

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

## **15th Meeting of the Fachbeirat**

**Berlin, 22nd - 24th November 2009**



## **Reports**







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

**15th Meeting of the Fachbeirat  
Berlin, 22nd – 24th November 2009**

**Reports**



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Head: K. Reuter

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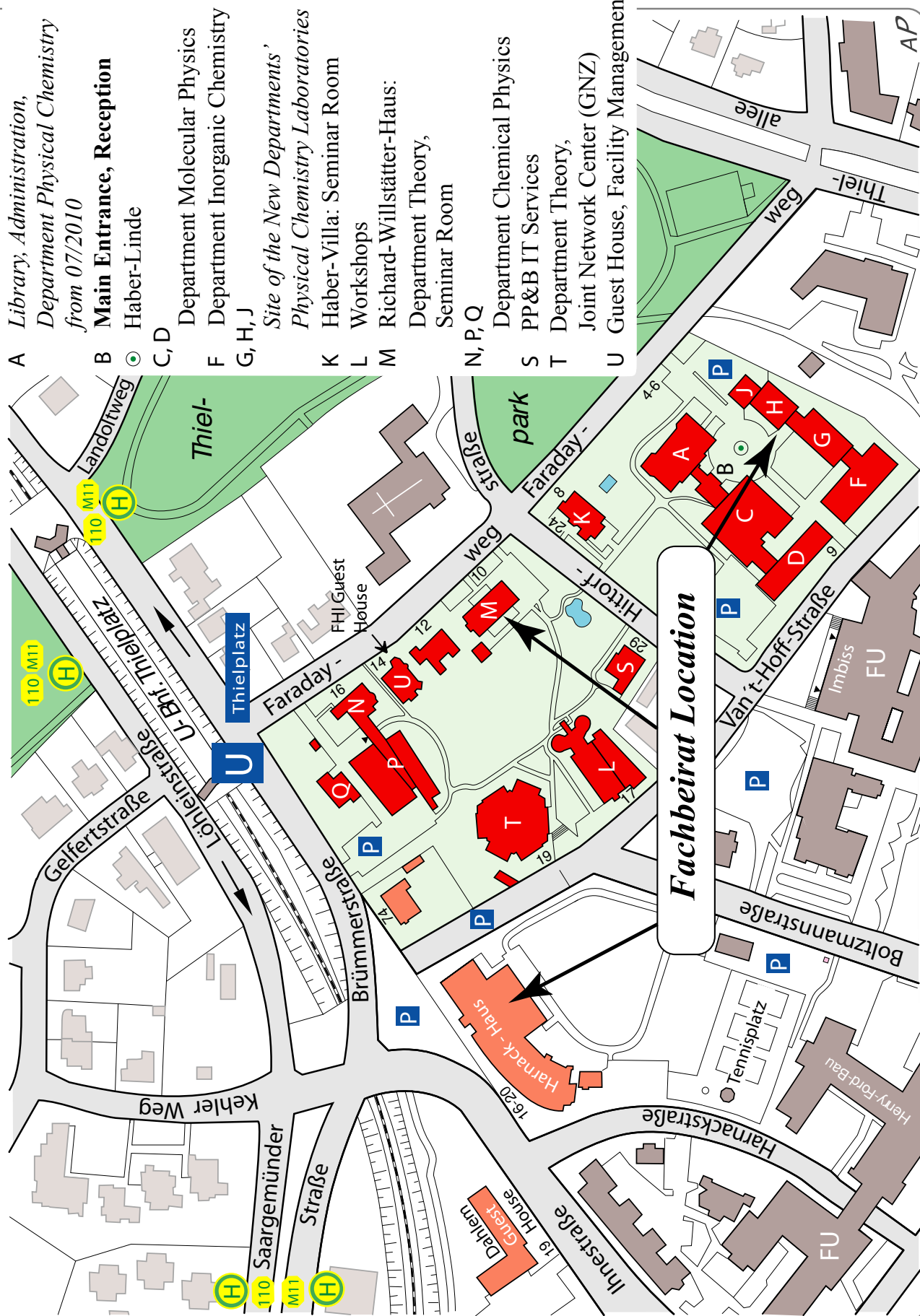
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# Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

- A Library, Administration, Department Physical Chemistry from 07/2010
- B Main Entrance, Reception
  - Haber-Linde
- C, D Department Molecular Physics
- F Department Inorganic Chemistry
- G, H, J
- Site of the New Departments' Physical Chemistry Laboratories*
- K Haber-Villa: Seminar Room
- L Workshops
- M Richard-Willstätter-Haus: Department Theory, Seminar Room
- N, P, Q Department Chemical Physics
- S PP&B IT Services
- T Department Theory, Joint Network Center (GNZ)
- U Guest House, Facility Management







## Research Departments of the Fritz Haber Institute

Inorganic Chemistry	Chemical Physics	Molecular Physics	Physical Chemistry	Theory
Robert Schlögl	Hajo Freund	Gerard Meijer	Martin Wolf	Matthias Scheffler
Staff Scientists				
Malte Behrens	Markus Heyde	Knut Asmis	Markus Eiswirth	Volker Blum
Frank Girgsdies	Helmut Kuhlbeck	Uwe Becker	Christian Frischkorn	Klaus Hermann
Axel Knop-Gericke	Niklas Nilius	Horst Conrad	Leonhard Grill	Sergey Levchenko
Dirk Rosenthal	Thomas Risse	André Fielicke	Alexander Mikhailov	Xinguo Ren
Olaf Timpe	Svetlana Schauer mann	Bretislav Friedrich	Bruno Pettinger	Patrick Rinke
Detre Teschner	Shamil Shaikhutdinov	Gert von Helden	Julia Stähler	Alexandre Tkatchenko
Annette Trunschke	Martin Sterrer	Karsten Horn		Mina Yoon
Sabine Wrabetz	Thomas Schmidt	Jochen Küpper		Angel Rubio
Raimund Horn (Indep. Res. Group)		Adela Marian		Karsten Reuter (Indep. Res. Group)
		Bas v. d. Meerakker		
		Melanie Schnell		

