECD measurement via velocity map imaging. PECD can lead to a forward/ backward intensity asymmetry (with respect to the direction of light propagation) for photoelectrons emitted from a chiral anion. Right: Photoelectron spectrum of the [alaninol-H]- anion and comparison to the calculated binding energies of the uppermost valence orbitals.

After photodetachment of an anion, an electron and a chiral neutral molecule are left behind which is different to the common measurements of PECD in the ionization of a neutral molecule, which leads to an electron and a cation. In photodetachment, the missing long-range interaction of the Coulomb potential may disclose the impact of short-range interactions between the electron and the neutral chiral molecule on PECD. Preliminary theoretical investigations by the groups of Christiane Koch (University of Kassel) and Robert Berger (University of Marburg), applying a plane wave Ansatz for the emitted electron and generalized Dyson orbitals, have demonstrated the absence of PECD for photodetachment processes. Therefore, further efforts are concentrated on slow electrons, for which the plane wave Ansatz for photodetachment is no longer appropriate.

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Guest Researcher in the Department of Molecular Physics
Prof. Dr. Kevin Pagel

Associate Professor of Bioorganic Chemistry at FU Berlin (since 2017)
Assistant Professor at FU Berlin (2014)
Research Associate at FHI (2011)
Post Doctoral Researcher at University of Oxford (2010)
Post Doctoral Researcher at University of Cambridge (2008)
Dr. rer. nat., FU Berlin (2007)

Sugars in the Gas Phase – From Structure to Reaction Mechanisms

The research of the Pagel group is dedicated to the analysis and structural characterization of biological macromolecules and their complexes in the gas phase. There is a long-standing collaboration with the MP department, and in particular the group of Prof. Gert von Helden, with vast mutual interests in ion mobility mass spectrometry (IM-MS) and gas-phase IR spectroscopy. Most of the performed experiments make use of unique capabilities of the FHI-FEL and would not be possible anywhere else.

In the last two years, the Pagel group successfully continued to use gas-phase analytical techniques for the analysis of biomolecules such as amino acid clusters[1] and peptide aggregates,[2] but also non-biological systems such as supramolecular complexes.[3] Without doubt, the most intensely studied class of biomolecules, however, were carbohydrates.

Motivation and Background

Carbohydrates are ubiquitous in nature and represent the most abundant biopolymers found on earth. Historically, they are associated with their prominent roles as structural scaffolds, for example in cellulose, or energy sources as in starch. Most of these polysaccharides are highly regular and exhibit little structural diversity. However, in most living systems shorter and less regular sugar chains, often referred to as oligosaccharides or glycans, are even more important. They play a major role in the sensing of inter- and intramolecular interactions such as in immune responses and are typically altered during disease processes. Similarly to proteins, the function of glycans is directly linked to their structure. In contrast to proteins and oligonucleotides, however, their biosynthesis is not template driven. Instead, it is based on a large number of consecutive assembly and disassembly steps often resulting in branched structures that are characterized by a diverse monosaccharide composition, regio- and stereochemistry. This complexity represents a major challenge for both the chemical synthesis and the analysis of glycans and is one of the reasons why the glycome has remained largely under-explored when compared to the genome and proteome.

A couple of weeks before the last visit of the Fachbeirat, the groups of Kevin Pagel and Gert von Helden showed that gas phase IR spectroscopy experiments can yield surprisingly well-resolved vibrational fingerprints for carbohydrates when performed at low temperature.[4] The obtained spectra are of high analytical value, as they are diagnostic to minute structural changes such as the orientation of a single OH group. This enables the unambiguous identification of oligosaccharides, which cannot be distinguished using established techniques.

Reaction Intermediates from Sugar Chemistry

Aside from the obvious use of cryogenic IR spectroscopy in oligosaccharide analysis, the exceptional resolution recently opened a completely new field of application: the mechanistic elucidation of glycosylation reactions. The chemical synthesis of oligosaccharides has traditionally been very cumbersome and much more elaborate than that of peptides. Most glycosylation reactions proceed via a typical S_N1 mechanism with a key cationic intermediate termed *glycosyl oxocarbenium ion*. These ions exhibit an sp^2-hybridised carbon at the anomeric center, to which a nucleophile can be attached from both sides. As a result, anomeric mixtures, *i.e.* mixtures of the corresponding α and β glycosides are obtained. Even though there are several empirical strategies to direct the configuration of glycosylation products, full stereocontrol is difficult to achieve and a detailed mechanistic understanding is lacking. This is largely a result of the short-lived nature of the reactive glycosyl oxocarbenium intermediates, which cannot be characterized sufficiently using established techniques.

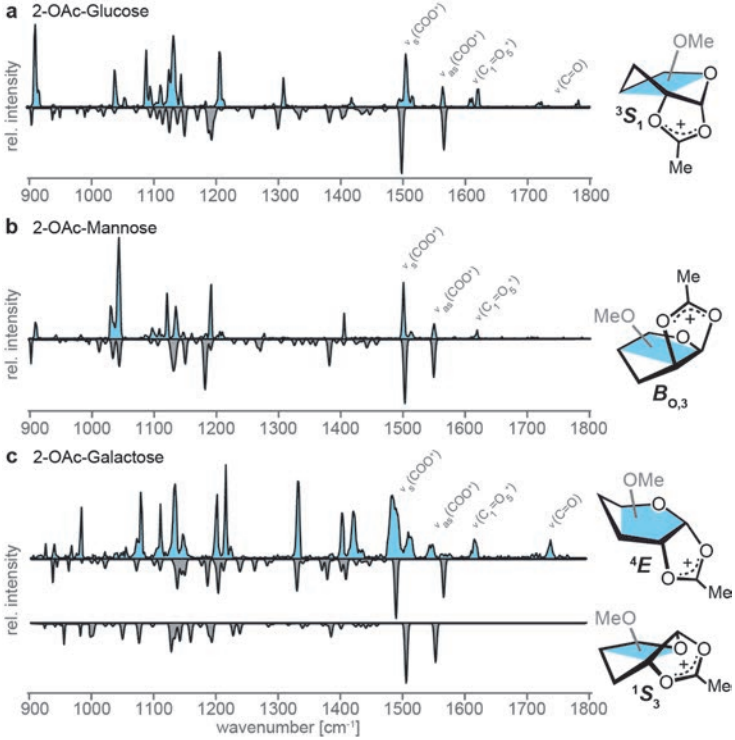

Figure 1: Experimental gas-phase IR spectra (top), theoretical spectra (bottom), and predicted structures (right) of permethylated and C2-acetylated glucose (a), mannose (b) and galactose (c). All monosaccharides form bicyclic acetoxonium ions, but differ significantly in the ring conformation.

In collaboration with partners from the FHI and the Max Planck Institute of Colloids and Interfaces in Potsdam, the Pagel group recently determined the first high-resolution structure of reactive oxocarbenium ions using a combination of cold-ion gas-phase IR spectroscopy and theoretical calculations (Figure 1).[5] The results provided direct evidence for the cation's chemical structure and confirmed two important hypotheses that were under debate for a long time. First, participating acyl protecting groups at the C2 carbon that are often used to control the stereochemistry of the reaction, directly interact with the anomeric carbon and form a covalent bond that leads to a C1-bridged acetoxonium ion. Second, the formation of this acetoxonium ion heavily distorts the ring conformation of the sugar and leads to distinctly different ring puckers such as skewers (S), boats (B), and envelopes (E) for each individual monosaccharide. This distortion of the ring pucker has a tremendous influence on the stereochemical outcome of glycosylation reactions. In a follow-up work, which was recently submitted for publication, it was shown that also participating protecting groups located at *remote* C4 positions can lead to the formation of acetoxonium ions, which in turn can be used to control the stereochemistry of the resulting products.

Elucidation of Sugar Fragmentation Pathways

A second promising application of cold ion IR spectroscopy, which emerged within the last two years, is the analysis of oligosaccharide is fragmentation pathways. Similarly to proteins, the vast majority of oligosaccharides characterized using tandem mass spectrometry based techniques. To do so, precursor ions are isolated in a mass spectrometer and fragmented under controlled conditions. Subsequently, a particular structure is derived based on the molecular mass of the precursor and its fragments. However, the fragmentation of oligosaccharides is compared to proteins considerably more complex and the underlying pathways are mostly unknown. This is further complicated by the frequent occurrence of isomers and unintended rearrangement reactions which can lead to erroneous assignments. As a result, a correct annotation of fragment spectra of oligosaccharides is currently extremely labor-intensive and cannot be automated as common practice in proteomics.

Due to the ionic nature of both precursor and fragments, cold-ion IR spectroscopy can provide valuable insight into the structure of fragment ions and their formation in the gas phase. As a result, the details of the fragmentation of oligosaccharides can be unraveled, which will make it predictable and eventually automatable in the future. As a first step in this direction, we recently elucidated the molecular details of the most prominent oligosaccharide rearrangement reaction in the gas phase: the intramolecular migration of the deoxy sugar fucose.[6,7]

Although fucose migration is generally associated with ion activation and fragmentation during tandem MS experiments, the results provided direct spectroscopic evidence that this reaction can also occur in intact glycan ions. The investigated regioisomeric trisaccharides Le^x and BG-H^2 show highly-resolved, distinct IR spectra as sodium adducts but, surprisingly, yield similar spectra as protonated ions. The results therefore indicate a proton-catalyzed rearrangement to an identical, but so far unknown chemical structure without explicit activation. Fucose migration is therefore a genuine issue in every tandem mass spectrometry experiment. Currently, it is not clear if this potentially ubiquitous rearrangement is a specific feature of a few exotic monosaccharides or if other, more common, building blocks such as mannose show a similar behavior. To approach this question, further experiments are currently in progress.

Perspective

The results obtained in the last two years revealed the exceptional value of cryogenic gas-phase IR spectroscopy in glycochemistry. This not only includes analytically-driven applications such as the sequencing of oligosaccharides, but also the elucidation of fundamental aspects in sugar chemistry such as currently poorly understood reaction and fragmentation mechanisms. In the future, cold-ion IR spectroscopy will therefore be increasingly applied to unravel the chemistry of oligosaccharides. A central aspect of these efforts will be the development of a simple, easy to use experimental setup which can be operated by non-specialists and used in routine applications.

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Prof. Dr. Gert von Helden

Scientist at the FHI (since 2003)
Honorary Professor at the Radboud University Nijmegen,
The Netherlands (since 2017)
Research group leader, FOM-Institute for Plasmaphysics, Nieuwegein,
The Netherlands (2000–2003)
Post-doc at the Radboud University Nijmegen, The Netherlands (1995–1999)
PhD in Chemistry at the University of California at Santa Barbara, CA, USA (1994)

Structure and spectroscopy of gas-phase ions and their clusters

Optical spectroscopy is one of the key techniques to elucidate the structures of molecules and solids. However, many interesting species can only be produced in very low concentrations and traditional techniques that are based on the direct detection of the attenuation of the light that interacts with the sample are not sensitive nor selective enough. Methods that can be used instead are based on the detection of *what the light does to the molecule* and are often termed *action spectroscopy*.

In our research group, we develop action spectroscopy methods that are based on the combination of IR spectroscopy with electrospray ionization (ESI) mass spectrometry to isolate well-defined mass/charge selected species, ion mobility spectrometry (IMS) for the analysis and separation of the geometrical shape and helium droplet isolation techniques to perform IR spectroscopy at ultralow (0.4 K) temperatures.

In this report we highlight two recent experiments that are performed in collaboration with other departments of the FHI and give a brief overview of other ongoing experiments and an outlook on future research.

In one project, we investigate the chemistry of free unsolvated fluoride ions with CO_2 and water. The high proton affinity and small ionic radius of fluoride promote the formation of strong ionic hydrogen bonds in the complexation of fluoride with protic molecules. Fluoride can also act as a potent nucleophile and for example undergo an exothermic reaction with carbon dioxide to yield fluoroformate, FCO_2^-, forming a covalent bond between F and C. We explored the chemistry of F^- with CO_2 and H_2O by applying mass spectrometry coupled to infrared spectroscopy of ions in liquid helium droplets and state-of-the-art *ab-initio* molecular dynamics simulations. The theory part is performed in close collaboration with Dr. Rossi who leads an Otto Hahn group and who is associated to the Theory Department at the FHI.

A second project focusses on polyoxometalate clusters. Condensed-phase polyoxometalates possess unique catalytic and electromagnetic properties and their structure and function is dictated by complex oligomerization processes, which in turn depend on the solution conditions. In a collaborative project with the research group of Dr. Trunschke from the FHI Inorganic Chemistry Department, we used MS, IMS as well as IR action spectroscopy to investigate the condensation process by studying the structures of small molybdenum and vanadium based polyoxometalate clusters.

Reactivity of fluoride ions with CO_2 and water [1,2]

Recently, we observed that gas-phase fluoroformate can be produced by nano-electrospray ionization of aqueous sodium fluoride in the presence of gas-phase carbon dioxide [1]. The mass spectrum obtained when monitoring this process is shown in the left part of Fig. 1. In addition to the observation of fluoroformate (FCO_2^-) at m/z 63, intense signals are observed at m/z 61 and 81. The signal at m/z 61 is readily identified as hydrogen carbonate, HCO_3^-, but the identity of the ion at m/z 81 is not so obvious. Formally, it corresponds to the addition of one water molecule to fluoroformate. The observation that this peak is the strongest in the mass spectrum and that the corresponding ions survive the complex chemistry at the atmospheric pressure side of the ion source as well as the transfer through the instrument indicate an extraordinary stability of the corresponding ions. To elucidate its structure, IR spectroscopy on the m/z 81 ion can be performed. For this, the ions are mass selected and trapped in a radio frequency (RF) ion trap. The trap is traversed by a beam of liquid helium droplets that are at an equilibrium temperature of 0.4 K and superfluid. The droplets can pick-up an ion, cool it to 0.4 K and transport it out of the trap. The doped droplets are then overlapped with the IR-beam of the FHI-FEL. When the IR photons are resonant with a transition of the ion, absorption of light can take place, leading to evaporation of helium atoms. Monitoring the evaporation as a function of photon energy gives an IR spectrum of the ion.

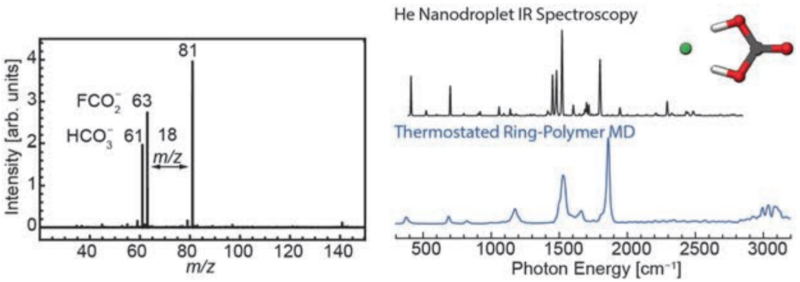

Figure 1 ESI mass spectrum (left) and IR spectrum (right, top) for the m/z 81 ion. Shown on the right. bottom is the theory prediction for carbonic acid complexed with F^-.

The top trace on the right side of Fig. 1 shows the experimental spectrum for the m/z 81 ion. A theory-based structure search revealed a surprisingly large number of different possible structures that are low in energy. To complicate matters, it is observed that standard methods to calculate IR-spectra which are based on the harmonic approximation perform poorly as the dynamics of the species involve strong anharmonic couplings as well as large amplitude vibrations. Therefore, infrared spectra derived from *ab-initio* molecular dynamics simulations were calculated which yield good agreement with experiment and capture the vibrational anharmonicity and mode coupling in the system.

Interestingly, the lowest energy structure is not a complex of the fluoroformate ion at m/z 63 with a water molecule but a carbonic acid molecule complexed with an F⁻ ion (shown in Fig. 1). Its calculated *ab-initio* molecular dynamics derived IR spectrum is shown in the lower trace on the right side in Fig. 1 and agrees well with the experimental spectrum. In this complex, the strong hydrogen-bonding interactions between the fluoride ion and the hydroxy groups of the carbonic acid result in strong anharmonic effects that require high-level quantum chemical methods to be predicted accurately [2].

The structures of small polyoxometalate clusters [3]

Small gas-phase polyoxomolybdate nanoclusters ($(HMo_nO_{3n+1})^{1-}$, n = 1–8, and $(Mo_nO_{3n+1})^{2-}$, n = 2–8) were investigated after nanoelectrospray ionization of an acidified solution of ammonium heptamolybdate heptahydrate by ion-mobility spectrometry–mass spectrometry (IMS – MS), infrared multiple photon dissociation (IRMPD) spectroscopy, and infrared action spectroscopy in helium nanodroplets.

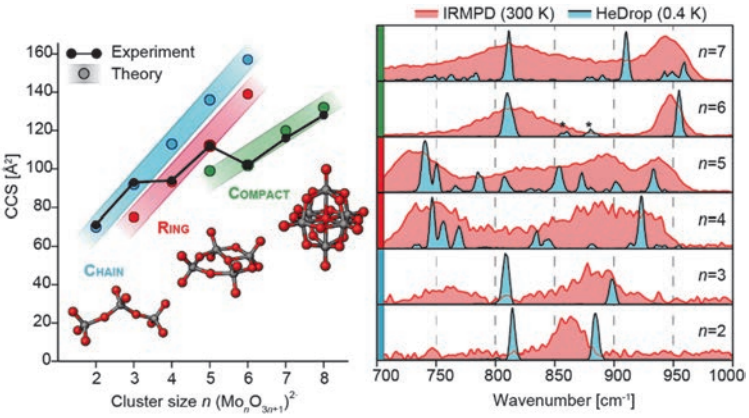

Figure 2: Experimental and calculated CCS values (left) and IRMPD spectra (right, red) as well as He-droplet (right, blue) IR spectra for $(Mo_nO_{3n+1})^{2-}$ clusters.

IMS allows for the determination of the absolute value of the angle-averaged collision cross-section (CCS) in Å². Shown in the left part of Fig. 2 are the experimental cross-sections for the $(Mo_nO_{3n+1})^{2-}$ species as black circles. Notably, the CCS does not increase smoothly with the number of Mo atoms but rather exhibits prominent discontinuities between n = 3 and 4 and between n = 5 and 6 where the CCS actually decreases while the number of atoms increases. The observations are interpreted in terms of a transition between chain (n = 2–3), ring (n = 4–5), and compact three-dimensional (n ≥ 6) structures as the number of atoms increases. This interpretation is confirmed by theory and the circles in color correspond to calculated CCS values for theory-derived structures having chain, ring and compact geometries [3].

Shown on the right side of Fig. 2 are experimental IR spectra taken in two different setups. The broad spectra in red are obtained using IRMPD spectroscopy on room-temperature clusters while the spectra in blue are obtained on clusters that are cooled by trapping them in helium droplets (see previous section). Clearly, the resolution and information content in the helium droplet spectra is much higher, compared to the IRMPD spectra. In both types of spectra, a qualitative difference for the spectra with n= 2 and 3, n = 4 and 5 as well as n = 6 and 7 can be observed, consistent with a global change in structure between these three groups. For the n = 6 cluster, a particular simple spectrum is observed. The observed band pattern is expected for a highly symmetric structure, and indeed, theory predicts the highly symmetric Lindqvist structure to be lowest in energy. Its calculated spectrum features only two bands with frequencies that are in qualitative agreement with the experiment (not shown).

Other ongoing and future projects

Other projects are in the framework of a fruitful collaboration with the group of Prof. Pagel (FU Berlin and FHI guest). This collaboration primarily focusses on the investigation of biological molecules in the gas phase. The systems investigated involve peptides and proteins as well as their aggregates and, more recently, carbohydrates. Especially the spectra of carbohydrates allow for structural differentiations and assignments that are still surprising to us and we will continue along these lines.

Presently, the IMS machine works extremely well and allows to perform spectroscopy on a large range of very well-defined species. However, the machine also has two shortcomings. First, the mass resolution in the time-of-flight mass analyzer is clearly limited. Having now the expertise from other machines, we will upgrade the IMS machine with a more capable mass analyzer. Further, it is clear that IR spectra benefit a lot from the ions being cold as both the spectral resolution and the signal-to-noise ratio are far superior then. To this end, we refined over the last years the helium droplet isolation technique from initially being exotic and difficult-to-perform experiments to a routine technique that works extremely well for both cations and anions in the size range of a few atoms up to proteins containing thousands of atoms. It is planned that in the near future, the IMS setup will be upgraded to allow for spectroscopy on cold ions.

A recent modification in the helium droplet setup allows to vary the temperature of the ions *before* pick-up. Using model systems, we have seen that if two (or more) isomers/conformers are in thermal equilibrium, the equilibrium population can be shock-frozen and retained when being cooled in the helium droplets. The resulting spectrum is then a superposition of the spectra of the individual components, which can be accurately disentangled using machine learning algorithms. This allows to determine the individual spectra as well as populations, and a subsequent van't Hoff analysis allows to deduce thermodynamic information and we will exploit those possibilities for chemically important systems.

Further, very soon the upgrade of the FHI-FEL will allow to perform two-color experiments. This will enable a large range of novel experiments with the (for us) maybe most interesting (but also most challenging) experiment being two-color pump-probe experiments of ions in helium droplets. The helium droplet setup seems ideal for such experiments, as it allows the counting of the number of photons absorbed (by monitoring the number of helium atoms evaporated) while ensuring that each (rapidly following) pulse pair sees re-cooled ions at 0.4K.

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Dr. Sandra Eibenberger-Arias

Group Leader at FHI, Department of Molecular Physics (since 2018)
Post Doc Harvard University, Department of Physics (2015–2018)
Dr. rer. nat. with distinction, University of Vienna, Department of Physics (2015)
Mag. rer. nat. with distinction, University of Vienna, Department of Physics (2010)

Controlled molecules

The Eibenberger group has been established in early 2018. The scientific research in this group is targeted at spectroscopy and control of cold gas-phase molecules. A specific focus is the development of new experimental techniques to spectroscopically investigate and manipulate chiral molecules. For this purpose, a new experimental setup has been developed and, since very recently, first experimental results using microwave spectroscopy and resonant multiphoton ionization spectroscopy have been obtained.

Enantiomer-specific spectroscopy and state transfer of cold, chiral molecules

Chiral analysis remains a challenge in modern chemistry and physics and enantiomer-sensitive detection of gas-phase chiral molecules is especially intriguing. Methods for the determination of enantiomeric excess include optical circular birefringence, circular dichroism, vibrational circular dichroism, Raman optical activity and photoelectron circular dichroism. Most methods to date share the difficulty of identifying enantiomers in mixtures of different chiral molecules. Recently, enantiomer-specific microwave spectroscopy was developed [1,2], a method which is species-, conformer-, isotopologue-, and enantiomer-specific, even in mixtures of different molecules. In conventional microwave spectroscopy, the phase of the recorded free induction decay signal is typically disregarded. Opposite enantiomers possess the same rotational constants and also the magnitudes of the dipole components $|\boldsymbol{\mu}_a|$, $|\boldsymbol{\mu}_b|$, and $|\boldsymbol{\mu}_c|$ are equal. This results in identical rotational spectra. However, the product $(\boldsymbol{\mu}_a \times \boldsymbol{\mu}_b) \cdot \boldsymbol{\mu}_c$ has an opposite sign for the left- and right-handed enantiomers of a species of the C_1 point group. This is utilized in enantiomer-specific microwave spectroscopy, where closed triads of transitions are used which include all three dipole components. The phase of the signal depends upon the signs of the molecules' dipole-moment components and can be used to identify enantiomeric excess.

A natural extension of identification of enantiomeric excess in a sample is the physical separation of the enantiomers. Typical current enantiomer separation methods are based on enantiomer-specific interactions with auxiliary substances [3,4]. These have to be developed and optimized for different molecular species in intricate processes. Recently, enantiomer-specific population transfer using an all-coherent method was demonstrated [5,6]. A three-pulse scheme using phase-controlled microwave pulses that drive electric-dipole allowed a-, b-, and c-type rotational transitions produces state-specific enantiomeric excess in a chosen rotational state.

Current experiments for enantiomer-specific population transfer in cold, gas-phase molecules have solely used microwave radiation. The achievable state-specific enantiomeric excess is mainly limited by the initial thermal population difference in the involved rotational states, resulting in significant population of the undesired enantiomer.

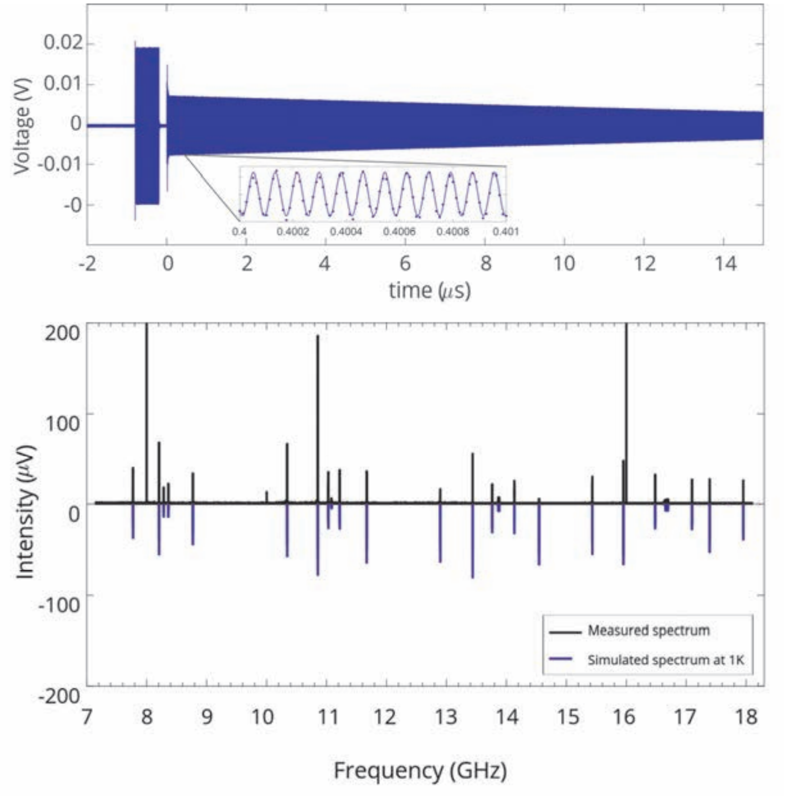

Figure 1: Rotational spectroscopy experiments for characterization of the new experimental apparatus. Upper panel: The noise level of the microwave circuit is low enough to observe a clear free induction decay for OCS molecules. Lower panel: Broadband rotational spectrum of benzonitrile alongside the simulated spectrum at 1 Kelvin.

The Eibenberger group is working on implementing a new, optimized experimental setup for enantiomer-specific spectroscopy and control of chiral molecules. For this, a compact microwave spectroscopy setup including microwave inputs with three perpendicular polarizations has been designed, built and preliminarily characterized. This new experiment allows for microwave spectroscopy experiments in the 2-25 GHz regime, making studies of a large variety of molecules possible. For initial tests of the new apparatus the molecule OCS was used and a free induction decay signal of this molecule's rotational transition at 12163 MHz is shown in the upper panel of figure 1. In the lower panel of figure 1 an experimental rotational spectrum of benzonitrile is shown alongside of its theoretical prediction at 1 Kelvin. These measurements lay an important foundation for future, enantiomer-sensitive measurements with chiral molecules.

When this new tool for enantiomer-specific state transfer is further developed it can be exploited in the future not only for tests of fundamental physics like parity violation in chiral molecules - an effect that so far has been elusive to experimental studies even though it has been predicted for a long time. Also, with extensions using for example electrostatic of dynamic deflection, it will be interesting to study the possibility of its use for physical separation of enantiomers from a mixture.

Electronic spectroscopy of cold, chiral molecules

Resonance-enhanced multiphoton ionization (REMPI) is commonly used for sensitive spectroscopy experiments. It allows for conformer-specific molecular spectroscopy and has been used in the Eibenberger group in combination with time-of-flight mass spectrometry. Therefore, a dye laser which is pumped by a frequency-tripled Nd:YAG laser has been implemented. This method has been chosen to characterize the newly built molecular beam apparatus in which a molecular supersonic jet expansion is created by an adapted pulsed General valve. The adaptations include a heatable sample holder where gaseous, liquid, and solid samples can be seeded into the carrier gas. Various molecular species have been investigated, of specific interest is the molecule 1-indanol. 1-Indanol is a relatively rigid and simple alcohol that has a chiral center and an aromatic ring, making it an attractive molecule to explore. Experiments were performed using Helium, Neon, and Argon as carrier gases. The choice of carrier gas determines the abundance of different conformers of a molecule, as seen in the REMPI sepectra presented in figure 2. When using argon as a carrier gas, only the lowest-energy isomer of 1-indanol is present in the beam. For potential future experiments using rotationally resolved UV spectroscopy it is crucial to know the lifetime of the excited electronic state. The lifetime determines the intrinsic linewidth of the transition and therefore defines whether it is possible to record a UV spectrum with sufficient rotational resolution. For this purpose double resonance experiments were performed. First, a low intensity resonant electronic excitation is achieved using the pulsed dye laser system. With tunable time delay this is followed by off-resonant excitation and ionization using an ArF

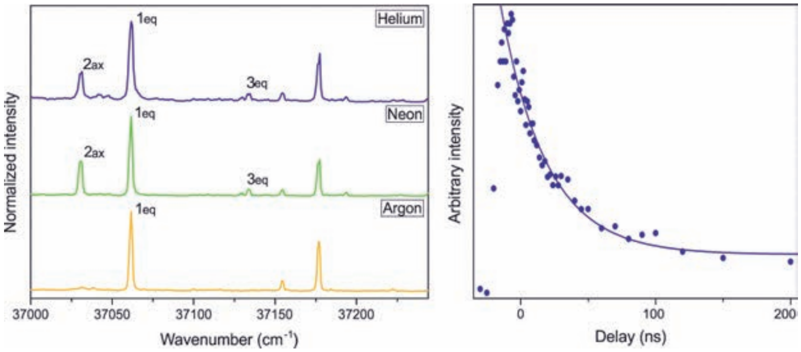

Figure 2: REMPI spectroscopy of 1-Indanol molecules. left: Depending on the used carrier gas, different conformers are present. With Argon as a carrier gas only the lowest energy conformer is observed. right: Lifetime measurement of the excited electronic state S_1 using consecutive irradiation with UV light from a dye laser (37060 cm^{-1}) and an ArF excimer laser (51800 cm^{-1}).

excimer. The resulting time-dependent ion signal is shown in figure 2. The lifetime of the excited electronic state of the lowest energy conformer of 1-indanol is seen to be around 34 ns. Similar measurements have been performed for two other conformers.

Development of a novel slit valve design based on piezoelectric stack actuators

Controlled sources for cold gas-phase molecules are often needed and used in experimental molecular physics and physical chemistry. Pulsed supersonic jet valves are very abundantly implemented for this purpose. Typically, these valves have a pinhole aperture, since these can be opened and closed easily, fast, and efficiently. However, for many spectroscopic experiments it would be desirable for the pulsed valves to exhibit a long, narrow slit as an aperture since slit valves have favourable expansion properties. The technical implementation of such slit valves has shown to be challenging, therefore most past slit valve designs have not found wide application. In the molecular physics department, a new slit valve design based on piezoelectric stack arrays was developed, built, and implemented. The Eibenberger group performed characterization experiments of this new design using atomic Argon as a gas and miniature capacitive microphones for detection. First results are promising for future applications of this pulsed slit valve design in molecular spectroscopy experiments.

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Emeritus Group Leader
Prof. Dr. Bretislav Friedrich

Honorary Professor at the Technische Universität Berlin (2006)
Habilitation Charles University Prague (1996)
PhD in Chemical Physics, Czech Academy of Sciences (1981)

Over the reporting period 2018-2019, the research group carried out work on two projects co-funded by the DFG: (1) Supersymmetry, entanglement, and dynamics of polar paramagnetic molecules in combined electric, magnetic, and optical fields (jointly with Burkhard Schmidt, Freie Universität Berlin); (2) Configurations of van der Waals complexes controlled via London dispersion forces as revealed by means of Stark spectroscopy in He-nanodroplets (jointly with Alkwin Slenczka, Universität Regensburg).

Project (1) concerned the analytic solvability of the quantum pendulum eigenproblem (1a) as well the study of the dynamics of molecules subject to time-varying fields acting on polar and polarizable molecular rotors (1b).

(1a) The quantum pendulum is a prototypical system that lurks behind numerous problems in physics and chemistry. Molecules subject to electromagnetic fields are a most common realization of the quantum pendulum. Unlike other key quantum prototypes, such as the harmonic oscillator, the quantum pendulum lacks, in general, exact eigenproperties, and so its energies and wave functions have to be obtained by solving the corresponding Schrödinger equation numerically. In our previous work based on supersymmetric quantum mechanics (SUSY QM), we found several classes of analytic solutions for both the planar and spherical pendulum as well as established (i) a general connection between the conditions of analytic solvability and the topology of the eigenenergy surfaces, and (ii) a connection between the classes of analytic solutions and the irreducible representations of the pendulum's symmetry group.

Our effort has culminated during the present reporting period in a generalization that relies on the Quantum Hamilton-Jacobi theory (QHJ). We have shown that QHJ (which amounts to taking SUSY QM into the complex plane) provides a systematic way of identifying quasi-analytic solutions of the pendulum eigenproblem and retrieved the conditions of quasi-solvability and the closed-form solutions derived previously within the framework of SUSY QM. Moreover, by applying QHJ, we found a cornucopia of additional closed-form solutions and the conditions under which they obtain.[1]

Furthermore, we showed that both the exact and numerical spectra of the trigonometric pendulum exhibit patterns that are intrinsically related to those of the eigenproblem obtained by the anti-isospectral transformation that converts the trigonometric functions in the pendulum's potential to their hyperbolic counterparts.[2] We note that the analytic solutions found may serve as benchmarks for numerical analysis and that the polynomial Ansatz they suggest offers itself for perturbative calculations in regions of the parameter space where analytic solutions are not available.

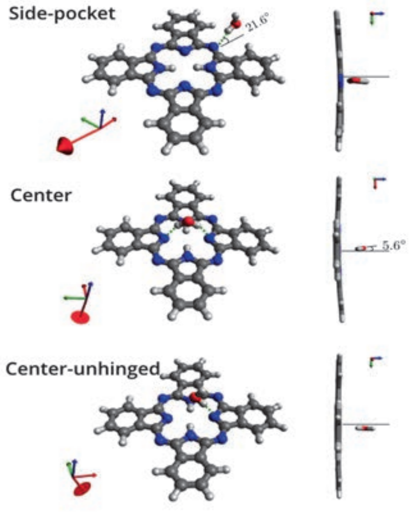
(1b) Understanding the dynamics of quantum systems subject to strong time-dependent electromagnetic fields has been central to research areas ranging from molecular to ultra-fast laser physics and from stochastic to condensed-matter physics. In particular, the study of the effects on atoms and molecules of ultra-short ($\Delta\tau \ll$ picosecond) laser pulses and the kicks, whether single or multiple, they exert has matured into a broad field of research with a plethora of applications in science and technology.

During the reporting period, our work on the dynamics of molecules subject to time-varying fields concentrated on polar polarizable molecular rotors interacting with unipolar pulses, i.e., few or single-cycle pulses with a bias.[3] “Unipolar” pulses are a boon to manipulating molecular rotation: (i) Their short duration (typically less than a picosecond, as compared to nanosecond rotational periods of typical small molecules) ensures a sudden interaction that results in recurring post-pulse orientation/alignment; (ii) The pulse interacts simultaneously with both the permanent and induced electric dipole moments of the molecule, whereby the advantageous combined interactions technique of manipulating molecular rotation is automatically implemented.

In the sudden, non-adiabatic limit, $\Delta\tau \ll \tau_r$, we derived analytic expressions for the rotor’s wavefunctions, kinetic energies, and field-free evolution of orientation and alignment. These provide valuable insights into the workings of kicked-rotor dynamics. We verified the analytic results by solving the corresponding time-dependent Schrödinger equation numerically and extended the temporal range of the interactions considered all the way to the adiabatic limit, $\Delta\tau > \tau_r$, where general analytic solutions beyond the field-free case are no longer available. The effects of the orienting (due to the permanent dipole) and aligning (due to the induced dipole) interactions as well as of their combination on the post-pulse populations of the rotational states were visualized as functions of the orienting and aligning kick strengths in terms of population quilts. Quantum carpets that encapsulate the evolution of the rotational wavepackets provide the space-time portraits of the resulting dynamics. The population quilts and quantum carpets reveal that purely orienting, purely aligning, or even-break combined interactions each exhibit sui generis dynamics. In the intermediate temporal regime, we find that the wavepackets as functions of the orienting and aligning kick strengths show resonances that correspond to diminished kinetic energies (“rotational arrest”) at particular values of the pulse duration.

Project (2) dealt with the solvation and rotation of molecular complexes formed and probed in superfluid helium droplets. The spectra of molecules embedded in helium nanodroplets reflect purely molecular characteristics, helium-mediated attributes, and purely helium-induced features. In numerous cases, the details of the helium-attributed features are either not resolved or rendered insignificant compared with the dominant molecular features that manifest themselves within the zero-phonon line (ZPL). However, it is the helium-induced spectral features that provide valuable information on helium microsolvation, i.e., the interaction of the quantum fluid with a foreign species (impurity) on a molecular scale. Besides the well-known phonon wing (PW), helium-induced features reveal themselves via spectral line shapes, including line splitting. The strength and the anisotropy of the interaction between the helium atoms and the dopant determines the size of the solvation shell(s), thereby directly affecting the rotational behavior of the many-body rotor.

During the reporting period, we undertook a study of the helium-induced features of phthalocyanine[4] and porphine,[5] which revealed that these occur chiefly as two kinds of excitations distinguished by their linewidths and their dependence on the droplet size.



At quasi-bulk conditions achieved with droplets in excess of a million helium atoms, we found that none of these dopants yields an optical spectrum that can be assigned to a plausible rotational band structure at the droplet temperature of 0.38 K. Moreover, the spectral width of each of the peaks observed in the optical spectra is about a half of the width expected for a freely rotating solvation complex in helium droplets. In order to gain insight into this behavior, we invoked the Angulon Theory (AT),[6] developed by Mikhail Lemeshko et al. (IST Austria). Preliminary calculations suggest that the pure rotational excitation spectrum of the angulon (a rotating quasiparticle resulting from the coupling of the rotational degrees of freedom of an impurity dressed by a bosonic bath) is indeed significantly squeezed-in owing to an enhanced centrifugal distortion of the solvation shell. Extended by *ab initio* molecule-helium potential energy surfaces in the ground and excited states, we expect AT to quantitatively explain the observed rotational band structure. An additional study of the glyoxal-helium *ab initio* PESs both in the ground and the lowest excited state is aimed at garnering clues regarding the quasi-free rotation of the glyoxal-helium complex as observed in the optical spectra.

In order to probe inter-molecular dispersion interactions inside the helium environment, we set out to study a polar dopant cluster that could be subject to Stark spectroscopy (which provides structural information via dipole moments and moments of inertia), apart from being of interest in its own right.

The cluster synthesis occurs via consecutive pick-up of the cluster building blocks by the helium droplet, and their subsequent coalescence within the droplet. The effective collision cross section of the building blocks is determined by the helium droplet size and thus exceeds by orders of magnitude that of a reactive collision in the gas phase. Moreover, the cryogenic helium environment as a host promotes the formation of metastable cluster configurations that often elude observation under gas-phase conditions. Our study dealt with clusters of single phthalocyanine (Pc) molecules with single water molecules.[7] A large fluorophore such as Pc possesses several sites where the water molecule can attach. The resulting isomeric variants of the Pc-H_2O complex could be identified by electronic spectroscopy. We compared the experimental electronic spectra of the Pc-H_2O complex with high-level quantum chemical calculations on the same cluster under gas-phase conditions (a basic potential screening DFT approach identifies four possible locations for the water molecule; SOS-CC2 in the density-fitting approximation predicts three stable isomers: side pocket, center, and center unhinged; see figure). Surprisingly, the number of isomeric variants observed in the helium droplet experiment came out the same as that obtained from the above gas-phase calculations.

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Dr. Jesús Pérez Ríos

Group leader in the MP department of the FHI (since 2019)
Assistant Profesor, Turabo University, Puerto Rico (2018)
Postdoctoral researcher, Purdue University, Indiana (2013–2016)
Postdoctoral fellow at the École Normale Supérieure, Paris (2012–2013)
Dr. rer. nat., Universidad Complutense de Madrid, Madrid (Spain) (2012)

Cold and ultracold chemistry

At very low temperatures ($T \lesssim 1K$) it is believed that chemical processes will show its inherent quantum mechanical nature, which would allow understanding the ultimate nature of different chemical reactions. This inherent quantal nature may be exploited to design and control chemical reactions, otherwise unachievable at room temperature. Moreover, ultracold molecules may have applications in quantum information and condensed matter physics [1]. In general, for most of the chemical reactions, at $T \sim 1mK$ only a handful of partial waves contribute to the cross section leading to a full quantal behavior. Thus, for chemical reactions at $T \lesssim 1mK$, it is customary to classify them as ultracold chemistry, whereas reactions at $1mK \lesssim T \lesssim 1K$ are classified as cold chemistry.

In our group, we are interested in the development of different theoretical frameworks to study cold and ultracold chemical reactions involving atoms, molecules, and ions. In particular, we develop theoretical approaches to study the dynamics of charged-neutral systems at (ultra-) low temperatures [1]. We calculate the underlying potential energy surfaces for ultracold molecules by means of *ab initio* quantum chemistry calculations, and by exploring novel inversion techniques to extract molecular potentials from spectroscopy data [2]. We calculate also the dynamics of ultracold molecules in external fields relevant for slowing and cooling of molecules and its scattering properties with different targets. In this line of research, the collaboration with experimentalists is of great importance to develop the proper tools and achieve the ultimate understanding of the intriguing world of chemistry at very low temperatures.

Theoretical cold chemistry

Techniques inherited from classical and semi-classical methods have been adapted to the study of cold ion-neutral-neutral and molecular ion-neutral scattering problems [1,3]. Thanks to this, we can deal with problems that are computationally intractable from a full quantum mechanical treatment, such as the vibrational relaxation of highly excited molecular ions. The new direction in our group is to extend these techniques to the study of vibrational relaxation of molecules in the presence of ions, which are relevant for cold chemistry experiments. We also plan to study three-body recombination of molecular ions and neutrals, which is important for action spectroscopy techniques for molecular ions [4]. These ideas are fueled by fruitful discussions and collaborations with Prof. G. Groenenboom and Prof. S. Brüncken (Radboud University, Nijmegen).

Ultracold chemistry: quantum chemistry, light-matter interactions and scattering

In our group, we calculate accurate ground and excited state properties for molecules relevant for ultracold chemistry experiments through the *ab initio* quantum chemistry methods such as the Muti-Reference Configuration Interaction (MRCI) for excited states, and the Coupled Clusters with Single and Double excitations and Triplet excitations treated perturbatively CCSD(T) method for ground states. These calculations are benchmarked against the available spectroscopy to understand the origin of theoretical uncertainty and how it can be reduced.

In the near future, we plan to develop the potential energy surface for AlF +He and AlF+AlF to study different scattering processes relevant for current experiments in the group of Dr. Truppe. At the same time, we will keep working on modeling laser-AlF interactions to understand and optimize the cooling and trapping of such molecules.

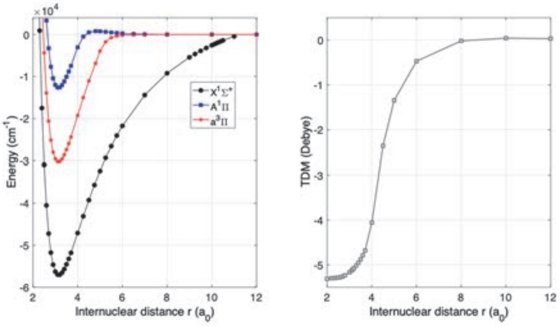

Figure 1: Ab initio quantum chemistry calculations. Left panel, potential energy curves for the relevant electronic states for laser cooling of AlF molecules. The ground electronic state has been calculated at the CCSD(T) level of theory whereas the a and A sates are calculated at the MRCI level of theory. Both calculations are carried out employing the av5Z basis set. Right panel, transition dipole moment for the X-A transition in AlF at the MRCI level of theory.

Physics beyond the standard model with atoms and molecules

The field of molecular physics has fantastically evolved in the last two decades leading to measurements of fundamental properties of atoms and molecules with unprecedented precision as well as to an exquisite control over their internal degrees of freedom. With these developments, atoms and molecules are the perfect playgrounds to test some aspects of the standard model of particle physics, unable to be elucidated within the paradigm of accelerator particle physics [7]. In the same vein, atoms and molecules may be suitable to search for the existence of new physics beyond the standard model [7].