<b>Administration</b>	Karsten Horn
Human Resources Accounting Purchasing Travel	
Facility Management	

### Service Groups

Electron Microscopy	IT Services (PP&B)	Free Electron Laser	Electronics Workshop	Joint Network Center (GNZ)
Library	Crystal Lab	Mech. Workshop		







## Report of the Executive Director

Within the reporting period from late 2007 to late 2009 the Institute continued to generate a large number of important and well-received scientific findings in its research area, as illustrated by the following reports of the individual departments which describe the research agenda and the individual achievements in detail.

The institute has continued to further strengthen its collaborative efforts, and to achieve an even greater coherence of the research activities pursued by the different departments. The institute covers, in its experimental and theoretical studies, a wide range of phenomena of Physical Chemistry ranging from heterogeneous catalysis via surface science of nanostructures and clusters to the study of spatio-temporal dynamics of chemical reactions and their elementary processes, and to the manipulation and control of gas phase molecules. In all these fields, the institute has developed focal points of common research interests, engaging the wide spectrum of competences available in the different departments.

The resulting unified view on research topics in the Kollegium helped the institute to become involved in multiple and leading roles within collaborative activities in the research landscape of the Berlin region. A highlight of these activities was the start of activities within the cluster of excellence (COE) *“Unifying Concepts in Catalysis”* that was funded by the special “Exzellenzinitiative” of the Federal Government, and started successfully within the reporting period. All departments of the FHI actively participate in this cluster. The CP department focuses the participation and represents the Institute in the governing board of the COE. In parallel to this substantial effort, the institute continues to participate actively in 4 other collaborative research centers of the Deutsche Forschungsgemeinschaft (SFB: Sonderforschungsbereich: *SFB 450, 546, 555, 658*) in which strong and focused collaborative activities connect the institute with all three Berlin universities and other research institutes.

The most spectacular and exciting single event in the reporting period was the award of the Nobel Prize for chemistry to G. Ertl in 2007. The fact was already known at the meeting of the last Fachbeirat but the award was presented to G. Ertl

on December 10, 2007. The laureate was kind enough to invite the Kollegium and the president of the MPG as personal guests to the ceremony and to multiple surrounding events. This week at Stockholm will be unforgettable for all of us. The invitation was also extended to the - at the time - candidate for the vacant director position Prof. M. Wolf who also can be seen on the photographs taken around the event.



The Kollegium created the *Gerhard Ertl Lecture* as a named lecture series on scientific aspects related to Gerhard Ertl's work. The lecture, kindly sponsored by *BASF ES Ludwigshafen*, will be held annually around the day of the Nobel prize ceremony. It is awarded in collaboration with partnering universities of the **UniCat** cluster (**TUB, HUB, FUB**) and held at locations of the partnering universities. A selection committee with representatives from all partnering

organizations awarded the first lecture in 2008 to Prof. G. A. Somorjai and the lecture in 2009 to Prof. J. K. Nørskov.

The FHI also initiated, in collaboration with the German Physical Society (DPG), and sponsored by *Elsevier Publishers*, the ***Gerhard Ertl Young Investigator Award*** that will be presented for the first time at the DPG spring meeting in 2010.

The Noble Prize awarded to G. Ertl created a long wave of additional honors and awards for the laureate. The FHI is proud and very happy that G. Ertl continues to be actively engaged in the institute and to pursue his scientific activities.

#### Selected honors of G. Ertl for the reporting period 2007- 2009

2007	Honorary Fellow	Royal Society of Chemistry
2008	Honorary Member	Physikalischer Verein, Frankfurt a.M.
2008	Honorary Member	European Academy of Sciences and Art
2008	Honorary Member	Berliner Wissenschaftliche Gesellschaft
2008	Honorary Member	GDCh (German Chemical Society
2008	Honorary Member	Dechema (German Society of Chemical Technology)
2008	Honorary Member	Deutscher Hochschulverband
2007	Otto-Hahn-Preis	Gesellschaft Deutscher Chemiker, Deutsche Physikalische Gesellschaft and the City of Frankfurt/M.
2008	Verdienstmedaille	Land Baden-Württemberg
2008	Dr. honoris causa	Queen's University Belfast
2008	Dr. honoris causa	Technische Universität München
2008	Großes Bundesverdienstkreuz mit Stern	President of the Federal Republic of Germany
2008	Nicolaus Copernicus Medal	Polish Academy of Sciences
2008	Diesel Gold Medal	Deutsches Institut für Erfindungswesen
2009	Dr. honoris causa	Humboldt-Universität zu Berlin
2009	Dr. honoris causa	Comenius University, Bratislava
2008	Ertl Center for Electrochemistry and Catalysis (Gwangju Institute of Sciences and Technology, S. Korea)	
2008	Integrierte Gesamtschule Gerhard Ertl, Sprendlingen/Rheinhessen	
2008	Gerhard Ertl Building (Faculty of Chemistry & Pharmacy, Ludwig-Maximilians-Universität, München)	

A most important event was the successful conclusion of the appointment process of *M. Wolf* to the position of Director of the Department of Physical Chemistry. The Beirat was informed about the nomination at its last meeting. In the meantime, the appointment process progressed smoothly, and the appointment negotiations were concluded in mid-2008. Prof. *M. Wolf* will report on his views and activities in a separate presentation at the opening session of the Beirat meeting. For the initial scientific activities see the report of the PC department.