In our group, we exploit the unique properties of atoms and molecules to propose new ways to put constraints on the available parameter space for the existence of new physics beyond the standard model, which is explained in some detail below. In particular, we make use of the fact that molecules have energy levels on the meV - 10 eV, which makes them perfect candidates to explore the existence of light-dark matter [8], otherwise unachievable with conventional accelerator particle physics techniques. Moreover, we use high precision spectroscopy of atoms and molecules to study new physics beyond dark matter such as the existence of a fifth force [9]. Therefore, in our view, molecular physics arises as a complementary field to high energy physics for elucidating the open questions in cosmology and particle physics.

Dark matter detection through molecular excitations

We propose to use molecules as detectors for light dark-matter by looking at the excitation spectra of the molecules under very well-controlled conditions. The main idea is to use the fact that dark-matter colliding with a molecule may induce a vibrational excitation through momentum exchange with the nuclei of the molecule as illustrated in Fig.2. Then, the excited molecule will decay by emitting several photons depending on the pressure and temperature of the gas, which is the to-be-detected signal. In particular, we employ CO owing to its unique collisional properties and its very well-known spectroscopic parameters. Our approach is sensitive to spin-independent as well as to spin-dependent dark matter-nucleus interaction models [8].

Currently, we are exploring the possibility of using spectroscopic data for CO from radio-astronomy to put constraints on the different dark-matter models, using star-forming and cooling rates and supernovae properties.

Precision spectroscopy in exotic atoms as a probe for new physics

Leptonic atoms such as positronium (Ps, the bound state of a positron and an electron) and muonium (Mu, the bound state of an antimuon and an electron) offer a clear playground to constrain the parameters space for new physics models owing to the absence of nuclear effects that may complicate the energy spectra of the atom. As a result, we find that the Ps atom may not be a good candidate based on

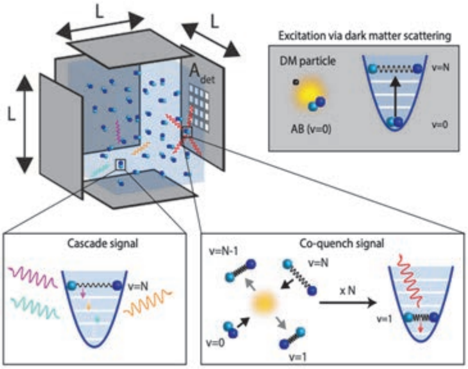

Figure 2: Scheme for dark matter detection with molecules. We envision a tank filled with diatomic polar molecules in gas phase. The temperature of the gas is chosen to ensure that most of the molecules are in their vibrational ground state. Then after a dark matter (DM) particle hits a molecule it gets excited (upper right panel). After this, the molecule will de-excite by emitting a different number of photons through to main decay mechanisms (lower panels), which is our readout signal.

the current state of the art precision spectroscopy, but Mu is [9]. Currently, in collaboration with Prof. D. Cassidy from University College of London, we are exploring the possibility of enhancing the precision spectroscopy techniques in Ps to be sensitive to new physics.

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Dr. Wieland Schöllkopf

Head of the FHI FEL Facility (since 2009)
Group leader FHI Dept. MP (since 2004)
Postdoc FOM Institute Rijnhuizen, NL (2003)
Postdoc Harvard University & Harvard-MIT Center for Ultracold Atoms, Cambridge, MA, USA (2000–2002)
Dr. rer. nat., Universität Göttingen (1998 with Prof. J.P. Toennies)

Introduction

In our Atom Optics project we take advantage of the wave-particle duality of atoms and molecules, which is arguably one of the most profound features of quantum mechanics. We investigate diffraction and other wave-specific phenomena such as, e.g., quantum reflection of a molecular beam from a solid sample. The sample can be either a micro-structured solid (diffraction grating) or a homogeneous surface of particular interest such as, for instance, hexagonal boron nitride (h-BN). In our experimental setup the molecular beam scatters from the sample under grazing incidence conditions with a glancing angle on the order of magnitude of 1 mrad (see Fig. 1). Under these extreme conditions the velocity component normal to the surface is very small and can be continuously adjusted by varying the angle of incidence. Hence, the incident atom's or molecule's de Broglie wavelength corresponding to the normal component can be very large. As a result, grazing incidence geometry allows us to observe quantum effects, in particular diffraction and quantum reflection, as it would otherwise be possible only at ultracold temperatures, as long as the translational motions normal and parallel to the surface stay decoupled.

These experiments are carried out at the FHI in long-term collaboration with Prof. B.S. Zhao and his group from the Ulsan National Institute of Science and Technology (UNIST), South Korea. Students from this group have joined our lab repeatedly for periods ranging from a few weeks to several months.

Matter-wave diffraction from a periodic array of half planes

In one line of experiments we have observed reflection and diffraction of beams of He atoms and D_2 molecules from square-wave gratings of a 400-μm period and strip widths ranging from 10 to 200 μm at grazing-incidence conditions. In each case we observe fully resolved matter-wave diffraction patterns including the specular reflection and diffracted beams up to the second diffraction order. With decreasing strip width, the observed diffraction efficiencies exhibit a transformation from the known regime of quantum reflection from the grating strips to the regime of edge diffraction from a half-plane array (see Fig. 1b). The latter is described by a single-parameter model developed previously to describe phenomena as diverse as quantum billiards, scattering of radio waves in urban areas, and reflection of matter waves from microstructures. Our data provide experimental confirmation of the widespread model.

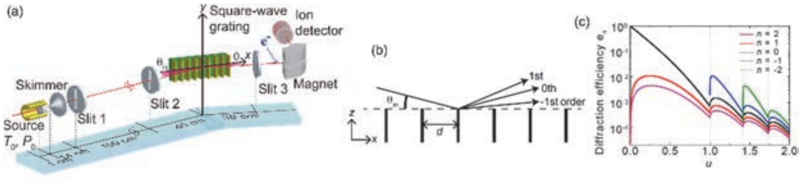

Figure 1: (a) Schematic of the experimental setup. Incidence angle θin and detection angle θ are measured with respect to the grating surface plane (xy plane). The reflection gratings are 50-mm-long micro-structured arrays of 4-mm-long parallel strips made out of 1-μm-thick photoresist patterned on a commercial gold mirror. The centre-to-centre distance of the strips defines the period d = 400 μm identical for all gratings. Gratings with different strip widths of 10, 30, 100, or 200 μm have been used. (b) Schematic of the idealized situation of diffraction from an array of half planes (corresponding to vanishing strip width). (c) Diffraction efficiencies calculated by the single-parameter theory of half-plane array diffraction (Bogomolny-Schmid model), which we confirmed in the experiment.

In addition, our results demonstrate that neither classical reflection nor quantum reflection are essential for getting coherent reflection of matter waves from a structured solid, but it can result exclusively from half-plane edge diffraction. Thus, we have identified edge-diffraction as a third viable mechanism for coherent matter-wave reflection in addition to classical and quantum reflection. This opens the possibility to achieve enhanced reflectivity for atoms and molecules that exhibit inefficient classical or quantum reflection. We have now applied this purely diffractive reflection mechanism to enhance the reflectivity of fragile He_2 and He_3.

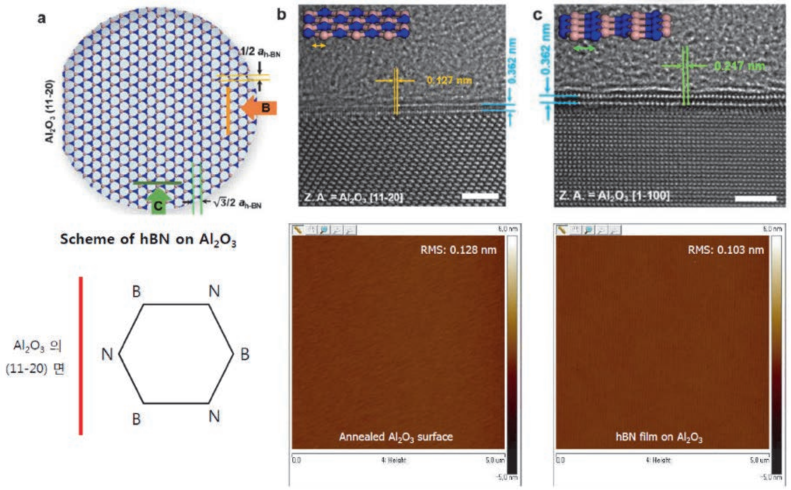

Figure 2: Few-layer hexagonal boron nitride (h-BN) samples have been made for our experiment at UNIST facilities in Ulsan, Korea. (a) The highly ordered h-BN is fabricated on top of a sapphire substrate. (b) STM images of the substrate indicate the high quality (small roughness) of the sapphire. (c) A trilayer h-BN film was formed atop the sapphire. It is characterized by excellent smoothness over a macroscopic surface area of 3 x 3 cm^2.

Scattering of helium atom beams from hexagonal boron nitride

In a new line of experiments we have studied quantum reflection of atoms and molecules from a hexagonal boron-nitride (h-BN) surface. Recently, few-layer h-BN has found interest from theory and experiment alike, because of its unusual electronic and structural properties. Due to the latter, this material is a good candidate for efficient quantum reflection of atoms or molecules. In quantum reflection a particle's wave-function is reflected at the attractive particle-surface Casimir-van der Waals potential. It can only be observed at extremely low incident kinetic energies. We employ grazing incidence of a highly collimated molecular beam onto a h-BN surface to achieve an extremely small perpendicular component of the incident momentum. This allows us to observe quantum reflection of He atoms or D_2 molecules at levels ranging up to tens of percent.

Large-area samples of high-quality h-BN have been fabricated for our experiment at a facility at UNIST in Korea. Figure 2 shows images of a tri-layer h-BN film on a sapphire substrate. Both h-BN and sapphire surfaces are characterized by a small level of roughness. However, only the h-BN surface shows a peculiar (and unexpected) behaviour when we measure the coherent, specular reflectivity of a He atom beam. In contrast to the surface of the sapphire substrate (and in contrast to other surfaces we have studied in the past), we find pronounced oscillations in the reflectivity curves. Figure 3 shows the He reflectivity plotted as a function of the normal component of the helium atom's incident wave-vector for a variety of incident kinetic energies expressed in terms of the incident de Broglie wavelength. All curves exhibit oscillations with the minima forming sharp resonances for some conditions.

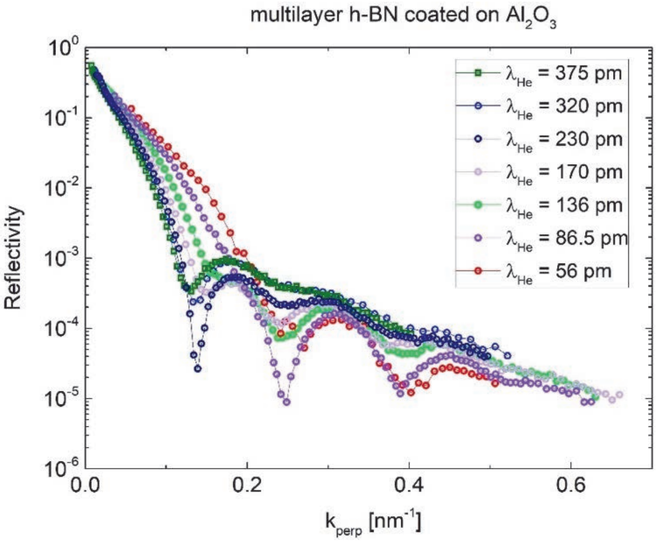

Figure 3: Observed specular reflectivity of He atoms from a tri-layer sample of h-BN as a function of the normal component of the incident wave-vector. Different colors indicate different He atom beam velocities expressed in terms of the He atom's de Broglie wavelength. For some conditions pronounced and recurring minima (resonances) are observed.

The origin of these resonances has not yet been identified. Possible explanations could be related to selective adsorption, to phonon interactions, or to interference effects between the channels of classical reflection and quantum reflection. As the h-BN surfaces are of high quality with respect to roughness, adsorbates, contamination, we consider it conceivable that relevant information about the h-BN layer and/or the interaction between the He atom and the h-BN can possibly be revealed. We plan to extend the measurements to other probes including Ne atoms or D_2 molecules and to other h-BN samples as e.g. mono-, bi-, or multi-layer h-BN. Furthermore, we hope to gain more insight from theoretical studies of the h-BN—He system.

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Dr. Stefan Truppe

Group Leader at Fritz-Haber-Institut, Molecular Physics (since 2017)
Postdoctoral Researcher, Imperial College London (2015–2017)
EPSRC Doctoral Prize Fellow, Imperial College London (2014)
Ph.D., Imperial College London (2013)

Cold and ultracold molecules

The main focus of the research group is cooling molecules to ultracold temperatures of 1 mK and below using laser light. Laser cooling of dilute atomic gases has revolutionized modern atomic physics. It enabled new technologies such as the most precise atomic clocks, new sensitive magnetometers, gyroscopes, gravity gradiometers, and many more. It also enabled breakthroughs in fundamental science such as the first Bose-Einstein condensate, the atom laser, and the first quantum computers and simulators. Ultracold gases afford unprecedented energy resolution and are now routinely used to test general relativity, quantum electrodynamics, the Standard Model of particle physics and even new theories of dark matter and dark energy. The high resolution also enables to probe and manipulate the interactions between the constituent particles of these ultracold gases. When the particles collide, the energy spectra show sharp resonances because their de Broglie wavelength is comparable to their interparticle spacing. The density of these resonances scales dramatically with the increasing complexity of the particles. This behavior gives rise to random fluctuations and states of ultracold matter that are driven by quantum chaos.

Cooling molecules to ultra-cold temperatures will have a similar impact on the field of molecular physics and physical chemistry. Ultracold molecules can be used to study chemistry and collisions at ultracold temperatures, to test fundamental symmetries through precision measurements to provide a new platform for quantum information. The strong and long-range dipole-dipole interaction of polar molecules offers unique possibilities to investigate the properties of strongly interacting quantum matter, to realize quantum computation and simulation protocols.

Direct laser cooling of molecules

The direct laser cooling of molecules is still in its infancy but progressing at a rapid pace. The first magneto-optical trap (MOT), the workhorse technique in cold-atom physics, has been demonstrated in 2014 for the diatomic radical SrF [1]. Two more species, CaF [2,3] and YO [4], have been trapped and cooled in a MOT since then. The laser cooling of YbF, BaF, BaH, TlF, MgF and the polyatomic species SrOH, CaOH, and YbOH are currently being pursued. Since the first demonstration of a molecular MOT, the achievable temperature of a molecular gas has decreased from 2 mK [1] to 5 μK [6, 7], and the density at such low temperatures has increased from 600 cm^{-3} [1] to 10^5 cm^{-3} in a magnetic trap [7] to 10^8 cm^{-3} in an optical dipole trap [6]. The molecules are cold enough to be used as sensitive probes for time-reversal and parity symmetry violating forces or to test a potential time variation of fundamental constants such as the fine-structure constant or the proton-to-electron mass ratio. To be able to study new quantum phenomena, even lower temperatures, and higher densities are required. For example, to observe a phase transition to a degenerate gas of polar molecules a phase-space density $\rho = n\lambda_{dB}^3 > 1, \lambda_{dB} = \sqrt{2\pi\,\hbar^2/(m\,k_B\,T)}$ is required. Here n is the density of the molecules and λ_{dB} is their thermal de Broglie wavelength. Currently, ultracold molecular samples produced by laser cooling have a phase-space density of about 10^{-12}-10^{-10}. To improve this, both, the number of molecules delivered to the MOT must increase significantly, and the temperature must be lowered by another order of magnitude.

Laser cooling aluminium monofluoride (AlF) molecules

We decided to investigate the direct laser cooling of aluminium monofluoride (AlF) molecules to address these issues. This molecule offers many new possibilities. The ground electronic state is a $X^1\Sigma^+$ state and the molecule has a binding energy of 6.9 eV. It forms as a stable constituent of aluminium-fluorine systems at high temperatures. These properties are ideal for producing a particularly bright molecular beam, either pulsed or continuous. For direct laser cooling to work a molecule must undergo about 10^4 cycles of photon-absorption and emission. The $A^1\Pi$, v=0 state of AlF has a lifetime of 1.9 ns, which is about ten times shorter compared to CaF and SrF. The $A^1\Pi$, v=0 ← $X^1\Sigma^+$ v″=0 transition occurs near 227.5 nm and has a very diagonal Franck-Condon matrix. The short lifetime, short transition wavelength, and favorable Franck-Condon factors permit applying an exceptionally strong optical force to the molecules. This reduces the stopping distance for a molecular beam with a speed of 150 m/s to a few cm only. Two lasers are required; one to drive the strong Q(1) line of the $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band and a second laser to address molecules that are optically pumped to $X^1\Sigma^+$, v″=1. The MOT has an exceptionally large capture velocity of > 40 m/s, limited by the currently available laser power in the UV. Once captured in the MOT, the molecules cool rapidly to the Doppler temperature $T_D = \hbar\Gamma_A/(2k_B) = 2\ \mathrm{mK}$, where $\Gamma_A = 1/\tau_A$ is the linewidth of the transition and τ_A the lifetime fo the $A^1\Pi$, v=0 excited state. To decrease the temperature further, the molecules can be cooled on the much narrower $Q_2(1)$ line of the $a^3\Pi_1$, v=0 ← $X^1\Sigma^+$, v″=0 band near 367 nm. This line is so narrow that it permits Doppler cooling of the molecules to the recoil temperature $T_r = \hbar^2k^2/(2mk_B) = 4\ \mu\mathrm{K}$. Narrow-line cooling is a very powerful tool to decrease the temperature and increase the density rapidly. This technique is used successfully to increase the phase-space density of laser-cooled alkaline earth atoms by over five orders of magnitude compared to a MOT that operates on a strong transition. It is so powerful that it permits laser cooling directly to quantum degeneracy [8]. However, narrow-line cooling has not been used to cool molecules yet.

Spectroscopy first

Strong absorption bands of AlF have been recorded already in 1939 by heating AlF_3 in a graphite furnace. Since then, spectroscopic measurements have identified seven triplet and eight singlet excited states. Precise spectroscopic parameters to describe the rovibronic structure in both singlet and triplet manifolds have been determined, but the hyperfine structure remained elusive. Prior to laser cooling experiments, it is essential to measure the hyperfine structure in the ground state, the lowest singlet and triplet excited states, the degree of spin-orbit coupling between the electronic states, the vibrational branching ratios and the electric dipole moments. We set up a compact molecular beam machine to obtain all the information we needed for subsequent laser cooling and trapping experiments.

We started by measuring the spin-forbidden $a^3\Pi_1$, v′=0 ← $X^1\Sigma^+$, v''=0 band because its long radiative lifetime allows high resolution. We drive the transition with a frequency-doubled pulsed dye laser followed by ionization using an ArF excimer laser. We mass-select the ions in a time-of-flight mass spectrometer and detect the AlF^+ parent ions using a microchannel plate. The spectra do not reveal the hyperfine structure but show that this band becomes predominantly allowed due to spin-orbit coupling with the $A^1\Pi$ state. To reach a higher resolution, we use a frequency-doubled, CW Ti:Sa laser to excite the molecules. These high-resolution spectra partially reveal the hyperfine structure in $a^3\Pi_1$, v=0, J=1. We also measure the weak spin-forbidden $a^3\Pi_0$, v′=0 ← $X^1\Sigma^+$, v''=0 band with a frequency-doubled dye laser and the very weak $a^3\Pi_2$, v′=0 ← $X^1\Sigma^+$, v''=0 band using a frequency-doubled pulsed dye amplifier. The spectra show that the interaction with $^1\Sigma$ states is about one order of magnitude weaker compared to the interaction with the $A^1\Pi$ state.

Using two ArF lasers in a pump-probe configuration, we determine the ionization cross-section at 193 nm to be 36 ± 5 Mbarn. We also use a frequency-doubled pulsed dye laser for state-selective resonance-enhanced multi-photon ionization from the $a^3\Pi$, v=0 state via the $c^3\Sigma^+$ state. This ionization technique enables us to detect background-free radio-frequency and microwave transitions between Λ-doublet components in the $a^3\Pi$, v=0 state. We record a total of 138 laser-radio-frequency-laser triple resonance spectra of AlF in the $a^3\Pi$, v=0 state for rotational levels up to J=7. This way, we determine the hyperfine levels with kHz accuracy. By fitting the energy levels to the eigenvalues of an appropriate Hamiltonian, we determine the hyperfine spectroscopic parameters for the $a^3\Pi$, v=0 state for the first time. Using the obtained spectroscopic parameters, we calculate the hyperfine levels with kHz accuracy in all three Ω-manifolds of $a^3\Pi$, v=0 and for rotational levels up to J=10. Using the measured hyperfine intervals we calculate the magnetic g-factors with high accuracy and find excellent agreement between theory and experiment.

We measure laser-microwave-laser-laser quadruple resonance spectra of the $X^1\Sigma^+$, v=0 state to determine its hyperfine structure and rotational constants with kHz accuracy. The detailed knowledge of the $a^3\Pi$, v=0 state enables us to resolve hyperfine splittings in the $X^1\Sigma^+$, v=0 state that are comparable to the widths of the rf and microwave transitions. We confirm that the hyperfine splitting in the $X^1\Sigma^+$, v=0 state is smaller than the linewidth of the main laser cooling Q(1) line of the strong $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band.

We measure laser-induced fluorescence spectra of the $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band to determine the hyperfine interaction, rotational constants and lifetime of the $A^1\Pi$, v=0 state. The spontaneous decay rate from the $A^1\Pi$, v=0 state is measured to be $\Gamma_A = 2\pi \times (83.8 \pm 1.3)\ \mathrm{MHz}$. The hyperfine structure in the J=1 level resembles the hyperfine structure in the J=1 level of the $a^3\Pi$, v=0 state. All Q-lines of the $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band are rotationally closed and can be used for laser cooling. There is a small residual rotational branching due to the mixing of rotational levels via the hyperfine interaction. We calculate the relative loss from the optical cycling transition using the measured hyperfine interaction energies to be below 10^{-5}.

We measure the vibrational branching ratio to $X^1\Sigma^+$, v″=1 to be $(0.56 \pm 0.02) \times 10^{-2}$. To compare the experimental results with theoretical predictions, we construct accurate potentials using our, and previously measured data. To predict the vibrational branching ratio with high accuracy, we include the variation of the transition dipole moment with the internuclear distance. This way, we find good agreement between theory and experiment. By addressing the vibrational loss channel with a repump laser it is possible to scatter about 10^4 photons before the molecules are optically pumped into the $X^1\Sigma^+$, v″=2 level. We observe the weak $R_1(0)$ and $Q_1(1)$ lines of the spin-forbidden $A^1\Pi$, v=0 ← $a^3\Pi$, v′=0 band of AlF for the first time. We measure their intensity relative to the R(0) and R(1) lines of the $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band to determine a relative loss from the optical cycling transition to 10^{-7}.

To conclude the spectroscopic measurements of AlF we record laser excitation spectra of the $a^3\Pi_1$, v′=0 ← $X^1\Sigma^+$, v″=0 band and of the $A^1\Pi$, v=0 ← $X^1\Sigma^+$, v″=0 band in electric fields of up to 150 kV/cm to determine the electric dipole moments. In the $X^1\Sigma^+$, v=0 state, in the $a^3\Pi$, v=0 state and in the $A^1\Pi$, v=0 state we find $\mu(X) = 1.515 \pm 0.004$ Debye, $\mu(a) = 1.780 \pm 0.003$ Debye and $\mu(A) = 1.45 \pm 0.02$ Debye, respectively. Knowing the energy level structure and dipole moments in each of the electronic states enables us to simulate the Stark spectra for fields up to 150 kV/cm.

Cryogenic buffer gas molecular beam

Motivated by the positive outcome of the spectroscopic measurements, we set up a new cryogenic buffer gas molecular beam machine. Compared to a supersonic molecular beam, a buffer gas source typically produces a significantly brighter molecular beam with a lower mean velocity. The source design follows the one presented in reference [9]. A continuous flow of cryogenic helium gas is mixed with SF_6 (300 K) and flows through a copper cell that is cooled to 3 K. We use a pulsed Nd:YAG laser to ablate an aluminium rod that sits inside the copper cell. The hot aluminium reacts with the SF_6 and forms hot AlF molecules. The molecules cool via collisions with the cryogenic helium and exit the cell through a small aperture in the cell. We routinely produce molecular beams that contain 5×10^{12} molecules/sr/pulse, a mean forward velocity of 170 m/s, and a rotational temperature of 4 K. This AlF beam is about 100 times brighter than the equivalent CaF molecular beam [9]. It is so bright that we can measure a peak density of 10^8 cm^{-3} via absorption of a resonant laser beam at a distance of 35 cm from the source.

Conclusion

The spectroscopic measurements show that AlF is an excellent candidate for laser cooling and electric field manipulation [10]. The strong optical force, in combination with an exceptionally bright molecular beam source, and the possibility for narrow line cooling will allow efficient laser cooling to very low temperatures and a high density.

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Dr. Bernd Winter

Group Leader at Fritz-Haber-Institut, Molecular Physics (since 2017)
Staff Scientist - Deputy Head of Division, Helmholtz-Zentrum Berlin (2008–2016)
Staff Scientist, Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin (1994–2008)
Postdoctoral Researcher, Max Planck Institute for Plasma Physics (IPP), Garching (1991–1994)
Postdoctoral Researcher, Argonne National Laboratory, USA (1989–1991)
Dr. rer. nat. (Physics), Freie Universität Berlin (1988)

Liquid-jet photoelectron spectroscopy

Research in the Winter group focuses on the electronic structure interactions in liquid water and aqueous solutions of common electrolytes, many organic and inorganic solute molecules, including amino acids, DNA, and of (transition-) metal nanoparticles dispersed in water. In our experiments we apply liquid-microjet photoelectron spectroscopy (LJ-PES), mostly in conjunction with monochromatized soft X-rays from synchrotron light facilities, BESSY, DESY, SOLEIL, or Spring-8.

Electronic structure information is intimately connected with the fundamental properties of liquid water and aqueous solutions. For example, we measure lowest ionization energies from water solvent and from solutes which directly relate to chemical reactivity. [1] On the other hand, core-level PES from aqueous solutions, often measured at some ionization threshold (opening multiple unique electronic relaxation channels, local and non-local), [2] reveals information on the local chemical environment. We can then quantify, *e.g.*, ion pairing, charge states, dynamical hydration configuration, hydrogen bond strength, intermolecular charge and energy transfers, ultrafast nuclear dynamics and chemical transformation, the density profile of solute species across the aqueous solution–vacuum interface, interfacial and bulk-solution chemical equilibria. Moreover, experimental photoelectron angular distributions (PAD) reveal the effect of hydrogen bonding on orbital character of aqueous species. This refers to the commonly measured PAD in the dipolar plane from which the β_2 anisotropy parameter is obtained. *[3]*

Terrestrial organisms display differentiated responses to chiral molecules encountered in their environment (pheromones, odors, pharmaceuticals) and in very many cases these interactions may incorporate (partial) solvation effects. This generates interest in fundamental investigations conducted in such conditions. We plan to extend the ability of LJ-PES to probing chirality in aqueous phase by introducing photoelectron circular dichroism (PECD; see below) to LJ-PES.

Our group has also a strong interest in advancing the LJ-PES technique by developments of unique and efficient electron detectors compatible with liquid jets, and we also work on novel designs of flat microjets. The latter is

indispensable for PAD measurements and also provides means for inducing slow chemical reactions by mixing of solutions.
Herein, a few selected activities are briefly described.

Unique liquid-jet PES setup for angular distributions

We are currently commissioning a novel LJ-PES setup "*EASI*" (Electronic structure from Aqueous Solution and Interfaces), consisting of a SCIENTA HiPP3 electron analyzer, a unique architecture of the principal interaction chamber, and novel liquid jet designs. *EASI* is capable of detecting PADs from aqueous solution in the dipolar plane. [3] An additional unique and novel feature is that PADs can be measured in the direction of light propagation, enabling the detection of the chiral parameter, β_1.

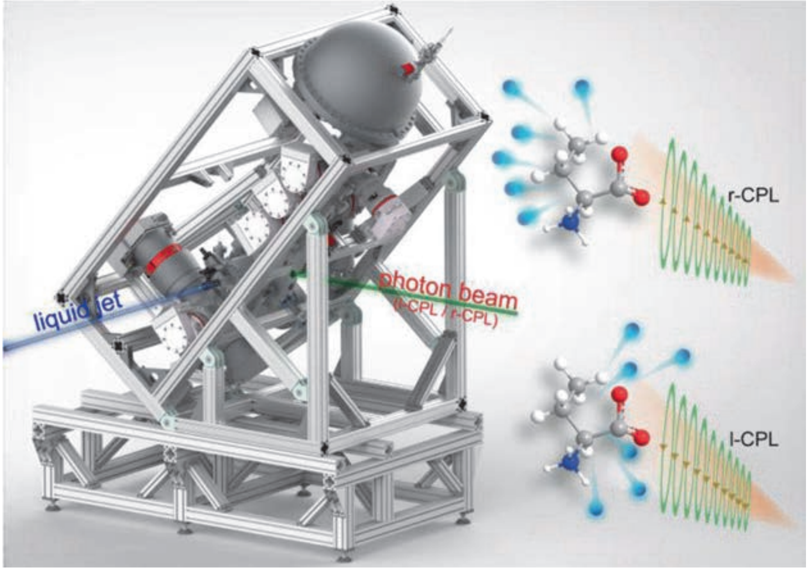

Figure 1: *EASI* setup. In the off-dipole plane geometry shown (one of several possible arrangements) electrons are detected in the opposite direction of propagation of the left, right circularly polarized light. Detection angle is fixed near the magic angle.

Specifically, we aim at detecting photoelectron circular dichroism (PECD) [4] from chiral molecules in aqueous solution. Photoionization of a chiral molecule by left- or right- circularly polarized light (l,r-CPL) introduces a forward – backward asymmetry in the flux of the ejected electrons (illustrated in Figure 1) with respect to the direction of light propagation. The difference seen between l,r-CPL, for a given enantiomer and given detection angle, defines the actual PECD. It exhibits the strongest (from a few to a few tens of percent) chiroptical asymmetry that can be observed in randomly oriented systems, and thus exceeds conventional circular dichroism by 2-3 orders of magnitude. This is because PECD arises from pure electric dipole interactions. PECD can be used to specifically probe chiral properties of each orbital contributing to the electronic structure without prerequisites, while at the same time retaining information on electronic charge distributions and oxidation states known from PES.

We now combine novel photoelectron circular dichroism (PECD) and LJ-PES to detect enantiomer-specific electronic structure. In our first experiments, aiming at demonstrating liquid-phase PECD for valence and core-level ionization, we study liquid fenchone; fenchone is a liquid at room temperature, and is thus well suited for LJ-PECD studies. Subsequent LJ-PECD studies will be performed from amino acids and sugars in water.

Another unique characteristic of *EASI* is the capability to detect the full PE spectra from aqueous solution, providing access to the solution work function.

Aqueous-phase nanoparticles

We have recently studied the intermediate metal-oxo oligomers that lead to nanoparticle (NP) formation in aqueous solutions, exemplarily for iron-(III) aqueous solutions at various pH. Here, addition of NaOH initiates Fe^{3+} hydrolysis, followed by the formation of iron-oxo oligomers. By a combination of direct PES and resonant PES (RPES) at the Fe 2p edge we could identify the electronic signature of these precursors. These studies led us to investigate the interaction of water with iron-oxide hematite, α-Fe_2O_3, 6 nm diameter nanoparticles (NP), a material of large interest in current energy research, with focus on its use in photo-electrochemical water splitting. The unique advantage of using NPs dispersed in liquid water (an “all-in-solution” surface-study approach) is that the NP surface is exposed to true bulk liquid solution environment, enabling controlled variation of pH. [5]

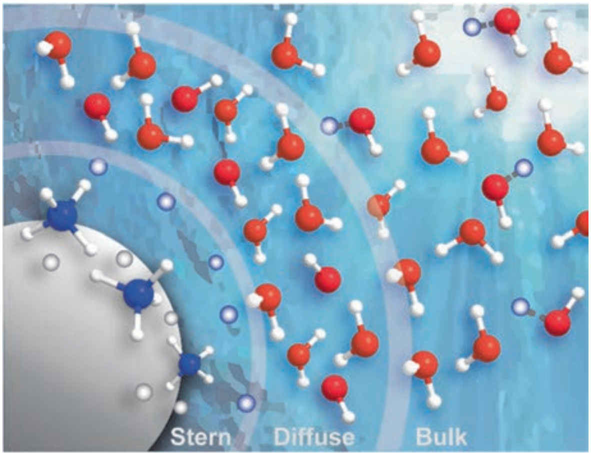

Figure 2: Model of the charge (NH_4^+, OH^-) distributions in the electric double layer (EDL) around a TiO_2 NP in 0.3 M NH_4OH aqueous solution (required to stabilize the NPs in water). An unexpectedly high concentration of OH^- ions, from water dissociation, can be accommodated within the diffuse layer. We argue that some of the protons from water dissociation are responsible for neutralization reactions in bulk solution.

Our work on Fe_2O_3 NPs has motivated the current investigations on aqueous-phase anatase TiO_2 NPs (20 nm); as low as possible NH_4OH concentration was used to stabilize the NPs in solution. By a combination of resonant and non-resonant PES at the oxygen 1s and nitrogen 1s edges (and including the respective resonant inelastic X-ray scattering, RIXS, measurements), water is observed to adsorb molecularly on the NP surface in acidic solution. [6] However, at slightly basic pH water dissociates, building up a remarkably large amount of OH^- localized within the electric double layer (EDL), and not contributing to pH. Moreover, our data suggest a prevailing 3-coordinated OH^- hydration structure, $OH^-(H_2O)_3$ (unlike in bulk water), within the diffuse layer surrounding the NP Stern layer.

Absolute energetics of aqueous solutions

Valence electrons govern chemical reactions, with their energies determining the solution environment's influence on bonding and antibonding states responsible for covalent bonding. This explains our interest in the characteristic aqueous-phase lowest ionization energies (IE). [1] These are the vertical ionization and detachment energies, VIE and VDE, as well as the respective adiabatic energies, which are measures of the propensity to detect an electron under equilibrium conditions. Surprisingly, though, these energies are not very accurately known which is due to the way they have been determined. Any electron binding energy from a given aqueous solution reported to date, almost exclusively acquired from LJ-PES measurements, is referenced to the vacuum energy. There are several reasons why this is not a satisfying procedure [7]. With *EASI* we will be able to establish a more robust energy reference. This entails to access, from solution, the absolute work function, based on the ability to measure for the first time the low-energy electron cutoff. It also provides access to surface dipoles resulting from the orientation of molecules residing at the solution – vacuum interface. Another crucial implication of an accurate absolute energy determination is the ability to probe the effect of solute on liquid water electronic structure which has been elusive so far [7].

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Physical Chemistry

Department of Physical Chemistry
Prof. Dr. Martin Wolf

Director at FHI and Scientific Member of the Max Planck Society (since 2008)
Professor, Freie Universität Berlin, Department of Physics (2000–2010)
Habilitation, Fritz Haber Institute of the MPG with Prof. Gerhard Ertl (1998)
Visiting Scientist, IBM Yorktown Heights & Columbia University
with Prof. Tony Heinz (1993, 1999)
Postdoc, University of Texas at Austin with Prof. Mike White (1991–1992)
Dr. rer nat., Freie Universität Berlin (1991)

Recent Development of the Department of Physical Chemistry

General remarks

In early 2018, the Department of Physical Chemistry became fully operational in its new building, which provides a very high quality laboratory infrastructure and an excellent working environment with close interaction between all members of the department. In this stimulating atmosphere we have sharpened our research profile with a stronger focus on light-matter interaction and elementary processes. This development is supported by the implementation of new techniques and instrumentation in the various research groups headed by younger scientists. We celebrated the opening of the new building in an inauguration ceremony on March 21, 2018 with scientific lectures, speeches, lab tours and an opening reception (see Fig. 1).

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

- *Dr. Yujin Tong* started a new research group in January 2018 on “Non-linear Spectro-electrochemistry” to investigate electrochemical reactions and molecular species at electrified interfaces by vibrational sum-frequency generation spectroscopy.
- *Dr. Matthias Koch* started a new research group in July 2018 entitled “Quantum Transport and Nanoelectronics“ to develop experiments for electronic transport in nanostructures on a silicon platform combining top-down with bottom-up techniques in low temperature scanning microscopy.
- *Prof. Kramer Campen* received an offer for a W3 professorship in physics at the University of Duisburg-Essen and started in this position in July 2019. He will move his group to Duisburg early next year. In addition, Dr. Yujin Tong will take up a permanent scientist position in his group, but will continue in parallel with his research at the FHI to pursue spectro-electrochemistry experiments at the FHI FEL exploiting the newly-developed capabilities for MIR-Vis vibrational SFG spectroscopy.
- In December 2018 *Dr. Michael Zürch* assumed a W2 position to set up a new independent Max-Planck-Research-Group (MPRG) for attosecond time-resolved X-ray absorption and diffraction experiments on solids. Soon after, he received an offer for an assistant professorship from the University of California at Berkeley and started on this tenure track position in July 2019. He will finish the construction of an experimental chamber at FHI during a

phase-out period and will set up his experiments in the new labs at Berkeley in 2020.

- Most recently *Dr. Julia Stähler* received an offer for a W3 professorship at the Humboldt University Berlin and will likely relocate her activities to the HU Chemistry Department in the next two years.

The Mechanical Workshops of the institute are associated with our department and are now headed by *Franck Kubitz*. Their service and high quality output is well received by all scientists. In the context of a necessary reconstruction of workshop building, we have developed a concept for future reorganization, which will in- corporate the activities of the crystal lab and will enable improved workflow and machine infrastructure.

Figure 1: The inauguration ceremony for the new building of the Department of Physical Chemistry took place on March, 21st 2018 (front page of the invitation).

Promotion of younger scientists

Guidance and promotion of younger scientists in their career development is an important goal of our 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). During the last two years a remarkable number of younger scientists in the department received academic offers, awards, distinguished research grants or fellowships. This can be considered as an indicator demonstrating the success of the department in the promotion of younger scientists:

Kramer Campen (ERC consolidator grant 2018, W3 professorship, University of Duisburg-Essen, Dep. of Physics 2019), *Sarah King* (AvH fellowship 2018, assistant professorship with tenure track, University of Chicago, Dep. of Chemistry 2018), *Julia Stähler* (offer for W3 professorship, Humboldt University Berlin, Dep. of Chemistry 2019), *Michael Zürch* (Max Planck Research Group (MPRG) 2018, assistant professorship with tenure track, University of California at Berkeley, College of Chemistry), *Helene Seiler* (SNF postdoc mobility grant, Switzerland 2019), *Samuel Beaulieu (*Banting postdoctoral fellowship, Canada 2019), *Chris Nicholson* (Carl-Ramsauer-Award for excellent PhD thesis, Physical Society Berlin 2018), *Daniela Zahn* (Physics Study Award 2018, Physical Society Berlin 2018).

An important career development for advanced postdocs and junior group leaders is gaining experience with grant applications and becoming project leader with grants from, e.g., German Research Foundation (DFG), European Research Council (ERC), or Japanese Science and Technology Agency (JST). In particular, establishing an independent junior research group with substantial own funding is one major achievement and career step for younger scientists. The department has been very successful in this regard as currently six research groups receive such independent funding and are hosted by the department: ERC Group of *Kramer Campen,* ERC Group of *Ralph Ernstorfer,* ERC Group of *Tobias Kampfrath,* DFG Emmy Noether Group of *Laurenz Rettig,* Max Planck Research Group of *Julia Stähler,* and Max Planck Research Group of *Michael Zürch.* Four of these group leaders have recently been appointed as professors (or received offers). In addition, several group leaders are project leaders in DFG funded collaborative research centers (Sfb 951, Sfb 1109, TRR 227), the DFG research unit FOR 1700 or have received individual research grants funded by DFG, JST, or from the European Commission.

Research profile and structure

Our research focusses on the dynamics of elementary processes at surfaces, interfaces and in solids aiming at a microscopic understanding of the coupling between various degrees of freedom (electrons, spins and phonons/vibrations). The goal is to obtain mechanistic insights at an atomistic or molecular level into various dynamic phenomena like ultrafast phase transitions, excited state dynamics or molecular processes and (electro-)chemical reactions at interfaces. Our strategy is to address these problems from several sides using complementary approaches, in particular by the development and application of various time- or spatial-resolved spectroscopic techniques dedicated to the specific physical questions. Research in the department is performed by small teams with specific, complementary expertise, creating various synergies and exchange between the different groups.

The current research topics of the department consist of three pillars: (1) Ultrafast dynamics of elementary processes and phase transitions in solids with specific focus on the coupling between electrons, phonons and spins. These processes are probed on their relevant time scales by *time-resolved spectroscopy* using ultrashort laser pulses from THz to XUV and ultrafast electron diffraction (UED). (2) A rather recent development is our new focus on localized excitations and transport phenomena at the nanoscale. Here we employ *scanning probe microscopy* to investigate plasmonic excitations and light confinement and inelastic scattering in STM junctions as well as electronic transport. The increasing emphasis on spatial-temporal phenomena combining ultrafast lasers with local scanning probe techniques is nicely complemented by ultrafast diffraction methods like UED. (3) The third pillar addresses molecular structure of adsorbates, electro-chemical reactions and dynamical processes at interfaces and in (molecular) liquids. These are probed by *nonlinear optical techniques,* in particular IR-vis vibrational sum frequency generation and nonlinear THz spectroscopy. Based on these pillars the department currently supports the following groups:

Time-resolved Dynamics of Solids: Electrons, Phonons and Spins

- Dynamics of Correlated Materials (*Laurenz Rettig*)
- Structural & Electronic Surface Dynamics (*Ralph Ernstorfer)*
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)

Localized Excitations and Transport

- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Ultrafast Scanning Probe Microscopy (*Melanie Müller*)
- Quantum Transport & Nanoelectronics (*Matthias Koch*)

Molecular Processes and their Dynamics

- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- Nonlinear Spectro-Electrochemistry (*Yujin Tong*)
- THz Driven Molecular Dynamics (*Mohsen Sajadi*)

Max-Planck-Research Groups

- Electron Dynamics (*Julia Stähler)*
- Transient X-ray Spectroscopy & Diffraction (*Michael Zürch)*

This structure reflects a number of new research topics developed over the last few years, which are often linked with the development of new techniques and instrumentation together with the inauguration of new research groups. This includes: (1) Far-infrared nonlinear optical spectroscopy of solids and photonic structures of phonon polaritons) at the FHI FEL and development of laser synchronization at the FEL by *Alexander Paarmann*. (2) Spectro-electrochemistry of electrochemical interfaces employing vibrational SFG and dedictated sample cells by *Kramer Campen* and *Yujin Tong* (3) Generation of high field THz pulses to study THz driven molecular dynamics in liquids and confined environment by *Mohsen Sajadi*, (4) Light coupling into a custom designed low-temperature STM for atomic-scale optical spectroscopy and studies of plasmon-mediated physical and chemical processes in nanocavities by *Takashi Kumagai*. (5) Ultrafast THz scanning probe microscopy developed by *Melanie Müller* and (6) Electronic transport and scanning gate microscopy using nanoscale integrated circuits on silicon performed by *Matthias Koch*. As several senior group leaders will move onto academic positions in near future, the number of research groups will consolidate. However, we will continue with our policy to create new groups headed by young scientists with their specific profile as pursued in the past.

Furthermore, we also provide lab space for the new experimental setup of *Hendrik Bluhm* (FHI Department of Inorganic Chemistry), who proposes challenging surface science experiments to probe chemical reactions on liquid surfaces (like water) using high pressure photoemission (HPXPS) and other characterization tools. We are looking forward to collaborate with him and plan to add an interface-sensitive, phase-resolved SFG spectroscopy setup to this experiment in a later stage.

Research Highlights of the Department

The following topics give a selection and comprehensive overview of research achievements as well as instrument developments in the department, obtained in the last two years. For more details see reports by the individual research groups:

- Multidimensional time- and angle-resolved photoelectron spectroscopy has been developed combining a 500 kHz extreme ultraviolet (XUV) laser source with a time-of-flight momentum microscope. Together with novel multi-dimensional data analytics, this development enables the reconstruction of the equilibrium and non-equilibrium electronic band structure of solids with exceptional high sensitivity and paves the way for future experimental electronic structure benchmarking [*Rev. Sci. Inst.* 90, 023104 (2019)].
- The sensitivity of the core level spectral function to excitonic excitations in the semiconductor WSe_2 has been demonstrated using the free-electron laser FLASH at DESY in conjunction with a momentum microscope. Based on an analytical model for the screening of the core holes by the excited states, the dynamics of a Mott transition could be revealed.
- Photo-induced chemical reactions and phase transitions are typically governed by dynamics on a Born-Oppenheimer potential energy surface, which depends on the transient electronic structure and its occupation. Using XUV time- and angle-resolved photoemission spectroscopy in conjunction with *ab-initio* molecular dynamics simulations, a detailed reaction pathway of a structural phase transition of In/Si(111) nanowires could be unraveled, revealing a close correspondence between changes of bonds in real space and the electronic band structure [*Science* 362, 821 (2018) & *Phys. Rev. B* 99, 155107 (2019)].
- The microscopic origin of non-equilibrium properties of ZnO was resolved by the combination of several complementary time-resolved spectroscopies. Previous conflicting results originate from the competition of intrinsic and defect-related relaxation dynamics of charge carriers and excitons. This first comprehensive picture of quasiparticle dynamics in ZnO offers the possibility of making use of the materials' susceptibility to defects that can be exploited to manipulate relaxation pathways on ultrafast timescales. [*Structural Dynamics* 6, 034501(2019)].
- Yttrium iron garnet (YIG) is a model insulating ferrimagnet with interesting applications in spintronics. The flow of energy and angular momentum between electron spins and ionic lattice has been directly probed after ultrafast resonant lattice excitation with intense THz pulses. On the 1-ps time scale, spins and phonons reach quasi-equilibrium in terms of energy through phonon-induced modulation of the exchange interaction. On the much slower, 100-ns scale, the excess of spin angular momentum is released to the crystal lattice, resulting in full equilibrium [*Science Advances* 4, eaar5164 (2018)].
- Spin angular momentum can be also transported out of YIG by just heating an adjacent metal layer. The initial steps of this spin Seebeck effect was analyzed with <27 fs time resolution using THz emission spectroscopy on YIG|Pt bilayers. After excitation of Pt with an infrared laser pulse, the spin Seebeck current rises on the same ~100 fs time scale on which the metal

electrons thermalize and subsequently follows their temperature. This instantaneous response arises because the metal spins have a correlation time of only ~4 fs and deflect the ferromagnetic moments without inertia. In a first application, we used this principle to characterize spin-to-charge-current in various alloys [*Nature Communications* 9, 2899 (2018) & *Nano Letters* 18, 1064 (2018)].

- Only recently discovered antiferromagnetic metals such as CuMnAs are currently in the focus of magnetism research as their magnetic order parameter (the staggered magnetization or Neel vector *L*) can be rotated by 90° and back by simply applying an electrical current parallel to *L*. It has been demonstrated that such reversible switching can even be obtained by driving the current with an ultrashort terahertz electric-field pulse as stimulus [*Science Advances* 4, eaar3566 (2018)].
- Femtosecond time-resolved resonant soft-X-ray diffraction is used to systematically investigate the ultrafast magnetization dynamics in various members of the rare-earth (RE) intermetallics family $RERh_2Si_2$. Demagnetization timescales varying by almost three orders or magnitude reveal a fundamental dependence of the angular momentum transfer rate on the strength of indirect RKKY exchange interaction in this prototypical class of antiferromagnets.
- Nanoscale heterostructures show rich structural dynamics in non-equilibrium states. Hot-electron induced atomic disordering and ultrafast nanoparticle motion has been revealed by femtosecond electron diffraction in Au nanocluster-thin film heterostructures [*ACS Nano* 12, 7710 (2018) & *Nanoscale Horizons* 4, 1164 (2019)].
- Inelastic light or electron scattering contains information on the momentum distributions of fundamental excitations in a material. Employing femtosecond electron diffraction, the time-dependent inelastic (diffuse) scattering reveals the localization of transient phonon distributions in momentum space arising from electron-phonon coupling or photo-induced phase transitions. This new approach has been successfully applied to different layered semiconductors and semimetals with thicknesses down to monolayers.
- In atomic-scale heterostructures, the macroscopic properties can be strongly influenced by the hetero-interfaces, due to the large interface-to-volume ratio. For optical phonons in Nitride semiconductor heterostructures, pronounced frequency shifts and the emergence of new interface modes have been demonstrated providing the possibility to modify the infrared dielectric function [*ACS Nano* 2019, 136, 6730].
- Strong coupling phenomena are ubiquitous in many areas of physics, providing hybrid modes with new physical properties. In ultrathin polar crystal films, the epsilon-near-zero phonon polariton hybridizes with the polar substrate polariton, resulting in a novel kind of hybrid polariton in the mid-infrared. [*Nano Letters* 2018, 18, 4285].
- Scanning probe microscope (SPM) pulling has the advantage that the structure of a molecule can be characterized before performing transport measurements. The influence of individual defects on the electromechanical properties of single graphene nanoribbons was obtained by combining SPM-Pulling experiments with atomistic simulations [*Phys. Rev. Lett.,* 121, 047701 2018].

- Plasmon-assisted resonant electron transfer under cw laser excitation has been demonstrated in nanoscale junctions of gold or silver tips and Ag(111). Resonant electron tunneling is induced from the tip to field emission resonances of Ag(111) through localized surface plasmon excitation in the STM junction [*Phys. Rev. Lett.* 121, 226802 (2018)].
- Near-field-induced tautomerization in single porpycene molecules on Cu(111) is mediated by photogenerated carriers and the reaction cross section is significantly enhanced in the presence of a Au tip through localized surface plasmon excitation [*Nano Lett.* 18, 152 (2018)].
- Using focused ion beam nanofabrication of gold tips, spectral features of a plasmonic STM junction can be manipulated. An exemplary Fabry−Pérot type resonator of surface plasmons is demonstrated by producing the tip with a single groove on its shaft and the spectral response is characterized by scanning tunneling luminescence [*Nano Lett.* 19, 3597 (2019)].
- Tip-enhanced resonant Raman scattering (TERRS) was demonstrated on ultrathin zinc oxide layers epitaxially grown on a Ag(111) surface. In this process both physical and chemical enhancement mechanisms support efficient TERRS with exceptional high (1-nm) spatial resolution arising from local variations of the electronic structure [Nano Lett. in press].
- Multi-angle reflectance measurements on Germanium in the extreme ultraviolet are used to recover the complex-valued index of refraction in unprecedented resolution. Besides resolving formerly undetected transitions, experimental proof is provided that critical angle reflectivity is largely insensitive to the electronic structure [*J. Opt. Soc. Am. B*, 36, 1716 (2019)].
- Sum frequency generation spectroscopy is interface specific within the electric dipole approximation for bulk phases with inversion symmetry. However many systems of interest may either have large quadrupole responses in the bulk or are non-inversion symmetric. A novel approach to quantitatively separate the two contributions from surface and bulk was demonstrated by taking advantage of the differing symmetries of bulk and surface contributions and performing high accuracy phase resolved SFG measurements. [*J. Chem. Phys.* 151, 064707 (2019)].
- Probing the mechanism of electro-catalytic reactions experimentally requires time domain characterization after rapid initiation of a reaction of interest. By quantifying photocurrents induced by fs optical pulse excitation we show the reactivity of Pt surfaces towards H_2 generation requires consideration of both ultrafast charge transfer and more slowly evolving electrolyte structural dynamics. [*ChemElectroChem.,* 6, 2675 2019].
- The potential dependent Stark shift in vibrational line shapes of adsorbates in electrochemical systems is typically described as a linear function of applied bias where deviations from linearity are often attributed to changes in surface structure or electrochemistry. For (bi)sulfate on a Pt(111) electrode SFG spectroscopy reveals such a nonlinear Stark shift. A microscopic model accounting for dipole-dipole coupling of adsorbates was developed showing that deviations from linearity are likely to occur in the absence of chemical or structural change. [*Surface Science* 678, 78–85 (2018)].
- Ion polarizability is important in understanding adsorption thermodynamics at liquid interfaces but has proven challenging to quantify. Using polarization resolved, vibrationally resonant sum frequency spectroscopy the anisotropy of perchlorate's polarizability at the air/water interface has been quantified,

providing constrains on the anion and solvation shell structure as function of surface coverage [*Nature Communications* 9, 1313 (2018)].

- Low-frequency collective molecular motions in the terahertz (THz) and sub-THz frequency range are decisive to the thermodynamic properties and chemical reactivity of liquids. It is demonstrated that the microscopic nature of the collective molecular dynamics of liquids, as complex as methanol, can be revealed by comparing their THz pulse and optical pulse induced Raman responses. [*J. Phys. Chem. Lett.* 9 1279-1283 (2018)].

Outlook

Aiming at spatial-temporal resolution at atomistic length and ultrafast time scales we will *enhance our activities in scanning probe microscopy coupled with local optical excitation and spectroscopy* by several measures (e.g. low temperature operation in THz STM, fs-laser implementation to a LTSTM or significantly improved spectral resolution and sensitivity in TERS). Complementary to such local probes are diffraction techniques (like *ultrafast electron diffraction*). Here we plan to implement advanced detector technology to cover a much higher dynamic range for detection of very weak diffuse scattering together with the intense Bragg peaks. We also consider supporting a new junior research group in this area.

A further important direction will be the development of *nonlinear vibrational spectroscopy and microscopy* at the FHI FEL enabling investigations of (Chi(2) and Chi(3)) non-linear optical processes at wavelength not accessible with typical laboratory sources. In addition we will further develop phase-sensitive SFG spectroscopy and implement a new laser system. This will enable, e.g., spectroscopy of protons at liquid interfaces or oxide formation at electro-chemical interfaces.

Furthermore we will improve our infrastructure and capabilities for sample preparation techniques for 2 D materials and heterostructures.

Emmy Noether Group Dynamics of Correlated Materials
Dr. Laurenz Rettig

Group Leader, Fritz-Haber-Institut der MPG, Berlin (since 2016)
Postdoc, Paul Scherrer Institute, Switzerland (2013–2015)
Postdoc, Universität Duisburg-Essen (2012–2013)
Dr. rer. nat., Freie Universität Berlin (2012)
Diploma in Physics, Freie Universität Berlin (2008)

Dynamics of Correlated Materials Probed by trARPES and X-ray Diffraction

The Emmy Noether group Dynamics of Correlated Materials focusses on understanding the ultrafast dynamics of complex materials with many interacting degrees of freedom after optical excitation, and on characterizing photo-induced phase transitions and out-of-equilibrium states using momentum-resolved techniques such as femtosecond time-resolved photoelectron spectroscopy (trARPES) or time-resolved (resonant) X-ray diffraction. Using a combination of such techniques, we aim at understanding the interactions between the various degrees of freedom inside such materials (e.g. electrons, spins or lattice), which in complex materials often lead to novel ground states with fascinating physical properties.

Multidimensional photoelectron spectroscopy

Many of the group's activities are performed in close collaboration with the ERC group of Ralph Ernstorfer, with which we share our high-repetition rate XUV trARPES setup. A new electron detector, a momentum microscope (SPECS Metis), was installed during the last two years allowing simultaneous and very efficient detection of transient electronic band structures in the complete surface Brillouin zone (BZ) of most materials. This development of multidimensional photoelectron spectroscopy (MPES) enables a completely new approach towards the investigation of transient electronic band structures and their properties, as well as its dynamics, treating three (energy, k_x, k_y) or even four dimensions (including time) on the same footing (see also report of the Ernstorfer group).

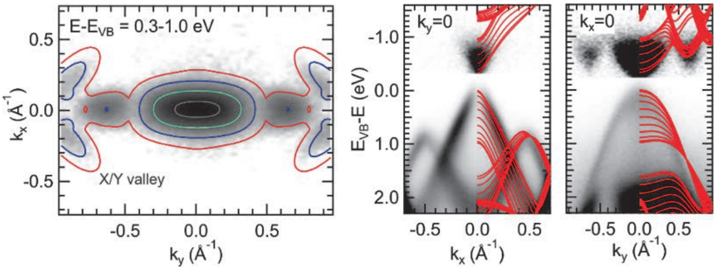

Figure 1: Time-resolved ARPES data of black phosphorous. Left: Constant energy contour of the conduction band states, showing the "hidden" X/Y valleys close to the BZ boundary. Right: Energy-momentum cuts along the armchair (k_x) and the zigzag (k_y) direction. Overlaid red lines are DFT calculations for different k_z values.

This approach is particularly useful for the investigation of anisotropic electronic systems, such as e.g. the layered semiconductor black phosphorous (Fig. 1). This material shows strong in-plane anisotropy associated with a glide-plane symmetry, leading to a large polarization contrast in the photo-absorption cross-section. Using MPES, we could identify a new “hidden” Y/X valley in the conduction band dispersion off the high symmetry directions, which was not observed before, and which plays an important role for the relaxation of excited carriers. Owing to the full momentum and energy information obtained, we could carry out a detailed analysis of the carrier relaxation between the different valleys, and for different excitation conditions, and reveal a long memory effect of the initial carrier distribution on the final state, governed by the glide plane symmetry in the system.

Photoinduced phase transitions

The spectroscopic access to the momentum-resolved unoccupied electronic band structure provided by MPES is also particularly useful to investigate photoinduced phase transitions (PIPTs) in complex materials, e.g. of changes in the topology of the electronic structure or from an insulating ground state into a metallic excited state. A key goal is to reveal the underlying reaction mechanisms and pathways. In addition, by comparison of the experimental data to electronic band structure calculations, their validity for predicting excited state band dispersion and potential deviations e.g. due to many-body phenomena can be assessed.

A fascinating system that we recently studied is the type-II Weyl semimetal T_d-$MoTe_2$, where a strong sensitivity of the γ conduction band pockets on the electron-electron interaction has been predicted by DFT calculations (Fig 2, c-d), leading to a Lifshitz transition. Such a scenario can also happen in a photoexcited semiconductor or semimetal, where the photoexcitation of a large number of free carriers strongly enhances electronic screening and thereby suppresses electronic correlations. Indeed, using MPES, we observe the emergence of additional pockets on the Fermi surface after strong infrared photoexcitation (Fig. 2 b), supporting this scenario. The strong correlation of the excited state carrier population and the energy position of the γ pocket provide further evidence, supported by theory.

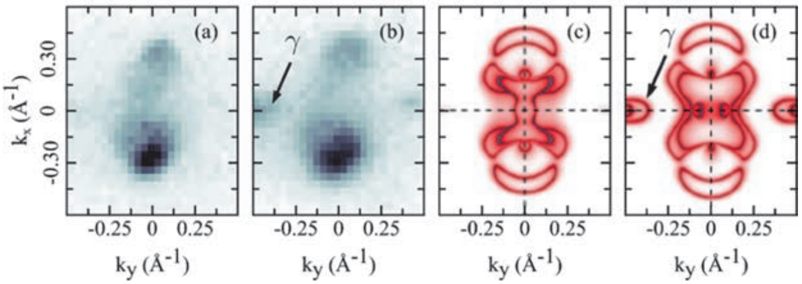

Figure 2: Time-resolved Fermi surface spectroscopy of $MoTe_2$. Fermi surface of $MoTe_2$ before (a) and at 500 fs after (b) excitation with 1030 nm pump pulses (0.64 mJ/cm^2). DFT+T calculated Fermi surface with (c) U=3 eV and (d) U=0 eV. Calculations adapted from PRL 121,136401 (2018).

A model system for a structural phase transition, concomitant to an insulator-metal transition, are In nanowires on a Si(111) surface. In this system, a detailed comparison of the unoccupied electronic band structure to DFT and GW calculations revealed a distinct momentum-dependent deviation pointing towards excitonic contributions in the low temperature phase. Furthermore, the structural PIPT has been probed by trARPES and a detailed reaction pathway with several distinct timescales of the transition in the electronic structure identified. Remarkably, the momentum-resolved dynamics is completely determined by the transient electronic temperature after excitation.

A similar mechanism is present in the prototypical charge density wave (CDW) model system $TbTe_3$, where large energy gaps open up in the energy dispersion due to a coupled structural and electronic instability. Using the momentum microscope, we are now able to investigate the transient electronic fingerprints of this transition in a wide energy and momentum range throughout the BZ, including the unoccupied band structure (Fig. 3a), which is well described by DFT band structure calculations. Upon optical excitation, the CDW distortion is transiently suppressed, as seen by a large transfer of spectral weight on the Fermi surface, and closing of the energy gaps (Fig. 3b). A detailed investigation of the fluence dependent dynamics of the spectral weight in the gapped regions yields access to the dynamics of the electronic order parameter of the CDW (Fig. 3c). Within a time-dependent Ginzburg-Landau model, we can extract the time and fluence dependent transient energy potential, which we find to be dominated by the evolution of the energy content in the electronic system. In conjunction with time-resolved structural dynamics of the CDW superlattice reflections measured by time-resolved X-ray diffraction, this model yields a detailed description of the dynamics of CDW suppression and recovery.

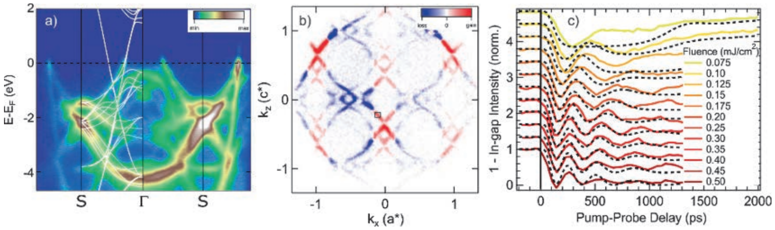

Figure 3: Ultrafast CDW dynamics in $TbTe_3$: (a) Band structure along the Γ-S high symmetry direction in a wide energy range, alongside with DFT band structure calculations (for YTe_3). (b) Differential Fermi surface, at 250 fs after excitation with 800nm laser pulses. The transfer of spectral weight from the metallic (blue) to the gapped (red) Fermi surface regions indicates the transition into the high-temperature state. (c) The coherent dynamics of the spectral weight inside the gap (black box in (b)) is well described by a modified time-dependent Ginzburg-Landau model.

Ultrafast dynamics of antiferromagnetic systems

The technique of time-resolved resonant soft X-ray diffraction is sensitive to the dynamics of magnetic ordering, in particular, of antiferromagnetic (AFM) systems. We have performed a series of experiments at the FemtospeX slicing source of BESSY II to investigate the ultrafast demagnetization dynamics of prototypical rare-earth (RE) intermetallic antiferromagnets, $RERh_2Si_2$. In this system, the rare-earth ions are enclosed in a fixed crystal lattice of Rh and Si atoms (Fig. 4a), and replacing the RE ions changes the electronic and magnetic properties relatively little. Therefore, this system is ideally suited to study the influence of the indirect RKKY exchange interaction on the demagnetization dynamics in an antiferromagnetic system. The transient diffraction intensity of the (001) magnetic reflection shows a drastically different behavior for different rare-earth ions in the system, ranging from a sub-picosecond demagnetization in $SmRh_2Si_2$ up to several 100 ps in $PrRh_2Si_2$ (Fig. 4b). In addition, we find a pronounced critical slow-down of the dynamics upon approaching a critical fluence in all materials (Fig. 4c). This strongly varying demagnetization behavior can be well understood by considering the transfer rate of angular momentum, and its dependence on the strength of the RKKY interaction, which we parametrize by the de Gennes factor (g-1)2 J(J+1). Thereby, our systematic study of AFM demagnetization dynamics in this system reveals the indirect exchange interaction as the fundamental process responsible for angular momentum transfer. In addition, in $GdRh_2Si_2$, we could identify a coherent in-plane rotation of the whole AFM structure after excitation, due to a transient change of the magnetocrystalline anisotropy.

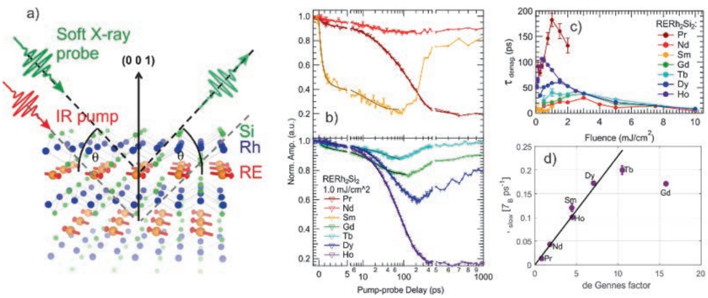

Figure 4: Time-resolved resonant x-ray diffraction in $RERh_2Si_2$. (a) RE atoms are embedded in a fixed Rh/Si matrix, and always order in a similar AFM structure. Soft x-rays tuned to the RE M4/5 absorption edges are used to detect the out-of-plane (001) magnetic diffraction peak. (b) Normalized magnetic diffraction signal for various $RERh_2Si_2$ compounds. Lines are biexponential fits. (c) Extracted slow time constants as a function of excitation fluence. (d) Derived angular momentum transfer rate as a function of the de Gennes factor.

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ERC Group Structural & Electronic Surface Dynamics
Dr. Ralph Ernstorfer

Group Leader, Department of Physical Chemistry (since 2017)
ERC CoG project FLATLAND (since 2016)
Max Planck Research Group, Department of Physical Chemistry (2010-2017)
Scientist, TU Munich and MPI for Quantum Optics (2007-2010)
Postdoctoral Fellow, University of Toronto (2005-2007)
Dr. rer. nat., Freie Universität Berlin (2004)

Ultrafast Dynamics of Electrons and Lattice in Nanoscale Matter

The Structural & Electronic Surface Dynamics Group aims for a microscopic understanding of fundamental interactions in nanoscale condensed matter, ultimately on the level of individual quantum states. To achieve this, we develop and employ experimental techniques providing momentum-resolved information on transient states of the electronic structure and the atomic structure. This methodology is applied to a broad spectrum of material systems ranging from thin-film (semi-) metals and semiconductors to nanoscale heterostructures and nanocrystals. We closely collaborate with the Dynamics of Correlated Materials Group headed by Laurenz Rettig.

Development of multidimensional photoemission spectroscopy

In recent years, we developed time- and angle-resolved photoemission spectroscopy (trARPES) based on a femtosecond extreme ultraviolet (XUV) laser source, which provides access to the non-equilibrium electronic structure in the entire Brillouin zone of crystalline materials. We extended this approach by adding a momentum microscope detector, which enables four-dimensional trARPES as depicted in Fig. 1(a). The high repetition rate (500 kHz) of the XUV source provides enough statistics for mapping the weak and transient excited state signal in addition to the occupied states in the material's valence band. This is illustrated in panels b and c, showing two snapshots from a 3D movie of the formation and evolution of excitons in WSe_2, a prototypical layered semiconductor. Additional examples of use of this approach can be found in the report of the Dynamics of Correlated Materials Group.

The combination of a high-repetition rate light source and an every-electron detection scheme generates large data volumes. Making such data accessible to a broader community, for instance for benchmarking electronic structure calculations, represents a new challenge for the photoemission community. Within the BiGmax Research Network, we develop unsupervised learning algorithms for extracting experimental band structure from multidimensional data sets. We share this development with the community by developing a general multidimensional photoemission data analytics toolbox (https://github.com/mpes-kit).

Complementary to the study of ultrafast dynamics of valence electrons with trARPES, we investigated the response of core levels to excitations of the valence states in WSe_2. Using a momentum microscope and the free-electron laser FLASH at DESY, we probe the spectral function of W 4f core levels during the formation and evolution of excitons, see Fig. 1(d). The evolution of the spectral function is well reproduced by an analytic model, which extends the Doniach-Sunjic line shape model to excited semiconductors. The time-dependence of the spectral function is governed by the core-valence Coulomb interaction, which differs largely between excitonic and single-particle excitations of the valence electrons. Core-level photo-emission spectroscopy proves to be a sensitive tool for the investigation of electronic phase transitions like, as shown here, a Mott transition in a photo-excited semiconductor.

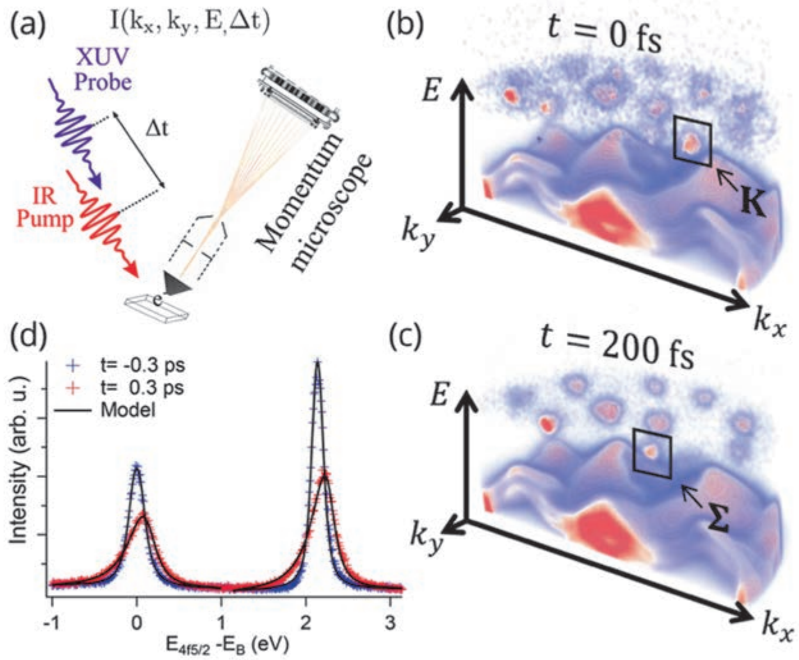

Figure 1: Multidimensional photoemission spectroscopy. (a) Illustration of the trARPES scheme with a momentum microscope spectrometer, which resolves the photoelectrons in energy, both parallel momentum dimensions and (pump-probe) time. Panels (b,c) show snapshots of the electronic structure of WSe_2 during the formation of an A exciton in the K valleys of the Brillouin zone (b) and after scattering of the bright A exciton to optically-dark excitons (c). The electronic contribution to the dark-exciton wave function is localized in momentum space near the Σ valleys of the conduction band. (d) Time-resolved spectral function of the W 4f core levels before (blue) and 300 fs after optical excitation of the A exciton resonance. The solid lines show fits with a time-dependent Doniach-Sunjic model, which reveals a Mott transition through the temporal evolution of the core-valence interaction

Elastic and inelastic femtosecond electron diffraction

Time-resolved diffraction techniques have primarily been employed for retrieving structural dynamics from elastic scattering signals, which reveal the net effect of all phonon modes on the atomic motion. Only recently, the analysis of inelastic scattering signal has been established as technique for obtaining momentum-resolved information on transient phonon populations. We employ this approach to study electron-phonon and phonon-phonon interactions as well as phase transitions in strongly coupled electron-lattice systems like charge density wave materials and certain topologically nontrivial semimetals. Fig. 2 shows exemplary data of the anisotropic semiconductor black phosphorous. The diffraction difference between excited and ground states shows the momentum distribution of the inelastic scattering, which reflects the transient phonon distribution in momentum space. After 300 ps, the pattern reflects a hot, yet thermal phonon distribution, see panel (b). On the sub-100 ps timescale, however, the inelastic scattering reveals nonthermal phonon distributions and highly anisotropic phonon population dynamics, as shown for small-momentum phonons in the armchair (red) and zigzag (black) crystalline directions, panel (c).

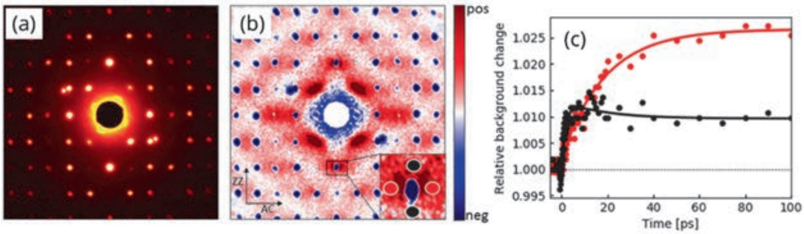

Figure 2: Femtosecond electron diffraction of a black phosphorous thin film. (a) Raw diffraction pattern showing the anisotropic structure in the armchair-zigzag plane. (b) Diffraction difference observed 300 ps after optical excitation of the electronic structure. Red signal: increase of star-shaped inelastic scattering, which reflects the transient phonon population at this time. The anisotropy of the phonon dynamics is retrieved from the momentum-dependent scattering signal, e.g., along the armchair (red dots) and zigzag (black dots) directions in the vicinity of elastic scattering peaks (see inset). Panel (c) shows the pronounced differences in the phonon dynamics along these high-symmetry directions (color code relates to the inset in (b)). These are explained by the anisotropy of the electron-phonon scattering phase space, which we independently measured with complementary trARPES measurements.

Ultrafast diffraction and microscopy of nanoscale materials

The large scattering cross section of nonrelativistic electrons allows for the investi-gation of structural dynamics in nanocrystals. We investigated size-selected magic-number Au clusters composed of ~920 atoms, which were soft-landed on different thin film substrates like graphene, see Fig. 3(a, b). The time-resolved diffraction patterns of these nanoscale heterostructures revealed the ultrafast flow of energy within each constituent as well as across the boundary and a hot-electron-assisted surface-melting mechanism. In the case of Au clusters on graphene, the dynamics of ultrafast restricted rotations, i.e., librations, could be extracted from the diffraction data. Molecular dynamics simulations reveal efficient coupling between flexural phonons of graphene and rotational motion of the cluster as quasi-impulsive driving mechanism of the librations.

Complementary to the momentum-space technique trARPES, we also aim to observe ultrafast dynamics in real space with femtosecond electron point-projection microscopy. This technique is sensitive to the electric potential in the vicinity of nanostructures; time-resolved experiments hence reveal changes in the electric potential and allow the reconstruction of the underlying motion of charges. To enhance the sensitivity of the technique towards the limit of a single elementary charge, we aim to realize femtosecond electron holography. Improvements of the mechanical stability of the microscope and optimization of the photoemission process from nanotips in terms of source coherence have recently allowed us to record first images with clear signatures of electron interference, see Fig. 3.

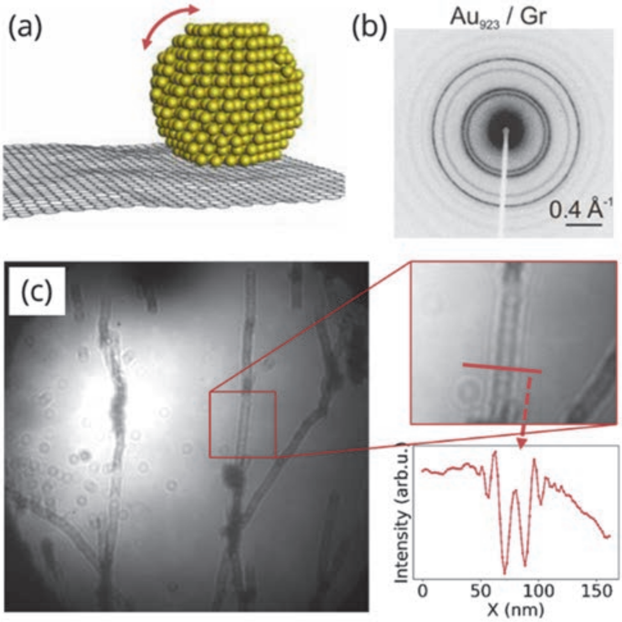

Figure 3: (a) Illustration of librational motion of Au-932 clusters on graphene. (b) The diffraction pattern of this 0D-2D heterostructure shows separa-ted graphene and Au peaks, which allows retrieving ultrafast energy flow in the heterostructure. Deviations from Debye-Waller dynamics in the diffraction data could be identified as rotational motion of the entire nanocrystals. (c) Electron transmission image of free-standing graphene recorded with 220 eV electrons. A crack in the graphene causes single-slit scattering and single-electron interference (top right and lineout profile).

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Lattice Dynamics Group
Dr. Alexander Paarmann

Group Leader, Department of Physical Chemistry (since 2014)
Postdoctoral Fellow, FHI, Department of Physical Chemistry (2010-2013)
Ph.D., University of Toronto (2010)
Diploma, TU Berlin (2005)

Nonlinear Phonon Spectroscopy using Infrared Free-Electron Lasers

The Lattice Dynamics group uses the FHI infrared Free-Electron Laser (FEL) to study optical phonons in polar dielectric crystals, and the associated resonances in the nonlinear-optical response of materials in the mid- to far-infrared spectral region. Specifically, we are interested in phonon polaritons in hetero- and nano-structures, where we use the structure to control the resonances while the polaritonic field confinement leads to enhancement of the nonlinear-optical signals. For these studies, we develop novel experimental approaches and instrumentation, as for instance FEL-based far-infrared surface-vibrational spectroscopy and microscopy. These new methods will, for instance, also be applied to investigations of transient structural motifs in electrochemical systems and domain structure in correlated oxide heterostructures in the future.

Phonon polaritons in polar dielectric heterostructures

Phonon polaritons – phonon-light coupled quasiparticles - arise in thin films or at surfaces of polar dielectric crystals due to the infrared-active optical phonons. They are supported in the negative permittivity region between transverse and longitudinal optical phonon resonances - the so-called Reststrahlen region. The long lifetimes of these excitations offer unique advantages for infrared nano-photonics over lossy, short-lived plasmon polaritons. However, a major drawback arises from the limited, material-specific spectral range over which phonon polaritons are supported, as well as their limited tunability. The Lattice Dynamics group follows various approaches to lift these restrictions by means of planar heterostructures, where the polariton modes can be tuned either via polariton-polariton coupling between the different layers, or even by phonon hybridization at the material interfaces in atomic-scale heterostructures.

For ultrathin polar dielectric films of 10-100 nm thickness, the phonon polariton dispersion is strongly modified, resulting in a unique mode that naturally resides at the zero-crossing of the dielectric function (epsilon-near-zero, ENZ). This ENZ condition has many attractive properties otherwise only accessible through carefully designed metamaterials, such as infinite phase velocity, scatter-free propagation, and drastically enhanced nonlinear-optical effects. When brought onto a polar dielectric substrate, the ENZ polariton in the thin film can hybridize with the substrate polariton, to generate strongly coupled modes with unique properties of both surface and ENZ polaritons.

In contrast, a (non-polar) dielectric ultrathin film placed on a polar crystal surface results in a compression of the substrate polariton dispersion. This is particularly interesting when using phase change materials like GST as the dielectric, where this compression can be modulated, see Fig. 1. Additionally, the perpendicularly polarized waveguide mode was found to, due to the polar crystal substrate, have very similar (polariton-like) properties, making the GST/polar crystal heterostructure an extremely attractive platform for infrared nanophotonics.

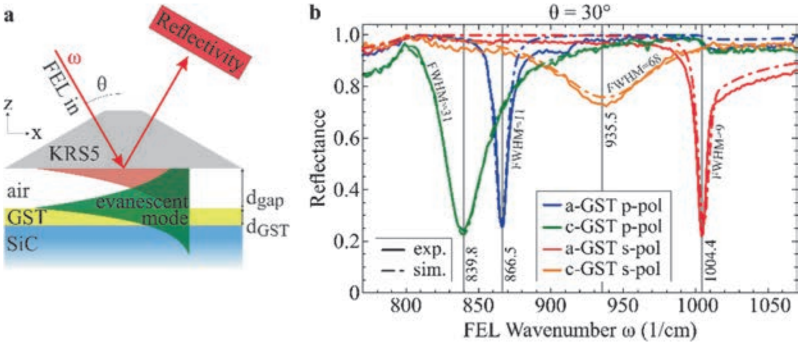

Figure 1: Tuning of phonon polariton resonances: (a) Schematic of Otto-type prism coupling experiment that allows mapping of the polariton dispersion in heterostructures. (b) For ultrathin layers of the phase-change material GST, switching of the of the GST phase results in tremendous tuning of the GST-compressed surface polariton (p-pol, blue/green) and the newly discovered polariton-like waveguided mode (s-pol, red/orange).

For heterostructures with ultrathin film thicknesses approaching atomic length scales, the modified chemical bonding at the layer interfaces additionally leads to hybridization of the optical phonons, and thereby modulation of the phonon polaritons. Simultaneously, due to strong anisotropy (in-plane vs. out-of-plane modes) of the heterostructure, this new material now also supports so-called hyperbolic polaritons – volume-confined modes with unbound momenta. As such, atomic-scale heterostructures establish a new way to design materials specifically for phonon-polariton-based nanophotonics.

Far-Infrared sum-frequency generation spectroscopy and microscopy

Infrared-visible sum-frequency generation (SFG) spectroscopy is a powerful tool to reveal the structure and symmetry of interfaces. This technique is well established in the mid-infrared range using table-top laser sources providing access to high-frequency vibrations. This has led to many major discoveries, for instance regarding the surface structure of liquid and solid water, or the transient interface structure in electrochemical systems. Using the FHI FEL, the Lattice Dynamics group is now pushing SFG spectroscopy into the far-infrared range, opening up a whole new field of exciting possibilities, owing to the vibrational and electronic excitations in that spectral range which are currently inaccessible. This applies for instance - but is by far not limited to - most optical phonon modes in the large class of metal oxides. Therefore, far-infrared SFG spectroscopy could be employed to study many important problems in, for instance, aqueous oxide chemistry or strongly correlated oxide heterostructures.

Many interface problems in physics, chemistry, and even biology involve significant spatial heterogeneity. Therefore, spatially resolved information about the interface structure and symmetry can tremendously enhance the understanding of underlying mechanisms. Notably, SFG is perfectly suited for infrared microscopy, whereby the spatial resolution is limited only by the wavelength of the visible SFG photons, i.e., well below the diffraction limit for infrared radiation. Motivated by these possibilities, we have started to implement FEL-based far-infrared SFG spectroscopy and microscopy.

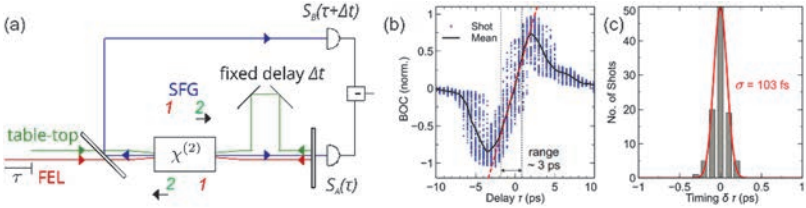

Figure 2: Timing tool for the FHI FEL: (a) Concept of balanced optical cross correlation (BOC) used for online monitoring of the relative arrival time of visible and FEL pulses. (b) BOC signal when scanning the delay time τ between FEL and visible laser. (c) The timing distribution function yields a timing jitter of ~ 100 fs.

To enable far-infrared SFG using the FHI FEL as the powerful far-infrared light source, a time-synchronized visible laser system is required. The Lattice Dynamics group has, over the last 4 years, established the respective instrumentation. A radio-frequency timing infrastructure at the FEL facility was installed, which was demonstrated to allow synchronization of a low-power fiber laser to the FEL pulses with ~100 fs precision (see Fig. 2). We also developed a new concept for and implemented a timing tool for online-monitoring of the relative timing between the two lasers, a crucial advantage of the current approach over earlier attempts at other FEL facilities.

Using the synchronized low-power visible laser for a proof-of-concept experiment, SFG spectroscopy and microscopy measurements were performed, see Fig. 3. Here we took advantage of the polaritonic field confinement in phonon polariton sub-diffractional resonators that leads to dramatic enhancement of the nonlinear signal, resulting in detectable signal levels despite the low visible laser power available. This also allowed for first far-infrared SFG microscopy experiments, here done with spatially scanning tightly focused beams.

To harvest the full potential of far-infrared SFG spectroscopy and microscopy, the department applied for and was recently granted financial support by the Max-Planck-Society to acquire a new high-power visible laser operating in burst mode, synchronized with the FEL. This new laser will be installed in early 2020, and our group will implement FEL-based SFG spectroscopy and microscopy as an experimental end station at the FHI FEL. Notably, the concept also includes to establish wide-field SFG microscopy. Once operational, this SFG end station will be used for many different experiments, ranging from infrared nanophotonics to quantum materials and electrochemistry.

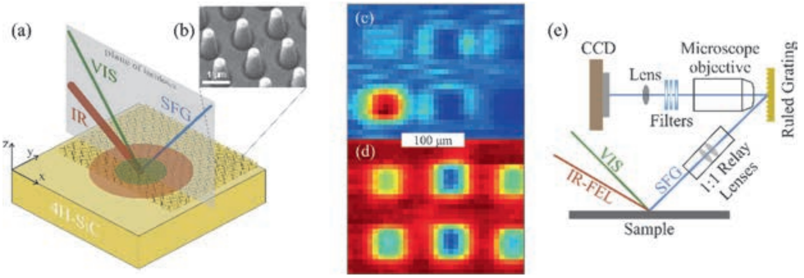

Figure 3: (a) Concept of scanning probe SFG microscopy of nanophotonic structures made of (b) Silicon Carbide nanopillars. Experimental resonant (c) and non-resonant (d) SFG images. (e) Concept for FEL-based wide-field SFG microscopy to be implemented

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ERC Group Terahertz Physics
Prof. Dr. Tobias Kampfrath

Full professor, Freie Universität Berlin (since 2016)
Group Leader, FHI, Department of Physical Chemistry (since 2010)
Postdoctoral Fellow, AMOLF Amsterdam/The Netherlands, University of Konstanz and Freie Universität Berlin (2006-2010)
Ph.D., Freie Universität Berlin (2010)
Diploma, Universities of Erlangen and Göttingen (2001)

Ultrafast Terahertz Spectroscopy of Complex Materials

The terahertz (THz) frequency range is attracting increasing interest for both applied and fundamental reasons. On one hand, bit rates in current information technology may soon approach the THz range. Therefore, it is warranted to study the behavior of materials at THz frequencies. This goal is, on the other hand, also highly interesting from a scientific viewpoint because its low photon energy (4.1 meV at 1 THz) makes THz radiation an excellent probe of many elementary excitations of solids, for instance lattice vibrations (phonons), electronic intraband transport, excitons and spin waves (magnons).

The Terahertz Physics Group makes use of ultrashort THz and optical laser pulses

- To gain insight into the interplay of low-energy excitations in complex materials. An example is the elusive interaction of lattice and electron spins in magnetically ordered solids.
- To push various physical effects so far studied at low frequencies into the THz range. Currently, the group has a strong focus on fundamental spintronic effects such as the only recently discovered spin Hall effect and the spin-type Seebeck effects. These studies are conducted in the framework of the PI's ERC Consolidator Grant project TERAMAG.
- 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.

Recent examples of these activities are illustrated below.

Ultrafast spin currents in magnetic bilayers

A fundamental operation of spintronic devices is the transport of spin information, for example from a magnetic layer into an adjacent nonmagnetic metal (see Fig. 1a). Remarkably, such spin current j_s can be triggered by simply heating the metallic layer, even if the magnetic layer is an insulator such as yttrium iron garnet (YIG).

To reveal the possibly ultrafast formation of this spin Seebeck effect in the model bilayer system YIG|Pt, we made use of a femtosecond laser pulse to instantaneously heat the Pt film (Fig. 1a). Note that any spin current j_c flowing from YIG to Pt is converted into a transient transverse charge current j_c by the inverse spin Hall effect of Pt. The time-dependent j_c gives rise to the emission of an electromagnetic pulse with frequencies extending into the THz range.

Using a highly sensitive electrooptic-sampling setup, we were able to measure the emitted THz pulse. We developed an inversion procedure to extract the ultrafast dynamics of the spin current $j_s(t)$ displayed in Fig. 1b. The decay of j_s on a 300 fs scale directly follows the cooling dynamics of the Pt electrons by the Pt lattice. Interestingly, the rise of j_s on a 100 fs scale is substantially slower than the 27 fs resolution of our setup. Analytical modeling and electron-dynamics simulations showed that this rise traces the thermalization of the Pt electrons. These findings are consistently explained by the formation scenario of the spin Seebeck effect that is summarized in Fig. 1c and its caption.

We have meanwhile confirmed these insights for other insulating ferrimagnets and take advantage of this scheme to rapidly characterize the strength of the spin Hall effect in various materials, to study the role of the interface and to understand how spin transport arises in the case of metallic rather than insulating magnetic layers.