The new department of Physical Chemistry has begun to actively pursue its work, partly on the premises of the institute, thanks to a joint effort of all other departments who contributed to a provisional solution for experimental space for the department. The main burden carries the MP department, where the long awaited experimental hall in building D after complete refurbishment was provisionally handed over to the PC department for the installation of new experimental facilities.

The research of Prof. *M. Wolf* requires exceedingly high standards for the laboratory environment. After detailed feasibility studies and extensive pre-planning it was decided to change the master plan of the FHI building and infrastructure renovation, and to construct a completely new building for the PC department at the location of the now existing buildings G, H, J which will be demolished. The original building A of the PC department is currently being refurbished to house, as a central institute facility, a newly designed library/common room, the administration and some additional central facilities. The first floor will house office space for the PC department.

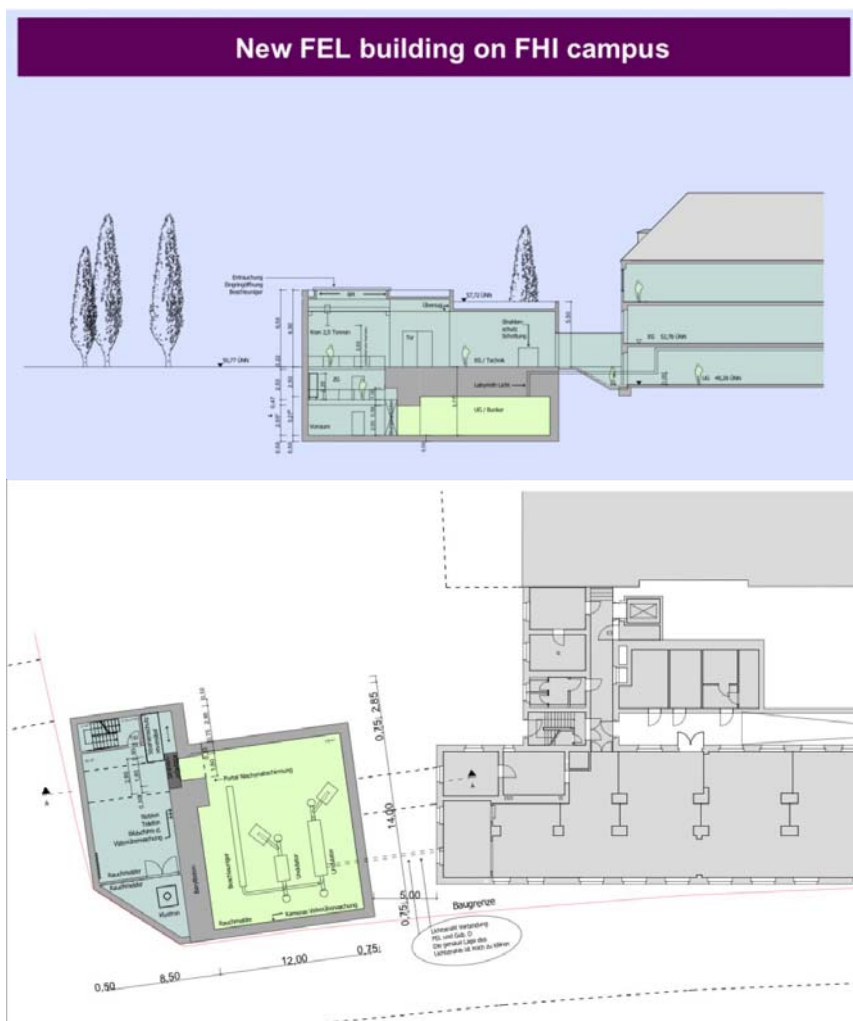
The preparations for installing a free-electron laser (FEL) infrared radiation facility have moved forward rapidly. Following the decision of the MPG to fund the construction of this facility at the FHI in August 2008, a team within the MP Department has been planning the FEL and the associated infrastructure on the campus. The envisioned IR-FEL, consisting of a 50 MeV electron linac and two undulator beamlines, is presented in detail on Poster MP21. For the design of the FEL, collaboration with Forschungszentrum Dresden-Rossendorf (IR-FEL facility FELBE) has been initiated. In a worldwide open tendering procedure, the US



company Advanced Energy Systems, Inc. (Medford, NY) has been chosen among three applicants to design, manufacture, and install the electron linac.

Since operating an electron beam at this energy produces a significant amount of  $\gamma$ -ray Bremsstrahlung, the FEL needs to be installed in a radiation-safe vault. To this end a new building, dedicated to house the FEL, has been planned. The FEL vault will be located in the basement such that efficient radiation shielding will be achieved by sand at three sides and a thick wall of special high-density concrete on the fourth side. In addition, a 2.5-m-thick concrete ceiling will limit radiation exposure in the building's ground floor to less than the maximum permitted dose levels. The institute submitted in June 2009 an application (including comprehensive radiation safety calculations) for an official permit to setup the FEL to the Berlin state authority. At the same time the architects submitted an application for getting the official permit for building construction ("Bauantrag"). Both permits are anticipated to be issued in November 2009, thereby allowing construction to start, according to schedule, in January 2010. We anticipate to occupy the building no later than December 2010; by then, design and fabrication of the FEL will be finished too. Thus, installation can start in early 2011 and commissioning could start in the summer of 2011.

The new building is depicted in the Figure below. It will be located on the present site of a parking lot next to building D. A walkway will bridge the 5 m separation between the buildings. While the FEL and all its auxiliary devices will be located in the basement, the ground floor will accommodate the infrastructure for air-conditioning, cooling water, etc. Experiments from all four experimental departments of FHI will be set up in Building D, where 425 m<sup>2</sup> of lab space are available in the basement and on the ground floor. The IR radiation will be steered by mirrors through a vacuum pipe from the FEL vault to Building D and further on to the user stations.



These major activities would not be possible without the constant and continuous scientific progress in all departments of the institute. These results are documented in the number of publications, appearing at a rate of about one paper per working day. A similar number of invited talks from staff scientists represent another focus of communication and dissemination activities. These activities are recognized by the community in a substantial number of citations (10225 in 2007, 12175 in 2008 and 9631 until 1.09.2009, 4221 average citations per year over 20 years) and in honors and appointments for members of the institute. A selected list of honours in the reporting period includes:

- *Hans-Joachim Freund* was elected as Member of the German Academy of Sciences Leopoldina, Halle, (April 2009). He also received the V. N. Ipatieff Lecture Award, Northwestern University, Center for Catalysis and Surface Science (March 2008), and was elected Chairman of the University Council, University Erlangen-Nürnberg (December 2007)

- *Thomas Risse* was awarded the Nernst-Haber-Bodenstein Award 2008 of the Deutsche Bunsengesellschaft für Physikalische Chemie
- *Jochen Küpper* was awarded the Nernst-Haber-Bodenstein Award 2009 of the Deutsche Bunsengesellschaft für Physikalische Chemie
- *Svetlana Schauermann* received the Fellowship of the Robert Bosch Foundation-Excellence and Leadership Program Fast Track (2008-2010)
- *Hendrick L. Bethlem* received an ERC Starting Grant and accepted a permanent position (“Universitair Docent”) at the Free University of Amsterdam, The Netherlands, in January 2008
- *Matthias Scheffler* was awarded the Ernst Mach Honorary Medal for Merit in the Physical Sciences by the Academy of Sciences of the Czech Republic in November 2008

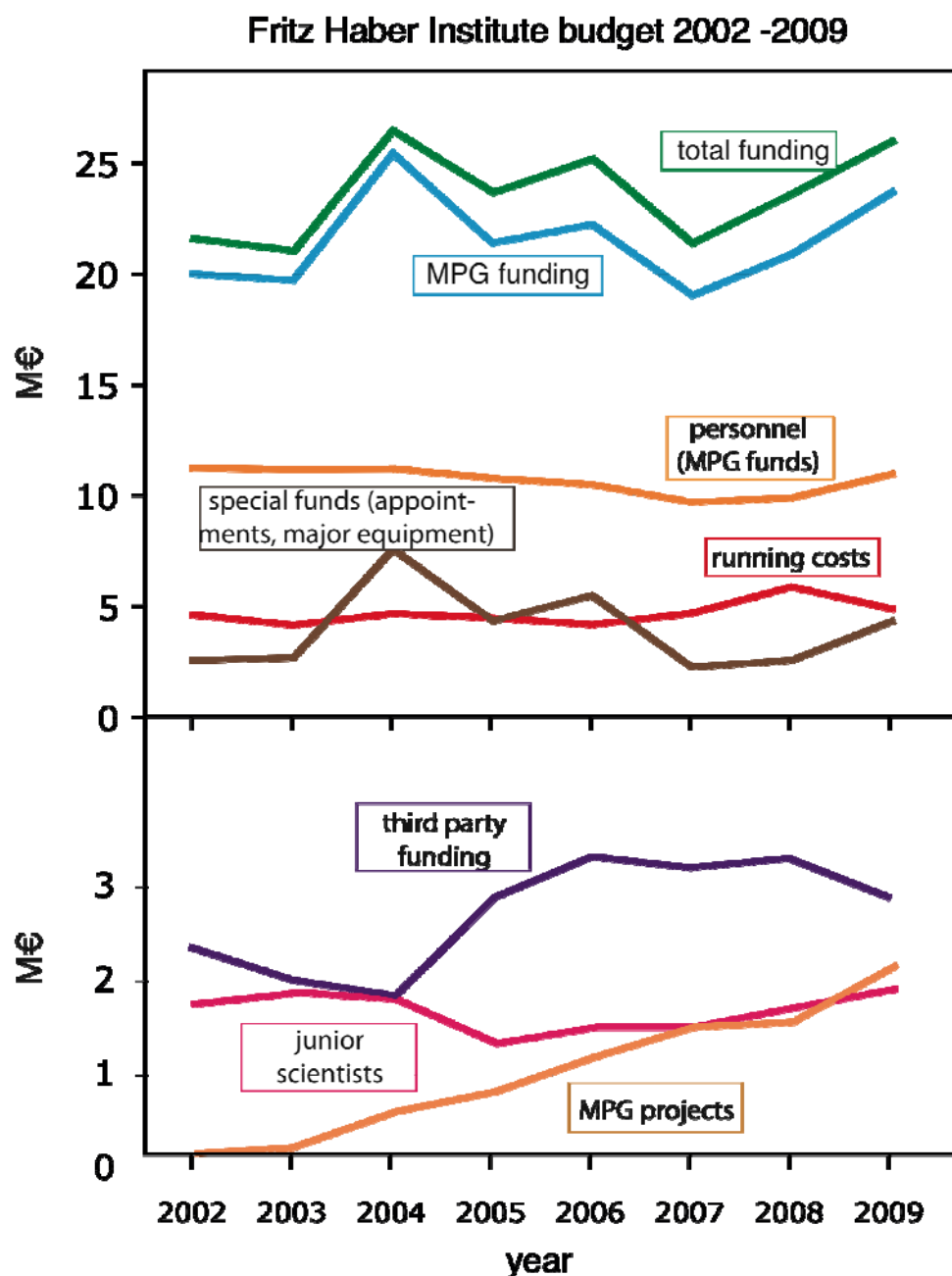
A number of graduate students of the institute received the Otto Hahn Medal of the Max-Planck society for excellent thesis work: *Dr. Tobias Schalow*, Department CP (2007), *Dr. Sebastiaan van de Meerakker* (2008), Department MP, *Dr. Sophie Schlunk* (2009), Department MP.