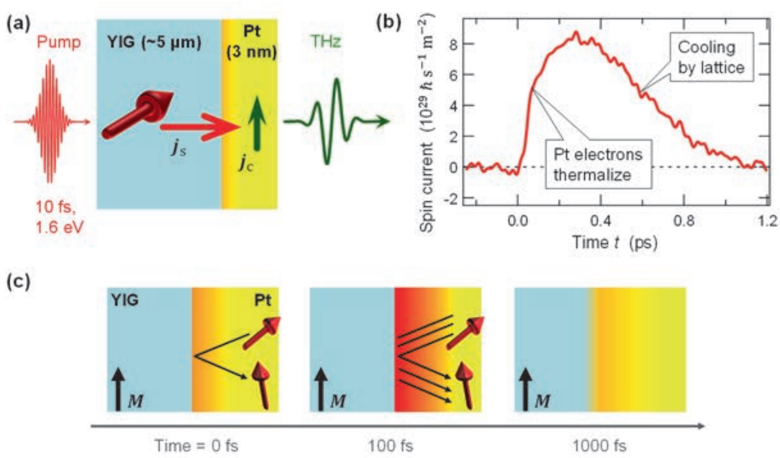

Figure 1: Ultrafast spin Seebeck effect. (a) Schematic of experiment. A pump pulse heats the Pt film, giving rise to a transient spin current js from YIG to Pt that is converted into a transverse charge current jc by the inverse spin Hall effect. Measurement of the concomitantly emitted THz pulse allows us to extract (b) the temporal dynamics of the transient spin current js(t) through the YIG-Pt interface. (c) Scenario of the formation of the spin Seebeck current. After heating of the Pt layer at time 0 fs, hot electrons scatter off the YIG-Pt interface, thereby partially aligning with the YIG magnetization through interfacial exchange interaction and transporting spin angular momentum into the N layer. The scattering rate is proportional to the number of occupied incident Bloch states times the number of unoccupied reflected states. It rises when the number of electrons and holes grows (here by a factor of ~40) in the course of electron thermalization.

Spintronic operations with intense THz fields

We not only use THz radiation to probe spin and charge dynamics, but also employ intense THz pulses to drive and finally control dynamics. A recent result is the switching of magnetic order of antiferromagnets as illustrated by Fig 2. Our sample was a thin film of the only lately discovered metallic antiferromagnet CuMnAs. Since the antiferromagnetically coupled and, thus, oppositely oriented (staggered) spins are located at sites with locally broken inversion symmetry, CuMnAs has a remarkable property: Driving a charge current through the metal is like applying a staggered magnetic field to the two spin sublattices. This effective field exerts a uniform torque on all spins and rotates them coherently (see Fig. 2a). The degree of alignment of the spin system can be probed by electrical measurement of anisotropic magnetoresistance (AMR).

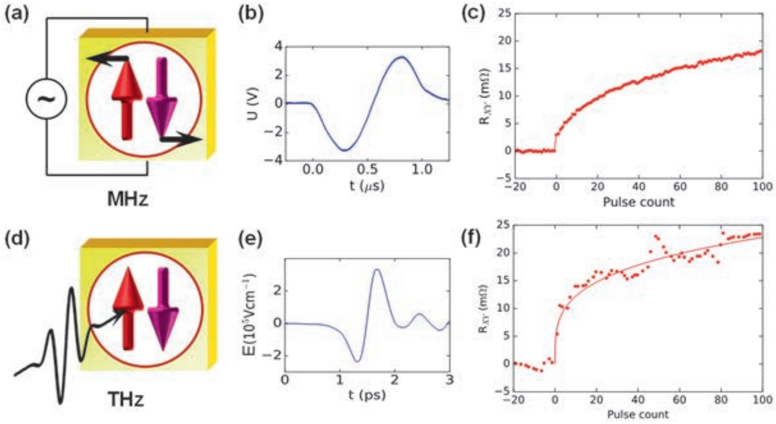

Figure 2: THz switching of antiferromagnetic order. (a) By applying an electric current pulse to the metallic antiferromagnet CuMnAs, a staggered magnetic field is applied to the antiferromagnetically coupled spin sublattices, resulting in coherent rotation of all spins. (b) Voltage vs time *t* of the electrical pulse applied to the Ohmic contacts of the sample. (c) AMR signal vs number of applied pulses. (d) Free-space THz pulses are applied to the sample to induce switching of antiferromagnetic order. (e) Transient electric field of the incident THz pulse. (f) AMR signal vs number of applied THz pulses.

To characterize our sample, we first applied microsecond voltage pulses (Fig. 2b) through Ohmic contacts to the sample. As expected from previous works of our collaborators, we observed that with every additional pulse, the AMR signal increased (Fig. 2c), indicating that an increasing number of spins had been rotated.

In a second experiment using the very same sample and setup, we excited the sample with free-space THz pulses (Fig. 2d) that featured a duration of ~1 ps and a peak field of ~0.3 MV/cm (Fig. 2e). Remarkably, we found the AMR signal to exhibit an increase when the number of applied pulses increased (Fig. 2f), fully analogous to the result of MHz-driving (Fig. 2c). Further checks showed that antiferromagnetic order of CuMnAs can indeed be switched (here rotated) using THz pulses. In complete analogy to the electrical approach (Fig. 2a), switching back was achieved by rotating the polarization of the THz beam by 90°.

We are currently working on time-resolving the switching dynamics. This goal requires the development of suitable ultrafast probes of antiferromagnetic order.

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Nanoscale Surface Chemistry Group
Dr. Takashi Kumagai

Group Leader, Department of Physical Chemistry (since 2013)
JSPS overseas research fellowship, FHI, Department of Physical Chemistry (2011–2013)
Ph.D., Kyoto University (2011)
Diploma, Kyoto University (2008)

Near-field Physics and Chemistry in Plasmonic Nanocavities

Near-field physical and chemical processes have gained increasing attention due to the potential for nanoscale imaging, ultrasensitive chemical analysis, and enhancement of photochemical reactions. Plasmonic nanocavities are key for various applications due to their strong field confinement and enhancement. The group of Takashi Kumagai has focused on investigation of near-field physics and chemistry in plasmonic nanocavities using a newly developed low-temperature STM for precise local optical excitation and detection (photon-STM). The photon-STM has been developed in collaboration with UNISOKU Co. Ltd. and was installed in the new STM laboratory in June, 2017. It has achieved high performance and the group has carried out the experiments described below. Part of this work is done in collaboration with the Ultrafast Scanning Probe Microscopy group of Dr. Melanie Müller.

Plasmon-assisted resonant electron tunneling

Light-induced electron transfer is of fundamental importance in nature and intimately related to energy conversion such as photovoltaics and photocatalysis. In particular, efficient electron transfer by visible light is a key to make use of solar energy. Plasmonic nanostructures can be used to harvest light and enhance photophysical and photochemical processes through surface plasmon excitation leading to dramatic enhancement of electromagnetic fields. Employng the photon-STM the group demonstrated plasmon-assisted *resonant* electron tunneling from an Ag or Au tip to field emission resonances (FERs) of a Ag(111) surface induced by irradiating an STM junction with a focused cw laser at visible wavelengths (Fig. 1a). As a hallmark of the plasmon-assisted resonant tunneling, a significant redshift of the FERs is observed whereby the shift of the first resonance equals the incident photon energy (Fig. 1b). STM-induced luminescence measurement for Ag and Au tips reveal a clear correlation between the laser-induced change in the FER spectra and the plasmonic properties of the junction. Our results demonstrate a novel resonant electron transfer mechanism in a plasmonic nanocavity (Fig. 1c).

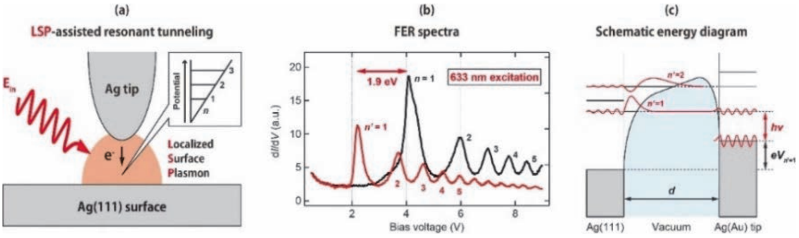

Figure 1: (a) Schematic of the experiment. (b) FER spectra with (red) and without (black) illumination. (c) Schematic energy diagram of plasmon-assisted resonant tunneling in the STM junction.

Near-Field manipulation in a scanning tunneling microscope junction with plasmonic Fabry-Pérot tips

Manipulation of near-field properties such as the spectral response, optical coupling to far fields, and local field enhancement, by metallic nanostructures is a is a key goal in plasmonics, providing a wide range of applications in nanooptics, single-molecule sensing, and enhancement of photovoltaics and photochemistry. Advances of nanoscale fabrication techniques have allowed to control surface plasmons at metal–dielectric interfaces, leading to the discovery of exotic properties of near-field optics, e.g., extraordinary high transmission through subwavelength holes. Plasmon excitation in nanoscale cavities is of particular importance due to dramatic enhancement and extreme confinement of an electromagnetic field, which result in strong light–matter interactions. The group demonstrated that the spectral features of a plasmonic STM junction can be manipulated by nanofabrication of Au tips using focused ion beam (FIB). An exemplary Fabry–Pérot type resonator of surface plasmons is demonstrated by producing the tip with a single groove on its shaft (Fig. 2a and 2b). Scanning tunneling luminescence spectra of these Fabry–Pérot tips exhibit spectral modulation resulting from interference between localized and propagating surface plasmon modes (Fig. 2c). The standing wave characteristic was reproduced by electrodynamic simulations (Fig. 2d). In addition, the quality factor of the plasmonic Fabry–Pérot interference can be improved by optimizing the overall tip shape. This approach paves the way for near-field imaging and spectroscopy with a high degree of accuracy. The group Furthermore, plasmonic FIB-tips we used to control single-molecule reactions and to demonstrate near-field action spectroscopy (Fig. 2e-i) which provides a unique way to characterize local field enhancement in plasmonic nanocavities. The FIB fabrication has been performed in close collaboration with Electron Microscope group in the AC department.

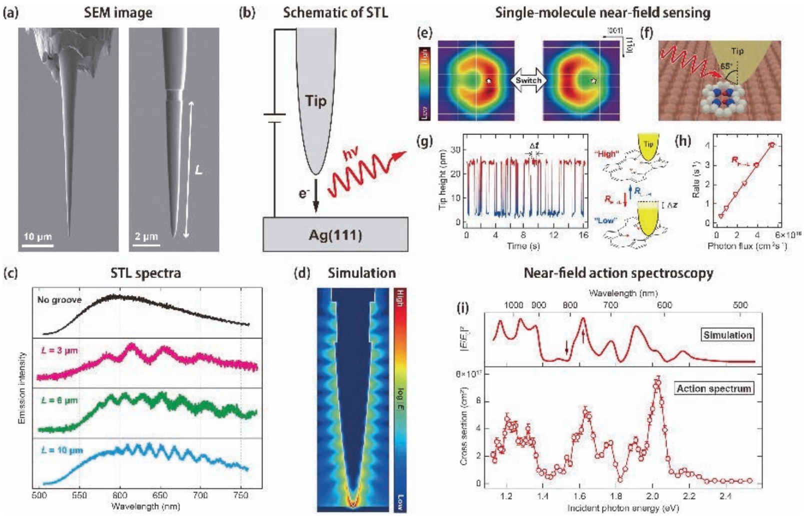

Figure 2: (a) SEM images of an Au FIB-tip with a single groove on the shaft at the distance L from the apex. (b) Schematic of STL. (c) STL spectra obtained for FIB-tips without the groove and with the groove at L=3, 6, 10 µm. (d) Electrodynamics simulation of plasmonic Fabry–Pérot interference in the grooved FIB-tip. (d) STM image of a single porphycene molecule on Cu8110) at 5 K, which acts as a nanoscale sensor to detect local field enhancement in plasmonic STM junctions. (e) Schematic of experiment. (f) Two-state switching of prophycene induced by localized surface plasmon excitation in the STM junction. (g) Fluence dependence of the tautomerization rate from which we can calculate the near-field cross-section. (h) Tautomerization cross section as a function of incident photon energy (near-field action spectrum).

Resolving the correlation between tip-enhanced resonance Raman scattering and local electronic states with 1 nm resolution

Low-temperature tip-enhanced Raman spectroscopy (TERS) enables chemical identification with single-molecule sensitivity and extremely high spatial resolution down to the atomic scale. The large enhancement of Raman scattering obtained in TERS can originate from physical and/or chemical enhancement mechanisms. Whereas physical enhancement results from strong near-field enhancement through excitation of localized surface plasmons, chemical enhancement is governed by resonance in the electronic structure of the sample, which is also known as resonance Raman spectroscopy. The group applied tip-enhanced resonance Raman spectroscopy (TERRS) to ultrathin ZnO layers epitaxially grown on a Ag(111) surface (Fig. 3a and b) and demonstrated that both enhancement mechanisms are operative. Furthermore, in combination with scanning tunneling spectroscopy (STS), it is demonstrated that the TERRS intensity strongly depends on the local variation of electronic states at the ZnO/Ag(111) interface (Fig. 3c and 3d). It was reveal that the spatial resolution of TERRS is dependent on the tip–surface distance and reaches nearly 1 nm in the tunneling regime (Fig. 3e and 3f). This can be rationalized by strong field confinement resulting from an atomic-scale protrusion on the tip apex. Comparison of STS and TERRS mapping clearly shows a correlation between resonantly enhanced Raman scattering and the local electronic states at near-atomic resolution. These results suggest that

TERRS can provide a new approach for the atomic-scale optical characterization of local electronic states.

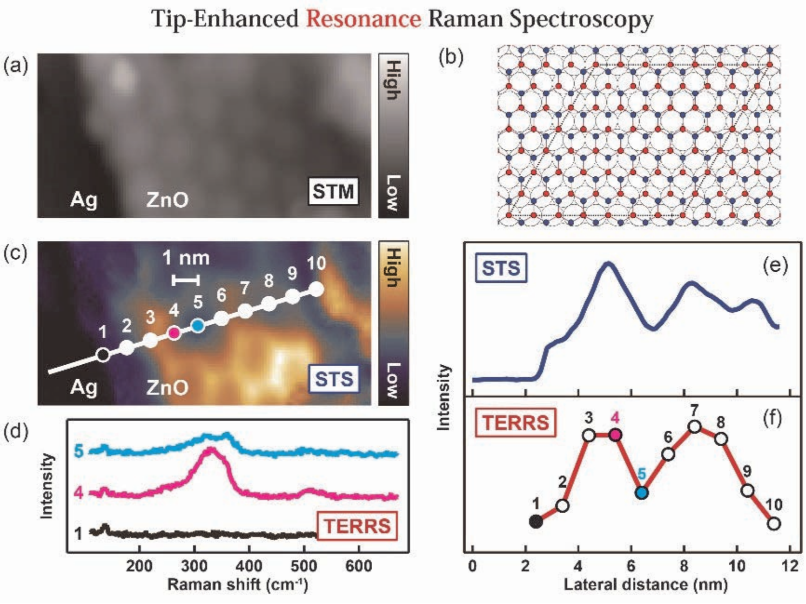

Figure 3: (a) STM image of ultrathin ZnO layers epitaxially grown on a Ag(111) surface. (b) Schematic structure of the ultrathin ZnO layer. (c) STS mapping over the ZnO layer. (d) TERRS spectra obtained at different positions. (e) Profile of the STS and TERRS intensity along the line in (c).

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Ultrafast Scanning Probe Microscopy Group
Dr. Melanie Müller

Visiting Scientist, University of Colorado, Boulder (2019)
Group Leader, Department of Physical Chemistry (since 2017)
Ph.D., Freie Universität Berlin (2017)
Diploma, Johannes-Gutenberg Universität Mainz (2010)

THz-gated Scanning Tunneling Microscopy of Photoexcited Nanostructures

Since the start of the *Ultrafast Scanning Probe Microscopy Group* in 2017, much of our work concentrated on the development and implementation of a THz-gated Scanning Tunneling Microscope (THz-STM) specifically designed for the combination of broadband optical and THz excitation, respectively. The main goal of our research is to probe the local femtosecond dynamics of photoexcited systems like nanostructures or surfaces on the nanometer scale down to atomic length scales. Understanding the role of the local environment and surface conditions on ultrafast carrier dynamics and their relaxation pathways is a longstanding goal in surface dynamics. In this regard, using THz-STM we aim at combining femtosecond spectroscopic information with atomic spatial resolution, complementing the wide variety of time-resolved surface science techniques available in the department of physical chemistry.

In close collaboration with the group of Takashi Kumagai and Unisoku Co., Ltd. we developed an ultrahigh-vacuum STM/AFM system with two large-aperture motorized parabolic mirrors integrated on the SPM platform in UHV for broadband excitation and light detection covering the full spectral range from the visible to the THz. The setup is operational at room temperature since February 2019 and is fully compatible to be upgraded to cryogenic temperatures down to 5K. For ultrafast gating of the tunnel junction we employ broadband single-cycle THz pulses generated from a metallic spintronic emitter (STE), as developed in our department in the THz-group of Tobias Kampfrath. A broadband OPCPA laser system, shared with the group of Ralph Ernstorfer, with variable repetition rates from 0.2 – 2 MHz at few μJ pulse energies is used for THz-generation and simultaneous photoexcitation of the STM junction.

First experiments include the investigation of THz near-field coupling to the tip, which requires time-domain sampling of the THz electric field directly in the STM junction as accomplished via ultrafast gating of photocurrents. Moreover, in this context we could probe nano-localized dynamics of photocarriers in a metallic STM junction on femtosecond timescales, manifested as deviations of the measured waveform from the real THz near-field. In terms of setup development, we analyzed the performance of the spintronic emitter using a curved-wavefront excitation geometry implemented for efficient pumping with few-femtosecond optical pulses at the μJ-level.

Waveform sampling of THz near-fields via ultrafast photocarrier gating

The transient electric field of a THz pulse acts as a quasi-static voltage applied to the STM, controlling current flow on femtosecond timescales. Optimal operation of a THz-gated STM evidently requires exact knowledge of the THz near-field waveform, which can differ significantly from the far-field waveform due to tip antenna effects. Moreover, the *local* waveform of the THz pulse critically depends on the position of the point-like tip in the THz focus, which additionally can suffer from strong chromatic aberrations, originating for instance from imperfect frequency-dependent collimation of the radiated THz beam. Whereas the tip itself acts as a low-pass filter to the THz pulse, the point-like character of the tip makes it difficult to compare the near-field to the far-field waveform measured via spatially integrating electro-optic sampling. It is thus essential to routinely measure the THz waveform directly in the STM for given settings of the setup.

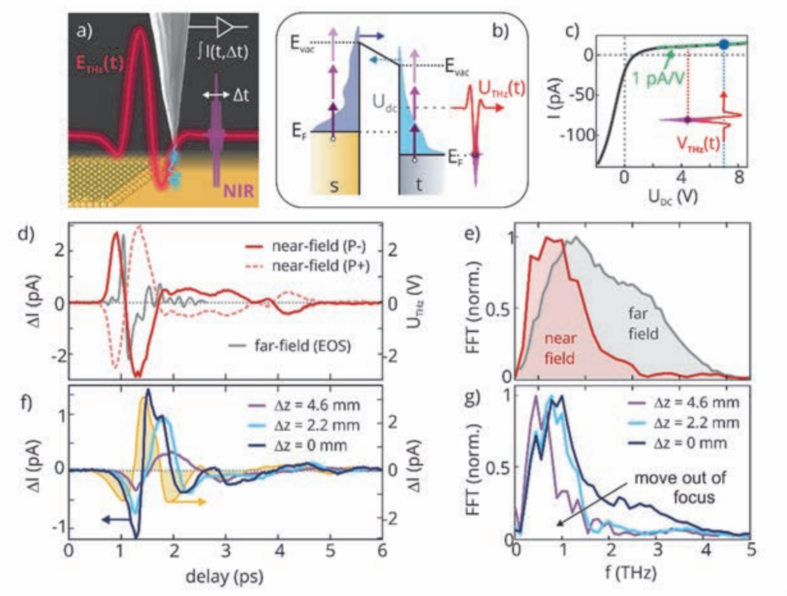

Figure 1: (a) Concept of photoexcited THz-STM. (b) Modulation of the potential barrier in the STM junction by the transient electric field of the THz pulse. (c) Photocurrent-voltage characteristics of the photoexcited junction of a W-tip on HOPG at few nm distance and illustration of transient bias modulation by the THz pulse. (d) THz-induced photocurrent modulation at 7 V bias and for opposite THz pulse polarities, sampled in the linear part of the photocurrent-voltage curve. The THz near-field waveform and applied THz voltage is revealed indicating a significant low-pass filter effect, as evident also from the corresponding spectra (e). (f) Change of the THz waveform as the tip is moved out of the THz focus by a distance Δz, and corresponding FFT spectra in (g). The yellow filled curve shows the waveform by tuning the Gouy phase shift at a fixed tip position in the THz focus via the incident THz beam divergence.

In this regard, much of our effort was invested to show that the THz near-field waveform can be sampled via THz-induced modulation of photoemission currents through the STM junction excited by femtosecond optical pulses, as sketched in Fig. 1. This type of THz-VIS crosscorrelation sampling can be routinely used independent of the type of sample and at all temperatures. However, care has to be taken to exclude temporal broadening due to non-instantaneous effects such as long-lived photocarriers and electron-propagation effects. In their absence, the delay-dependent THz-induced change of the photocurrent is determined by the instantaneous THz electric field, with a dependence dictated by the photocurrent-voltage characteristic, as seen in Fig. 1c). In the particular case of a linear IV dependence, knowledge of its slope allows for easy quantitative calibration of the applied THz voltage. For the example shown in Fig. 1d) peak THz voltages of 4 V_{pp} are obtained in the junction.

Employing this method, we characterized the THz near-field dependence of the relative position of tip and THz focus, as shown in Fig. 1f) and 1g), where we see low-pass filtering due to frequency-dependent spatial overlap. We further can use the Gouy phase shift to tune the THz waveform from sinus-like to a cosine-like pulse (yellow curve). Together with straightforward control of the THz polarity and polarization via magnetization of the STE, our setup allows us to precisely tune the THz waveform according to the requirements for THz-STM.

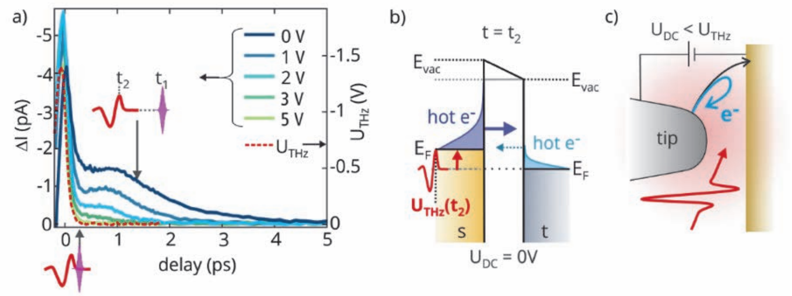

Figure 2: Dynamics of photocarriers measured for a W-tip and HOPG sample in a IR-pump - THz-probe scheme. (a) THz-induced photocurrent modulation for different sample biases at tunneling distances (I_{set} = 200 pA, U_{set} = 10 V). Note that the x-axis is reversed compared to Figures 1 (d) and (f). The red dashed line shows the first half cycle of the applied THz transient (right y-axis). Signal observed before arrival of the THz pulse can originate from either (b) long-lived hot electrons inside tip and sample, or (c) from slow photoelectrons decelerated back into the tip or sample by the THz field at low DC voltages $U_{DC} < U_{THz}$, for which photoelectron propagation is dominated by the spatio-temporal distribution of the THz field.

Beyond characterization of the THz near-field, we started to investigate the dynamics of photoexcited charge carriers in the STM junction. Depending on sample bias and THz polarity, we find carrier dynamics on femtosecond to few picosecond timescales to contribute to the signal. For the example shown in Fig. 2a) using a W-tip and HOPG sample, photocarrier dynamics are observed several ps before arrival of the THz pulse. Whereas photoemission is a nearly instantaneous effect suitable for waveform sampling, tunneling of long-lived hot electrons at energies closer to the Fermi level requires convolution of the waveform with their respective lifetimes. Furthermore, for DC biases smaller than the applied THz voltage, slow photoelectrons can be decelerated back into the tip (or sample). To understand the observed dynamics, further modeling of photo-assisted tunneling through a time-dependent junction and calculation of photoelectron trajectories within the THz near-field is required. These experiments are a first step to demonstrate the ability of THz-STM to probe ultrafast carrier dynamics with femtosecond time resolution on THz sub-cycle timescales.

Curved-wavefront excitation of a spintronic THz emitter

Optimal operation of a THz-STM requires variable repetition rates between 100's kHz to few MHz, with μJ pulse energies for generation of THz pulses with sufficient field strength. Optically pumped emitters such as photoconductive antennas and spintronic emitters are very attractive for THz-STM as they allow for simple adjustment of the THz polarity and polarization, but they suffer from saturation effects and low damage thresholds. In the case of a spintronic emitter pumped with μJ optical pulses, depending on the pump spot size both ablation and thermal suppression of THz emission might occur. In this regard, placing the STE in the convergent or divergent part of a focused pump beam, we aimed for a flexible setup enabling tunable pump spot sizes which can be optimized for a specific repetition rate and pump pulse energy, respectively.

We find that the THz field strength decreases by more than 90% close to the pump focus independent of the pulse energy, excluding thermal heating effects. We attribute this large drop to a superposition of sub-wavelength emission (causing decreased radiation coupling to the far field) and THz beam propagation effects. Further investigation taking into account propagation of the THz beam are underway.

Further directions

After an initial period of implementation and experimental characterization of the setup, we will focus on using THz-STM as a nanoscale platform to study high-field THz-driven nonequilibrium states in matter with high spatial resolution using high repetition rate THz sources. We recently started to study room-temperature electroluminescence of p-doped GaAs out of the STM junction, aiming for the spatio-temporal investigation of THz-driven luminescence from semiconductor surfaces on sub-cycle timescales. Moreover, we are planning first time-resolved imaging experiments on photoexcited semiconductor surfaces and metal-semiconductor interfaces at room temperature. Furthermore we will upgrade our STM to cryogenic temperatures, which is necessary to access not only a wider class of samples, but also to improve the stability of the illuminated STM junction. This is a key aspect for experiments which conceptually do not require low temperatures, but which suffer from thermal instabilities of the tip and thermal drifts at room temperature.

Quantum Transport & Nanoelectronics Group
Dr. Matthias Koch

Group leader, FHI, Department of Physical Chemistry (since 2018)
Postdoctoral Fellow FHI, Department of Physical Chemistry (2016-2018)
Postdoctoral Fellow, University of New South Wales, Sydney (2014-2016)
Dr. rer. nat., Freie Universität Berlin (2013)
Diploma, Freie Universität Berlin (2009)

High Resolution Scanning Gate Microscopy

Quantum transport on the nanoscale is often probed by electrical conductance measurements. However, these measurements typically lack spatial resolution and the observable, the current, is averaged over the whole junction. Especially at nanometer length scales the environment as well as the precise chemical composition of the junction will influence the measurement and the electronic properties of the material. Therefore, having utmost control over the junction is of importance. In our group we want to combine commercially available scanning probe microscopy (SPM) methods with additional electrodes integrated into the sample system, parallel to the surface, to electronically contact/gate nano-scale materials with nanometer precision. These additional electrodes in close proximity to the surface extend the functionality of the SPM to perform scanning gate microscopy, pointometry as well as Kelvin probe microscopy. In this manner the high spatial resolution of SPM can be combined with sophisticated transport experiments. In a nutshell, the detailed composition of the junction can be characterized by SPM while performing transport experiments. Furthermore, SPM enables modification of the structure or adsorbed molecules with atomistic precision.

The core of this technique are electrodes which bridge the gap from mm scale patches to µm wide contacts in the center of the silicon sample. It is of particular importance that these electrodes stay intact especially after the high temperature treatment necessary for preparation of Si(100), by several short annealing steps at 1000°C or higher. Therefore, antimony, which has a low segregation speed, was ion-implanted in close proximity to the surface. Key is that the silicon host material becomes insulating at low temperature whereas the implanted electrodes stay metallic because of their high dopant density. The precise arrangement of the ion-implanted electrodes is defined by the experimental question. For example, a narrow spacing between two electrodes is desired for conductance experiments while a larger separation is favored when using them to apply an electric field for gating purposes (see Fig. 1).

For this project we have designed and set up a home-build ultra-high vacuum system optimized for semi-conductor preparation which we extended with a commercially available low-temperature SPM from Createc GmbH. Most importantly we have developed a sample holder matching the needs of high quality semi-conductor surface preparation and in-situ transport measurements: Four insulated contacts are integrated into the sample clamping system of the sample holder, equipped with direct heating possibilities. Each of the four clamps will be pressed against one of the four ultra-shallow electrodes for electrical contact.

Experimental characterization of the electrodes

We tested a first set of ion-implanted electrodes by comparing their temperature dependent resistivity with and without antimony wires. To avoid out-diffusion of the dopants the thermal budget must be limited to approximately 1050°C. In contrast to a reference sample without wires the four-probe resistance of a 1 µm wide wire does not rise continuously with decreasing temperature, but reaches a plateau at roughly 0.01M Ohm (see Fig. 2a). Furthermore, a characteristic Ohmic behavior is found for the implanted wires, which is desired to rule out contributions of the contacts to the conductance measurements (see Fig. 2b). This changes when annealing the sample above 1050°C. Out-diffusion of the dopants sets in and the resistivity increases and a non-linear IV dependence is observed.

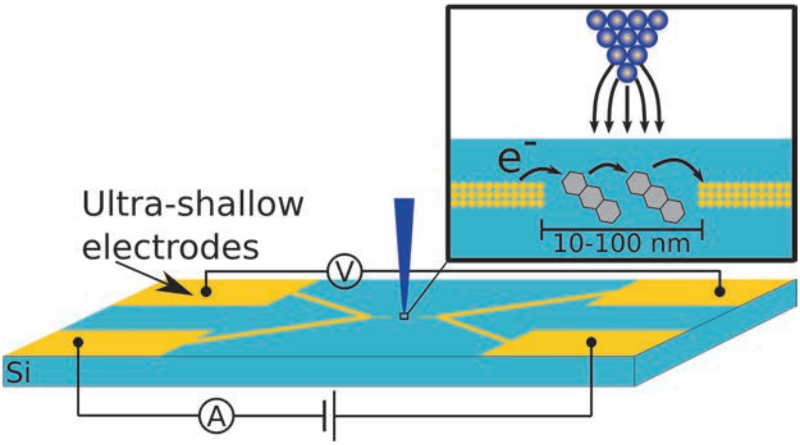

Figure 1: (a) Schematic illustration of the experimental setup: A Si(100) sample equipped with four ultra-shallow ion-implanted electrodes bridging the gap from mm to µm. These implanted electrodes can be subsequently extended with STM hydrogen resist lithography to the nm scale.

The lateral confinement of the implanted regions is confirmed by measuring the resistance of two electrodes separated by a narrow insulating region with varying width. Electrically this can be described as two p-n junctions in series, resulting in an open bipolar transistor. The IV traces are no longer Ohmic but have a large non-conducting region, which increases linearly with the separation (see Fig. 2 b and c). The narrow area between the two electrodes might limit the formation of the depletion layer and the device will be punched through. Interestingly, even when annealing the sample repeatedly to 1050°C the gap stays intact, demonstrating that lateral diffusion seems to play a minor role.

To locate the electrodes on the sample with the SPM tip a marker design, compatible with the high temperature treatment, was developed, which does not deteriorate the surface quality. The reactive ion etched markers allow us to position the SPM tip with nm-precision, even after taking the sample out of the SPM stage and growing a silicon encapsulation layer (M. Koch *et al.* 2019).

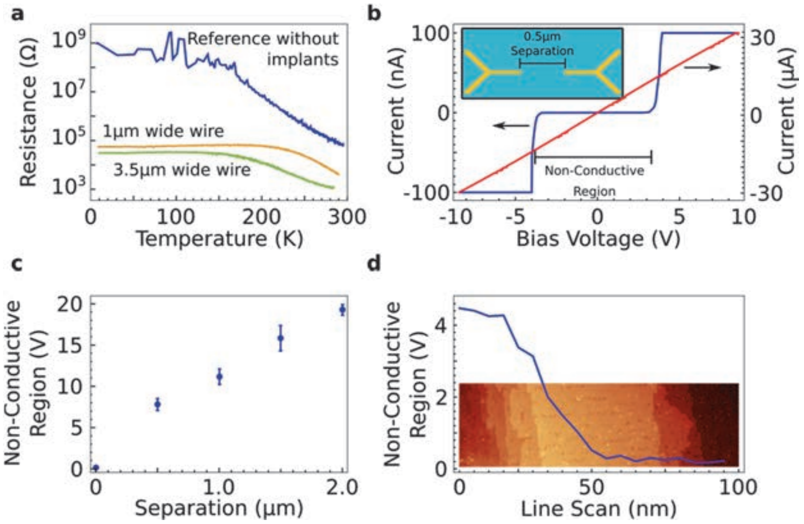

Figure 2: (a) Sample resistance as a function of temperature for a reference sample without implants and for two ion-implanted wires with a width of 1 and 3.5µm, respectively. (b) IV trace of a 1µm wide wire (red) and of two electrodes separated by 0.5µm weakly doped silicon (blue). (c) Size of the non-conductive region as a function of the electrode separation. (d) Non-conductive region extracted from STM spectroscopy. The inset shows the STM image of the same region. The sample temperature is 5K if not stated otherwise.

The enhanced conductance of the electrodes is visualized with STM spectroscopy. With increasing distance of the SPM tip to the electrodes a non-conductive gap opens which increases rapidly in size and a high bias voltage is required for STM imaging. However, we find that the presence of the electrodes does not influence the surface quality (Fig. 2 d).

Outlook

We have now successfully developed a platform with conducting electrodes on insulating Si(001), which bridge from mm length scale down to the (sub) µm scale. This versatile sample system will be used to study different scientific problems. For example, we will investigate the charge transport through organic molecules and nanostructures as well as electronic properties of nanoscopic 2D materials, like transition metal dichalcogenide (TMDC) flakes. To contact objects even down to the few nm scale we want to extend the ion-implanted ultra-shallow electrodes with STM patterned electrodes (STM hydrogen resist lithography) based on controlled phosphine adsorption. While the hydrogen passivated silicon surface is rather inert, the non-terminated (hydrogen free) Si(001) surface consists of unsaturated dangling bonds and is highly reactive. By controlling the surface passivation and removing hydrogen with atomic precision, the adsorption site of molecules can be steered. In the case of phosphine this has been perfected to pattern electronic circuits with STM. These truly nano-scale circuits will then be used to electrically contact for example organic assemblies to study their transport behavior.

By applying oscillating electric fields we intend to induce motion on the molecular level which will be studied by SPM. For this purpose we have designed a double-decker molecule with an integrated dipole moment, isolated from the substrate. SPM manipulation will allow to control the environment of the molecular rotor so that we can address the steric interaction between individual molecules.

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Interfacial Molecular Spectroscopy Group
Prof. Dr. R. Kramer Campen

Professor of Physics, University of Duisburg-Essen (since 06/2019)
Group Leader, FHI, Department of Physical Chemistry (since 2011)
Post-Doctoral Researcher, FOM Institute AMOLF, The Netherlands (2011-2007)
PhD, Pennsylvania State University, USA (2007)

Interfacial Molecular Spectroscopy

Much of the work performed in our group is done in collaboration with the Nonlinear Spectro-Electrochemistry Group of Dr. Yujin Tong, who was a post-doc with us until 2017. While there is substantial overlap of the interests of both groups, he has focussed to a larger extent on the steady-state characterization of other catalytically interesting systems. As of the winter of 2019/20 the activities of both groups will move to the University of Duisburg-Essen where Dr. Campen has been appointed as a W3 Professor and Dr. Tong will take up a senior scientist position.

The Goal: Mechanistic Insight into (Photo)electrocatalysis

(Photo-)electrocatalytic chemistry holds out hope for mitigating human effects on the climate system, more efficiently producing value-added chemicals and helping clean up polluted environments. Building the best possible catalysts for reactions of interest requires understanding the *mechanism* of the relevant heterogeneous chemistry and its change with catalyst material, solution composition and surface structure. Despite the clear need for this sort of insight there are very few catalytic systems where the mechanism of the relevant chemistry is well understood.

The absence of such insight can be largely attributed to three factors: (1) particularly for buried, solid/liquid, interfaces characterizing interfacial molecular structure is experimentally challenging, (2) most candidate catalytic materials have significant spatial structural heterogeneity and thus presumably strong spatial heterogeneity in reactivity, and (3) assuming the first two hurdles can be overcome, experimental characterization of interfaces under steady-state reactive conditions cannot unambiguously probe mechanism: one cannot know whether a particular species observed at an interface is an intermediate in the desired chemistry or an unwanted side product.

In the *Interfacial Molecular Spectroscopy Group* we focus on addressing these challenges for prototypical electrode/electrolyte and solid/gas systems. We are doing so by developing nonlinear optical, vibrationally resonant sum frequency generation (VSFG), and mixed optical/current measurements that allow the characterization of the solid/gas and electrified solid/liquid interface with *interfacial specificity*; by performing second harmonic generation (SHG) microscopy *to spatially characterize chemical reactivity operando* and *by performing femtosecond perturbation experiments* to overcome the limits of steady-state characterization of reactivity.

Building Interface-Specific Tools

From 2017–2019 we invested much effort in developing VSFG spectroscopy for application to (thin-film) spectro-electrochemistry. It was necessary to overcome a substantial number of technical obstacles (e.g. identifying materials that are suitable for both optics and electrochemistry, compensating for distortion of fs pulses, etc). In many of these we were largely successful: *e.g.* we have characterized the potential dependent structure of water and of sulfate on an Au and Pt electrodes and of ClO_4^- at the air/water interface [Tong 2017] [Zwaschka 2018] [Tong 2018].

Because we are interested in (photo)electrocatalytic systems with semi-conductor electrodes, and a central issue in such systems is the role of surface states, we have invested much effort in developing optical surface phonon spectroscopy by extending VSFG to MIR wavelengths. Part of the challenge here is relating this novel observable to microscopic surface structure. We have done so on α-Alumina single crystals, where, in collaboration with theory from Prof. Peter Saalfrank (University Potsdam) we have quantified the manner in which increasing coverages of water (from UHV to ambient) induce surface reconstruction.

Finally, conventional VSFG spectroscopy detects the intensity of the emitted sum frequency light, not the field. However, accurate extraction of the interface's nonlinear optical response, and in particular the separation of surface and possible bulk contributions, requires high precision measurements of both the amplitude and phase of the emitted sum frequency field. Performing this measurement, particularly for interfaces between two condensed phases, is extremely challenging. In this period we have developed a novel, collinear, time domain, balance detected heterodyned spectrometer [Thämer 2018] and demonstrated its application to the quantitative separation of surface and bulk signals in α-quartz [Thämer 2019], and for the characterization of the optical response of the metal electrode/ electrolyte interface.

Resolving the Spatial Heterogeneity of Reactivity

To address the challenge in understanding the *spatial heterogeneity* of electro-catalytic reactivity we initiated a collaboration with Prof. Sylvie Roke (at EPFL Lausanne). In proof-of-principle experiments we constructed in electrochemical cell inside an existing second harmonic generation (SHG) microscope and imaged the electrooxidation and oxygen evolution reactions on several Au electrodes *operando*. The exceptional signal-to-noise of this microscope made it possible to resolve the growth and detachment of O_2 bubbles, under mildly anodic conditions, in real-time. Given this capacity, we demonstrated that the reactivity of the surface is controlled by active sites that are 3-11 % of the surface area, as shown in Fig. 1, and are of least two different structural types. This is a new approach to electrocatalytic systems and is, to our knowledge, the first study to spatially resolve product formation in water splitting on an electrocatalyst.

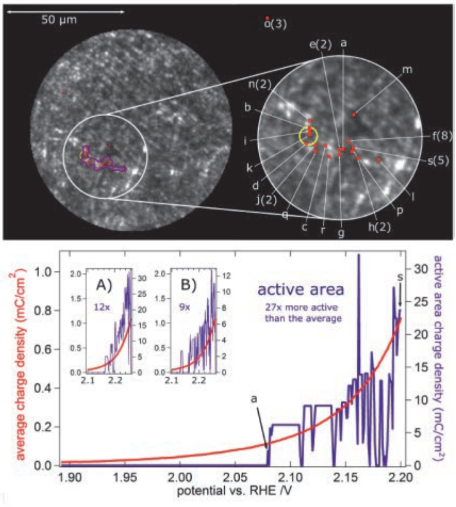

Figure 1: top left panel: circular FOV of the electrode at 1.8 V vs. RHE. Red dots are sites at which bubbles nucleate during the linear potential sweep shown in the bottom panel. Top right: magnification of active area showing the order of bubble appearance. Bottom panel: comparison of measured electrode charge density and bubble derived charge density for three different fields of view.

Moving Beyond Steady-State Reactive Conditions

We are currently moving beyond steady-state nonequilibrium characterization for the hydrogen evolution reaction (HER) on Pt and Au. We do so by performing perturbation experiments triggered, using fs optical pulses, on the fs timescale of electron transfer. As an initial step on Pt single crystal working electrodes we demonstrated the detection of photocurrents induced by femtosecond optical excitation as a function of bias [Zwaschka 2019]. This approach allows separation of current induced by the femtosecond duration elementary step of charge transfer from that induced by slower, picosecond, electrolyte structural dynamics. The results of its application to the HER on Pt suggest that ease of electron transfer may control previously observed trends in H_2 generation activity with change of Pt crystal face. Current work is devoted towards spectroscopic characterization of the interface after excitation using VSFG.

Using a similar approach, we also characterized the mechanism of H_2 generation at the Au electrode/water interface. In contrast to Pt, hydrogen adsorbs very weakly on Au and thus we initiate adiabatic electron transfer by forming an interfacial solvated electron (which reduces water forming H_2 over longer timescales). We have observed this solvated electron in a novel two pulse photovoltage scheme in which we form the solvated electron with an initial femtosecond UV pulse, illuminate the interface with a second fs pulse, and measure the photovoltage as a function of delay between the two pulses and the wavelength of the second pulse. This scheme, some results from the application of which are shown in Fig. 2, in conjunction with more conventional UV pump – VSFG probe measurements, allows us to extract the spectrum of the solvated electron at a metal water interface and show how the surface bias alters its local structure.

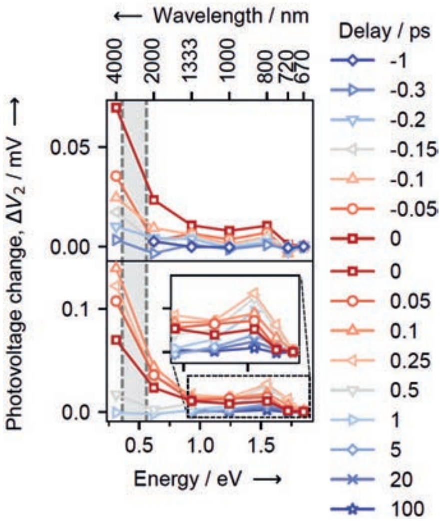

Figure 2: Photovoltage induced by a 4.56 eV UV pulse and a second pulse of variable photon energy plotted as a function of photon energy and delay between the two femtosecond pulses. The presence of a photoinjected conduction band electron near 0 fs Is clear (adsorption in the far infrared) and its localization over 200 fs (shift of spectral position towards 800 nm). The resulting localized solvated electron is long-lived and its spectral response, which is 200 meV red shifted from its bulk value, reflects the electrons partial desolvation at the interface.

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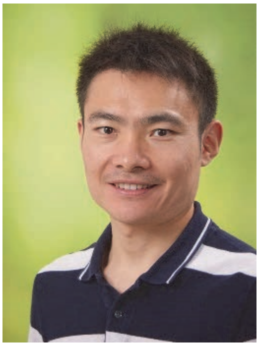

Nonlinear Spectro-Electrochemistry Group
Dr. Yujin Tong

Group Leader, FHI, Department of Physical Chemistry (since 2018)
Postdoctoral Fellow, FHI, Department of Physical Chemistry (2012-2017)
Post-Doctoral Researcher, FOM Institute AMOLF, The Netherlands (2011)
PhD, Hokkaido University, Japan (2010)

Nonlinear Optical Spectro-Electrochemistry

A deep understanding of electrochemical processes generally requires a combination of electrochemical and spectroscopic methods. While electrochemical analysis can provide the potential, current and charge information, the spectroscopies can reveal the electronic and vibrational properties of the reaction intermediates or products. The combination is referred to as *spectro-electrochemistry*. Among the modern spectro-electrochemical techniques, vibrational spectrsocopy such as Infrared absorption and Raman scattering are powerful in terms of providing structural and chemical information of interfacial species and have thus been widely employed for *in situ* spectro-electrochemical characterization. However, IR and Raman spectroscopies are not surface specific. When the surface and the bulk have similar chemical compositions, i.e. bulk solvents and anions adsorb to the electrode surface, it is very challenging to selectively probe the adsorbed species and discriminate from those of the bulk. Vibrational sum frequency spectroscopy (VSFS), based on the 2nd order nonlinear optical process, is intrinsically surface specific hence an excellent tool in probing buried interfaces. Our group employs VSFG to study fundamental processes in electrochemistry, whereby a majority of work has been done in collaboration with Interfacial molecular spectroscopy group of Dr. R. Kramer Campen.