Several members of the institute left during the reporting period to take up academic positions:

- *Friederike Jentoft* took up a professorship at Oklahoma State University in 2008
- *Christian Hess* took up a W3 professorship at Darmstadt University in 2008
- *Kazuo Watanabe* left the group effective November 01, 2009, to accept a postdoctoral associate position at Oak Ridge National Laboratory
- *Dario Stacchiola* was appointed to an Assistant Professorship at Michigan Technology University
- *Zhihui Qin* was appointed Associate Professor at Wuhan Institute of Physics and Mathematics (WIPM) of the Chinese Academy of Sciences
- *Hiroko Ariga* was appointed Associate Professor at Hokkaido University, Japan
- *Steven Hoekstra*, post-doc since May 2005 and group leader since early 2008, accepted a tenure-track Assistant Professor position at the KVI in Groningen, The Netherlands, starting November 2009

- *Andreas Osterwalder* received a “Förderprofessur des Schweizerischen Nationalfonds”, or SNSF Professorship, at the EPFL, Switzerland, effective May 2009
- *Hong Jiang* accepted an offer for a professorship from the College of Chemistry at Peking University (Institute for Theoretical and Computational Chemistry) (June 2009)
- *Karsten Reuter* was offered full professorships by the University of Kiel (Germany), the University of Amsterdam (Netherlands), and the Technical University of Munich (Germany). He accepted the latter offer for a chair in theoretical chemistry, but will stay with us “im Nebenamt” with a 20% appointment for one more year. His plan is to move fully to Munich in the Summer 2010
- *Hardy (E.K.U.) Gross* has been a Max Planck Fellow at the institute since 2006. Recently, he accepted the offer to become a Director at the Max Planck Institute for Microstructure Research in Halle. He has been there since October of this year, and consequently his Max Planck Fellow status and his group have just ended

The institute finds itself in a stable financial situation. The flexible accounting system permits to operate the budget according to scientific needs. The Figure below shows the development of the budget over the last 7 years. Omitting the special effects through large grants (“special funds”), the institute operates on a stable basis of about 20 M€a from central funding.



The essential additional flexibility in research comes from funding based upon grant applications to external funding sources, but also increasingly through peer-reviewed MPG-internal project actions. External funding comes from a wide variety of sources, ranging from the Deutsche Forschungsgemeinschaft (DFG) and the EU and network-funded activities with the national ministry of research (BMBF) to purely industry-sponsored bilateral projects. Should this trend towards a substantial role of application-based funding apparent in the reporting period

continue, then the character of activities in the institute may change from the solely curiosity-driven research to a larger fraction of program-oriented research. The numerous large-scale activities that are ongoing in the institute have led the Kollegium to agree on a master plan for administering the “special funds” section of the budget. A long-term planning until the year 2013 was proposed, and has been accepted by the president of the MPG. It bundles the expenditures for the running appointment grants (G. Meijer and M. Wolf) together with grants for the free electron laser and its research infrastructure. A substantial upgrade of the SMART project to be carried out in 2009/2010 is also included in the planning. The effects of this investment plan can only be seen gradually in the budget figures but will become manifest throughout the next 4 years with large sums of investments hiding the trend that was mentioned above.

Execution and administration of the budget has become increasingly more complex for the institute. Apart from the ever-increasing number of externally funded projects with their partly extensive regulatory burdens, the internal operation of the budget has also become increasingly more regulated, requiring the observation of substantially more rules and procedures. All this is handled by the administration without additional personnel.

The head of administration *Mr. R. Fink* left the institute in 2009 to take up a new position within the MPG. His instrumental support for the institute was taken over for an interim period by the Administrative Director *K. Horn* and by the heads within the administration. The position of *R. Fink* was filled with *N. Jakubzig* who joined the institute on October 1<sup>st</sup>, 2009. The institute aims at improving the existing operational and technical safety measures; these include a personalized web-based safety training, improved safety instruction at experiments and FHI-standards for laboratory notebooks.

The collaborative actions of the institute extend also to areas of supporting scientific activities. The institute is engaging in many initiatives within the MPG, both on the level of the directors and on the level of scientific, administrative and technical staff. The FHI is “pilot institute” for many new activities from the central administration such as for the cost-oriented accounting procedures “Kosten- und Leistungsrechnung” (KLR), for the electronic self-archiving

activities of the MPDL (eSciDoc) and also creates useful networking activities amongst Max Planck Institutes. An example is the initiative of the head of our electronics department, *G. Heyne*, who organized a 3-day meeting for the electronics development engineers of the Max Planck Society at the FHI in the summer of 2009. The idea behind this meeting was to establish direct contacts between the – often highly specialized – electronics engineers of the various institutes, and to provide a format for the exchange of ideas and expertise. A total of 33 colleagues from 21 MPIs came to Berlin, where they informed each other about „typical“ ongoing projects at their home-institutions in short presentations. These presentations were followed by lively discussions during which it became clear that often-similar tasks and problems need to be tackled, and that similar approaches exist at the different MPIs. Possibilities for initiating and optimizing the collaboration between the MPIs in the field of electronics development were discussed. In view of the positive resonance from all participants of this first meeting it was decided to hold such a meeting annually.

For the renovation of its buildings and its technical infrastructure, a master plan has been effective since the year 2000. In the reporting period, the workshops were relocated to a central facility (building L) and the refurbishing of the second building of the MP department (building D) was completed. The first master plan finishes with the refurbishment of building A. It should be mentioned that the budget limit of the first master plan was met exactly despite the execution time of 9 years.

The redirection of the usage of building A, the installation of the new PC department and the construction of the FEL source led to the creation of a second master plan, and to the assignment of substantial additional funding for building activities on campus.

The appointment of a new team of architects and civil engineers has permitted, for the first time, the application of modern planning tools such as finite element simulation of buildings, and for a complete analysis of the technical infrastructure including all media supplies. A package of individual measures will be put into operation in order to upgrade the campus, with a strict timeline dictated by the necessity to fully provide the new department of *M. Wolf* with laboratory space

and infrastructure as fast as possible, and to complete these tasks on time for the centennial anniversary of the institute in 2011. Intense and complex planning activities are currently ongoing to prepare for the practical action beginning in spring 2010 with the completion of building A. All agreements of the MPG internal bodies have been obtained and the building permission of the new research building is pending with the national authorities.

### *Facility management*

The extensive construction activities lying ahead, and the resulting creation of a large number of novel infrastructural systems underline the importance of the facility management team in the institute. *U. Tisini*, our technical facility manager, and *U. Reppnow*, an expert for construction activities, head this unit. The team further encompasses 5 technical workers who are in charge of sanitation, climatization, cooling and electrical supply systems, and 3 gardeners who take care of the park on the campus. The work of the facility management team gradually shifts from service and minor modifications of the infrastructure to advising the external engineers in planning, controlling construction, and operating of the increasingly complex computer control systems of the technical infrastructure. The building automation and control network that is under development in the institute has been made a pilot project for the entire Max Planck-Society, and requires substantial planning, programming and operation by the team. It was already reported at the last Beirat meeting that the institute engages in the development of such a system that will suit the needs of the scientific departments in controlling a media infrastructure with strongly varying requirements and with rapidly changing technical specifications. The PP&B computer support team, headed by *H. Junkes* adapts this software according to the needs of the institute. This project has already started before the last Beirat meeting; is still ongoing and has led to many changes in technical specifications and in hardware of the technical infrastructure. Through this activity, the institute also plays a prominent role in efforts of the Max Planck Society for energy conservation, and for innovative planning of research infrastructure.



We expect that this will enable the institute to cope with the challenging complexity of facility management brought about by the increasing demands of the experimental facilities and by the need to save on energy resources. To this end the facility management team was able to significantly reduce the energy consumption and costs of the institute by technical measures, and by negotiating better contracts with suppliers at a time where the rising energy cost needs to be compensated from the research budget.

The managing director wishes to thank the Fachbeirat - on behalf of the whole Kollegium and the whole Fritz Haber Institute - for its continuous support and advice over the years and for the intense efforts during the coming meeting. I wish all of us a stimulating and fruitful session and warmly welcome you all in Berlin in November 2009.

Robert Schlögl







# International Max Planck Research School

## Complex Surfaces in Material Science

### Spokesperson:

Hans-Joachim Freund

### Coordinator:

Thomas Risse

### Members:

Klaus Christmann, FU  
Hans-Joachim Freund, FHI  
Paul Fumagalli, FU  
Klaus Hermann, FHI  
Karsten Horn, FHI  
Gerard Meijer, FHI  
Klaus Rademann, HU  
Karsten Reuter, FHI

Harm-H. Rotermund, FHI (until 12/07)  
Joachim Sauer, HU  
Matthias Scheffler, FHI  
Robert Schlögl, FHI  
Reinhard Schomäcker, TU  
Helmut Schwarz, TU  
Helmut Winter, HU  
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FHI: Fritz-Haber-Institut*

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Rosa Arrigo, *Italy (until 08/09)*  
Martin Baron, *Germany*  
Hadj M. Benia, *Algeria (until 11/08)*  
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David Blauth, *Germany*  
Tom Cotter, *New Zealand (since 07/07)*  
Carsten Enderlein, *Germany*  
Gang Feng, *P.R. China (since 01/09)*  
Philipp Giese, *Austria (since 04/09)*  
Anastasia Gonchar, *Russia (since 07/08)*  
Mathis Gruber, *Austria*  
Philipp Grüne, *Germany (until 02/09)*  
Jan-Frederick Jerratsch, *Germany (since 01/08)*  
Ki Hyun Kim, *Korea (until 05/09)*  
Patrick Kirchmann, *Germany (until 02/09)*  
Karolina Kwapien, *Poland*  
Tanya Kumanova Todorova, *Romania (until 09/07)*