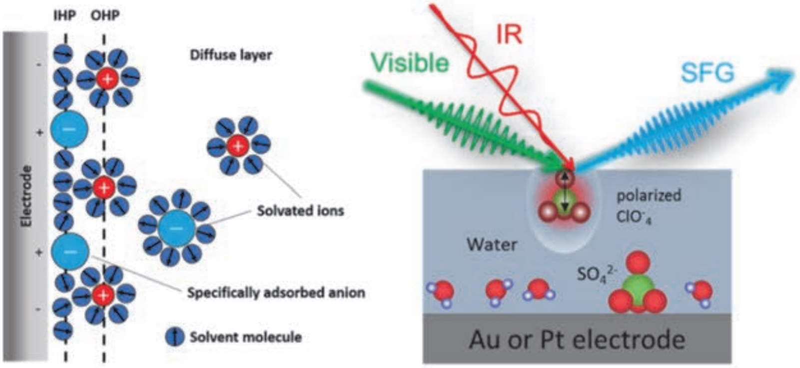

Figure 1: Left panel: Electric double layer structure according to the Gouy–Chapman–Stern model. Right panel: Example systems studied with VSFS in our group: hydrophobic water on gold; sulfate adsorbed on a Pt(111) single crystal electrode and solvated perchlorate at the air/water interface.

Structure of the electric double layer

Electric double layer is the key component of electrochemistry, where reactants, products, ions and solvents follow certain spatial distribution at the interface. Currently the most accepted model is the Gouy-Chapman-Stern model (Fig. 1 left), in which the interface has been divided into three regions: the inner Helmholtz plane, where solvent and specific anions adsorb directly to the electrode; the outer Helmholtz plane, where solvated cations present; and the diffuse layer, where ions follow Poisson- Boltzmann distribution. However, this model is depicted based essentially on the thermodynamic measurements, i.e. the electrocapillary curve, surface excess, differential capacitance, etc. The molecular level information is still insufficient and many of the recent observations cannot be explained by this qualitative model. For example, why different ions can affect the efficiency and selectivity of CO_2 reduction? To gain such information, we have to directly probe the molecules and ions in the electric double layer. This is what we are doing in our group. A few examples are shown in the right panel of Fig. 1. With VSFS, we have successfully probed the bias dependent structure of water on gold electrode, the chemical and physical nature of sulfate anions on Pt(111) surface, and also the anisotropic properties of the polarizability of perchlorate at the air/solution interface where weak electric double layer present.

Structure and chemistry of adsorbates under potential control

Electrochemistry is about the chemical reaction under bias control. In the ideal case, one would like to follow the evolution of all the structure and chemistry of the reactants and products during the reaction. Here we demonstrate with a model system of pyridine derivative (Dimethylaminopyridine) to monitor the deprotonation and phase transition processes with VSFS. As demonstrated in Fig. 2, the spectroelectrochemical approach can provide fruitful information to reveal the detailed physical chemistry actions that happen as a function of bias.

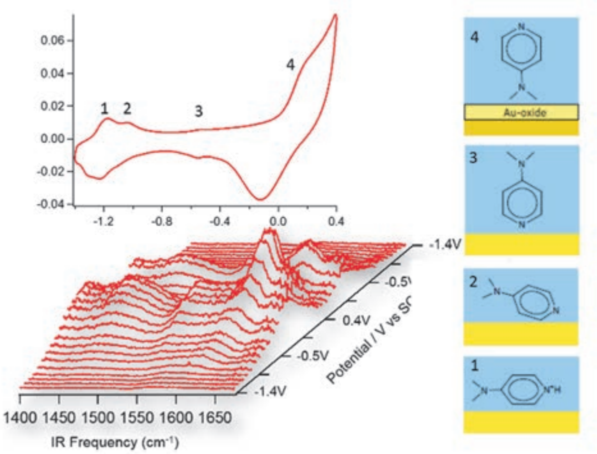

Figure 2: Top left: Cyclic voltammetry of gold electrode in 0.1M $NaClO_4$ solution containing 1mM Dimethylaminopyridine (DMAP). The Numbers indicate features related to the interaction of DMAP with the gold electrode; Bottom left: potential dependent VSFG spectra of DMAP; Right panel: The corresponding chemical and structural changes as suggested from the spectroelectrochemical measurements.

Toward ultrafast electrochemistry

Many electrochemical and photo-electrochemical related processes take place on pico- or even femtosecond time scales. However, a three electrode system coupled to a conventional potentiostat has a rather poor time resolution of, at best, 10 ns. To overcome this resolution problem, we have combined the photocurrent or photovoltage detection with ultrafast laser excitation. As demonstrated in Fig. 3 left, using a sequence of two ultrashort laser pulses of different photon energies and detecting the laser induced change in photovoltage as a function of time delay between the two incident pulses, ultrafast electrochemical processes on femtosecond timescales can be resolved.

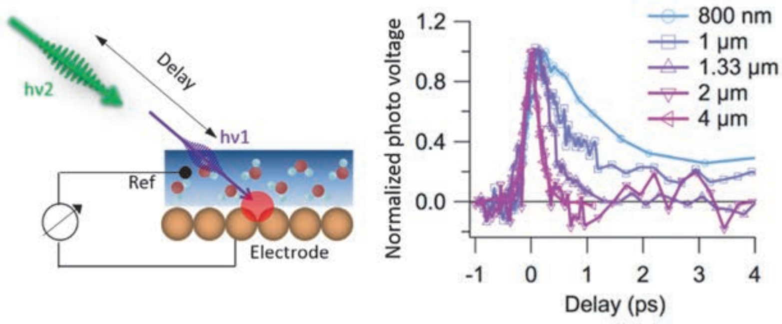

Figure 3: Left panel: scheme for newly developed photo voltage detection scheme to follow ultrafast processes at electrochemical interfaces. Right panel: time dependent photo voltage measured for gold solution interface as trigger by a UV laser (267 nm) followed by a second layer pulse with the indicated energies. The dynamics consistent with the evolution of solvated electron at the interface.

This method can be employed to study the evolution of the interfacial charge carriers which are directly relevant to photo-electrochemistry. Since the measured quantity is the charge/voltage instead of photons, the experimental geometry will be less restricted by the spectroscopic requirement, hence this method can be directly used for *in situ* characterization of the photovoltaic devices. The right panel of Fig. 3 shows as an example of such study, whereby photoinjected solvated electrons at the gold/solution interface are monitored. The excitation laser was chosen at 267nm, whicle the probe laser (2nd pulse) was tuned from mid infrared to the visible frequency region. The induced photovoltage induced by the 2nd pulse is plotted as a function of delay in Fig. 3, right panel. The wavelength dependence is attributed to the different degrees of localization of solvated electrons at the interface. The results suggest that with such ultrafast laser excitation, sub picosecond time resolution could be achieved at the electrochemical interface.

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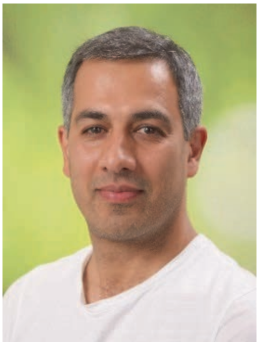

THz-Driven Molecular Dynamics Group
Dr. Mohsen Sajadi

Group Leader at FHI (since 2017)
Postdoc at FHI (2013–2016)
Postdoc at Humboldt Universität zu Berlin (2012)
Dr. rer. nat., Humboldt Universität zu Berlin (2008–2012)

Terahertz Spectroscopy of Molecular Systems

Collective and cooperative molecular motions are decisive to the physical and chemical properties of molecular systems. The spectral fingerprint of these dynamics lies in the low-frequency terahertz (THz) and sub-THz frequency range. We aimed to develop novel spectroscopic techniques by which the entire THz dynamics of liquids can be obtained and further gain microscopic insights on intermolecular interactions.

Ultra-Broadband THz time-domain spectroscopy

We have employed THz time-domain spectroscopy (THz-TDS) to obtain the dielectric loss and permittivity spectra of liquids. In our approach the THz spectra of liquids in the 0.5 THz - 16 THz range are obtained, using an inherent property of the newly developed spintronic emitter. As shown in Fig. 1, upon femtosecond excitation, the spintronic emitter radiates a THz pulse inversely proportional to the complex refractive indices of the surrounding materials (namely diamond and a liquid). Relative to the refractive index of air, the ultra-broadband complex refractive index of liquids is obtained with unprecedented accuracy[7].

Time resolved nonlinear THz spectroscopy

To overcome the limitations of linear THz spectroscopy to characterize the intermolecular interactions and dynamics we employ nonlinear THz spectroscopy by which the intermolecular degrees of freedom are resonantly driven with intense THz pulses.

THz Kerr Effect (TKE). Here, we measure the THz-pump induced ellipticity of an optical pulse traversing the liquid samples as function of the time delay between the THz pump and the optical probe pulses. The third-order nonlinear response of the TKE signal, scales with the square of the permanent dipoles of the liquid at the THz pump frequency and its polarizability anisotropy at the probe frequency. The latter relation was directly corroborated in our TKE studies of molecular gases.

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[7] To keep the novelty of the spintronic THz spectrometer for a patent application, we appreciate if this information is treated as confidential.

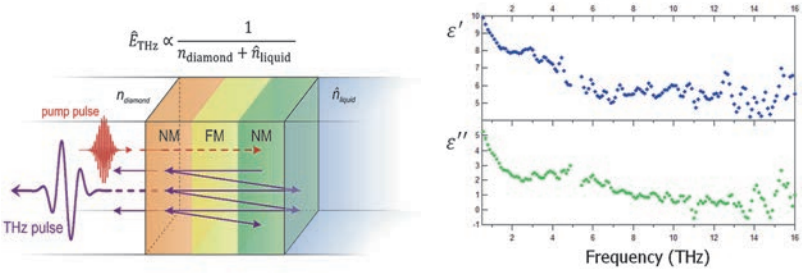

Figure 1: Top) The radiated THz pulse from a few nm thick spintronic emitter is inversely proportional to the refractive indices of the materials sandwiching the metallic stack. We used this feature to obtain the complex refractive index $\hat{n}_{\text{liquid}}$ of liquids. When a liquid is in contact with the metallic stack, its $\hat{n}_{\text{liquid}}$ is printed on the radiated THz pulse due to the Fabry–Pérot effect. Below) The ultra-broadband dielectric permittivity ε' and loss ε'' spectra of liquid water are obtained by the spintronic emitter approach. The covered bandwidth of the measured response depends only on temporal duration and the stability of the laser pulse that pumps the spintronic emitter.

Ultrafast Energy Dissipation in Water. Due to its ability to form hydrogen bonds, water exhibits rich low-frequency intermolecular dynamics within a spectral bandwidth of more than 1000 cm^{-1} (~30 THz). The different intermolecular degrees of freedom associated with the H-bonding network of water facilitate ultrafast and efficient dissipation. Using the TKE approach, we resolved the real-time energy fellow within the H-bonding network of water. As shown in Fig. 2, the bipolar TKE signal of water manifests intermolecular energy transfer between the rotational and the translational degrees of freedom. MD simulations[8] corroborate the experimental findings. A significant THz field induced molecular alignment is found, but no relaxation is resolved. However, we observe a relaxation tail resembling the tail of the TKE signal of water, in the translational degrees of freedom of water molecules.

Nonlinear THz spectroscopy of aqueous ionic solutions. The symbiotic relation of water and ions is vital to the bio-functionality of both partners. Water shields the giant electric field of ions which otherwise strongly polarizes their surrounding and in return its H-bonding network is disrupted. However, the extent of this cooperativity and mechanism of ionic solvation are not exactly known. To this end, we measured the TKE response of a large series of aqueous ionic solutions. Notably, as the TKE response of aqueous solutions originates from a water-water interaction, it can directly probe the structural deformation of water around ions. In general, relative to the pure water signal, we observe a reduction (enhancement) of the TKE signal amplitude for anions (cations) which signifies the different cationic versus anionic solvation mechanisms. Cations are repelled by the H-bonding network and interact electrostatically with the water electron lone pairs, resulting in stronger H-bonding between water molecules.

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[8] In collaboration with Thomas Kühne, Paderborn University and Roland Netz, Free University Berlin.

In contrast, negatively charged anions accommodate themselves in the H-bonding network, disrupting the water-water coupling.

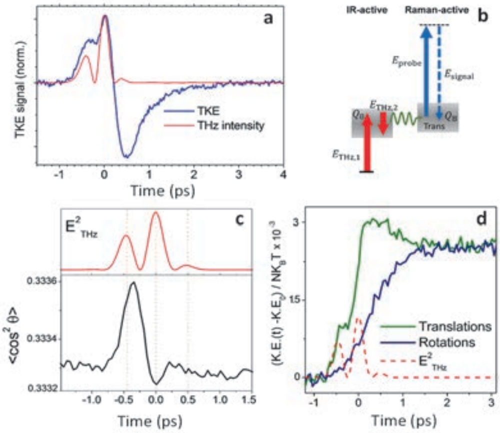

Figure 2: a) Water has a peculiar bipolar THz Kerr effect (TKE) signal with a feature resembling the THz field squared around time zero followed by a relaxation tale with flipped polarity. b) Two-field interaction changes the rotational distribution of molecules (coordinate Q_θ) from a disordered into a partially aligned molecular system. The energy/momentum of this interaction is transferred into the restricted translational motion (coordinate Q_B) of the neighboring molecules, shown as a wavy arrow. The relaxation of the latter mode is observed in the TKE signal via a Raman interaction. c) MD simulations reveal a significant molecular alignment due to the THz electric field torque on the molecular dipoles however, with no relaxation tail. d) Dynamics of the kinetic energy declare relaxation of the molecular translational degrees of freedom (green line) analogous to the TKE signal relaxation tail. The step-like increase of the kinetic energy exhibits the 100 mK temperature rise due to THz absorption.

THz-Magnetic-field induced Faraday Rotation in Molecular Liquids. Upon copropagation of a THz pulse, with ~1T magnetic field strength and 0.5ps duration, and a short optical pulse through molecular liquids, we resolved an ultrafast Faraday rotation of the optical pulse. Analog to the electric Hall effect, the polarization rotation is explained by the deflection of an optically induced instantaneous electric polarization by the Lorentz force originated from the THz magnetic field. The resolved effect scales linearly with the THz magnetic field and quadratically with the molecular polarizability. Nonpolar liquids (e.g. n-hexane) and long chain alcohols (e.g. 1-hexanol) show strongest Faraday rotation.

Rotational dynamics of encapsulated water molecules. Fullerene based molecular cages provide a unique opportunity to study the dynamics of confined molecules. For example, the dynamics of different spin isomers of water can be accessed in $H_2O@C_{60}$. To this end, as shown in Fig. 3 we obtained the THz transmission spectra of $H_2O@C_{60}$ at 8K and remarkably resolved the onset of ortho (total spin *I*=1) to para (total spin *I*=0) conversion of water spin isomers[9]. We have also measured the THz pump/THz probe response of $H_2O@C_{60}$ at 220K. The latter signal shows the real-time dynamics of the encapsulated molecule. Further measurements are underway to capture the entire spin conversion dynamics of $H_2O@C_{60}$ and resolve the non-saturated rotational transition line shapes. The latter information will enable us to realize the impact of the highly polarizable C_{60} cage structure on water dynamics. Moreover, we will perform THz pump/THz probe experiment at 77K to resolve both the coherent and the non-coherent dynamics of ortho and para spin isomers of water.

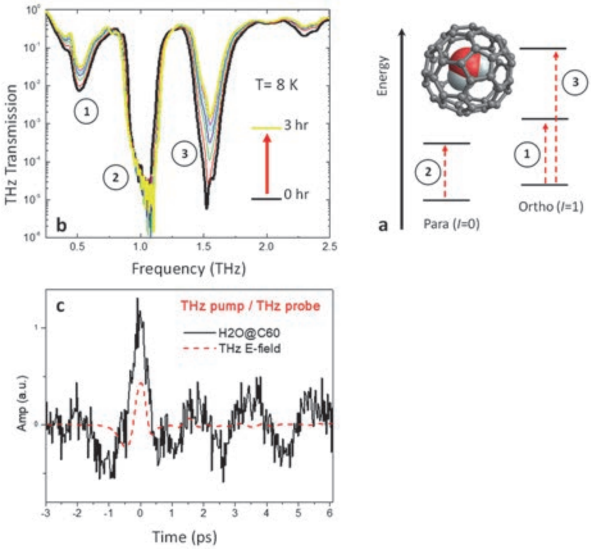

Figure 3: a) The diagram of the rotational transitions of ortho and para spin isomers of water. b) THz transmission spectra of $H_2O@C_{60}$ at 8K shows the rotational transitions of the encapsulated molecule and reveals the ortho to para spin conversion of water. c) THz pump/THz probe signal of $H_2O@C_{60}$ at 220 K shows the real-time coherent dynamics of the confined water molecules.

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[9] In collaboration with Richard Whitby and Malcolm Levitt, University of Southampton and Boris Gorshunov, Moscow Institute of Physics and Technology.

Max Planck Research Group Electron Dynamiχ
Dr. Julia Stähler

Independent Max Planck Research Group Leader at the FHI (since 2015)
Group Leader, FHI Berlin (2009-2015)
Visiting Scientist, Columbia University (2011)
Postdoc, University of Oxford (2008-2009)
Visiting Scientist, University of Pittsburgh (2007)
Dr. rer. nat., Freie Universität Berlin (2007)

Scientific Scope of the Electron Dynamiχ Group

The group's research focus lies on the non-equilibrium dynamics in materials and at their surfaces as well as interfaces launched by ultrafast optical excitation. Using a broad selection of femtosecond time-resolved (TR) spectroscopic techniques, we investigate how particles, quasiparticles, and the electronic structure of matter react to photoexcitation on an ultrafast timescale. With this approach, we do not only characterize elementary relaxation mechanisms and determine how different subsystems interact; the research is consciously tailored to identify and understand the differences in bulk and interface properties of materials and, ultimately, create transient functionality at interfaces by the exploitation of the evanescent properties of so-called "hidden" or "unconventional" states of matter.

Ultrafast Quasiparticle Dynamics in (Quasi-)2D Systems

Exciton dynamics in monolayer WS_2

In WS_2, multiparticle states like excitons or trions are present even at room temperature and dominate the optical response. Optical excitation of a transition metal dichalcogentite (TMDC) and the resulting transient change of quasiparticle density in the system strongly affects the screening of the Coulomb interaction, reducing the binding energy E_B of the multiparticle states and, simultaneously, decreasing the quasiparticle band gap leading to red and/or blue shifts of optical resonances (Fig. 1b) that are unpredictable *a priori*. We investigated the photoinduced change of the optical response of a pristine monolayer of WS_2 on SiO_2 under different excitation conditions. The broadband reflectivity contrast (RC, Fig1a) shows two overlapping optical resonances, the A exciton (X_A) at 1.95 eV and the trion (T^-) at 1.91 eV. The non-equilibrium dynamics of their energy position, width, and intensity after (i) resonant ($h\nu_{\mathrm{pump}}$ = 1.96 eV) and (ii) above-resonant ($h\nu_{\mathrm{pumo}}$ = 3.1 eV) expose a complex multi-exponential character. While (i) resonant excitation, which solely generates excitons in the material, leads to an overall *blue* shift of the X_A resonance, (ii) above-resonance excitation, which initially primarily excites quasi-free carriers in the system, first results in a *red* shift that later emerges to a blue shift (Fig. 1c). We conclude that the E_B reduction induced by exciton screening is stronger than the excitons' impact on the quasiparticle band gap, while the free carrier screening of the Coulomb interaction leads to a stronger band gap renormalization than E_B decrease. Based on a very simple rate equation model, we find - in agreement with literature - that exciton formation occurs within

$\tau_F = 0.9$ ps, competing with quasi-free electron-hole recombination with a time constant of $\tau_D = 1.6$ ps. The initial exciton population decay happens within $\tau_X = 5.9$ ps, likely *via* an Auger process.

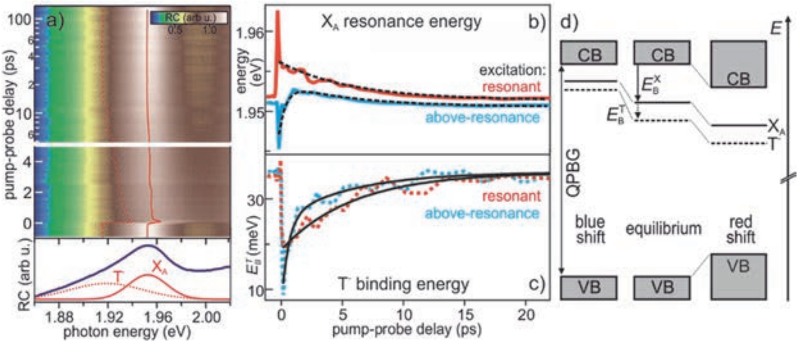

Figure 1: a) Top: Reflectivity contrast (RC) in false colors as a function of photon energy and pump-probe time delay, solid and dashed red curves indicate the peak position of the X_A and T^- resonance position respectively. Bottom: Spectrum at $t < 0$ (blue) and corresponding X_A and T^- fits. Time-dependent evolution of b) the X_A resonance energy and c) the trion binding energy for resonant and above-resonance excitation. d) illustrates how screening of the CIA can lead to red and blue shifts of optical resonances

This work demonstrates the fragile balance of free carrier and exciton screening of the Coulomb interaction that determine the complex non-equilibrium optical properties of TMDC monolayers and highlights the different interactions of excitons and trions with photogenerated quasiparticles [Calati *et al*., in prep.].

Inhibition of a photoinduced structural phase transition in TNS

We used fs TR mid-IR reflectivity to investigate the electron and phonon dynamics occurring at the direct band gap of the excitonic insulator Ta_2NiSe_5 (TNS) below the critical temperature of its structural phase transition from a monoclinic to an orthorhombic high-*T* phase. The phonon dynamics show a strong coupling to the excitation of free carriers at the Γ point of the Brillouin zone. The optical response saturates at a critical fluence of 0.3 mJ/cm^2 due to optical absorption saturation. This limits the excitation density such that the system cannot be pumped sufficiently strongly to undergo the structural phase transition [Mor 2018].

Complex Non-Equilibrium Dynamics in Transition Metal Oxides

Ultrafast generation and decay of a surface metal in ZnO

Photoinduced phase transitions occur in strongly correlated systems due to coupling between electronic, lattice, and spin degrees of freedom. Also, semiconductor-to-metal transitions occur in many "conventional" semiconductors upon doping, e.g. in phosphorous-doped Silicon. ZnO undergoes a such a transition, too, when the surface is "doped" with hydrogen resulting in downward surface band bending causing a partially filled conduction band (CB).

We succeeded in driving an ultrafast semiconductor-to-metal transition at the ZnO(10$\bar{1}$0) surface [publication in preparation]. A first laser pulse (hν_{pump}) generates holes in the valence band (VB) and depletes deep-lying in-gap states caused by surface defects, which induces downward surface band bending (Fig. 2a). The resulting dynamics near the Fermi energy (E_F) are probed by a time-delayed second fs laser pulse hν_{probe} by angle-resolved photoelectron spectroscopy (ARPES). Photoexcitation causes the generation of density of states (DOS) below E_F (Fig. 2b, top) and, simultaneously, to a downward shift of the VB (bottom), indicative of a photoinduced downward surface band bending. This is an *inverse* surface photovoltage effect due to a transient increase of surface charge by photo depletion of defect states.

The non-equilibrium state of ZnO exposes all footprints of a transient metal: DOS below E_F (Fig. 2b) of a partially filled dispersive band (m_{eff} = 1.6(4) m_e), showing the same build-up (20 fs and 1.25 ps) and decay dynamics (224 ps) as the up- and downward shifting of the VB (Fig. 2c), respectively, and an electron distribution following Fermi-Dirac statistics that thermalizes with the lattice within 200 fs (not shown). This work demonstrates that ultrafast semiconductor-to-metal transition can be photoinduced in "ordinary" semiconductors in the absence of strong correlation effects. Complementary to previous studies, which showed the ultrafast formation of *metal-like semiconductors* (e.g. Si or GaAs) after strong photoexcitation with quasi-Fermi energies in the CB and VB through photoexcited carriers at densities exceeding the Mott density of the respective material, our results reveal the formation of a *transient metal* with a Fermi-Dirac distribution centered at the equilibrium E_F of the ground state semiconductor [Gierster *et al.*, submitted to *Nature*]. This finding is of great relevance for industrial applications, in particular combined with the ultrafast back-switching to the semiconducting ground state, which could not be demonstrated for photoinduced phase transitions in strongly correlated systems so far.

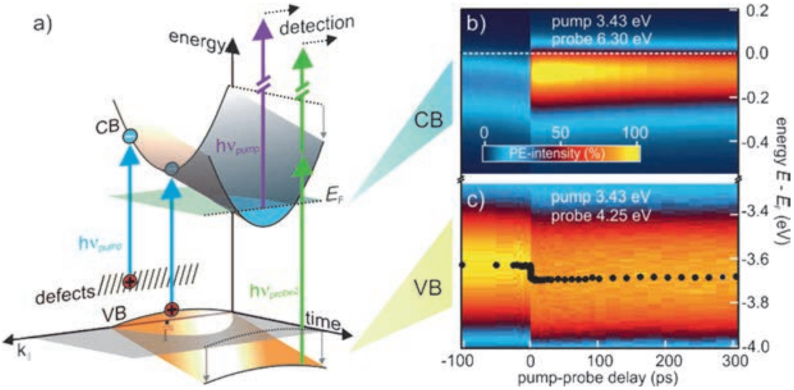

Figure 2: a) Experimental scheme and observed processes. Photodepletion of defect states causes a transient downward surface band bending via an inverse surface photovoltage effect. The resulting time-dependent population of the CB, which is shifted below E_F, and the down-shift of the VB are depicted in b) and c), respectively. Build-up and decay of both effects occur on coinciding timescales and behave similar to the formation and relaxation of the nearly-free electron mass of the transient surface electron signal (not shown).

First TR photoemission experiments of Hematite (1$\bar{1}$02) surfaces

To date, all measurements of excited states in hematite (α-Fe_2O_3), which is the most stable iron oxide in nature, lack an absolute energy scale. We are conducting TR-ARPES of (i) the bulk-like (1x1) and (ii) the oxygen-deficient (2x1) surface termination of the (1$\bar{1}$02) surface. In good agreement with previous UPS work, the equilibrium VB maximum lies at (i) 1.58(5) and (ii) 1.77(5) eV below E_F and an occupied state attributed to Fe^{2+}-like cations of the (2x1) structure is found at 1.13(5) eV. We observe a fluence-*independent* reduction in surface potential, presumably caused by adsorption of residual hydrogen gas or oxygen defect formation, and an additional fluence-*dependent* component of surface potential decrease which is interpreted as a reduction of intrinsic upward surface band bending owing to a surface photovoltage effect.

Interfacial Electronic Structure & Elementary Excitations in Hybrid Systems

Disentanglement of a hybrid exciton in the time domain

The notoriously low charge separation efficiency at ZnO-organic interfaces was suggested to result from weak electronic coupling of the LUMO to the ZnO CB or from the formation of a hybrid charge transfer state, which favors recombination at the interface. Using TR–ARPES, we disentangled the key processes in the charge separation sequence at the interface of a ZnO single crystal and *p*-quinquephenyl-pyridine (5PPy, inset in Fig. 3a). Characterization and comparison of the interfacial electronic structure of pyridine/ZnO(10-10) with the one of 5PPy/ZnO(10-10) reveals an occupied in-gap state directly below E_F, an extraordinarily strong work function reduction >2 eV, and a 5PPy LUMO around 2 eV above E_F [Vempati 2019]. In order to disentangle the contributions of pure electronic coupling of the LUMO to the ZnO CB and to reveal the influence of the electron-hole interaction on the charge separation dynamics at this inorganic/organic interface, we used two different excitation schemes to transiently populate the LUMO: Interfacial excitation from the in-gap state (Fig. 3b) causes population decay due to pure wave function overlap with the ZnO CB within only 70 fs (Fig. 3a, green), while intramolecular excitation (Fig. 3c) results in a lifetime increase by a factor of five (Fig. 3a, blue) as a result of the on-site electron-hole interaction in the molecule.

Note that this lifetime enhancement by the local Coulomb interaction in the molecule is not sufficient to explain the comparably low charge separation efficiency of ZnO-based inorganic/organic hybrid systems, as lifetimes on the order of only few hundreds of fs are clearly resulting from strong electronic coupling. The origin of the low charge separation efficiency phenomenon lies in the build-up of the hybrid charge transfer exciton 0.5 eV below E_F (Fig. 3e), which builds up on a 100 ps timescale, exhibiting a lifetime that exceeds 5 μs. In this work, we do not only provide a comprehensive understanding of the structural, electronic, and non-equilibrium properties of a model inorganic/organic interface and the first observation of a hybrid charge transfer exciton at a buried interface in the time domain [Gierster *et al.*, in prep.], but also offer – by the selective interfacial and intramolecular excitation – a unique tool to disentangle elementary processes at buried inorganic/organic interfaces [Vempati 2019].

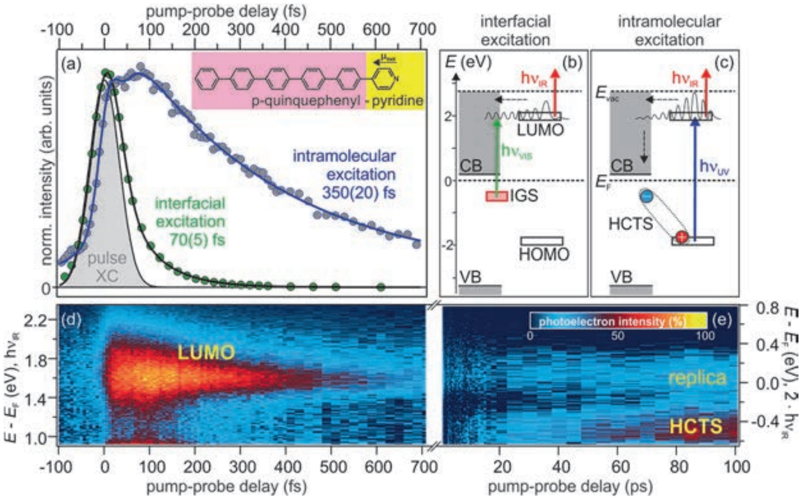

Figure 3: a) Comparison of LUMO population decay for interfacial (scheme in b) and intramolecular photoexcitation (scheme in c). (d) Exemplary time-resolved 2PPE experiment for intramolecular excitation. (e) Build-up of the hybrid charge transfer exciton on ps timescales. The replica of the hybrid charge transfer exciton is probed by pump photons.

Terrylene – a textbook dye

TR investigations of charge and energy transfer processes across organic-TMDC interfaces require organic dye molecules with appropriate HOMO-LUMO gaps and sufficiently long excited state lifetimes to allow for interfacial phenomena to take place. We characterized the optical properties of terrylene molecules in para-xylene solution. The combination of polychromatic transient absorption spectroscopy with time-correlated single photon counting experiments shows that excitation at the absorption maximum leads to photoluminescence and ground state bleaching that decays within 3.7 ns. Above resonance excitation is followed by internal vibrational relaxation on a 100 ps timescale [Tanda Bonkano *et al.*, in preparation]. Without any surprising or ground-breaking new properties terrylene may not attract significant research interest on its own. However, the complete absence of any unexpected behavior and the simplicity of its non-equilibrium properties make this unpretentious molecule an ideal species for the study of complex charge and energy transfer studies at organic/inorganic interfaces.

Further studies

- Development of the first comprehensive picture of intrinsic and defect-related charge carrier and exciton dynamics in ZnO [Foglia 2019]
- Revelation of the elementary steps of charge injection, localization, and solvation across the electrochemically relevant DMSO/Cu(111) interface [King 2019]
- Triplet-triplet annihilation through autoionization on microsecond timescales in an organic chromophore [Vempati et al., submitted to JCP]

Future Perspectives

The Electron Dynamiχ Group is – after the laboratory move and maternity leave in the previous evaluation period – growing again and preparing for future challenges. These will likely involve our move to the Department of Chemistry at the Humboldt University Berlin following a call to a W3 professorship.
One major strength of the group is the complementarity of its femtosecond time-resolved experimental techniques (photoemission, transient transmission and reflection, photoluminescence, electronic sum frequency generation) that allows the disentanglement of the bulk, surface, and interface properties of a given material system. This sets the basis for the study of very diverse research questions, ranging from strong correlation phenomena in condensed matter physics to electrochemistry, as the respective fundamental interactions and elementary processes in these areas are strongly related and in some cases even similar. Our curiosity-driven, complementary approach will be continued in the future and is reflected in the breadth of the forthcoming research topics in the fields of Physics, Chemistry, and Material Science. In order to even extend the access of the group's experimental suite to spatio-temporal dynamics relevant for nano science and most applications, capabilities will be expanded by a novel femtosecond time-resolved scanning probe technique.

Toward TR interferometric optical nanoscopy

The femtosecond electron dynamics in 2D materials and at surfaces can exhibit significant variation at the nanometer scale. We are developing TR interferometric optical nanoscopy (TRION), where a scattering-type scanning near-field optical microscope (s-SNOM) is used for TR optical spectroscopy. This technique will exploit near-field enhancement close to a metallic tip to achieve spatial resolution (<40 nm), while the temporal resolution is obtained using femtosecond laser pulses in a pump-probe scheme (~40 fs). This technique has yet to be demonstrated in the visible spectral range, while it has been used in the IR region previously by other groups. Using TRION, we will investigate the spatial dependence of the relaxation rates and spectral dynamics in TMDC monolayers as well as in TMDC/organic lateral heterojunctions.

Forthcoming research topics

- The susceptibility of 2D materials (e.g. TMDCs) to local changes of the dielectric function through the substrate or adsorbates will be used to manipulate the electronic structure and optical response on the nm scale and on ultrafast timescales.
- Charge and energy transfer processes across TMDC-based inorganic and organic hybrid interfaces and along nano-structures on dielectric templates will be studied and exploited for advanced opto-electronic or light-harvesting functionalities.
- Transient phenomena at catalyst surfaces (e.g. ZnO) like charge accumulation or metallization may be used to trigger or enhance desired chemical processes and to study their – often stochastic – dynamics on the relevant ultrafast timescales.
- The injection of charges into electrolytes near oxide surfaces is a key process in (photo-) electrochemistry. We will bridge the gap between what

is known for ultrafast charge carrier dynamics across well-defined solid/frozen solvent interfaces under UHV conditions and solid/liquid systems.

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Max Planck Research Group Transient X-ray Spectroscopy & Diffraction
Prof. Dr. Michael Zürch

Assistant Professor of Chemistry, University of California Berkeley, College of Chemistry (since 07/2019)
Max Planck Research Group Leader, FHI (12/2018 - 06/2020)
Independent Junior Research Group Leader, FSU Jena (2018)
Feodor Lynen Fellow, University of California Berkeley, (2015 - 2017)
Ph.D. in Physics, Friedrich Schiller University Jena (2014)
Diploma in Physics, Friedrich Schiller University Jena (2010)

Ultrafast Carrier and Spin Dynamics Probed by Transient X-ray Spectroscopy and Diffraction

The Max Planck Research Group Transient X-ray Spectroscopy and Diffraction experimentally explores structural, carrier and spin dynamics in novel quantum materials, heterostructures and on surfaces and at interfaces to answer current questions in materials science and physical chemistry. For this we pursue a multidisciplinary research program that combines the exquisite possibilities that ultrafast X-ray spectroscopy and nanoimaging offers and closely interface with material synthesis and theory groups. In the lab, we develop and employ attosecond XUV and soft X-ray sources to perform transient absorption spectroscopy and time-resolved X-ray diffraction experiments. We further develop novel nonlinear X-ray spectroscopies at large-scale facilities with the goal to gain interfacial and surface sensitivity combined with the material specificity provided by X-rays on femtosecond time scales. We are interested in experimentally studying and controlling material properties on time scales down to the sub-femtosecond regime and on nanometer length scales to tackle challenging problems in quantum electronics, information storage and solar energy conversion. The Max Planck Research Group Transient X-ray Spectroscopy and Diffraction officially started in March 2019 after a 3-month preparational phase beginning in December 2018. The group is currently moving to the University of California at Berkeley, where Dr. Michael Zürch has been appointed as assistant professor with tenure-track and new labs will be set up in early 2020.

Attosecond diffraction spectroscopy

In our group we develop a new scheme that we refer to as attosecond diffraction spectroscopy, which is a multimodal approach to probe the long-range spin order and the electronic and lattice dynamics in magnetic thin films. For this, we generate isolated attosecond pulses in a broad spectral range covering several absorption edges present in the multilayer thin films and interrogate the spin order by resonant magnetic diffraction, while the electronic-structural response is simultaneously measured with atomic specificity by transient absorption spectroscopy (Fig. 1a). Using this scheme enables us following the ultrafast optical excitation of the carriers out of equilibrium and the subsequent demagnetization. This provides insights into the complex correlation between magnetism and electronic excitation. With this we seek to contribute to the experimental and theoretical efforts to understand

and control this phenomenon, acknowledging the prospects ultrafast spin control has for novel fast and efficient memories and spintronic devices.

A first experiment was conducted in collaboration with the group of Prof. Leone at the University of California at Berkeley and evaluated during the first few months of the MPRG. In the experiment, 4-fs optical pump pulses and extreme ultraviolet (XUV) attosecond probe pulses covering the core-level absorption edges of cobalt and platinum, the constituents of the magnetic multilayer under investigation, between 50 and 75 eV are employed (Fig. 1b, top). The two pulses are collinearly focused onto a Co-Pt multilayer thin film with stripe-like oriented magnetic domains (domain size ~160 nm, inset Fig. 1a). The observed transient absorption spectra (Fib 1b, bottom) feature photo-induced red-shifts of the absorption edges indicating out-of-equilibrium excitation of the electrons (Fig. 1c, black and red curves for Co and Pt, respectively). The demagnetization, i.e. loss of magnetization M, observed in the diffraction signal peaks after ~200 fs and slowly recovers over a time scale of ~100 ps (not shown here), consistent with previous observations in Co-Pt multilayers. Intriguingly, it is observed that the onset of the demagnetization (Fig. 1c, blue curve) is delayed by approximately 4 fs with respect to time zero. To understand this observation, we initiated a collaboration with a theory group from the Max Born Institute. The observation can be explained by the fact that in the ground state the cobalt layers are responsible for the magnetization and the platinum layers become weakly magnetized at the interface. The optical excitation then drives a spin current from the cobalt into the platinum layers through a mechanism known in literature as optically induced spin and orbital momentum transfer causing a brief increase of the magnetization in the platinum layers, while cobalt demagnetizes. It is found that the total observed magnetization is nearly constant in this case. The observed time scale thus manifests the time scale before many body effects and scattering events disturb the coherence in this process.

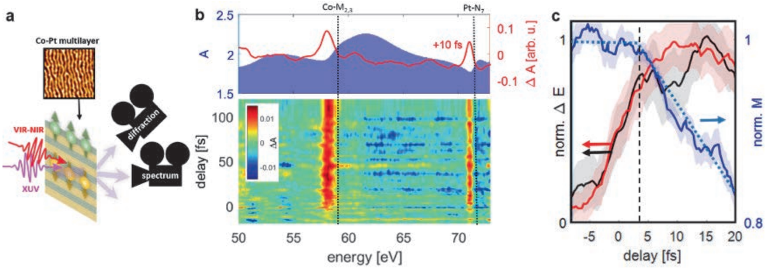

Figure 1: Scheme and application of attosecond diffraction spectroscopy to study ultrafast demagnetization. (a) Experimental scheme of attosecond diffraction spectroscopy. (b) Static absorbance and photo-induced absorption change (top) and transient absorption signal depending on the time delay (bottom). (c) Normalized absorption edge shift in Co (black) and Pt (red) upon laser excitation. The onset of demagnetization (blue) measured by resonant magnetic diffraction is observed at approximately 4 fs delay.

In the near future we hope to expand the analysis further as we have strong indication that we can separate the cobalt and platinum response in the diffraction data and, thus, gain a better insight into these complex dynamics. Following this first demonstration, we plan expanding this scheme to different physical problems that are of interest to research groups in the Department, for instance for quantifying charge density wave (CDW) dynamics where our scheme will allow to acquire structural and electronic details during the first femtosecond of CDW melting.

Nonlinear X-ray spectroscopy at Free-electron lasers

While our table-top studies are restricted to either study the bulk response of a system or investigate spatially confined, e.g. 2D, materials, for many application-relevant aspects the electronic structure at the surface is relevant and should be studied ideally with all advantages that X-ray spectroscopy offers. Unfortunately, access to surface spectra cannot be easily gained due to the relatively large penetration depth of X-rays. In optical spectroscopy, nonlinear techniques, such as SHG and sum-frequency generation, can overcome this limitation by exploiting the breaking of the symmetry at interfaces and surfaces as mastered by other groups in the Department. The challenge for transferring these techniques to the X-ray regime lies in the inherent need for high intensities to induce a nonlinear response. Attosecond sources are currently not powerful enough to push into a relevant intensity regime. Free-electron lasers in turn can achieve sufficient intensities as has been very recently demonstrated in a first surface-sensitive SHG measurement.

In our group we collaborate with various research groups from Japan and the USA and successfully apply for beamtime at Free-electron laser facilities around the world to perform proof-of-concept experiments concerning nonlinear spectroscopies and material responses in the X-ray regime and their application to surface/interface dynamics. During 2019 experiments were performed at FERMI (Triest, Italy; twice) and FLASH in Hamburg. For 2020 beamtimes have been scheduled at SACLA (Japan) and several proposals are currently under evaluation.

At FERMI we conducted a first experiment studying the nonlinear absorption of carbon under the influence of an ultrashort melting laser pulse. Graphite thin foils were placed in the overlap of the FEL beam and an optical laser. The transmitted light was measured for three different photon energies under (262 eV), at (286 eV) and above (309 eV) the K-edge of carbon. Additionally, the time-delay between the two light sources were varied to probe different states of carbon. As stated by Beer-Lambert law, the absorption coefficient is independent of the intensity of the incoming light. Due to the high intensity of the X-ray beam the graphite gets partially depleted of the 1s electrons and the transmission is higher than expected from Beer-Lambert law (Fig 2B). The absorption coefficient α is not sufficient to describe the behavior and is replaced by a linear absorption coefficient α_L and an intensity-dependent nonlinear absorption coefficient α_{NL}. These two absorption coefficients were extracted from the experimental data and are plotted versus the time delay. Measurements were taken from -1 ps, at which the optical laser hit the sample first, up to +1 ps, at which the FEL hit the sample first. The linear absorption coefficient α_L shows wavelength dependence but no variations with time delay (Fig 2C). The nonlinear absorption coefficient (Fig 2D), however, shows additionally to the wavelength dependence a sensitivity for the time delay. This information is expected to lead to further understanding of different carbon states, including liquid carbon, which we currently model using time-dependent density functional theory.

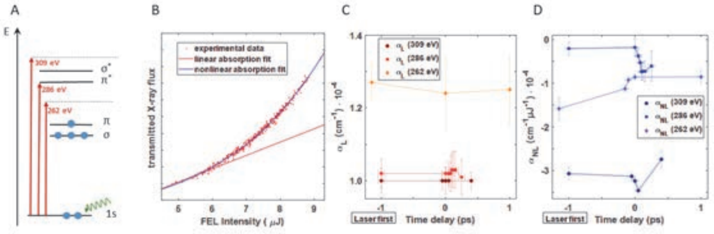

Figure 2: FEL-induced nonlinear absorption in graphite thin foils. (a) Three possible electronic excitations of the 1s electrons. Depending on the FEL wavelength the 1s electrons can be resonantly excited to the π* orbital, virtual below-edge states or higher-lying conductions band states. (b) Plot of the transmitted X-ray flux versus the FEL intensity. The data (red circles) shows clear nonlinear behavior (blue curve). Graphite becomes more transmissive as expected from a linear Beer-Lambert law (red curve). Extracted linear absorption coefficients α_L (d) and nonlinear absorption coefficients α_{NL} (d) are shown for different time delays of the optical laser to the FEL for three different photon energies. While α_L shows only a wavelength dependence, α_{NL} varies also with time delay.

Transition to the University of California at Berkeley

During the start-up phase of the MPRG and implementation of the new laboratory at FHI, the group leader received an offer to join the Faculty at the University of California at Berkeley within the College of Chemistry as Assistant Professor with tenure track. Following the successful negotiation and acceptance of the offer in May 2019, the appointment at Berkeley started in July 2019, which started a one-year transition phase of the MPRG effectively ending the MPRG in June 2020.