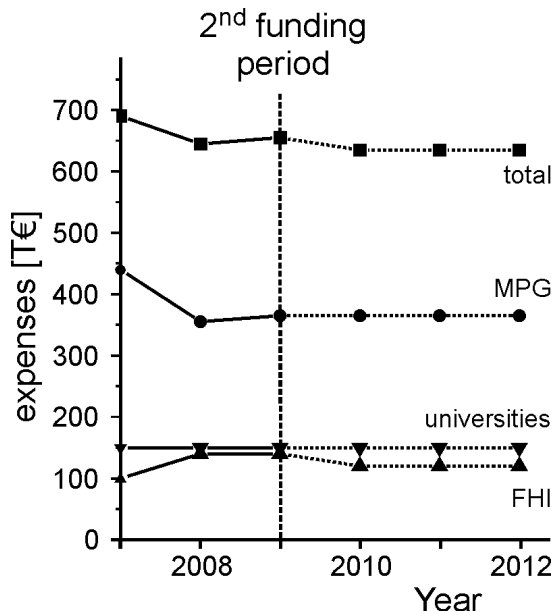
Bo Li, *PR China (until 12/08)*  
Xinzheng Li, *PR China (until 07/08)*  
Jichun Lian, *PR China (08/06 – 09/08)*  
Rhys Lloyd, *UK (until 06/08)*  
Erik McNellis, *Sweden*  
Norina A. Richter, *Germany (since 05/09)*  
Michael Rieger, *Germany (since 12/07)*  
Yuriy Romanyshyn, *Ukraine (until 06/09)*  
Alessandro Sala, *Italy (since 06/08)*  
Pablo Sanchez Bodega, *Spain (until 04/08)*  
Adnan Sarfraz, *Pakistan*  
Philip Schambach, *Germany (since 07/09)*  
Viktor Scherf, *Kazakhstan*  
Philipp Schmidt-Weber, *Germany (until 02/08)*  
Andreas Schüller, *Germany*  
Konrad von Volkmann, *Germany*  
Yongsheng Zhang, *PR China (until 05/08)*  
Hui-Feng Wang, *PR China (since 11/08)*



## General Remarks:

The International Max Planck Research School (IMPRS) “Complex Surfaces in Material Sciences” (<http://www.imprs-cs.mpg.de>) is a structured PhD program creating a platform for PhD students of currently 15 groups located at the Freie Universität Berlin, the Humboldt-Universität zu Berlin, the Technische Universität Berlin, and the Fritz Haber Institute. The school aims at creating a unique opportunity in terms of cutting-edge research and a thorough training in the physics and chemistry of surfaces by integrating the expertise of several research groups. This concept was successfully evaluated in late 2006 and the second 6 year funding period started in the beginning of 2009.

At the moment the school has 23 students, 12 being financed by funds from the IMPRS. One of the goals for all International Max-Planck Research Schools is to attract especially foreign students to participate in these schools. In accordance with this guideline, currently 52 % of all participants IMPRS are foreign students which cover a broad range of 11 nationalities.



**Budget of the IMPRS 2007 - 2012**

The Figure presented on the left shows the total budget of the IMPRS as well as the individual contributions of the different participating organizations for the years 2007-2009. In addition, the expected evolution for the forthcoming years is drawn. The budget declined in the last two

years. This decline results from a decrease of the MPG contribution to 365 T€ which was set as the upper limit by the general administration. This reduction of the budget has forced us to reduce the number of students financed by the IMPRS.

It should be noted at this point that the general administration has provided extra funds for the year 2008 in which the originally granted budget was substantially lower than the in previous years. This reduction of the budget in 2008 was caused by the funding scheme which provides lower fund at the end of a funding period. Due to the fact that the school was positively evaluated, this reduction was compensated by the general administration.

The plan of research of the IMPRS mirrors the development of the surface science in the last decades away from studies of highly idealized single crystal surfaces towards complex surfaces and interfaces. The later encompasses multi-phase systems such as layered systems, nanoparticles, and combinations between different material classes such as metal-oxide structures. Chemical processes on surfaces such as elementary processes in heterogeneous catalysis are one example for questions addressed within the school. This example can be amended by various other topics ranging from ultrafast electron dynamics to synthetic work in the field of carbon nanotubes. In addition to experimental work there is a broad range of theoretical efforts within this school and it is a particular aim of the school to foster the connection between theory and experiment.

Understanding of the properties of highly complex surfaces at an atomistic level is not only an interesting scientific subject. These questions are highly relevant for an ever-increasing number of technological applications. This is reflected, among other things, by the importance of modern surface analytical tools such as atomic force microscopy, X-ray photoemission by industry. This overlap of interest in surface processes creates a high demand for well-trained scientific personnel with an excellent command of the concepts and techniques of modern surface science.