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Theory

Theory Department
Prof. Dr. Matthias Scheffler

Director at FHI and Scientific Member of the Max Planck Society (since 1988)
Honorary Professor at the Freie Universität Berlin, Humboldt-Universität zu Berlin, and Technische Universität Berlin
Distinguished Visiting Professor at the University of California, Santa Barbara
Habilitation, Technische Universität Berlin (1984)
Dr. rer. nat., Technische Universität Berlin (1978)

Recent Developments in the Theory Department

On July 1, 2019, the FHI Theory Department turned 31 years old; its founding director has since become an Emeritus. He will head the department until the new director assumes office, which will probably be on January 1, 2020. Karsten Reuter from the Technical University of Munich has been identified for this position and was recently elected by the MPG Section for Chemistry, Physics, and Technology (CPTS). We are very happy with this development and hope that by the time of the meeting of the Fachbeirat, he may already have signed his contract with the Max Planck Society. Currently, it is planned that the upper floor of the T building will be cleared by January 1, 2020; the "Scheffler Group" will be located in the Richard Willstätter House (RWH) and, together with those parts of its projects oriented towards research-data infrastructure (see the NOMAD/FAIR-DI activities below), also at the Humboldt-Universität zu Berlin.

From the very beginning, research in the department has been concerned with fundamental aspects of the chemical and physical properties of surfaces, interfaces, clusters, and nanostructures. Obviously, this theme is sufficiently general and covers a wide range of topics, so that there has been little reason for change. Having said this, we note, however, that a group working in biophysics was added a few years ago. Moreover, since 2013, activities on a FAIR[10] data infrastructure and on (big) data analytics based on artificial-intelligence concepts have been systematically added. These activities have received considerable attention worldwide and are now affecting many of our new developments, as will be sketched below.

As of September 1, 2019, the FHI Theory Department is structured in 9 research groups, although most of the work in the department is performed as cross-cutting activities within this group structure. The groups and their leaders are:

1. *Unifying Concepts in Catalysis*, headed by **Sergey V. Levchenko**
2. *Heat and Charge Transport*, headed by **Christian Carbogno**

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[10] FAIR stands for Findable, Accessible, Interoperable, and Re-usable. The FAIR Data Principles: https://www.force11.org/group/fairgroup/fairprinciples. See also: C. Draxl and M. Scheffler, Big Data-Driven Materials Science and its FAIR Data Infrastructure. Plenary Chapter in Handbook of Materials Modeling (eds. S. Yip and W. Andreoni), Springer (2019). https://arxiv.org/ftp/arxiv/papers/1904/1904.05859.pdf

3. *Ab Initio Biomolecular Simulations*, headed by **Carsten Baldauf**
4. *Simulations from Ab Initio Approaches: Structure and Dynamics from Quantum Mechanics*, **Otto Hahn Group of Mariana Rossi**
5. *Big-Data Analytics for Materials Science*, headed by **Luca M. Ghiringhelli**
6. *Crystal-Structure Prediction and Heterogeneous Catalysis*, headed by **Matthias Scheffler**
7. *Novel Materials Discovery and a FAIR Research Data Infrastructure*, **Max Planck Fellow Group of Claudia Draxl** of the Humboldt-Universität zu Berlin
8. *Advanced Electronic-Structure Methods*, **Max Planck Partner Group of Xinguo Ren** at USTC in Hefei, China (in collaboration with Matthias Scheffler)
9. *Atomistic Simulations of Electrochemistry,* **Max Planck Tandem Group of Luana Pedroza** at UFABC, Santo André, Brazil (in collaboration with Mariana Rossi).

Furthermore, the Theory Department hosts Emeritus Alexander M. Bradshaw who 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. He plans to retire finally within the next three years on completion of a project with the University of Augsburg.

Ongoing organizational developments are summarized in the following:
Part of group 1 is moving to group 6, but the main part is being transferred to the renowned Skolkovo Institute of Science and Technology (Skoltech). This is a private graduate research institute in Moscow, Russia (established in 2011 in collaboration with the MIT), and Sergey V. Levchenko took up an Assistant Professorship there in November 2018. Group 2 will continue at the FHI, largely within Scheffler's **ERC** project **TEC1p**: *Big-Data Analytics for the Thermal and Electrical Conductivity of Materials from First Principles*. The TEC1p funding ends in September 2022. Group 3 is being transferred partly to group 4 and partly to the MP Department of the FHI. Mariana Rossi and her group 4 will move to the Max Planck Institute for the Structure and Dynamics of Matter in Hamburg, where she will set up her distinguished Lise Meitner Group. A small subgroup connected to the DFG-funded Collaborative Research Centre (CRC) 951 (HIOS)[11] will remain at the FHI, hosted by the "Scheffler Group" in the RWH. Groups 5, 6, 7 are key elements of the NOMAD (Novel Materials Discovery) Center of Excellence[12], the FAIR Data Infrastructure association (FAIR-DI e.V.)[13], and the activities of the Max Planck Network on Big-Data-Driven Materials Science (BiGmax)[14]. Some aspects are part of the Max Planck Graduate Center for Quantum Materials[15]. The materials science data infrastructure activities in NOMAD/FAIR-DI are strongly related to the FAIRmat consortium[16] which may

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[11] https://www.physik.hu-berlin.de/de/sfb951

[12] https://nomad-coe.eu

[13] https://fairdi.eu

[14] https://bigmax.iwww.mpg.de/scope

[15] https://www.quantummaterials.mpg.de

[16] https://fairdi.eu/fairmat

possibly become part of the NFDI (National Research Data Infrastructure)[17]; more information is given below. These groups (5-7) will remain, and their funding is planned at present for the period until fall 2025. Group 8 was favorably evaluated in December of last year, and its funding will continue until November 2020. Moreover, the funding of group 9 in Brazil will continue until July 2023. Concluding, by January 1, 2020, four groups will remain in Berlin: *NOMAD/FAIR-DI* (Claudia Draxl), *DFT and Beyond* (Matthias Scheffler), *Big-Data Analytics for Materials Science* (Luca M. Ghiringhelli), and *Heat and Charge Transport* (Christian Carbogno). They will occupy offices in the RWH and at the HU Berlin.

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 7 additional institutions. It focuses on networking, backup, virtualization, and security services. The GNZ is headed by Gerd Schnapka, and more information is given in the report of the GNZ in this booklet.

Groups 1, 2, 4, 5, 7, 8 are described by their respective group leaders in special chapters, following this general overview. At this point it is perhaps appropriate to mention a few highlights, in particular in those areas that are likely to comprise the future activities of the "Scheffler Group".

NOMAD and FAIR-DI

These activities started with the NOMAD (Novel Materials Discovery) Repository in 2013 (online since 2014), together with Claudia Draxl and the MPCDF (Max Planck Computing and Data Facility). They have developed into the highly successful NOMAD Center of Excellence (established in October 2015). In brief, NOMAD has five key components (see Fig. 1).

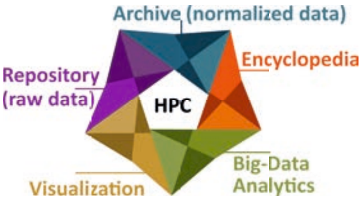

Figure 1: Structure of the NOMAD (Novel Materials Discovery) Center of Excellence which now is the biggest data base in computational materials science. For details see the report by Claudia Draxl and the respective poster.

With its combination of the Repository and Archive, it represents a FAIR[1] data infrastructure. FAIRness also implies the underlying metadata and ontology infrastructure, the NOMAD Metainfo. Many people have contributed here, but four of them should be mentioned explicitly: *Fawzi Mohamed, Luca M. Ghiringhelli, Claudia Draxl,* and *Markus Scheidgen.* The metadata and ontology

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[17] https://www.dfg.de/en/research_funding/programmes/nfdi/index.html

development will be advanced in the coming years, supported by the BMBF project STREAM (Semantische Repräsentation, Vernetzung und Kuratierung von qualitätsgesicherten Materialdaten).

Figure 2 shows a transparency that summarizes the worldwide leading data infrastructures in materials science as shown by James Warren, the director of the Materials Genome Program of NIST (USA) in his welcome speech at a workshop in Washington D.C. in August 2019. It not only includes NOMAD but also mentions the OPTiMaDe (Open Databases Integration for Materials Design)[18] project. OPTiMaDe aims to make various materials databases interoperational by developing a common REST API. This effort is led by Gian-Marco Rignanese from Louvain La Neuve, and FHI / NOMAD scientists form a significant part of the consortium. Further aspects of NOMAD are described in the report by Claudia Draxl and in the next paragraph on artificial intelligence for materials science.

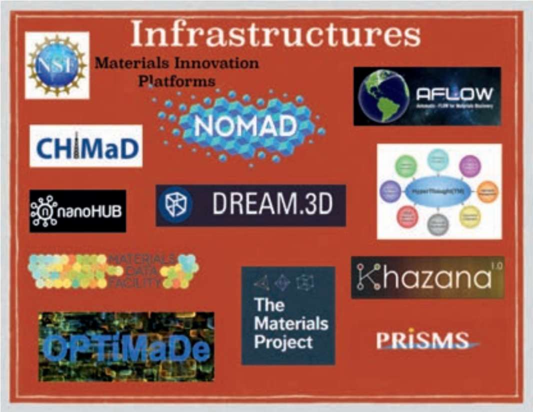

Figure 2: Slide listing the main materials science data infrastructures. This was shown in the welcome talk of the director of the Materials Genome Program of NIST in August 2019.

NOMAD also plays a significant role for the Max Planck Network on Big-Data-Driven Materials Science (BiGmax[14]; Fig. 3 left) in which several institutes of the Max Planck Society combine their know-how to further data-driven materials science. The aim is to develop concepts and methods for handling and analyzing large amounts of materials data. In its present funding period, BiGmax will run until February 2022. Together with Peter Benner (MPI for Dynamics of Complex Technical Systems, Magdeburg), Matthias Scheffler is coordinating the BiGmax network and the Theory Department is part of several cooperation projects.

In September 2018, institutions from the Netherlands and Germany founded the not-for-profit association FAIR-DI e.V.[13] (Fig. 3 right; “gemeinnütziger, eingetragener Verein” according to German law). It is headed by Matthias Scheffler (supported by two executive secretaries Carsten Baldauf and Alexander Brink (Radboud University)). Its mission statement reads: “Scientific

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[18] http://www.optimade.org

data are a significant raw material of the 21st century. To exploit its value, a proper infrastructure that makes it Findable, Accessible, Interoperable, and Re-purposable – FAIR – is a must. For the fields of computational and experimental materials science, chemistry, and astronomy, FAIR-DI e.V. sets out to make this happen. This enabling of extensive data sharing and collaborations in data-driven sciences (including artificial-intelligence tools) will advance basic science and engineering, reaching out to industry and society."

BiG max
MAX PLANCK RESEARCH NETWORK
on big-data-driven materials science

FAIR-DI
FAIR Data Infrastructure
for Physics, Chemistry,
Materials Science,
and Astronomy e.V.

Figure 3: Two important facilities co-lead by the FHI.

The FAIR-DI concept is largely identical with the goals of the planned large-scale German Data Infrastructure NFDI (the corresponding DFG call for proposals was published in June this year and successful submissions may expect funding from fall 2020 onwards)[17]. FAIR-DI's materials-science component will submit a proposal called FAIRmat[16] in October 2019. FAIRmat, coordinated by Claudia Draxl, is supported by the CPTS of the Max Planck Society, the Condensed Matter Section of the German Physical Society, and numerous research groups in Germany.

Artificial Intelligence for Materials Science

We realized early on that the direct impact of high-throughput screening of materials may remain limited as the amount of possible materials is practically infinite. Thus, two goals were defined: First, to construct "property maps of materials" analogous to the periodic table of the elements (see Fig. 4). Second, to note that the number of high-performance materials that may be suitable for a certain purpose, may be very small, e.g. just 10 or 100 out of the practically infinite number of all possible materials. Thus, the goal is not a statistical-learning process (or a "fit") of the big data but the identification of "statistically exceptional regions" in the data space ("needles in a haystack"). Two important methods have been developed for these purposes: a) SISSO (Sure Independence Screening and Sparsifying Operator) and b) Subgroup Discovery. In simple words, SISSO follows the spirit of LASSO (Least Absolute Shrinkage and Selection Operator), a popular method in compressed sensing (signal processing). However, there are several significant advancements. In LASSO, the selection is approximated by replacing the ℓ_0 by the ℓ_1 norm, since there are problems with ℓ_0 in actual calculations because of its NP hardness. Furthermore, LASSO becomes unstable when the number of features offered are correlated and/or exceed about 5,000, with about 100 data points, which is a typical number of data points in materials discovery. All these issues were resolved with SISSO: SISSO considers the ℓ_0 norm and the number of features can be huge, e.g. billions or trillions. For the one-dimensional feature selection, the result is even exact. And for higher dimensions we implemented an iterative approach. The key people behind this work are *Runhai Ouyang* and *Luca M.*

Ghiringhelli. More details are described in the report by Luca M. Ghiringhelli and on the posters.

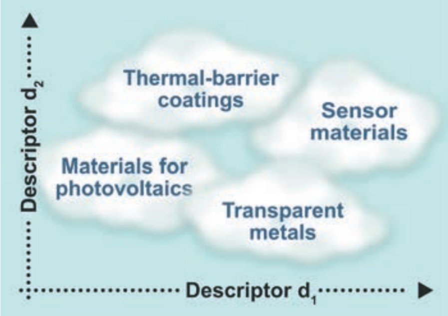

Figure 4: Big data of materials contain correlations and structure that are invisible in small data sets. Finding descriptors that determine a specific property or function of a material is a crucial challenge. Once this is in place, it will be possible to machine learn the data and eventually draw maps of materials.

The second highly important development is "subgroup discovery". As mentioned above, fitting, or machine learning, all available data with a single, global model means fitting the hay, where one may accidentally average away the special features of the interesting minority, namely, the needles. Using Boolean conjunctions, the method of subgroup discovery identifies statistically-exceptional subgroups in a large amount of data. The key developers of this approach were *Mario Boley, Jilles Vreeken (Saarland University), Luca M. Ghiringhelli,* and *Bryan Goldsmith*. A recent application of the approach was the identification of materials that may be good for catalytic CO_2 activation (turning a greenhouse gas into fuels and useful chemicals). This work was done with *Sergey V. Levchenko* and *Aliaksei Mazheika* (see also the report of *Sergey V. Levchenko*).

Thermal and Electrical Conductivity from First Principles

Thermal conductivity (TC) is a key characteristic of many materials, e.g. thermoelectrics, thermal-barrier coatings, and catalysts. However, TC is largely unknown − of the 225,000 identified inorganic semiconductor and insulator crystals, only 100 have any experimental TC data available. We started a high-throughput study of TC by first developing a rapid-decision algorithm on what materials actually exhibit strong anharmonic effects and thus low TCs. This revealed that for many of the technologically interesting materials anharmonic effects are large, so that the standard description in terms of perturbation theory and Boltzmann equation does not provide a reliable description. To investigate accurately these strongly anharmonic materials, we have developed and coded a full *ab initio* molecular dynamics description with a numerically efficient algorithm that enables convergence of the statistical mechanics in system size and time. Together with the decision algorithm mentioned above, this has allowed us to screen thousands of materials and to study the TC of several complex material classes, including half-Heuslers, inorganic halide perovskites, and ultra-insulating layered chalcogenides like SnSe.

Analogously, we have developed an *ab initio* theory of electrical transport for systems with strong electron-phonon coupling and/or strong anharmonic effects. At this point, our approach is the only one that does not involve perturbation theory – neither for the electron-phonon coupling nor for the nuclear dynamics. Rather, all anharmonic effects in the nuclear motion are accounted for via *ab initio* molecular dynamics, while electron-phonon coupling is treated to all orders by analyzing the evolution of the self-consistent electronic-structure along the anharmonic trajectory. The approach is being implemented and tested right now. The key developer behind these TEC1p methods is *Christian Carbogno* (see corresponding report).

Related to these studies we are also working on advanced exchange-correlation treatments, e.g. a self-interaction corrected SCAN (Strongly Constrained and Appropriately Normed) functional, RPA (Random-Phase Approximation) and coupled-cluster theory in order test the accuracy of the computed properties of strongly anharmonic systems. The key developers are *Igor Y. Zhang* and *Xinguo Ren* (see corresponding report).

Let us finish with a note on the recent scientific impact of the Theory Department, specifically on our NOMAD/FAIR-DI/AI activities. This may be measured by the number of invited, keynote, and plenary talks held by members of the Theory Department on related topics. For the last 2-year reporting period (from September 1, 2017 to August 31, 2019) the number was 76. And there were numerous contributed talks by our students and postdocs.

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, October 2014 - September 2018.
- 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, February 2016 - Januar 2019.
- BMBF – Federal Ministry of Education and Research (Germany), Semantische Repräsentation, Vernetzung und Kuratierung von qualitätsgesicherten Materialdaten (STREAM), coordination: Fraunhofer-Institut für Werkstoffmechanik IWM; project leaders: M. Scheffler, C. Baldauf, August 2019 - July 2022.
- BMWi – Federal Ministry for Economic Affairs and Energy (Germany), Cooperation Project within "Zentrales Innovationsprogramm Mittelstand": Entwicklung einer neuartigen Softwarekombination; FHI project leaders: M. Scheffler, S. Kokott, May 2019 - April 2021.
- DFG – German Research Foundation, CRC 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. A third funding period has been approved: July 2019 - June 2023, Current project: Temperature effects

on the atomic and electronic structure of organic/TMDC interfaces (A13), project leader: M. Rossi.

- EPSRC - Engineering and Physical Sciences Research Council (UK): International Centre-to-Centre Collaboration: New trimetallic nanoparticles as catalysts for the conversion of carbon dioxide to renewable fuels, coordinator: G. Hutchings; project leader: M. Scheffler, starting October 2019.
- ERC – European Research Council, Advanced Grant: Big-Data Analytics for the Thermal and Electrical Conductivity of Materials from First Principles (TEC1p), M. Scheffler, October 2017 - September 2022.
- EU – European Commission, E-Infrastructures: NOMAD (Novel Materials Discovery) Center of Excellence, coordinator: M. Scheffler; work package leaders: L. M. Ghiringhelli, C. Draxl, November 2015 - October 2018.
- FAPESP – São Paulo Research Foundation, Max Planck Tandem Group for Atomistic Simulations of Electrochemistry lead by L. Pedroza at UFABC in Santo André, Brazil, August 2018 - July 2023.
- Leibniz-Gemeinschaft – Leibniz-WissenschaftsCampi (LWC): Growth and fundamentals of oxides for electronic applications (GraFOx), spokesperson: H. Riechert; principal investigators: M. Scheffler, C. Draxl, 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; since 2013. Current project: Machine learning of experimental observables in surface and interface science, project leaders: M. Ceriotti (EPFL), M. Rossi.
- Max Planck Society - Central Funds – MP Fellow Group of C. Draxl, since July 2014. In July 2019, C. Draxl was appointed as MP Fellow of the Max Planck Graduate Center for Quantum Materials for 5 years, with her MP Fellow Group based at the FHI.
- Max Planck Society - Central Funds – MP Partner Group for Advanced Electronic-Structure Methods lead by X. Ren at the University of Science and Technology of China (USTC) in Hefei, December 2015 - November 2020.
- Max Planck Society - Central Funds – BiGmax, Max Planck Network on Big-Data-Driven Materials Science, coordinators: P. Benner, M. Scheffler; project leaders: C. Draxl, L. M. Ghringhelli, M. Rossi, M. Scheidgen, M. Scheffler, March 2017 - February 2022.
- Max Planck Society - Central Funds - Max Planck Graduate Center for Quantum Materials, speaker: B. Keimer; FHI coordinators: M. Rossi, M. Scheffler, since January 2019.
- Max-Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis ‘FUNCAT’, coordinators: G. Hutchings, F. Schüth, project leader: M. Scheffler, starting 2020.
- 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.

Additionally, Matthias Scheffler is Visiting Professor at the Institute for Catalysis, Hokkaido University, Japan, since 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 consortium of the MM1P.de node consists of the University of Bremen (represented by the Node Director T. Frauenheim and T. Wehling), the MPI Hamburg (represented by A. Rubio), Goethe University Frankfurt (represented by B. Winkler and R. Valenti), and the FHI (represented by M. Scheffler). The node will continue to exist at least until 2022.

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.

In the context of NOMAD and the FAIR-DI activities, the FHI has also established a collaboration with Shanghai University, specifically with its Materials Genome Institute on “Data Infrastructure and Materials Informatics”.

Personnel and Related Matters

Since the last visit of the Fachbeirat in November 2017 the following noteworthy developments have taken place:

- **Mariana Rossi** was selected as leader for a highly prestigious Lise Meitner Group which she will establish in January 2020 at the Max Planck Institute for the Structure and Dynamics of Matter in Hamburg. Additionally, she was accepted into the Elisabeth Schiemann Kolleg in June 2018. Within the Elisabeth Schiemann Kolleg scientific members of the Max Planck Society foster the careers of excellent female scientists after their postdoc phase, helping them to succeed on their way to an appointment as a tenured professor or as a director of a research institution.

- Since September 2018, **Carsten Baldauf** has been Visiting Professor (Professurvertretung Theoretische Chemie) at the Wilhelm-Ostwald-Institut, Fakultät für Chemie und Mineralogie, Universität Leipzig. Starting October 1, 2019, he assumes a permanent position in the administration of the FHI as representative of the board of directors.
- **Igor Ying Zhang** became Professor at Fudan University in March 2018.
- **Yang-Gang Wang** became Associate Professor at the Southern University of Science and Technology of China in September 2018.
- **Sergey V. Levchenko** assumed an Assistant Professorship at the Skolkovo Institute of Science and Technology in November 2018.
- **Honghui Shang** became Associate Professor at the Institute of Computing Technology of the Chinese Academy of Sciences in November 2018.
- **Runhai Ouyang** assumed a position as Associate Professor of Materials at the Genome Institute at Shanghai University in February 2019.
- **Jungho Shin** assumed a Senior Researcher Position at the Korea Research Institute of Chemical Technology in March 2019.
- In February 2019, **Matthias Rupp** became an Applied Scientist at Citrine Informatics, a leading company for data-driven developments of chemicals and materials.
- **Angelo Ziletti** accepted a position as Senior Data Scientist in the Artificial-Intelligence Lab of Bayer in April 2019.
- **Stefano Curtarolo** received the Friedrich Wilhelm Bessel Research Award of the Alexander von Humboldt Foundation in 2016 and spent a sabbatical year in Berlin from July 2017 - July 2018.

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 *GW* 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, 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, in Berlin and different international locations. This year we had more than 100 applicants but were only able to accept 74 participants (from 16 countries). The workshop in Beijing in 2018 was generously funded by the Sino-German Center for Research Promotion and the Max Planck Society. This workshop as well as the one in Barcelona in 2019 (funded by CECAM and Psi-k) were great successes, and Carsten Baldauf, the main organizer, did a very impressive job. As always, the whole Theory Department helped greatly.

Further activities in the last two years included:

- CECAM workshop Quantum-Chemistry Methods for Materials Science, Lausanne, Switzerland, November 8–10, 2017, organizers: I. Y. Zhang, M. Scheffler.
- NOMAD: Third Industrial Meeting, London, United Kingdom, February 5–6, 2018, organizers: A. De Vita (King's College London), A. Rubio (MPI for the Structure and Dynamics of Matter, Hamburg), M. Scheffler.
- Symposium on Managing and Exploiting the Raw Material of the 21st Century at DPG Spring Meeting in Berlin, Germany, March 11–16, 2018, organizers: C. Draxl, P. Fratzl (MPI of Colloids and Interfaces, Potsdam).
- Symposium on Frontiers of Electronic Structure Theory: Correlated Electron Materials at DPG Spring Meeting in Berlin, Germany, March 11–16, 2018, organizers: S. Biermann (École Polytechnique, Palaiseau), P. Kent (Oak Ridge National Laboratory), M. Scheffler.
- BiGmax Workshop 2018 on Big-Data-Driven Materials Science, Kloster Irsee, Germany, April 10–13, 2018, organizers: J. Neugebauer (MPI für Eisenforschung GmbH, Düsseldorf), P. Benner (MPI for Dynamics of Complex Technical Systems, Magdeburg).
- CECAM workshop Path Integral Quantum Mechanics: From the Basics to the Latest Developments, Lausanne, Switzerland, June 25–29, 2018, organizers: M. Rossi, J. Richardson (ETH Zürich), M. Ceriotti (EPF Lausanne), T. Markland (Stanford).
- Electronic Structure Theory with Numeric Atom-Centered Basis Functions - FHI-aims Developers' and Users' Meeting, Munich, Germany, July 9–11, 2018, organizers: V. Blum (Duke University, USA), W. Huhn (Duke University), H. Oberhofer (TU Munich), X. Ren (University of Science and Technology of China), M. Rossi.
- Hands-On DFT and Beyond: Frontiers of Advanced Electronic Structure and Molecular Dynamics Methods, Peking University, Beijing, China, July 30–August 10, 2018, organizers: X. Li (Peking University), C. Baldauf, X. Ren (University of Science and Technology of China), H. Jiang (Peking University), V. Blum (Duke University), M. Scheffler.
- HoW exciting! 2018, Humboldt-Universität zu Berlin, Berlin, Germany, July 31–August 9, 2018, organizers: C. Cocchi (HU Berlin), A. Gulans (HU Berlin), P. Pavone (HU Berlin), C. Draxl.
- Theory Department Workshop 2018, Ringberg, Germany, September 12–14, 2018, organizers: C. Carbogno, M. Rossi, M. Scheffler.
- Long Program on Science at Extreme Scales: Where Big Data Meets Large-Scale Computing at the Institute for Pure & Applied Mathematics, Los Angeles, USA, September 12–December 14, 2018, organizers: J. Buhmann (ETH Zürich), H.-J. Bungartz (TU Munich), E. Candes (Stanford University), C. Draxl, J. Hittinger (Lawrence Livermore National Laboratory), F. Jenko (MPI for Plasma Physics and UCLA), D. Keyes (KAUST), A. Lee (AMD), T. Warnow (University of Illinois).
- NOMAD Summer: A Hands-On Course on Tools for Novel-Materials Discovery, Lausanne, Switzerland, September 24–27, 2018, organizers: L. M. Ghiringhelli, M. Rampp (MPCDF, Garching), A. Ziletti, M. Scheffler.

- Exciting Shanghai School, Shanghai, China, November 17–22, 2018, organizers: W. Ren (Shanghai University), A. Stroppa (CNR-SPIN), C. Draxl, P. Pavone (HU Berlin).
- FAIRmat Meeting, FHI, Berlin, Germany, March 22, 2019, organizer: C. Baldauf, C. Draxl, M. Scheffler.
- Symposium on Frontiers of Electronic-Structure Theory: Focus on The Interface Challenge at DPG Spring Meeting in Regensburg, Germany, March 31–April 5, 2019, organizers: J. Nørskov (Technical University of Denmark), K. Reuter (TU Munich), M. Scheffler.
- NOMAD-FAIR-DI workshop: Shared metadata and data formats for Big-Data Driven Materials Science, Berlin-Adlershof, Germany, July 8–12, 2019, organizers: C. Draxl, L. M. Ghiringhelli, G. Hutchings (Cardiff University), J. Kermode (University of Warwick), C. Koch (HU Berlin), C. Liebscher (MPI für Eisenforschung GmbH, Düsseldorf), M. Tourdot de Oliveira (MPI for the Structure and Dynamics of Matter, Hamburg), G.-M. Rignanese (UCLouvain), M. Scheffler, C. Wöll (KIT).
- FAIRmat Meeting, Berlin-Adlershof, July 15–16, 2019, organizers: C. Baldauf, C. Draxl, M. Scheffler.
- Hands-On DFT and Beyond: High-throughput screening and big-data analytics, towards exascale computational materials science, Barcelona, Spain, August 26–September 6, 2019, organizers: F. Illas Riera (University de Barcelona), E. Ruiz Sabin (University de Barcelona), C. Baldauf, S. Kokott, V. Blum (Duke University), M. Scheffler.
- BiGmax summer school Big Data Summer, Platja d'Aro, Spain, September 9–13, 2019, organizers: G. Dehm (MPI für Eisenforschung GmbH, Düsseldorf), C. Draxl, M. Scheffler, J. Vreeken (CISPA – Helmholtz Center for Information Security).

Prof. Dr. Sergey V. Levchenko

Assistant Professor at the Skolkovo Institute of Science and Technology, Moscow, Russia (since 2018)
Group Leader at the FHI (2008-2019)
Postdoc at the University of Pennsylvania, PA, USA (2005-2008)
Ph.D. (Chemistry), University of Southern California, CA, USA (2005)

Activities of the "Unifying Concepts in Catalysis" Group

Our group studies surfaces and interfaces under realistic conditions of temperature (T), pressure (p), and doping using first-principles modelling combined with statistical mechanics. In particular, we investigate the surface stoichiometry and atomic structure of heterogeneous catalysts. Below, we describe the projects pursued in the last two years.

Accurate Single-Particle Energies and Band Gaps of Solids from Second-Order Møller-Plesset Perturbation Theory and Beyond

With: Maria Dragoumi, Igor Y. Zhang (Fudan University), and Matthias Scheffler

Previously, we have unveiled the important role that charge-carrier doping plays in defect formation at surfaces under realistic (T, p) conditions [1]. This has prompted us to develop a methodology for describing polarons in materials using *ab initio* methods [2]. As a continuation of this work, we develop a many-body perturbation theory method for accurate evaluation of polaron properties in solids. While local density/generalized gradient approximations to density-functional-theory (DFT) exchange-correlation (XC) functional suffer from the self-interaction error that influences charge-carrier localization energetics (an important property of a polaron), hybrid functionals contain adjustable parameters the values of which can be set by comparing with more accurate parameter-free methods. Therefore, we start from the Møller-Plesset second-order perturbation theory for quasiparticle excitations [3], but go beyond by solving the Dyson equation. This way, an infinite summation of diagrams is considered, including second-order exchange that cancels the one-electron self-interaction error. Calculations of the band gap for semiconductors and insulators with the new approach show that the Dyson equation is crucial for a proper treatment of single-particle energies. The new approach shows a competitive or even superior performance in comparison to hybrid functionals and the *GW* approximation, where the second-order exchange diagram is missing.

Oxidation of Elemental and Alloyed Transition-Metal Surfaces at Realistic Temperature and Pressure

With: Zhong-Kang Han, Santiago Rigamonti (HU Berlin), Maria Troppenz (HU Berlin), Claudia Draxl, and Matthias Scheffler

In this project, we study thermodynamics of elemental and alloyed metal surfaces under an oxygen atmosphere. The thermodynamics of oxidation and its dependence on the metal type and surface orientation are still not fully understood. We have performed a DFT study (comparing various XC approximations) for the adsorption of atomic and molecular oxygen on the (111) and (110) surfaces of Ag, Au, Pt, Rh, Pd, and Cu elemental metals, and on the Pd- or Pt-alloyed Cu(111) and Cu(110) surfaces. The effects of configurational entropy were evaluated by combining a cluster expansion (CE) model with Monte Carlo sampling [4]. To the best of our knowledge, this is the first study that takes into account configurational entropy for both alloy components and adsorbates simultaneously. It leads to a very large number of possible compact clusters in CE, so that machine-assisted selection of the clusters is required to find a predictive model. We showed that it is essential to take into account the Coulomb repulsion between oxygen anions to explain the stability of ordered structures of adsorbed O atoms on the (110) and (111) surfaces of elemental metals. The structures of adsorbed O at the Pd or Pt-alloyed Cu surfaces exhibit a larger variety of patterns depending on coverage; Pd/Pt segregate to the surface at low oxygen coverages, while at high oxygen coverages Cu segregates.

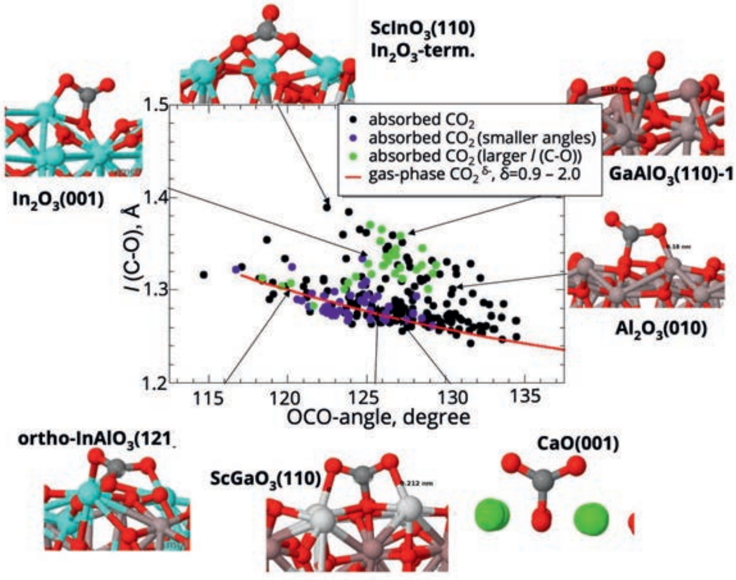

Figure 1: The correlation between the larger of the two C-O bond lengths (in case the two bond lengths are different) and the OCO-angle in charged gas-phase (red line) and adsorbed CO_2 (dots, blue – subgroup with small OCO-angles, green – subgroup with large l(C-O), black – the remaining samples).

A Route Towards Discovering Better Catalysts Using Artificial-Intelligence Analysis of *Ab Initio* Data Together with Experimental Data

With: Aliaksei Mazheika, Yang-Gang Wang, Rosendo Valero (University of Barcelona), Luca M. Ghiringhelli, Francesc Illas Riera (University of Barcelona), and Matthias Scheffler

In this project we have applied data-analytics techniques to systems relevant for heterogeneous catalysis [5,6]. In particular, we have studied the activation of carbon dioxide at oxide surfaces [6]. Uncontrolled emission of CO_2 into the atmosphere is one of today's major environmental threats. The most promising way to recycle CO_2 is to convert it to fuels and other useful chemicals using heterogeneous catalysis. For a rational design of catalytic materials for CO_2 activation, a reliable prediction of catalytic performance (e.g., reaction turn-over frequency, TOF) requires understanding and modelling the full catalytic cycle, which is currently not feasible. A way out is to find *indicators* for activation, i.e., common features of good CO_2-conversion catalysts. In order to be useful, these features should be much easier to evaluate than the TOF. We consider several physically motivated indicators for CO_2 activation, including the OCO bending angle and the C-O bond length $l(\mathrm{C\text{-}O})$ in the adsorbed CO_2 molecule. Overall, 71 different binary and ternary oxide materials, 141 surfaces, and 270 unique adsorption sites were considered. We then used the subgroup-discovery (SGD) [7] approach to identify subgroups of adsorption sites that provide a small OCO angle or a large C-O bond length. Interestingly, for the $l(\mathrm{C\text{-}O})$ subgroup, *all* experimentally tested materials are good CO_2-conversion catalysts. On the other hand, several materials that have been identified as unsuitable for CO_2 activation belonged to the “small OCO angle” subgroup. This is explained by the fact that the OCO angle is reduced on surfaces that also bind CO_2 too strongly. The longer $l(\mathrm{C\text{-}O})$ is achieved due to the binding of an O atom in the adsorbed molecule to a nearby surface cation, which provides an additional mechanism for weakening C-O bonds (Fig. 1). This suggests that C-O bond elongation might be used as an indicator for CO_2 activation. Based on these findings, we propose a set of promising new catalysts for CO_2 conversion, and a recipe to find more. In future, we plan to extend this work to other materials classes, including metal carbides.

Atomic and Electronic Structure of β-Ga_2O_3 Surfaces at Realistic Conditions

With: Konstantin Lion (HU Berlin), Matthias Scheffler, and Claudia Draxl

The transparent conducting oxide Ga_2O_3, which exhibits a band gap of about 4.9 eV, is a promising candidate for a number of applications, such as semiconducting lasers and transparent electrodes for UV optoelectronic devices and solar cells. As such, the bulk properties of its thermodynamically stable β phase have been extensively studied in the last two decades. The surface properties that play a vital role in epitaxial growth, electrical contacts, and gas sensors are, however, still not well understood. We performed DFT calculations for several β-Ga_2O_3 surfaces with the hybrid exchange-correlation functional HSE06, which mixes a portion of exact exchange from Hartree-Fock theory with exchange energy from a generalized gradient calculation. The mixing parameter was chosen as 26% exact exchange, which reproduces the experimental band gap. Surface structures were modelled as slabs in the supercell approach, including up to 140 atoms per supercell. Surface thermodynamic stability over a wide range of temperature and pressure conditions was characterized by the surface free energy. While the total energy is the dominating contribution to the free energies, vibrational contributions can potentially affect the relative stability of different surface orientations. Therefore, we also included vibrational contributions for the two most stable surfaces.

We found that the (100) surface is the most stable one, in agreement with previous reports, but, quite surprisingly, it is followed closely by the $(\bar{2}01)$ surface. Here, the topmost surface layers are significantly flattened upon relaxation, reducing the surface energy to 40% of the value of the unrelaxed surface. Vibrational contributions further slightly stabilize both surfaces but do not change their relative stability. This result explains recent experimental findings where ($\bar{2}$ 01) facets were found to form during homoepitaxial growth on off-oriented β-Ga_2O_3 (100) substrates [8].

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Dr. Christian Carbogno

Group Leader at the FHI (since 2015)
Deputy Group Leader at the FHI (2013-2015)
Post-doctoral Researcher at the University of California Santa Barbara, USA (2010–2012)
Dr. rer. nat., Universität Ulm (2009)

Activities of the "Heat and Charge Transport" Group

Heat and charge transport processes play a key role in materials science, e.g., in the discovery of novel materials for thermoelectric devices. Nonetheless, little is known about the actual mechanisms that drive or hinder heat and charge transport in complex materials under actual operational temperatures $T >$ 300 K. To date, perturbative formalisms based on an idealized, semi-harmonic description of the nuclear motion and its coupling to the electrons are still the most popular tool in materials science [1] – despite the fact that these assumptions are prone to failure in real materials and/or at elevated temperatures. The main focus of the *Heat and Charge Transport* group is to overcome these approximations by developing novel first-principles methodologies based on *ab initio* molecular dynamics (aiMD), so as to accurately account for **all** *anharmonic* effects in the nuclear motion and in its coupling to the electrons. These developments massively increase the range of materials, temperatures, and pressures, for which highly-accurate first-principles predictions are possible. We demonstrate this by applying the developed techniques – mostly in a *high-throughput* fashion – to fundamental, yet still unsolved, materials-science problems such as the design of improved thermoelectric materials. Accordingly, this research covers the fundamental challenges within the ERC-funded TEC1p project of Matthias Scheffler. To facilitate this, the group also addresses practical aspects of density-functional theory (DFT), e.g., decreasing its computational cost and estimating its numerical errors, in collaborative efforts.

Vibrational Heat Transport in Strongly Anharmonic Solids

With: Florian Knoop, Thomas A.R. Purcell, Maja-Olivia Lenz, Stefano Curtarolo, and Matthias Scheffler

In the last two years, the group has implemented a *high-throughput* framework for the efficient and high-precision prediction of vibrational thermal conductivities $\kappa(T)$ using the *ab initio* Green-Kubo (aiGK) approach [2]. This *ab initio* MD-based formalism developed earlier in the group is able to capture anharmonic effects to **all** orders and thus to accurately predict $\kappa(T)$ in solids, even at elevated temperatures and/or for strongly anharmonic materials, e.g., for materials close to a phase transition. Accordingly, this formalism is uniquely suited to aid and guide the search for novel thermoelectric materials, which require ultra-low $\kappa(T)$ and thus strongly anharmonic dynamics, well beyond the regime in which perturbative approaches are applicable. Clearly, an exhaustive *high-throughput* search for such thermal insulators is only possible if good conductors are disregarded early in the search process, even before computational time is invested in calculating their $\kappa(T)$. For this purpose, we have developed an analytical metric $r^2(T) \sim 1 - \langle (\boldsymbol{F}^{\mathrm{DFT}} - \boldsymbol{F}^{\mathrm{ha}})^2 \rangle$ that quantitatively captures the degree of anharmonicity in the nuclear dynamics. It relies on the statistical comparison of the fully first-principles anharmonic forces $\boldsymbol{F}^{\mathrm{DFT}}$ experienced by the nuclei under specific thermodynamic conditions $\langle\cdot\rangle$ with those forces $\boldsymbol{F}^{\mathrm{ha}}$ that would act in the *harmonic* approximation. Accordingly, an essentially harmonic system features $r^2(T)$ values close to unity, whereas strongly anharmonic systems feature $r^2(T)$ values below 0.8. Since $r^2(T)$ can be obtained in a robust fashion within few force evaluations – several orders of magnitude faster than $\kappa(T)$ – we are able to scan over the materials space in a *high-throughput* fashion, covering thousands of materials including several complex thermoelectric material classes (half-Heuslers, inorganic halide perovskites, layered chalcogenides, etc.). This reveals that strongly anharmonic effects are much more common than hitherto believed. As shown in Fig. 1 for a representative test set of known materials obtained via the *AFLOW Library of Crystallographic Prototypes* [3], many compounds are well described by a perturbative quasi-harmonic description at 300 K ($r^2 > 0.8$) For 900K, however, this only holds for 55% of the materials. Over 20% of them, especially complex functional materials like perovskites, feature $r^2(T)$ values lower than 0.8. Accordingly, harmonic and anharmonic effects are of the same order and anharmonic effects can thus no longer be treated in a perturbed harmonic theory. To obtain the thermal conductivity $\kappa(T)$ of such materials, we perform *high-throughput aiGK* calculations, revealing that these compounds indeed feature low and ultra-low conductivities $\kappa(T) \ll 10$ W/mK. We demonstrate that accounting for all orders of anharmonicity is critical in this regime to obtain correct insights, i.e., quantitative predictions and a qualitative understanding of the atomistic mechanisms.

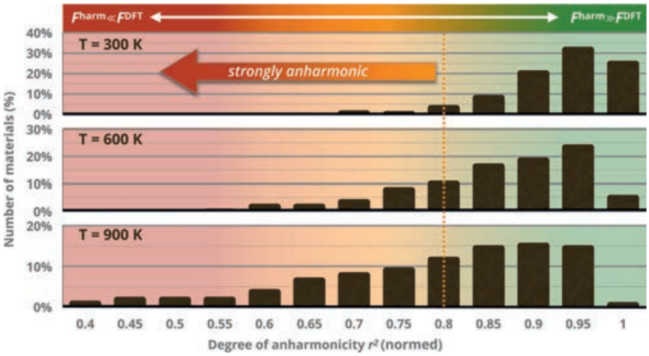

Figure 2: Degree of anharmonicity $r^2(T)$ obtained from first-principles with the PBE functional at 300, 600, and 900K for a representative set of over 300 materials, including over 100 perovskites structures. For compounds with $r^2(T) < 0.8$ (orange line) harmonic and anharmonic effects are comparable in magnitude.

Electronic Transport beyond Perturbation Theory

With: Marios Zacharias, Zhenkun Yuan, and Matthias Scheffler

The frequent emergence of strongly anharmonic effects in complex materials discussed above raises the question, to what extent these effects also determine electronic transport in solids. Existing perturbative formalisms [1] are unsuitable to resolve this doubt, since they intrinsically rely on a harmonic description of the nuclear motion. Furthermore, they rely on an additional, potentially problematic approximation [4], i.e., a first-order model for the electron-phonon coupling. To overcome **both** these approximations and to account for **all** orders of phonon-phonon and electron-phonon coupling, we have developed a first-principles theory of electronic transport, in which the electronic flux, i.e., the time derivative of the electronic polarization $\boldsymbol{P}(t)$, is computed along aiMD trajectories. Since $\boldsymbol{P}(t)$ requires computing the *Berry phase* on a dense $\boldsymbol{k}$-grid [5], this approach seems at first incompatible with aiMD calculations in large supercells . We circumvent this via a newly developed electronic-structure unfolding scheme: The time-dependent, single particle wave-functions $\Psi_{\boldsymbol{k},n}^{\mathrm{aiMD}}(t) = \sum_{j,\boldsymbol{G}} C_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{G}}^{n,j}(t)\, \psi_{\boldsymbol{k}+\boldsymbol{G},j}^{\mathrm{ref}}$ in the aiMD supercell are expressed in terms of a static reference $\psi_{\boldsymbol{k}+\boldsymbol{G},j}^{\mathrm{ref}}$, i.e., the wave-functions of the primitive unit cell. Here, $\boldsymbol{G}$ denotes the reciprocal vectors connecting the respective Brillouin zones. By this means, the Berry phase can be evaluated in the primitive unit cell; the time-dependent expansion coefficients $C_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{G}}^{n,j}(t)$ then modulate the individual contributions, thus capturing the anharmonic electron-phonon couplings. Eventually, the spectral function $A_{\mathbf{k},j}(\varepsilon, T) \sim \langle \sum_{n,\boldsymbol{G}} \left| C_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{G}}^{n,j}(t) \right|^2 \rangle$, i.e., the T-dependent electronic band-structure in the primitive unit cell, is computed from the thermodynamic average of $C_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{G}}^{n,j}(t)$ obtained via aiMD in supercells. Analogously, the lifetimes $\tau_{\mathbf{k},j}(T)$ are computed from the correlation functions of $C_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{G}}^{n,j}(t)$, thus providing a direct route to evaluate electronic transport. As an example, Fig. 2 shows the spectral function $A_{\mathbf{k},j}(\varepsilon, T)$ obtained for silicon at 0K as well as the T-dependence of the indirect band-gap, as extracted from a series of $A_{\mathbf{k},j}(\varepsilon, T)$ calculations for different T. For this validation calculation, a quantum-mechanical harmonic model is used for the nuclear motion, so that our approach is in excellent agreement with perturbative theoretical results. Disagreement with experiment becomes noticeable at higher temperatures. Since our approach is also fully compatible with anharmonic aiMD, ongoing investigations on simple as well as on complex functional materials aim at understanding the role of anharmonicity for electronic self-energies and for the resulting transport coefficients.

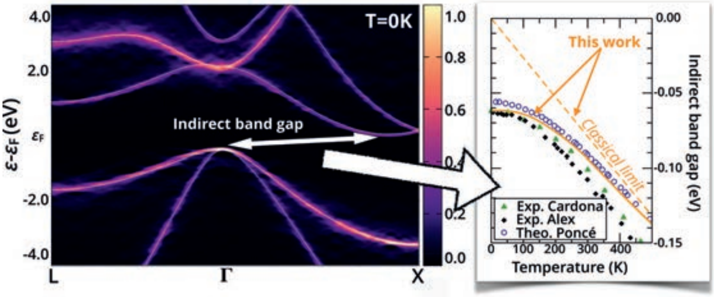

Figure 3: Spectral function $A_{\mathbf{k},j}(\varepsilon, 0\mathrm{K})$ (left) and temperature-dependence of the indirect band gap in silicon (right). All results obtained within the harmonic approximation for the nuclear dynamics to allow a direct comparison with the also shown perturbative literature results.

ELPA-AEO: Towards Eigensolvers for Materials Science at the Exascale

With: Hagen-Henrik Kowalski, Danilo S. Brambila, and Matthias Scheffler

The above described DFT calculations in extended supercells come at the cost of considerable computational effort; the bottleneck of which is solving (generalized) eigenproblems. To exploit existing and upcoming exascale high-performance architectures, e.g., hybrid CPU-GPU installations, the group participated in the BMBF-funded ELPA-AEO project[19], coordinated by Hermann Lederer (MPCDF), aimed at improving and optimizing the eigensolver library *ELPA*. In particular, the group was involved in guiding its development and evaluating the achievements. Due to this effort, *ELPA* nowadays *"outperforms ScaLAPACK on all architectures tested and all matrix sizes and concurrencies"*, as recently found by NERSC and Cray [6]. Furthermore, these advantages are accessible in an unprecedented user-friendly fashion, since performance-critical parameters are chosen in an automated way.

Numerical Quality Control for DFT-based Materials Databases

With: Björn Bieniek, Daniel Speckhard, Claudia Draxl, and Matthias Scheffler

Despite the widespread use of DFT calculations in *high-throughput* studies, little is yet known about code- and method-specific numerical errors that arise when the basis sets and $\boldsymbol{k}$-grids commonly chosen in such workflows are used. Hence, potentially uncontrollable uncertainties prevent re-using data from different sources or created for different target properties, in spite of the fact that the data may be publicly available. To overcome this, we have studied the convergence of different key properties (band gaps, total and relative energies) in four conceptually-different DFT codes (*exciting*, *FHI-aims*, *GPAW*, and *VASP*) for typical settings used in production calculations, but also for extremely precise settings that serve as fully converged reference to evaluate the numerical errors. On the basis of data obtained for 71 elemental solids, we have proposed an analytical model that allows total-energy errors for any compound to be estimated, as demonstrated for 73 binary and ternary solids. We are investigating the extensibility of our approach towards complex materials properties such as band gaps.

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Otto Hahn Group Leader
Dr. Mariana Rossi

Independent Otto Hahn Group Leader at the FHI (Oct. 2016–Dec. 2019)
Visiting Researcher, EPF Lausanne, Switzerland (2016)
Junior Fellow in St. Edmund Hall, Oxford, UK (2013–2015)
Dr. rer. nat., Technische Universität Berlin (2012)

Activities of the Otto Hahn Group "Simulations from Ab Initio Approaches: Structure and Dynamics from Quantum Mechanics"

General Remarks

The Otto Hahn Group, led by Mariana Rossi, is completing its third year in October 2019. In this period, the group has been pushing back the boundaries of atomistic simulations of weakly bonded systems at finite temperatures. The group's four PhD students and two postdocs are funded through the budget allocated to the Otto Hahn Group and through Dr. Rossi's third party-funding. This consists of a sub-project within the Collaborative Research Centre 951 (Hybrid Inorganic/Organic Systems for Opto-Electronics - HIOS), the Max Planck Research Network on Big-Data-Driven Materials Science (BiGmax) and the Max Planck-EPFL Center for Molecular Nanoscience and Technology. One student is funded through the International Max Planck Research School (IMPRS) for functionalized interfaces. Since August 2018, Mariana Rossi is also the main partner of the Max Planck Tandem Group on "Atomistic Simulations for Electrochemistry", led by Luana Pedroza at the UFABC, São Paulo, Brazil. The group has long-term collaborations with the experimental groups of Takashi Kumagai (PC Department, FHI) and Norbert Koch (Humboldt-Universität zu Berlin). New collaborations in the framework of the CRC-951 (third funding period, since June 2019) have been established with Katharina Franke (Freie Universität Berlin), Ralph Ernstorfer (FHI), and Christoph Koch (Humboldt-Universität zu Berlin). In the past two years, the group has also collaborated with other theory groups, for example those led by Jörg Behler (Georg-August-Universität Göttingen), Jeremy Richardson (ETH Zürich), Michele Ceriotti (EPF Lausanne), Patrick Rinke (Aalto University), and Volker Blum (Duke University).

In January 2020, the group will move to the Max Planck Institute for Structure and Dynamics of Matter in Hamburg, where Mariana Rossi will be taking up a tenure track position within the scope of a Lise Meitner Group. She will continue with a 20% appointment at the FHI for the duration of the third funding period of the CRC-951, which will end in June 2023.

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. Especially in weakly bonded systems, the nuclear fluctuations induced by temperature can completely change the structure, the thermodynamic equilibrium, and also the electronic structure of materials. In addition, given the ubiquitous presence of light nuclei in organic materials, not only the electrons but also the nuclear fluctuations must be treated within the first principles of quantum mechanics. We achieve an all-atom, all-electron quantum description of these systems by developing methodology and tools that allow joining density-functional-theory calculations to path-integral methods. We belong to the core developers of the FHI-aims electronic-structure package [1] and the i-PI software [2], which performs nuclear dynamics. As described in detail below, this combination has allowed us to solve questions related to level broadening in semiconductor interfaces, isotope effects in electron-phonon coupling and apparently contradictory observations in hydrogen-transfer reactions. None of this would be possible if the atomic structure of the systems was unknown or incorrect. This is why we also conduct exhaustive *ab initio* structure searches of single molecules and of self-assembled monolayers as well as augment genetic-algorithm program packages in order to make these searches more efficient (see Fig. 1).

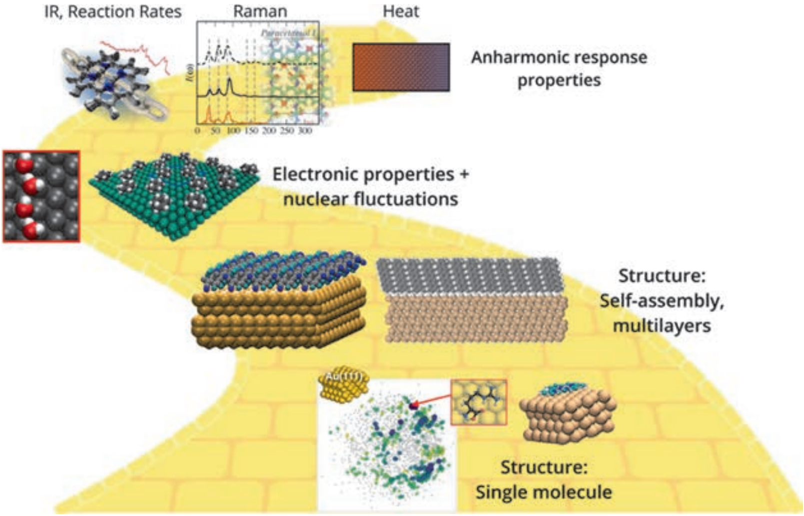

Figure 1: Research topics explored in the group. For isolated molecules on surfaces, we develop strategies for conformational space exploration that can handle the flexibility of the adsorbates. We address self-assembled organic structures at interfaces including the impact of atomic structure on the electronic-level alignments. We also include anharmonic nuclear quantum effects in electron-phonon coupling at weakly bonded interfaces. Finally, we develop novel techniques for the calculation of anharmonic nuclear response properties including nuclear quantum effects.

Research highlights

Hydrogen Transfer Reactions in High-Dimensional Anharmonic Systems

With: Yair Litman, Jeremy Richardson (ETH), and Takashi Kumagai (PC Department)

Intra- and inter-molecular hydrogen transfer is strongly impacted by zero-point energy and tunneling. The inclusion of these effects in high-dimensional anharmonic systems represents a considerable challenge in atomistic simulations. We implemented and derived optimizations for the ring-polymer instanton method [3] and thermostatted ring-polymer molecular dynamics [4] in the i-PI code. The former method gives access to reaction rates and the latter to vibrational spectra, both including zero-point energy and tunnelling effects, and are applicable to high-dimensional anharmonic systems. For the paradigmatic example of porphycene, a prototype molecular switch, experimental intramolecular hydrogen transfer reaction rates show a controversial coexistence of Arrhenius (classical) behaviour and a strong isotope effect. Our simulations are able to explain fully the experimental data (see Fig. 2a) – a feat that had not been previously achieved [5]. In particular, the failure of the classical-nuclei description and apparent controversies for reaction rates are fully explained by the vibrational coupling between quasi-classical thermally activated modes and high-frequency quantized modes in this system. The framework we developed is easily generalizable to even more complex situations.

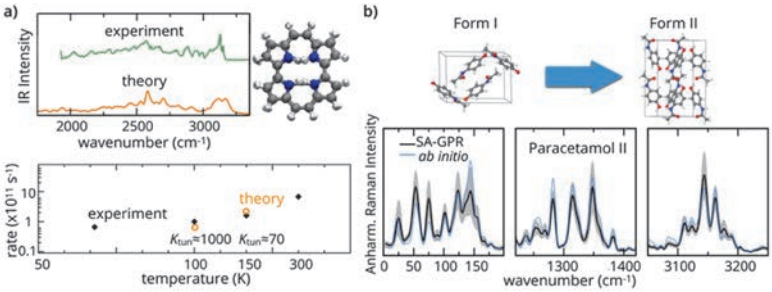

Figure 2: a) Top: Simulated anharmonic *ab initio* IR spectrum from approximate quantum dynamics and experimental spectrum at room temperature for the porphycene molecule. Bottom: Comparison between experimental tautomerization rates and simulated ones from approximate quantum dynamics, including the tunneling enhancement factors K_{tun}. See Ref. 3 and references therein. b) Gaussian process regression (GPR) prediction of the vibrational Raman spectrum of the paracetamol crystal. With the symmetry-adapted GPR (SA-GPR) framework, we obtained a model that is transferable between different polymorphic forms, see Ref. 4 and references therein.

Molecular Crystals at Finite Temperatures

With: Nathaniel Raimbault, Marcin Krynski, Andrea Grisafi (EPFL), and Michele Ceriotti (EPFL)

Structure prediction in molecular crystals is incomplete if the thermodynamic conditions (temperature, pressure) are not considered. Anharmonic contributions represent the largest contribution to free-energy differences of molecular crystal polymorphs composed of flexible molecular units. We have computed lattice changes at different conditions, confirming the essential role of van der Waals interactions for the stability and anisotropic lattice expansion and contraction of aspirin and paracetamol. Further, we have studied the accuracy of approximate methods to include anharmonic free-energy contributions (which were implemented in i-PI) for these systems, and found that methods based on normal-mode expansions fail when librational and rotational motion are present. Thermal free energies are especially sensitive to the low-frequency vibrational modes, which are also an important region to differentiate different crystal polymorphs. With the efficient density-functional-perturbation-theory implementation in FHI-aims, we were able to simulate anharmonic Raman spectra based on *ab initio* molecular dynamics trajectories. In order to cope with the added cost of calculating Raman intensities, we devised a machine-learning model based on a symmetry-adapted Gaussian process regression algorithm (SA-GPR) that makes use of models trained for isolated molecules to learn dielectric responses of crystals [6]. The models are very accurate with only a few hundred points and, importantly, are transferable between different polymorphs (see Fig. 2b).

Hybrid Organic-Inorganic Interfaces and Electron-Phonon Coupling

With: Haiyuan Wang, Sergey V. Levchenko, Karen Fidanyan, Svenja M. Janke (Duke University), Volker Blum (Duke University), Thorsten Schultz (HU Berlin), Norbert Koch (HU Berlin) and Matthias Scheffler

A major challenge in describing organic-inorganic interfaces is predicting and controlling the structure-function relationship. The weakly-bonded organic components show flexibility and polymorphism, which are exacerbated by the typical temperatures at which these systems operate. We have studied the impact of strain on interfaces of silicon and pentacene films, finding that even low strain can strongly change the frontier-orbital alignment. When silicon is interfaced with strong organic electron acceptors, we found that the level alignment is more robust but the structure itself is strongly dependent on the strength of van der Waals interactions. Moreover, we predict a broadening of frontier orbitals due to anharmonic nuclear fluctuations at room temperature that far surpasses $k_B T$ [7]. Anharmonic electron-phonon coupling also explains the isotope effect in work-function changes that has been measured in metal-organic interfaces, showing that finite temperature nuclear quantum effects are relevant also for the electronic structure

This work was performed partly within the framework of the DFG CRC-951 (HIOS) project.

Other Research Fronts

A major challenge in predicting structure of flexible organic films and solids is navigating the conformational space of not only the self-assembled structure but also of the individual molecular constituents. In collaboration with Carsten Baldauf and the PhD student Dmitrii Maksimov, we improved a genetic-algorithm-based structure search that can handle flexible molecules in order to work at interfaces. In addition, we are investigating how to bias these searches to favour regions of lower free-energy minima under specific thermodynamic conditions.

In collaboration with the Tandem Group led by Luana Pedroza (UFABC, São Paulo, Brazil) we are implementing a framework to capture nuclear quantum effects at water interfaces relevant for electrochemistry. In particular, we have a setup based on the i-PI code and a density-functional non-equilibrium Green's function code that performs path-integral molecular dynamics with (self-consistent) forces from simulations where the potential bias is included explicitly. This bias has a direct impact on the structure of water at the interface, while nuclear quantum effects can strengthen (or weaken) intramolecular H-bonds and metal-hydrogen bonds. These effects play a direct role on interface degradation at different voltage biases and on the efficiency of the cells at different temperatures, but simulations have so far not been able to combine these physical interactions.

Regarding heat transport through materials, we wish to perform simulations for regimes where strong anharmonicity and quantum effects play a significant role. These regimes are of particular importance for organic electronics due to the anharmonic (weak) interactions and the ubiquitous presence of light atoms. We collaborate with Christian Carbogno and David Manolopoulos (Oxford University), as well as with the students Hagen-Henrik Kowalski and Benjamin Sutherland to achieve novel frameworks based on calculations of thermal diffusivities from non-equilibrium simulations and thermal conductivities directly from the Green-Kubo formalism. With these developments, we hope to achieve a robust approximate method that is efficient in combination with *ab initio* simulations.

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Dr. Luca M. Ghiringhelli

Group Leader at the FHI (since 2011)
Postdoc at the FHI (2008–2010)
Postdoc at the Max-Planck-Institut für Polymerforschung in Mainz (2005–2008)
Dr. rer. nat., Universiteit van Amsterdam (2006)

Activities of the "Big-Data Analytics for Materials Science" Group

The group "Big-Data Analytics for Materials Science" was established in 2015 with the research focus on developing and applying methods for finding patterns, trends, and analytical relationships in materials-science data, in order to establish what has now become the field of "data-driven materials science". Primarily, the methods developed belong to the wide area of artificial intelligence (AI). AI is an umbrella term describing any technique that mimics (and potentially even surpasses) human intelligence, in particular its ability to infer regularities from empirical data. It embraces disparate areas from signal analysis, data mining, and statistical (or machine) learning. The developed AI algorithms are applied to relevant problems in materials science, in particular the identification of descriptors enabling the construction of simple *maps* (or *charts*) of materials properties (see Fig. 1 for an example). Below is a short account of the major advances within the group in the last two years.

SISSO, an Efficient, Massively Parallel Algorithm for the Compressed-Sensing- Based Identification of Materials-Property Maps

Method development with: Runhai Ouyang, Emre Ahmetcik, and Matthias Scheffler
Applications also with: Stefano Curtarolo, Christopher J. Bartel, Chistopher Sutton, Bryan Goldsmith, and Charles B. Musgrave (University of Colorado Boulder)

Building on the breakthrough introduction in 2015 of LASSO+ℓ_0, a method that combines symbolic regression[20] and compressed sensing[21] for identifying descriptors and accurate models from a set of candidate features, we developed SISSO [1]. This is a massively parallel algorithm that overcomes the limitation of LASSO+ℓ_0., i.e., it can cope with hugely and highly correlated dimensional feature spaces. SISSO stands for "Sure Independence Screening and Sparsifying Operator" and deals with feature spaces with billions or more elements. Together with the algorithm for identifying the best descriptor in the set of candidates, we also constructed a "self-diagnostic" technique that determines the maximum complexity of the descriptor by means of so-called cross validation[22]. Perhaps the most notable application was the identification

[20] Symbolic regression is a technique that searches the space of mathematical expressions in order to find the model (equation) that best fits a given data set. This is in contrast to parametric regression, e.g. the usual linear (least-square) regression, where only the parameters of fixed functional form are fit to the data.

[21] Compressed sensing is a mathematical technique developed in signal analysis for solving massively underdetermined (fewer equations than unknowns) linear systems.

[22] Cross validation is a family of techniques having in common the iterated splitting of the data set into training and test. The model is fitted to the training data, but the performance is

of a tolerance factor for predicting whether the ground-state crystal structure of a material with a given chemical formula within the prototype ABO_3 is perovskite [2]. Having been trained using about 600 experimental data points retrieved from literature, the descriptor found by SISSO utilizes the same input features as the hundred-year-old, famous Goldschmidt tolerance factor t, confirming that the sizes of the atoms (namely, their Shannon radii) determine their spacing and their stability as perovskites, but proposes a slightly more complex equation. The newly found descriptor, dubbed τ, outperforms Goldschmidt's t in terms of accuracy and crucially allows a monotonic probability to be assigned as to whether a material is a perovskite or not. In practice, for very small (large) values of τ, the material is predicted as certainly (not) a perovskite, while for intermediate values, the probability ranges from 100% to 0%. We have exploited the model found by SISSO by scanning all possible values of atomic radii and identified several perovskites candidates that were previously unknown. The model can be extended without loss of accuracy to double perovskites, by just inputting the average Shannon radii of the atomic species occupying the *A*/*A*′, (or *B*/*B*′) positions. The latter circumstance highlights one of the big merits of the SISSO-like descriptor and model learning: The relative simplicity of the descriptor learned and the very small number of fitting parameters (e.g., only one fitting parameter for τ) gives rise to a remarkable stability and extrapolation ability well beyond the training data set.

Learning Several Materials Properties Simultaneously from Incomplete Databases with Multi-Task SISSO

With: Runhai Ouyang, Emre Ahmetcik, Christian Carbogno, and Matthias Scheffler

The SISSO algorithm was generalized to so-called multi-task learning, a framework that allows for the simultaneous learning of several target properties by means of a family of models sharing certain characteristics. In the case of the newly developed multi-task (MT) SISSO, all predicting models (one per target property) have in common the same descriptor (as usual identified from a huge set of candidates), while they differ in the fitting coefficients. The remarkable characteristic of MT-SISSO is that it is not necessary to have information about all considered properties for all training data points. In fact, the training database can be rather incomplete and the enhanced robustness introduced by the simultaneous learning promotes the identification of an accurate model. MT-SISSO was applied, among other things, to *crystal-structure prediction* (within Scheffler's ERC project TEC1p) of the relative formation energy of several (5) crystal structures for octet binary materials, see Fig. 1. MT-SISSO promises to be a versatile approach, coping with incomplete databases and circumventing the present difficulty of single-task SISSO, where it is problematic to characterize materials found in different crystal structures. Instead of finding an explicit descriptor encoding the crystal structures, the problem is shifted to the fitting coefficients, which are implicit functions of the crystal structures.

evaluated over the test data. The minimization of the test error allows for choosing the so-called hyperparameters, that in the case of SISSO are those determining the complexity (how many input features and how many mathematical operators acting on them) of the learned formula.

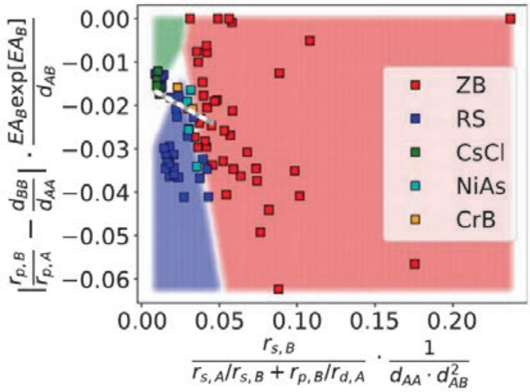

Figure 1: Map (phase diagram) of the ground-state crystal structure for octet binary materials. Five prototypes are considered: Zinc blende (ZB), rock salt (RS), CsCl, NiAs, and CrB. The extended colored regions correspond to the stability of the corresponding crystal phase, while the colored squares are the training points. The descriptor depends on *s,p,d* valence-orbital radii for the *A* or *B* component of the binary and the equilibrium distances of the isolated *AA*, *BB*, and *AB* dimers, and the electron affinity.

NOMAD Activity: The Kaggle Competition

With: Christopher Sutton, Angelo Ziletti, and Matthias Scheffler

In the context of the NOMAD (Novel Materials Discovery) Laboratory (see report of Claudia Draxl), a machine-learning competition was organized. By means of high-throughput density-functional-theory (DFT) calculations, the formation energy and band gap of 3,000 transparent conducting oxides (prototype formula, $Al_xGa_yIn_zO_3$, $x+y+z=2$) were calculated. The input data (chemical formula, atomic coordinates, and unit cell lattice vectors) were then provided to the participants of a competition hosted on the Kaggle platform for machine-learning contests[23]. The aim of this challenge was to identify the best machine learning (ML) model for the prediction of two target properties.

As many as 883 teams participated. The first three best-performing models are described in Ref. [4]. The first place solution is a novel approach, based on both crystal-graph representation and chain of words (*n*-grams) borrowed from natural-language processing.

This competition is unprecedented in materials science and the possibility to analyze AI models designed and trained by independently working teams revealed valuable information, since the bias introduced by one team selecting AI models due to personal preferences is removed by the crowd-sourcing approach.

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[23] https://www.kaggle.com/c/nomad2018-predict-transparent-conductors

Subgroup Discovery for the Analysis of the Performance of Machine-Learning Models.

With: Mario Boley (Monash University), Christopher Sutton, Matthias Rupp (Citrine Informatics), Jilles Vreeken (Helmholtz Center for Information Security), and Matthias Scheffler

In 2017, we adapted subgroup discovery (SGD) to materials-science problems. SGD is a data-mining technique that identifies subsets of the data with outstanding values of a given target property; the subgroups are described by means of descriptors identified within a set of candidates, in a spirit similar to SISSO. However, rather than fitting the target property, the algorithm looks for statistically exceptional subsets, where the target property exhibits, e.g., a narrow distribution of values and its average is much smaller than for all data points. In a recent project (paper to be submitted), we trained 3 ML models on the same dataset as for the Kaggle competition and analyzed the distribution of *test (prediction) errors*. In practice, we identified what we define *domains of applicability (DA)* of the three models, described in terms of the input parameters (e.g., the lattice vectors). These are regions of the data space where the model performs better, in terms of reduced prediction root mean-square error. This (meta)analysis of AI models by means of another AI algorithm can be used to guide the development and improvement of ML representations through the identification of their systematic strengths and weaknesses.

NOMAD Activity: Analytics Toolkit

With: Emre Ahmetcik, Angelo Ziletti, Benjamin Regler, Ádám Fekete (King's College London), Fawzi Mohamed, and Matthias Scheffler

In the context of the NOMAD Laboratory, the Analytics Toolkit was first introduced in 2017. This is an online library of python notebooks illustrating step-by-step AI projects developed within the NOMAD team. The projects described above, in particular SISSO, the winners of the Kaggle competition, and more are available at https://analytics-toolkit.nomad-coe.eu/. Users can reproduce the results published in the related papers, starting from the raw training data; furthermore, they can interactively modify the training parameters to build an understanding of their effect on the trained models.

Robust Crystal-Structure Recognition via Deep Learning

With: Angelo Ziletti, Andreas Leitherer, Devinder Kumar (University of Waterloo and Vector Institute of AI Toronto), and Matthias Scheffler

Automatically recognizing local arrangements of atoms in order to assign crystal-structure prototypes by similarity and localizing boundaries among crystalline regions is a challenging, as well as important, application of AI. Existent and widely applied methods are not robust, since they typically rely on human-defined tolerance and/or are limited to few prototypes. Furthermore, it is desirable to recognize the parent structure also in case of heavily defected (e.g., by the presence of vacancies or atomic displacements). By designing a suitable descriptor, based on the Fourier transform of the atomic structure, and by training a state-of-the-art deep convolutional neural network (ConvNet) developed in the image-recognition field, we have obtained a parameter-free algorithm able to classify several prototypes in possibly heavily defected structures [5]. Furthermore, by using a cutting-edge technique [6], we were able to interpret the reasoning of the trained ConvNet, which turns out to use bright spots in the input image as an experienced human crystallographer would do.

In a recent development, we have introduced an alternative local descriptor, based on the expansion of the local environment over spherical harmonics and then averaged over the observed sample. With this as input for a newly trained ConvNet, we achieved the contrast to classify more than a hundred prototypes, including lower dimensional ones. We are able now to investigate structural transitions such as the Bain path between fcc and bcc structures, where the intermediate structures along the path are smoothly assigned to the expected crystal-structure prototypes even though the network is trained only on pristine structures.

Ongoing Projects

- *(with Benjamin Regler)* Development of an information-theory based score for assessing the content of information in a set of features with respect to a target property. This approach does not assume or search for any functional form for the feature set → property relationship, but rather quantifies how much a set of features "knows about" a target property. This algorithm would run preliminary to a symbolic regression or in general a ML step where the actual model for the selected features is trained. For this project, the theoretical development is essentially fulfilled, and few proof-of-concept applications are being carried out.
- *(with Emre Ahmetcik)* Development of a ML empirical potential for crystal-structure prediction (within Scheffler's ERC project TEC1p) across chemical space, such that the fitting parameters depend explicitly on the chemical species involved. These are characterized, for example, by their row and column in the periodic table, electronegativity, etc. The purpose is to be able to transfer the interacting potential from species to species with a sparse database, where only (relatively) few data points for each species and configuration are available. Preliminary tests show very promising results.
- *(with Yuanyuan Zhou)* Development of a potential-energy-surface efficient sampling technique in the grand-canonical ensemble. Based on the extension of the replica-exchange framework to the grand-canonical ensemble, this method is developed having in mind the unbiased and beyond-harmonic study of reactive surfaces in reactive atmospheres at finite temperature and pressure. An extensive application to the Si(111) surface in contact with H_2, modeled at the gradient-corrected DFT level, is under development. This work is going to be part of the Max-Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis 'FUNCAT'.

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Max Planck Fellow
Prof. Dr. Claudia Draxl

Max Planck Fellow of the MP Graduate Center for Quantum Materials (since July 2019)
Max Planck Fellow at the FHI (July 2014–June 2019)
Einstein Professor at the Humboldt-Universität zu Berlin (since 2011)
Habilitation Universität Graz (1996)
Dr. rer. nat., Universität Graz (1988)

Activities of the Max Planck Fellow Group

The main focus of the Max Planck Fellow group centers on data-driven research, covering all important aspects, from the creation of high-quality benchmark data to the design of FAIR [1] data infrastructure and the development and application of artificial-intelligence (AI) tools. Through the close interaction with the FHI, the NOMAD Laboratory has developed into a world-leading platform for materials discovery (see also Poster *From NOMAD to FAIR-DI*).

The NOMAD Laboratory

The Novel Materials Discovery (NOMAD) Laboratory is a unique user-driven platform for sharing and exploiting computational materials science data for speeding up research in materials and engineering. With the NOMAD Repository[24] and the NOMAD Archive, its code-independent and normalized form, the NOMAD Laboratory represents the worldwide largest data collection in this field. Based on its FAIR (findable, accessible, interoperable, reusable) data infrastructure, various services are offered, comprising the NOMAD Encyclopedia[25], advanced visualization, and artificial-intelligence tools as realized in the NOMAD Analytics Toolkit[26]. Prerequisite for all this is the NOMAD metadata, a hierarchical description of the data produced by all important computer codes in the community. Users can request a DOI to make data citable.

NOMAD is orthogonal to, but interacts synergistically with, other data collections worldwide. A new pipeline for automatic ingest from the *Materials Project* (MP)[27] input and output files is currently installed, which can be downloaded by interested users from NOMAD. Likewise, data from the *Automatic FLOW for Materials Discovery* (AFLOW)[28] and *The Open Quantum Materials Database* (OQMD)[29] have all been ingested into NOMAD.

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[24] https://repository.nomad-coe.eu

[25] https://encyclopedia.nomad-coe.eu

[26] https://analytics-toolkit.nomad-coe.eu

[27] https://materialsproject.org

[28] http://aflow.org

[29] http://oqmd.org

The NOMAD Laboratory – in the meantime well established – has recently been incorporated into a non-profit association, FAIR Data Infrastructure for Physics, Chemistry, Materials Science, and Astronomy e.V. (FAIR-DI e.V.)[30]. Although an association under German law, it is international in nature and has close connections to the European Open Science Cloud (EOSC). The latter initiative is dedicated to providing a stable and sustainable data infrastructure that hosts and further develops the NOMAD Repository, Archive, and Encyclopedia, so as to guarantee long-term viability, independent of the individual research projects currently driving it. It also forms an ideal basis for advancing data-driven science, for example, also addressing experimental studies. First steps in this direction have already been taken and also involve other departments at the FHI: Together with Ralph Ernstorfer and Martin Wolf (PC Department) we are tackling the FAIRness of time-resolved angle-resolved photoemission spectroscopy (tr-ARPES) data, while with Annette Trunschke and Robert Schlögl (Inorganic Chemistry) we focus on catalysis data.

All the above are components of FAIRmat[31] a consortium, led by Claudia Draxl and co-led by Matthias Scheffler, with significant involvement of Carsten Baldauf, which is running for the National Research Data Infrastructure (NFDI). This is a large-scale project of the BMBF (Federal Ministry of Education and Research, Germany) with a proposal deadline on October 15, 2019. FAIRmat brings together individual researchers, research institutions, joint research programs, and data and computing centers from all over Germany with the aim of establishing a FAIR data infrastructure for the wide field of materials science. The latter comprises all the sub-communities in condensed-matter science and reaches out to solid-state chemistry, catalysis, and soft matter. It covers synthesis, as well as experimental and computational materials science and will demonstrate its potential for selected applications such as batteries, heterogeneous catalysis, optoelectronics, spintronics, and AI.

We emphasize that such an infrastructure is the crucial basis for data science. After demonstrating the potential of compressed sensing for learning descriptors for materials properties, [2] i.e., parameters that capture the physical mechanisms underlying certain material properties, the methodology has been further refined [3] (see also the report by Luca M. Ghiringhelli). In the PhD thesis of Benedikt Hoock (co-supervised with Matthias Scheffler), this approach has been applied in order to predict lattice parameters and energetics of ternary alloys. In this context, various cross-validation-based model-selection strategies have been introduced and compared, at the same time probing various ways for choosing the feature space [4]. Other activities are dedicated to exploring similarities of materials in terms of properties and structures.

Critical for operating in a huge data space are validation and verification of the data. The most severe restrictions that may hamper interoperability concern the computational parameters that are used in different calculations, thus

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[30] https://fairdi.eu

[31] https://fairdi.eu/fairmat

affecting their numerical precision. Data are typically created for different purposes which may require different levels of convergence in terms of basis-set size and alike. We have to ask as well whether different codes aiming at the solution of one and the same problem give the same results. For the latter, the community effort led by Stefaan Cottenier showed for the equations of state for 71 elemental solids, that over a time span of a few years, many different *ab initio* electronic-structure packages finally led to basically the same answer [5]. While such investigations have set the stage towards a culture of benchmarking in the field of computational solid-state science, clearly, other properties like energy barriers, band gaps, spectra, etc., and systems like surfaces, interfaces and inorganic/organic hybrid materials, etc. will be much less forgiving than total energies of simple bulk solids and will make discrepancies more obvious. Also, the comparison of codes could only be made with parameter sets that represent full convergence, while calculations performed on a regular basis are often far from this optimal case. So, the question is how to compare and operate on data that have been obtained with different settings, e.g. in terms of basis sets, meshes for Brillouin-zone integrations, and other parameters. That this is, in fact, possible, i.e., that fully converged results of complex materials can be estimated by learning from errors of calculations of simple materials has been recently demonstrated by employing four different codes, two of them being developed in Berlin (`exciting` in Draxl's group, FHI-aims in Scheffler's group). For details, we refer to the report by Christian Carbogno.

Finally, we note that Claudia Draxl has been an organizer of the Long Program *Science at Extreme Scales: Where Big Data Meets Large-Scale Computing* (Sep.12–Dec. 14, 2018) at the Institute for Pure & Applied Mathematics (IPAM) at the University of California, Los Angeles (UCLA) to bring together innovators and pioneers from applied mathematics, computer science, and various applications areas to catalyze the new, emerging field linking HPC with Big Data[32].

The Cluster-Expansion Package CELL

With: Santiago Rigamonti (HU Berlin), Maria Troppenz (HU Berlin), Martin Kuban (HU Berlin), Axel Hübner (HU Berlin), Christopher Sutton, Luca M. Ghiringhelli, and Matthias Scheffler

Predicting stability and properties of alloys is a challenging task due to the need to evaluate relative energies of many atomic configurations accessible at realistic temperatures. A direct *ab initio* approach is typically hampered by the significant amount of time required to evaluate these energies. By mapping the configuration-dependent properties of the material to an Ising-like Hamiltonian parametrized with *ab initio* data, the cluster expansion (CE) approach reduces this time by several orders of magnitude. Still, for complex alloys with large parent cells, traditional CE approaches are not feasible.

The python package CELL[33] has been devised to deal with such situations by allowing for an iterative solution of the CE and, as a result, can handle materials with complex primitive cells comprising 30 atoms and more. An impressive

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[32] http://www.ipam.ucla.edu/programs/long-programs

[33] https://sol.physik.hu-berlin.de/cell

example for this capability has been demonstrated by predicting ground-state configurations and electronic properties of thermoelectric clathrates [6]. CELL can be applied to a broad variety of cases, covering one-, two- and three-dimensional materials, as well as multi-component and multi-lattice systems. A joint ongoing project between Draxl and Scheffler is on the *ab initio* atomistic thermodynamics of adsorbed atomic hydrogen at the (10-10) ZnO surface (in preparation).

Other joint activities

Claudia Draxl and Matthias Scheffler co-supervise three PhD students: Benedikt Hoock, working on data analytics (see work on compressed sensing above); Daniel Speckhard, working on verification and validation aspects of computational materials data (going beyond what is described above); Konstantin Lion, within the LeibnizCampus GraFOx on surfaces and growth of group-III oxides (see report by Sergey V. Levchenko).

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Max Planck Partner Group Leader
Prof. Dr. Xinguo Ren

Max Planck Partner Group Leader (since 2015)
Professor at the University of Science and Technology of China (since 2013)
Postdoc at the FHI (2006–2012)
Dr. rer. nat., Universität Augsburg (2006)

Activities of the Max Planck Partner Group on "Advanced Electronic-Structure Methods"

Introduction

The Max Planck Partner Group on Advanced Electronic-Structure Methods was set up in December 2015 at the University of Science and Technology of China (USTC). Xinguo Ren was appointed as the Head of this Partner Group. The group is hosted by the FHI Theory Department, led by Matthias Scheffler. The basic task of the Partner Group is to develop cutting-edge electronic-structure methods and the corresponding computer code to deal with challenging problems in computational materials science. During the past few years, the Partner Group has collaborated closely with the Theory Department of the FHI on multiple common projects, facilitated amongst other things by several mutual visits.

Below, we describe the research efforts of the Partner Group, on both implementing existing electronic-structure methods in a new numerical framework, and developing new concepts and methodologies.

Implementation of Periodic G_0W_0 within an All-Electron, Numerical Atomic Orbital Basis-set Framework

With: Florian Merz (Lenovo HPC Innovation Center), Hong Jiang (Peking University), Hermann Lederer (MPCDF), Volker Blum (Duke University), and Matthias Scheffler

We have implemented the periodic G_0W_0 method for quasiparticle energy calculations within an all-electron, numerical atomic orbital (NAO) basis-set framework. A straightforward implementation of such correlated methods within a NAO framework results in a computationally expensive code. Here we employ a localized variant of the resolution of identity (RI) approximation, enabling a significant reduction of the required CPU time and memory consumption. We demonstrate that the error arising from the localized RI approximation is controllable and can be made negligibly small by enhancing the set of auxiliary basis functions (ABFs). A particularly effective algorithm, suitable for the NAO framework, has been developed to deal with the Coulomb singularity in the Brillouin zone sampling.

Our implementation is carried out within the FHI-aims software package. In Fig. 1, we present the computed G_0W_0 band gaps, on top of the PBE starting point, versus the experimental values for a selected set of semiconductors and insulators. The three sets of all-electron G_0W_0 results presented here are obtained by the FHI-aims code with a standard NAO *tier* 2 basis set, and by the FHI-gap code with the linearized augmented plane wave (LAPW) basis as well as with the LAPW complemented by high-energy localized orbitals (HLOs), respectively. For most of the materials, our implementation yields band gap values in close agreement (within 0.2 eV) with those obtained by the LAPW+HLOs framework. However, for systems with a strong ionic character, such as LiF and ZnO, previous investigations indicate that the standard LAPW basis set is not sufficient to converge the G_0W_0 gap. Adding HLOs significantly enlarges the band gap up to 0.7 eV for ZnO and 0.9 eV for LiF. Our standard NAO basis set, though surpassing the standard LAPW basis set in performance, suffers from a similar under-convergence issue. We are currently working to resolve this issue by complementing our standard *tier* 2 basis set with highly localized Slater-type orbitals (STOs). Preliminary results for ZnO shows that this strategy works rather well.

Implementation of Periodic RPA within a NAO Basis-Set Framework

With: Florian Merz (Lenovo HPC Innovation Center), Igor Ying Zhang (Fudan University), Hermann Lederer (MPCDF), Volker Blum (Duke University), and Matthias Scheffler

Our periodic RPA (Random-Phase Approximation) implementation follows a similar numerical algorithm as G_0W_0, and has been used to compute the binding energy curves of bulk materials and layered materials. Benchmark calculations for a set of 14 solid materials have been reported previously [1]. We would like to point out our periodic RPA implementation also includes a correction arising from renormalized single excitation contributions (rSE) [2], which can further increase the accuracy of binding-energy calculations. In Fig. 2 we present benchmark RPA and RPA+rSE calculations for bilayer boron nitride (BN), compared with results from other functionals.

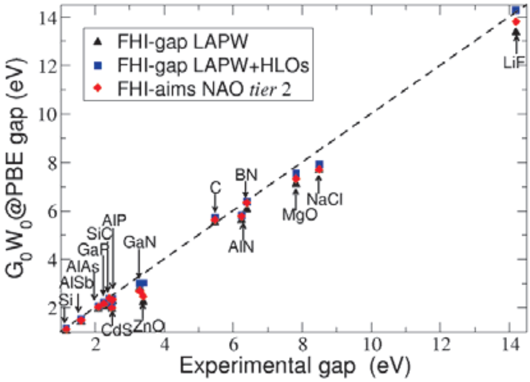

Figure 1: The calculated G_0W_0 @PBE band gaps versus the experimental gap for a sequence of semiconductors and insulators. Presented theoretical results are obtained by the FHI-aims code using the NAO *tier* 2 basis set (red diamonds, this work), and by the FHI-gap code with the LAPW (black triangles, and LAPW+HLOs (blue squares) basis sets

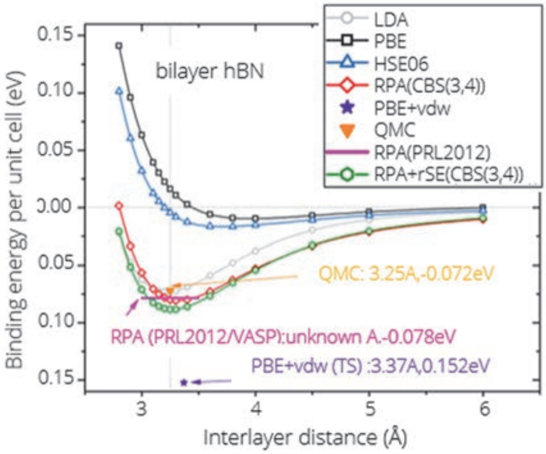

Figure 2: Binding energy curves of a double-layer BN obtained by Local Density Approximation (LDA), Perdew-Burke-Ernzerhof (PBE) Generalized Gradient Approximation, Heyd-Scuseria-Ernzerhof (HSE) hybrid funcitoinal , RPA, and RPA+rSE [2].

Particle-Particle RPA and Its Combination with Standard Particle-Hole RPA

With: Muhammad N. Tahir (USTC)

In nuclear physics, the usual RPA used in condensed matter physics and quantum chemistry is called particle-hole RPA (ph-RPA). In addition to the ph-RPA, a particle-particle channel of RPA (pp-RPA), corresponding to the ladder diagrams, has also been discussed. Weitao Yang's group from Duke University has played a pioneering role in bringing the pp-RPA to the attention of the electronic-structure community [3]. It seems that pp-RPA does not suffer from the charge delocalization error as the ph-RPA does. We implemented pp-RPA in FHI-aims, with the aim to develop a computational scheme that combines pp-RPA and ph-RPA. We analyzed the critical role of the exchange-type interactions, which are included in pp-RPA and usually not in ph-RPA. Unfortunately, although pp-RPA and ph-RPA are diagrammatically distinct, a straightforward combination of the two RPA channels does not work well. We carried out an analysis which helps us to understand why this is the case [4]. At the moment, we are trying to combine the two channels of RPA in a range-separation framework, which has been shown to work for a homogeneous electron gas.

Force Calculations within the RPA method

With: Muhammad N. Tahir (USTC), Tong Zhu (Duke University), and Volker Blum (Duke University)

The RPA force calculation is an important step in developing RPA into a viable method in computational materials science. In complex systems where different bonding mechanisms compete with each other, the geometry often cannot be reliably determined. Geometry relaxations with the RPA method should be very helpful in such situations. In the literature, RPA force implementations based on the Gaussian orbital basis sets and the projector augmented wave (PAW) method have been reported. In the present work, we have derived the RPA force formalism within the NAO framework and implemented it in the FHI-aims code.

Benchmark results for small molecules indicate that our derivation and implementation are correct. At the moment we are working to improve the implementation efficiency in order to treat more complex and interesting systems. Next, we will extend the implementation to periodic systems.

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Chemical Physics

Department of Chemical Physics
Prof. Dr. Hans-Joachim Freund

Director at FHI and Scientific Member of the Max Planck Society
(1996–2019)
Honorary Professor Ruhr-Universität Bochum (since 1997), Freie Universität Berlin (since 1997), Technische Universität Berlin (since 1998), Humboldt-Universität zu Berlin (since 1998), School of Physics and Astronomy, University of Birmingham (since 2006)
Habilitation Universität zu Köln (1983)
Dr. rer. nat., Universität zu Köln (1978)

Recent Developments in the Department

General remarks

The present report covers mainly the time between November 2017 and end of March 2019. On April 1st, 2019 the Department of Chemical physics has been terminated due to the retirement of the former Director Hans-Joachim Freund, who is now Emeritus Director and has been awarded an Emeritus Group by the President of the Max-Planck Gesellschaft for two years until March 31st 2021, with the perspective to get prolonged after review. The instrumentation developed during previous years within the Chemical Physics Department have been transferred to the newly founded Interface Science Department with the exception of the instrumentation connected with the ERC Advanced Grant (PI: Hans-Joachim Freund) as well as the setup containing the photon-scanning tunneling microscope. For those instruments, laboratory space has been assigned in building C (Molecular Physics Department), but, so far, the instruments have not been moved.

Since the last visit of the Fachbeirat the following changes occurred among the technical staff:

- Werner Hänsel-Ziegler reached his retirement age.
- Matthias Naschitzki and Burkhard Kell were allowed to shift their retirement by one extra year.

There were no changes among the scientific staff.
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 partner groups will be terminated at the end of 2019.

Honors and Awards

Hans-Joachim Freund

- Lecture at the Hefei Forum of Great Minds (2017)
- Japan Society for the Promotion of Science Microbeam Analysis 141 Committee Award (2017)
- CAS (Chinese Academy of Sciences) President's International Fellowship for Distinguished Scientists (2019)
- 2019 ACS Award in Surface Chemistry (2019)

Francesca Mirabella

- Otto Hahn Medal (2018)

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, as well as instrument development in the Department of Chemical Physics. There are collaborations with the Department of Theory of the Institute as well as with Chair of Physical Chemistry II, Friedrich-Alexander-University of Erlangen-Nuremberg. The Department has also participated in a number of projects funded from outside sources:

- Cluster of Excellence “Unifying Concepts in Catalysis” (UniCat) funded by the German Science Foundation until its termination,
- Collaborative Research Center (SFB1109) “Understanding of Metal Oxide/Water systems at the Molecular Scale: Structural Interfaces and Dissolution”, funded by the German Science Foundation until its termination, both in collaboration with the three Berlin Universities. Both have ended.
- “Selective Hydrogenation of triple bonded Hydrocarbons by Ceria” in collaboration with the group of Professor Weixin Huang, funded by the German Science Foundation and the National science Foundation of China until end of 2019 (?)
- “Structure and Reactivity of Nanoparticles on Silica” funded by the German-Israeli-Foundation (has ended)
- “The Crystal-Vitreous Transition in Two-dimensional Silica” funded by an Advanced Grant of the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Program (Grant Agreement No. 669179).

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 Fisicas (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, Cardarache

Collaboration within Germany:
H.-J. Freund, M. Heyde and N. Nilius, Universität Oldenburg, Oldenburg
H.-J. Freund, M. Heyde, S. Shaikhutdinov, S. Schauermann, H. Kuhlenbeck and J. Sauer, Humboldt-Universität zu Berlin, Berlin
H.-J. Freund, H. Kuhlenbeck und V. Staemmler, 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
H.-J. Freund, Th. Schmidt and M. Sierka, University Jena
H.-J. Freund, Th. Schmidt, D. Usvyat, HU Berlin, and M. Schlutow, FU Berlin

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 Sweden:
H. Junkes and T. Korhonen, ESS, Lund

Collaboration with Poland:
Th. Schmidt and M. Lewandowski, NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Poland

Collaboration with the UK:
H.-J. Freund, H. Kuhlenbeck, N. de Leeuw, University of Cardiff
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.-J. Freund, M. Heyde, K. M. Burson, Hamilton College, Clinton, NY
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 instrument development:

- The success of the FEL based development of the surface action spectroscopy (SAS) depends on the development of the sample holder cooling. Through the efforts in Helmut Kuhlenbeck´s group it has been possible to use molecular hydrogen and its isotopic variations to study the surface states of oxide surfaces.
- Coupling theory (involving collaborators from the FHI Theory Department and Paul Bagus at the University of North Texas) with experiment we succeeded to study surface core level shifts at CaO surfaces and demonstrate deficiencies of standard techniques employed in their calculations using density functional calculations.
- Hydrogen interacting with $CeO_2(111)$ has been studied for the fully oxidized and the reduced surface. Hydrogen has been shown to adsorb on the surface and also absorb underneath the surface (in collaboration with the group of Professor Fukutani/University of Tokyo using resonant-Nuclear Reaction Activation r-NRA). The absorbed hydrogen is shown to oxidize reduced ceria by forming a hydride.

- Electron Energy Loss Spectroscopy has been used to unambiguously demonstrate that the valence electron structure of stoichiometric ceria is restored by absorbing hydrogen into the bulk of ceria demonstrating the oxidation of the ceria lattice by absorbed hydrogen, probably via hydride formation.
- A well-ordered iron sulfide film with a well resolved STM monitored surface structure has been prepared and studied using I/V LEED. A collaboration with Professor deLeeuw/Cardiff University is under way to elucidate the structure.
- In collaboration between the working groups of Thomas Schmidt, Markus Heyde and Shamil Shaikhutdinov a new two-dimensional silica phase has been identified, which was called the zig-zag-phase due to its STM morphology. In collaboration with the theory group of Denis Usvyat at HU Berlin the structure has been resolved.
- Germania bi-layer films have been prepared and characterized via STM and I/VLEED. A transition between a crystalline and a vitreous structure has been observed and characterized in detail in comparison with an earlier analysis for silica.
- The crystal-vitreous transition in two-dimensional silica has been studied via LEEM and the apparent activation energy and transition temperature has been identified. In collaboration with the group of Professor Sierka /University Jena a model for the transition is being developed on the basis of theoretical calculations.
- Using the SMART microscope developed at BESSY in the working group of Thomas Schmidt a recipe has been developed to prepare mixed Germania-Silica films, as well as metal (iron) substituted silica and Germania films.
- Water formation in confined space, i.e. underneath a silica film prepared on an oxygen covered Ru(0001) surface has been studied further in collaboration with Dr. Usvyat/HU Berlin and Dr. Schlutow/FU Berlin to analyze the kinetic information.
- Water adsorption has been studied and compared on two magnetite surfaces, i.e. $Fe_3O_4(111)$ and $Fe_3O_4(100)$ using TDS, IRAS and LEED in collaboration with the group of Professor Parkinson/TU Vienna and the theory group of Dr. J. Paier/HU Berlin.
- Similar to EELS, XPS has been used to demonstrate that absorbed hydrogen may oxidize reduced ceria.
- Carbondioxide adsorption on magnetite and CaO has been studied using STM, XPS, TPD and IRAS.
- We had previously proven the formation of oxalate at the rim of a Au island deposited on an MgO(100) thin film. We have now upgraded the LT-STM(4K) to record Inelastic Electron Tunneling Spectra (IETS) and show first results on CO adsorbed on Au atoms on Ag(100).
- A microscopic analysis of the so-called carpet-growth of the SiO_2 bilayer on Ru(0001) across steps on the metallic surface is being undertaken and we try to correlate the results with the measurements the bending rigidity of 2D-silica reported in collaboration with Bodil Holst/Bergen Univ., Norway.
- A major successful effort had been undertaken to prepare and characterize a 2D Germania film on several metallic substrate in order to compare growth mode, crystal vs. vitreous properties, and Germania substrate interaction with the equivalent properties of 2D-silica.

- AFM studies of a reconstructed-quartz(0001) surface under liquid water has been undertaken and close to atomic resolution images have been obtained, which provide benchmark information of such surfaces in contact with a polar liquid.
- A novel STM is being developed to study the crystal-vitreous transition in 2D-Silica and 2D-Germania within the ERC Advanced Grant CRYVISIL.

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

Dr. Markus Heyde

Research Group Leader, Department of Interface Science (since April 2019)
Research Group Leader, Department of Chemical Physics (2007–2019)
Habilitation Humboldt-University in Berlin (2015)
Postdoctoral Scholar, Lawrence Berkeley National Laboratory (2001–2003)
Fritz-Haber-Institute (2003–2007)
Dr. rer. nat. Humboldt-University in Berlin (2001)

Scanning Probe Microscopy Group

Members: K. M. Burson, L. Gura, M. Heyde, B. Kell, D. Kuhness, A. L. Lewandowski, P. Marschalik, J. Pal, C. N. Ryczek, W.-D. Schneider, F. Stavale, G. Thielsch, H.-J. Yang, Z. Yang

The atomic scale characterization of thin oxide film systems in the context of model catalysis by using scanning probe microscopy techniques has been the focus of our group. In particular, the silica and germania network structures as well as their physical and chemical properties are ongoing highlights in our research efforts. Furthermore, we continued to establish inelastic tunneling spectroscopy measurements for the characterization of molecular species interacting with metal clusters on ultrathin oxide films supported on a metal single crystal.

Binding behavior of Carbonmonoxide to Gold Atoms on Ag(001)

The first step in a heterogeneous catalytic reaction is the adsorption of a molecule at a specific binding site on a surface. A pertinent example in this respect is CO oxidation at Au-clusters. Early investigations of size-selected Au clusters supported on MgO suggested that the adsorption and oxidation of the CO molecules take place on the cluster rim in contact with the underlying oxide surface. The decisive role of the oxide-nanoparticle interface for charge transfer activating a catalytic reaction has been reviewed recently.

In order to obtain microscopic insight into of the adsorption behavior of CO molecules on Au-clusters, we considerably simplified the situation and modelled the adsorption characteristics of a single CO molecule at a single Au atom supported on a Ag(001) single crystal surface. To this end scanning tunneling microscopy and spectroscopy, as well as inelastic electron tunneling spectroscopy have been demonstrated to be an excellent experimental technique to probe binding states of single molecules.

For CO on Ag(001) it is found to be very weakly bound. In contrast to the CO adsorption behavior observed so far for single adatoms and metal islands, where CO molecules are predominantly bound on top of the Au adatoms and to the rim of Au islands, we find two different configurations - one on top and the other one at the side of individual Au atoms on Ag(001). Moreover, inelastic electron tunneling spectroscopy reveals different low-energy vibrational energies observed between tunneling voltages of 10 and 30 meV for the two binding sites of CO to Au as compared to the one at 16 meV for the single CO molecule bound to Ag(001). The latter value corresponds closely to the one reported previously, identified as the frustrated rotational mode of CO. Supporting density functional theory calculation are currently performed by the group of Hannu Häkkinen from the University of Jyväskylä in Finland for verification of our findings.

The Carpet Growth-Mode of Silica Thin Films

With the two-dimensional silica bilayer films a new class of film system was discovered that revealed atomic sites of amorphous oxide network structures for the first time. Subsequently, the characterization of this specific film system has become a fascinating research topic.

In our previous work we were able to show that it is possible with a mechanical exfoliation process to transfer a large-scale silica bilayer from the original growth substrate to another one. The process has been patented. These bilayer films interact only through van der Waals forces with the metal substrate. In fact, the weak coupling to the substrate is responsible for the randomly-oriented unit blocks of silica tetrahedron that give rise to amorphous networks. Also experiments like the lift-off process emphasize a strongly interconnected film structure, but a week interaction with the metal substrate.

Still one open question is the growth-mode of the film across step edges. In a recent approach we have performed a detailed study of a ring sizes and atomic neighboring distances across step edges. Our analysis based on highly resolved scanning tunneling microscopy images emphasizes a smooth connection of the silica network over some step edges. We are now comparing the experimental results to density functional theory calculations performed by Gianfranco Pacchioni from the Università di Milano-Bicocca in Italy.

Determination of Silica and Germania Film Network Structures on Ru(0001)

Depending on the preparation conditions, the silica bilayer film can be tuned between its crystalline and amorphous state. So far, this is the only oxide network film system that has shown such unique structural properties.

However, silica is not the only prominent amorphous oxide network former. Comparisons with other glass formers, such as germania or boron oxide, can provide new insight into glassy structure. In a recent attempt, we have successfully grown germania monolayer films on a Ru(0001) metal substrate. Recently, we presented the first data on amorphous germania bilayers and compared common structural network features for monolayer as well as for bilayer silica and germania films. We compared monolayer films and structural motifs observed in their domain boundaries and then analyzed bilayer film coverages.

Both monolayers exhibit a similar atomic structure. They consist of tetrahedral unit blocks for silica and germania. They are strongly coupled to the substrate by forming purely crystalline films. A wider set of ring size combinations is observed for germania monolayer films in their domain boundaries. Density functional theory calculations predict a strong interaction between the germania bilayer and the substrate, while the silica bilayer is farther apart from the substrate and interacts only weakly with it through van der Waals interactions. This factor plays a key role in the observed structural differences.

We were also able to prepare amorphous germania bilayer films for the first time. These layers compensate for the strain by forming a buckled structure that could involve different Ge coordination numbers, direct bonds to the metallic substrate, different ring sizes in the direction perpendicular to the substrate, or others. In order to assign all ring sizes in the germania bilayer film, a complete atomic model would be needed, which is difficult to establish directly by scanning probe methods due to the corrugated film and the affected resolution. Therefore, further experiments aim to prepare flatter bilayer germania films by diminishing the film-support coupling by, e.g., changing the substrate. The fabrication of germania bilayers on Ru(0001) represents the first step in this direction.

From Crystalline to Amorphous Germania Bilayer Films on Pt(111)

Following previous attempts to prepare amorphous germania bilayer films, we have investigated the growth of ultrathin germania films on a Pt(111) single crystal surface. This metal substrate has been chosen, because it has a similar lattice constant compared to Ru but a lower oxygen affinity. The latter should lead to a weaker film-substrate interaction favoring the structural stability of a bilayer germania film.

Bilayer films of germania have been prepared and studied by scanning tunneling microscopy as well as density functional theory calculations. This two-dimensional germania film opens up opportunities to compare its material properties at the atomic scale as well as its crystalline-vitreous phase transition conditions to silica. Both materials are important reference materials for the potential synthesis of silica-germania mixtures.

By varying the preparation conditions crystalline and vitreous structures have been created, imaged and characterized in real space. One significant difference between the germania film discussed here and the earlier presented silica film is the lower glass transition temperature. This is known for the bulk materials and has also been verified now for the film systems.

This work opens up experimental avenues to study the dynamics of those transitions at the atomic scale. Importantly, for the germania bilayer structure on Pt(111) it has been found experimentally, that a unit cell consisting of a 558 ring-combination is the most stable one, thus confirming density functional theory predicting this as the preferable structure. In perspective, we are approaching a more general understanding of the structure of oxide network forming glasses.

Assessing the Film-Substrate Interaction in Germania Films on Au(111)

The structure and properties of metal-supported thin oxide films are strongly influenced by the nature of the metal substrate. A good example of this are previously discussed differences in the atomic arrangements adopted by silica and germania ultrathin films when prepared on different metal substrates.

Following the argument that the interaction between film and substrate diminishes with the oxygen affinity of the substrate, preparing films either of silica or germania films on Au(111) represents an interesting extreme case, due to its chemical inertness.

The preparation of germania films on Au(111) is based on our previously reported germania films. We were able to prepare partial coverages of germania bilayers supported on Au(111). It was possible to derive from the scanning tunneling microscopy images structural similarities to previously reported measurements from silica on Pt(111). The germania film grows atomically flat and consists of an amorphous network of different ring sizes. A ring-size distribution from 4- to 8-membered rings is observed. From the scanning tunneling microscopy images the herringbone reconstruction on the free metallic sites can be visualized and analyzed.

The herringbone reconstruction has been widely used to test the interaction at the organic-metal interface between molecules and the Au(111) surface, but has so far not been used to directly address the interaction with thin oxide films. However, it has been observed that oxide films, like MgO, TiO_2, ZnO_2, MoO_3 lift the herringbone reconstruction. This effect can be studied via scanning tunneling microscopy, in submonolayer films, where the soliton walls wind themselves up avoiding the unreconstructed gold below the oxide islands. On the contrary, NaCl films on Au(111) do not affect the herringbone reconstruction.

Interestingly, by comparison with the pristine herringbone Au(111), the gold reconstruction is disturbed by the presence of the germania film. Currently, the images are being analyzed and compared to density functional theory calculations performed by Gianfranco Pacchioni from the Università di Milano-Bicocca in Italy.

Morphology and Structure of the Reconstructed a-Quartz(0001) Surface

We started a real space structure study of α-quartz(0001) surfaces prepared at high temperature in air. High resolution atomic force microscopy images recorded in humid air, dry nitrogen, water and ethanol as well as supplemental low energy electron diffraction and X-ray photoelectron spectroscopy provide insight into surface morphology and reconstruction. In particular we take advantage of the enhanced resolution capabilities of atomic force microscopy in liquid water to address the real space atomic scale structure of this surface when in contact with a polar liquid. Our findings are further expected to assist theorists in the development of more appropriate surface models.

Towards Resolving Dynamic Processes in Silica Thin Films

CRYVISIL - ERC Grant (2016-2020)

The possibility to follow chemical reactions at surfaces by scanning tunneling microscopy has been proven quite a few years ago by Joost Wintterlin and in the PC Department at the institute under the directorship of Gerhard Ertl. In a new project we attempt 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.

To this end, we are developing a high-speed scanning tunneling microscopy 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. Spiral scanning modes ensure efficient high-speed movements of the piezo setup and our group has recently already established scan rates of several images per minute using this method. Scanning tunneling microscopy measurements and low energy electron diffraction measurement are currently taken as a function of temperature. The structural characterization of the silica and germania film systems will be supported by intensity-voltage low-energy electron diffraction experiments.

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Dr. Helmut Kuhlenbeck

Chemical Physics Department (1996–2019)
Department of Interface Science (since April 2019)
Academic councilor, Ruhr-Universität Bochum (1994–1996)
Research associate, Ruhr-Universität Bochum (1988–1994)
Research stay at the University of Sherbrooke (1993)
Dr. rer. nat., Universität Osnabrück (1988)

Spectroscopy Group

Members: G. Berti, E. Davis, F. Feiten, W. Hänsel-Ziegler, H. Kuhlenbeck, M. Naschitzki, A. Plucienik, X. Song, W. Wachsmann, Z. Wu

Surface action spectroscopy (called SAS in the following) is a vibrational spectroscopy method where desorption of weakly bound messenger atoms is triggered by a vibrational excitation at the substrate surface. Therefore, a plot of the messenger desorption rate versus the photon energy of the exciting infrared radiation is a vibrational spectrum. The infrared radiation comes from the free electron laser of the Fritz Haber Institute which emits intense infrared radiation over a wide range of photon energies.

Compared to other vibrational methods, SAS has the merits that reference spectra are not required (unlike to the case of infrared spectroscopy) and that spectra of rough surfaces can be measured (unlike to the cases of infrared spectroscopy, HREELS [high-resolution electron energy loss spectroscopy] and HAS [helium atom scattering]). Selective decoration of surface areas with messenger atoms by control of the adsorption temperature may restrict the spectral information to these areas.

Some effort has been dedicated to technical improvements such as measures to enhance the rare gas detection efficiency in the quadrupole mass spectrometer, and a better protection of the sample against infrared radiation from the chamber walls and the hot QMS ionizer. The background behind the latter was to get the sample cold enough for helium adsorption. He binds very weakly to all substrates, which makes it a sensitive messenger for low-energy vibrations. At present ~1.5 K can be reached on the sample holder, which would be sufficient for He adsorption on many substrates, but the lowest sample temperature reached yet was 4.8 K which is too warm for He adsorption. There is still room for improvements by elaborate constructive measures to improve the thermal contact between the sample and the sample holder. The given temperatures are for a transferable sample holder. One way to achieve a better thermal contact between the sample and the sample holder would be to give up on the transferability, but this would be the last resort if everything else fails.

SAS is a suitable tool for the measurement of microscopic surface vibrations because reference spectra are not required. If reference spectra are required then they should be recorded from a sample without these surface vibrations, but everything else unchanged – such samples are not easily available. Another reference-free method is HREELS, but in this case spectra of ionic surfaces suffer from intense Fuchs-Kliewer excitations and multiple losses hereof, which may hide the desired information. HAS is well suited to measure surface vibrations, but its energy range is limited to 60 meV and the method requires very flat surfaces.

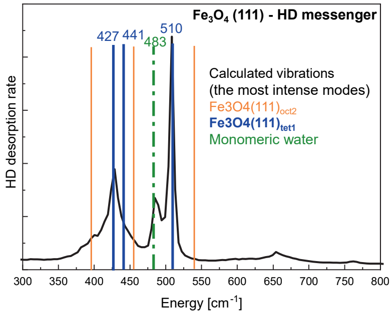

Figure 1: SAS spectrum of Fe_3O_4(111). The vertical lines mark the energies of the most intense modes as calculated by Joachim Paier and Xiaoke Li.

The surface vibrations of Fe_3O_4(111) films on Pt(111) were measured with the aim of testing the suitability of SAS for surface structure determination using the surface vibrational spectrum as a finger print. For this purpose, surface vibrational energies of the Fe_3O_4(111) oct2 and tet1 terminations (for the nomenclature see [1]) were computed by Joachim Paier and Xiaoke Li. These two terminations are the most commonly discussed ones and a recent IV-LEED study [2] came to the conclusion that the surface is tet1-terminated. This conclusion is supported by the SAS results (see Fig. 1). The measured peak positions are in agreement with the theoretical results for tet1 but not with those for oct2. One of the vibrations is assigned to monomeric water, which is a common contamination of Fe_3O_4(111). The peak at ~660 cm^{-1} is tentatively assigned to a CO_2 or H_2O vibration.

The surface specificity of the SAS spectra is also indicated by a collection of different iron oxide spectra (Fig. 2). Iron deposition massively damps the intensities of Fe_3O_4(111), while heating at 1000 K in oxygen leads to intense Moiré structures in the LEED pattern, similar to what is found for FeO(111) islands. The similarity of the SAS spectra of the heated film and the FeO(111) islands indicates that both surface structures are similar, which might be compatible with a dewetting of the Fe_3O_4(111) film such that the FeO(111) at the interface becomes visible. Oxidation of the FeO(111) islands to FeO_2(111) leads to new vibrational structures at around 500 cm^{-1}. As before, the band at ~660 cm^{-1} is tentatively assigned to CO_2 or H_2O contaminations. These data indicate again that SAS may be used profitably for surface structure determination using the microscopic surface vibrations as fingerprints.

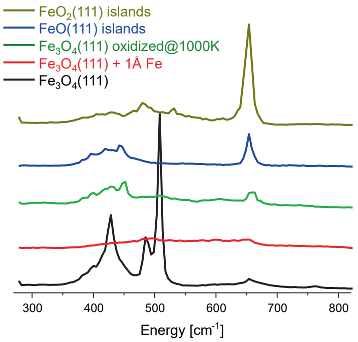

Figure 2: SAS spectra of different iron oxide systems.

Another topic of investigations was the dependence of the spectral intensities on the type of messenger gas. The energy to break the bond of the messengers to the surface is provided via vibrational coupling between the excited surface vibration and the vibration of the messenger-surface bond. An expected result of the studies was that only weakly bound messenger atoms are suited for SAS, since little energy is required for desorption. Another, somewhat less obvious result was that physisorbed molecular hydrogen is a more sensitive messenger than neon, despite the similar bonding strengths, which we tentatively attribute to the larger number of vibrational levels in the hydrogen/surface system. More vibrational levels means that more vibrational coupling channels are available for the energy transfer, which would make hydrogen molecules more sensitive messengers than Ne atoms.

Hydrogen in defective CeO_2(111)

As has been shown recently, hydrogen can be stored in defective CeO_2(111) [3]. This topic was investigated with HREELS and STM. The main result was that hydrogen can be incorporated as hydride into defective CeO_2(111), where it leads to an oxidation of the reduced cerium atoms from Ce^{3+} to Ce^{4+}. HREELS with loss energies of up to 10 eV was used to study the electronic excitations of the system (Fig. 3). Reduction of the oxide leads to significant changes in the electronic excitation spectrum, while exposure of the reduced film to 10 mbar of hydrogen at room temperature essentially re-establishes the spectrum of the stoichiometric film. Most of the intensity in the spectra stems from excitations of O2p electrons into empty cerium states [4]. The recovery of the spectrum means that not only the cerium oxidation state is re-established, but also the geometry of the cerium atoms, since the electronic structure and the geometric structure depend sensitively on each other. In agreement with this, it was observed that the LEED pattern improves when the film is re-oxidized by hydrogen.

The re-oxidation by hydrogen was also observed with XPS in the structure and reactivity group, and with different methods for ceria powder. Theoretical studies performed by Joachim Paier and Xiaoke Li support these results in that they indicate the presence of a bound hydride state below the surface of a defective oxide.

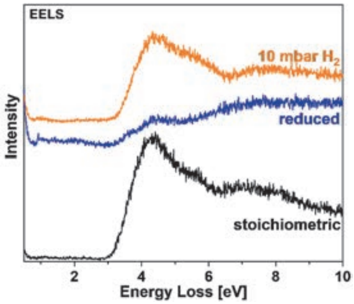

Figure 3: EELS spectra of differently prepared CeO_2(111) thin film surfaces. Reduction of CeO_2(111) to CeO_{2-x}(111) was achieved by annealing in UHV. The reduced CeO_{2-x}(111) was then exposed to 10 mbar H_2 at 300 K for 15 min. The spectra were recorded in sequence from the bottom to the top.

Well-ordered iron sulfur layers

The study of iron sulfide layer on Au(111) has been continued. XRD data taken in co-operation with the Stierle group in Hamburg reveal that the film has a NiAs-like structure (c-axis along the surface normal) with Fe vacancies, similar to iron sulfides such as pyrrhotite and smythite, although no indication of any ordering of these vacancies was observed. XPS data provide evidence for a large number of Fe vacancies also at the surface and they show that the film is sulfur-terminated. LEED and STM show that the film exhibits a 2×2 surface reconstruction, which was investigated with IV-LEED. However, a conclusive result could net yet be obtained.

These layers were studied with respect to the activation of CO_2. The as-prepared layers turned out to be rather unreactive in that only molecular CO_2 adsorption, but no reaction was observed. Following this, efforts were made to increase the iron concentration in the layers by deposition of iron. However, the annealing step which was required for film ordering led to the disappearance of the additional iron, probably by dissolution into the substrate. Further approaches involved the reduction of the surface with atomic hydrogen and attempts to block the diffusion of iron into the substrate by introduction of a FeO(111) layer between the substrate and the sulfide film. The latter approach worked to some extent, but in the course of the preparation it could not be avoided that gold became visible in the XPS data, probably due to diffusion of gold into the film. It could be shown that the presence of additional iron and gold together could activate the CO_2 at the surface such that it decomposed into carbon and oxygen. Gold without the additional iron (this could be prepared by annealing) and additional iron without gold (this could be prepared by reduction with atomic hydrogen) appeared to be unable to activate the surface. There is still a number of open questions around this system and its reactivity. At present this sulfide system is put to rest, but it is not excluded that it is revived at some later time. Then it might be advisable to use a different substrate to prevent the contamination of the layer with substrate material (gold in this case).

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Dr. Thomas Schmidt

Research Group Leader, Dept. of Interface Science (since April 2019)
Research Group Leader, Dept. of Chemical Physics (2009–2019)
Senior Scientist, University of Würzburg (1999–2008)
Postdoctoral Fellow, ELETTRA, Trieste (1996–1999)
Postdoctoral Fellow, University of Würzburg (1996)
Postdoctoral Fellow, Technical University of Clausthal (1994–1996)
Dr. rer. nat., University of Hannover (1994)

Spectro-Microscopy Group (SMART)

Members: A. Fuhrich, D. Gottlob, H. W. Klemm, D. Menzel, G. Peschel, S. Pohl, M. J. Prieto, Th. Schmidt, M. Springer, L. Tănase, E. Umbach

The activities of the group have been focused on the growth of thin oxide films and the observation of surface reactions utilizing these films. The chemical and structural properties of silica, iron silicate, iron germanate and germanium oxide films and the intercalation of reactive gases under the silica film have been studied in situ and in real time. Here, the temperature and pressure dependence of the observed front velocity allows for insights in the reaction kinetics. The investigations were carried out with the SMART microscope (Spectro-Microscope with Aberration correction for many Relevant Techniques) operating at a high flux undulator beamline at the synchrotron light source BESSY-II of the Helmholtz-Center Berlin (HZB).

Silica on Ru(0001)

Combining low energy electron microscopy (LEEM) with local low energy electron diffraction (µLEED) and x-ray photoemission electron microscopy (XPEEM) with local x-ray photoemission electron spectroscopy (µXPS) enables a comprehensive study of the growth processes of the silica film, involving oxidation, structure formation and structural phase transition. We have investigated the formation of various silica layers, defined and characterized their properties and their connected morphology, and followed their evolution. Two distinct chemisorbed monolayers and three bilayers (physisorbed crystalline and vitreous, and chemisorbed zigzag phases), and some transitions between them, have been studied. We found that, apart from the deposited silicon amount, the most important parameter for steering the evolution to a particular well-defined layer is the oxygen content at the Ru interface. Nucleation and growth of all layers have turned out to be homogeneous on the scale of our resolution and lead to rather small domains (20-40 nm), mostly of the same phase, which appear to be separated by defect lines. All our bilayer silica preparations start with the deposition of the corresponding amount of Si at room temperature on a Ru(0001)-3O support and subsequent annealing in 10^{-6} mbar of oxygen. At annealing temperature of about 625 K the film is completely oxidized but without structure. The crystalline structure is formed in a temperature range between 950 K (within an hour) and 1100 K (within seconds). Further annealing transforms this crystalline film into a vitreous film. Two special structures were intensively studied in the last two years and are discussed in the following.

Zigzag structure

Slow annealing (heating rate about 1 K/s) at 1080 K in UHV or fast annealing (heating rate about 10 K/s) in 5×10^{-6} mbar of O_2 yields the so-called zigzag structure, which has the density of the regular hexagonal bilayer. A structural model was developed within internal collaborations (with STM group of Markus Heyde and IRAS methods in the group of Shamil Shaikhutdinov) and with the theory group of D. Usvyat and M. Schütz (HU zu Berlin). In contrast to the physisorbed hexagonal silica bilayer, the zigzag structure is chemisorbed on the substrate via oxygen bonds and reveals a rectangular unit cell with a glide mirror plane observed in LEED. This symmetry causes the zigzag like appearance in the STM images. The zigzag structure occurs only under special (oxygen poor) preparation conditions during the annealing process. Once formed, it is stable under cooling down to RT or even to lower temperature. However, further annealing in oxygen at about 1050 K converts the zigzag into the hexagonal bilayer structure and subsequently into the vitreous structure. Once the vitreous or crystalline bilayer is formed, a reverse transformation towards zigzag by cooling or (chemical) removal of interfacial oxygen has not been observed.

Crystalline to vitreous phase transition

The investigation of the crystalline to vitreous phase transition was continued in the last two years, focusing on the influence of the interfacial oxygen on the Ru(0001) support. The transition has been observed in LEED in the temperature range between 1000 K and 1200 K both, in UHV and in 10^{-6} mbar of O_2. Whereas heating in UHV reduces the Ru(0001) support to a (2x2)-1O interface by thermal desorption (before the transformation starts), the heating in O_2 keeps the (2x2)-3O at the interface. The three times higher O concentration and, related to this, the larger interfacial dipole have an effect on the transition rate. The resulting apparent activation energy of 4.2 eV is the same in both cases, but the value of the pre-exponential factor in oxygen is 2.5 times larger than in UHV. The collaboration with the group of Marek Sierka (Univ Jena) leads to a further understanding of the observed process. DFT calculations for a free standing bilayer suggest a new path for the transformation by a modified Stone-Wales mechanism: instead of the simultaneous rotations of overall four coupled SiO_2 tetrahedra in both layers, the transformation first occurs in one plane of the bilayer, yielding an intermediate state, and then continues in the second plane. Introducing now the Ru support into the calculation might explain the observed influence of the oxygen at the interface by an entropic effect: a stronger interaction between support and the physisorbed bilayer might cause that always one of the two planes is transformed first, whereas with weak interaction (quasi free-standing) the transformation can start in both planes. This directly affects the entropic term and therefore the pre-exponential factor, without substantial change of the activation energy.

Germania films

The germania films are prepared by deposition of 0.6 nm of Ge at room temperature in UHV on a Ru(0001)-3O surface and subsequent oxidation at 600 K and 1×10^{-6} mbar O_2 pressure, observed in real-time and in-situ by LEEM, LEED and XPS. As a result, a completely closed GeO_2 monolayer was formed with a partially closed GeO_x layer on top. This excess GeO_x layer desorbs at temperature above 770 K.

Mixed germania-silica films

In order to tune the chemical (e.g. reducibility) and physical (stiffness) of silica films, mixed films of silica and germania were produced on a Ru(0001) support. Special interest was focused on the preparation conditions to form a homogeneously distributed and oxidized mixed film without segregation or domain formation or loss of material. Mixed layers with ratio of Si:Ge in the range between 75%:25% and 95%:5% were studied. Various recipes were not successful: (a) starting with a complete GeO_2 monolayer, followed by deposition of Si at RT and subsequent annealing in oxygen, formed separated domains of silica and germania and led to a partial loss of germania (at temperatures above 970 K), because the oxidation temperature of Si was too high to avoid Ge desorption. (b) starting with a complete SiO_2 monolayer, followed by Ge deposition at RT and annealing in oxygen also caused segregation with formation of separated domains. However, recipe (c) was successful: deposition of the corresponding amount of Si and Ge both at RT on a Ru(0001)-3O and subsequent annealing in oxygen, yielded an intermixed complete silica-germania film without domain formation (within the spatial resolution limit of 10 nm in these experiments). Interestingly, the addition of Ge reduces the oxidation and structure formation temperature from 950 K for pure silica down to 820 K for the mixed films.

Chemical reactions in confined space under a silica bilayer

The physical gap between the physisorbed silica bilayer film and the Ru(0001)-(2x2)-3O support was used to intercalate gases and to drive reactions in this confined space. Using LEEM, LEED and local XPS, water formation from adsorbed O and H_2 on a Ru(0001) surface covered with (crystalline or vitreous) SiO_2 bilayers were investigated and compared to the same reaction on bare Ru(0001). In both cases the reaction is characterized by moving reaction fronts. The reason for this might be related to the requirement of site release by O adatoms for further H_2-dissociative adsorption. Apparent activation energies (E_a^{app}) are found for the front motion of 0.59 eV without cover and 0.27 eV under cover. For both, the crystalline and the vitreous film, the activation energy is the same, but in the Arrhenius plot the pre-exponential factor for the vitreous layer is twice the value for the crystalline. We suggest that the smaller activation energy but higher reaction temperature for the reaction on the SiO_2 BL covered Ru(0001) surface is due to a change of the rate-determining step. One important point is the involved diffusion. Whereas the H_2 molecules can permeate the 6-member rings of the silica without a problem, the formed H_2O molecules can hardly leave the confined space through the 6-member rings but easily through 7-member or larger ring sizes. These larger ring sizes can be found in the crystalline film only at the domain boundaries, whereas everywhere in the vitreous layer. The variation of the H_2 pressure in the experimental chamber exhibited a square-root like dependence of the front velocity. A further temperature and pressure dependent observable parameter is the width of the reaction front.

Basing on these experimental results we developed a kinetic model described by rate equations, involving the processes of adsorption, diffusion, reaction, and desorption. Within the collaboration with the theory group of Denis Usvyat (HU Berlin) and with Mark Schlutow (FU Berlin) we found that the transition states are not affected by the silica cover. Instead, the observed difference can be explained by a diffusion effect: the silica cover might reduce the H_2O desorption and therefore increases the local concentration of adsorbed H_2O molecules nearby the reaction front. This increased H_2O concentration, in turn, can hinder the H diffusion between the O poor area, where it is dissociatively adsorbed, and the O rich area, where the H_2O is formed. The rate limiting step would be now this diffusion.

Chemical reactions in confined space under a mixed silica-germania bilayer

Based on molecular dynamics Marx et al. (PRL 119 (2017) 056002) found, that the water self-dissociation increases when water molecules are confined between two sheets of FeS mackinawiete. Interestingly, the same behavior is observed when the chemistry of the confining walls is taken out by simply substituting FeS by Lennard-Jones walls. This was the motivation to change the chemical composition of our silica cover to understand whether solely the physical confinement plays a decisive role or also the chemical property of the confining wall. We used the above mentioned mixed silica-germania bilayer films on Ru(0001)-3O to run the water formation reaction. At lower Ge amount (10 % Ge, 90 % Si) we observed large reactions fronts like in the silica case and determined the temperature dependence of the velocity. Interestingly, the apparent activation energy is the same as in the pure silica case, but with a three times smaller pre-exponential factor for the mixed films. As proven with local XPS, the oxygen at the Ru interface is reduced during the main reaction, as in the silica case. However, in a second step, also germania is partially reduced by hydrogen. That means, the integrity of the mixed film is not preserved during the reaction, but the film can be fully recovered by a subsequent oxidation.

Iron silicate and iron germanite films

Ultrathin iron silicate or iron germanate films grown on a Ru(0001) support are suitable model systems for catalytically active structures, such as zeolites. The growth and the chemical and physical properties of these films were comprehensively investigated by LEEM, µLEED, µXPS and XPEEM. Ultrathin iron silicate films consist of a monolayer of silica on top of a monolayer of iron oxide, supported by Ru. In particular, the measurements suggest that the number of iron atoms per silica unit cell is two (i.e. Fe:Si ratio is 1:1) and that an additional oxygen layer at the iron/ruthenium interface is present. The Fe-Fe distance is found to be adapted to the Si-O-Si distance in unstrained silicates, rather than being influenced by the ruthenium substrate. Moreover, the iron silicate structure was varied and prepared with two layers of iron oxide or two layers of silica, respectively. Both additional layers are found to be stable if grown as complete layers, and adapted to the monolayer iron silicate film structure.

Ultrathin iron germanate films exhibit almost the same structure as iron silicate films, i.e. a monolayer of germania is bound on top of a monolayer of iron oxide. However, as seen in LEED, the Fe-Fe distance is adapted to the length of Ge-O-Ge bonds in unstrained germanates. Different preparation methods show that these films are energetically stable in the investigated temperature (between 300 K and 840 K) and pressure (up to 10^{-6} mbar) range.

Dr. Shamil Shaikhutdinov

Group Leader, Department of Chemical Physics, Fritz Haber Institute, (2004–2019)
Postdoctoral Fellow, Fritz Haber Institute (1998–2004), University Hannover (1996), University Ulm (1994)
Research Associate, Boreskov Institute of Catalysis (Novosibirsk) 1987–1998
PhD., Moscow Institute of Physics and Technology (1986)

Structure and Reactivity Group

Members: U. Härtel, J. Hartmann, F. Ivars Barcelo, L. Li, F. Mirabella, S. Shaikhutdinov, X. Weng, K. Werner, E. Zaki, J.-Q. Zhong

The group carried out studies aimed at a deeper understanding of adsorption processes at oxide surfaces, in particular, with respect to the interaction of water and carbon dioxide both with non-reducible (CaO) and reducible (magnetite Fe_3O_4) oxides. For the iron oxide, more emphasis was put on the structural sensitivity of water adsorption by making use of the (111) and (001) oriented well-ordered thin films. Adsorption of CO_2 on both Fe_3O_4 and CaO surfaces was found to critically depend on the presence of water ad-species at the surface. In case of CaO(001), water ad-species considerably strengthen CO_2 bonding as monodentate carbonate. On Fe_3O_4, adsorbed CO_2 may even form bicarbonate species. Another project relates to recently reported superior activity of the ceria catalysts in the selective alkyne hydrogenation reactions. In order to rationalize unusual reactivity of ceria, we performed hydrogen and alkyne adsorption studies on CeO_2(111) thin films highlighting the key role of oxygen vacancies in these reactions.

Water adsorption on Fe_3O_4 surfaces

Well-ordered magnetite Fe_3O_4(111) and (001) thin films were grown on Pt(111) and (001) substrates, respectively. The films were characterized by LEED, AES, as well as by TPD and IRAS of CO as a probe molecule to prove the surface termination which is quite sensitive to the sample preparation. The Fe_3O_4(111) surface is terminated by a $^1/_4$ monolayer of tetrahedrally coordinated Fe^{3+} ions on top of a close-packed oxygen layer. The Fe_3O_4(001) surface terminated with an intact layer of oxygen and Fe_{oct} atoms. However, a rearrangement of the subsurface cations distorts the structure leading to a $(\sqrt{2}\times\sqrt{2})R45°$ super-structure. We monitored adsorption of water at different temperatures as a function of coverage using infrared reflection-absorption spectroscopy, temperature programmed desorption, and single crystal adsorption calorimetry.

The results showed that water molecules readily dissociate on Fe_3O_4(111) surface Fe_{tet1}-O ion pairs to form “monomers”, i.e., terminal Fe-OH and surface OH groups. Further water molecules adsorb on the hydroxyl covered surface non-dissociatively and form “dimers” and larger oligomers, which ultimately assemble into an ordered (2´2) hydrogen-bonded network structure with increasing coverage prior to the formation of a solid water film.

Adsorption on the (√2×√2)R45°-reconstructed surface of Fe_3O_4(001) is strongly influenced by the surface reconstruction, which remains intact at all coverages. Close to the completion of the first monolayer, however, the ad-layer adopts a longer-range (2×2) superstructure. The formation of ordered water ad-layer on these two surfaces was directly monitored by temperature programmed LEED (see Figure 1). The results showed that ordered structure on the (111) facet exists over a significantly larger range of temperatures and coverages than on the (001) surface.

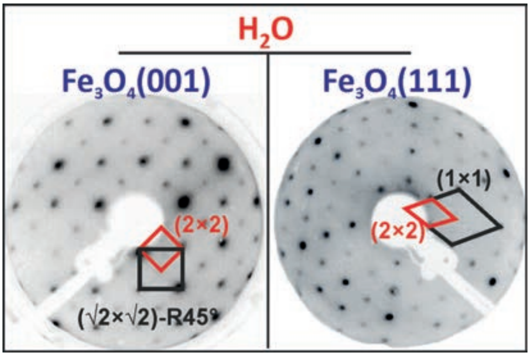

Figure 1: LEED patterns of the Fe_3O_4(001) and (111) surfaces showing the formation of ordered water ad-layer structures upon adsorption of 2 L water at 140 K and heating to 170 and 220 K, respectively.

In both cases, the long-range order is evidence that water-water interactions exert a significant influence on the structure already prior to the nucleation of the second layer. We conclude that the stability differences stem from the smaller unit cell on the (111) surface, and the ability of water to more easily form stable hexagonal ice like-structures on the hexagonal substrate.

CO_2 adsorption on oxides (CaO and Fe_3O_4)

We monitored the adsorption of CO_2 on well-ordered Fe_3O_4(111) films using IRAS and TPD. The results showed that CO_2 weakly interacts with the regular Fe_3O_4(111) surface, as it almost fully desorbs at temperatures above ~140 K. However, TPD and IRAS features corresponding to a more strongly bound, chemisorbed species were also observed. Their formation required relatively long CO_2 exposure times, which we associated with adventitious co-adsorption of residual water from the vacuum background. Since the Fe_3O_4(111) surface is known to be very sensitive towards water, we additionally investigated the correlation between water and CO_2 adsorption process and found that the degree of surface hydroxylation plays a crucial role on CO_2 binding to the Fe_3O_4(111) surface, ultimately leading to the formation of bicarbonate species.

Adsorption of CO_2 on well-ordered thin CaO(001) films, prepared on Mo(001) and Pt(001) single crystal surfaces, resulted in monodentate carbonates (CO_3^{2-}) at low coverages. TPD spectra showed pseudo-first order desorption kinetics with a maximum shifting from 500 to 470 K with increasing CO_2 coverage. However, at further increasing exposures, desorption maximum is shifted to the considerably higher temperatures (570 K), although CO_2 uptake remained almost the same. This unusual effect was found to correlate with dissociative adsorption of residual water in the UHV background as observed both by TPD and IRAS. Comparative analysis of spectral evolution on crystalline CaO(001) films and CaO nanoparticles favors the model, where surface hydroxyls only affect adsorption geometry of the carbonates rather than form bicarbonate species. However, hydroxyls show stabilizing effect on CO_2 binding to the CaO surface.

Interaction of hydrogen with CeO_2(111)

Cerium oxide (CeO_2) 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_2 using well-defined CeO_2(111) surfaces as thin films. The experiments performed by XPS, IRAS, and nuclear reaction analysis (NRA) suggested that H_2 dissociates on CeO_2(111) at elevated pressures and temperatures, and H atoms may migrate into the bulk of reduced CeO_{2-x}(111) films and not on fully oxidized CeO_2(111) films. Further studies clearly showed that hydrogen may form hydroxyls at the surface and hydride (Ce-H) species below the surface. However, hydride formation is only observed when oxygen vacancies are present in the oxide. Their formation is accompanied by the transfer of an electron from a Ce^{3+} species to hydrogen, which results in the formation of Ce^{4+}, and thus in oxidation of ceria.

Impressum

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