A variety of activities have been established to accomplish the goals of the school. Apart from the cutting edge science pursued in the individual PhD projects a variety of teaching efforts have been established to ensure a thorough training in the methods, concepts, and theoretical basis of the physics and chemistry of surfaces. First, block courses on basic as well as advanced topics taking place every semester (for typical content see attached schedules). As of the winter term 2009/2010 the introductory courses will be organized in collaboration with the center of excellence “Unifying Concepts in Catalysis”. The school recruits



students with different backgrounds (chemists, physicists, material scientist). The lectures pay particular attention to this aspect, thus providing a common experimental and theoretical knowledge base for more advanced topics and try to bridge the typical language barriers which exist between fields. The block courses are amended by lectures on special topics extending and deepening the knowledge provided in the compact block courses. (A list of lecture courses is attached below.) A central role plays the seminar program as well as a visiting researcher's program. Due to the extensive seminar program within the institute and the universities in Berlin the school does not have its own seminar series, however, the students are invited to actively participate in the selection of speakers. The lively exchange of ideas and an open atmosphere of discussion is a particularly important prerequisite for the success of such an integrated effort. To this end regular small workshops are organized. Within these workshops the students report on the current development of their projects and discuss the achievements as well as exchange ideas for the future progress of their project with the other participants of the research school. Excursions to industry (e.g. AMD, SulfurCell) offer the possibility to acquaint students with the industry perspective of surface problems. Since most of the students will later be working in industry, it provides the possibility to make contacts which may help in their future career.

Soft skills are often a key argument when recruiting scientists with similar scientific background. Among others this includes communication skills, proper time management, or the ability to manage a project efficiently. The school offers a variety of courses to improve these skills. These include e.g. courses on scientific presentation or training for job interviews.

Finally it is worth mentioning the two of the students from the school have been granted awards for their work pursued within the school. Julia Stähler has received the Klaus Tschira prize for understandable science "Klartext!" for communicating the results of her PhD thesis to the broader public. Katrin Domke has received the Wilhelm-Ostwald young scientist award of the Deutsche Bunsengesellschaft für Physikalische Chemie for her exceptional thesis entitled "Tip-enhanced Raman spectroscopy - Topographic and chemical information on the nanoscale."

### Current PhD-Projects within the IMPRS:

*Arndt, Sebastian:* Investigation of metal catalysts with defect structures for the activation of small molecules.

IMPRS, Germany, TU/FHI: Prof. Schomäcker/Prof. Freund

*Arrigo, Rosa:* Large scale synthesis of Carbon nanotubes.

IMPRS, Italy, FHI: Prof. Schlögl/Prof. Horn

*Baron, Martin:* Characterization of vanadia clusters on well defined CeO<sub>2</sub> films.

IMPRS, Germany, FHI/HU: Prof. Freund/Prof. Winter

*Bdzoch, Juraj:* Analysis and control of ultrafast reactions on metal surfaces.

IMPRS, Slovakia, FU/FHI: Prof. Wolf/Prof. Freund

*Blauth, David:* Oxidation of NiAl: structure and effects of ion influence emission of electrons.

IMPRS, Germany, HU/FHI: Prof. Winter/Prof. Freund

*Cotter, Thomas:* Synthesis and characterisation of molybdenum oxide-based model catalysts for the selective oxidation of C<sub>3</sub> hydrocarbons and oxygenates.

IMPRS, New Zealand, FHI/TU: Prof. Schlögl/Prof. Schomäcker

*Enderlein, Carsten:* High resolution photoemission of low dimensional systems.

IMPRS, Germany, FHI/FU: Prof. Horn/Prof. Fumagalli

*Feng, Gang:* Theoretical investigation on mechanism of catalytic transfer hydrogenation over Cu/gamma-alumina.

IMPRS, PR China, HU/FHI: Prof. Sauer/Prof. Freund

*Giese, Philipp:* Oxidative coupling of methane.

IMPRS, Austria, FU(UniCat)/FHI: Prof. Wolf/Prof. Freund

*Gonchar, Anastasia:* Chemistry and Physics of point defects on oxide surfaces.

IMPRS, Russia, FHI: Prof. Freund/Prof. Schlögl

*Gruber, Mathis:* Interaction and reaction of hydrocarbons on oxides: DFT model investigations of electronic structure and spectroscopic properties.

IMPRS, Austria, FHI/FU: Prof. Hermann/Prof. Freund

*Jerratsch, Jan-Frederick:* STM study of the adsorption properties of clean and chemically modified oxide surfaces.

IMPRS, Germany, FHI/FU: Prof. Freund

*Kwapień, Karolina:* Quantum chemical reactivity studies on supported transition metal oxides.

IMPRS, Poland, HU/FHI: Prof. Sauer/Prof. Freund

*McNellis, Erik:* First principles studies of molecular switches at surfaces.

IMPRS, Sweden, FHI/FU: Dr. Reuter/Prof. Wolf

*Richter, Norina Anna:* Reaction dynamics at lithium doped MgO (001).

IMPRS, Germany, FHI/TU: Prof. Scheffler

*Rieger, Michael:* CO oxidation on oxidized Pd surfaces: a combined DFT and kinetic Monte-Carlo study.

IMPRS, Germany, FHI/FU: Dr. Reuter/Prof. Wolf

*Sala, Alessandro:* Investigation of catalytically active nano-cluster with high-resolution spectro-microscopy.

IMPRS, Italy, FHI/FU: Prof. Freund/Prof. Christmann

*Sarfraz, Adnan:* Deposition of amino acids and derivatives on surfaces.

IMPRS, Pakistan, HU: Prof. Rademann/Prof. Freund

*Schambach, Philip:* Tip enhanced Raman spectroscopy.

IMPRS, Germany, FU/FHI: Prof. Wolf/Prof. Freund

*Scherf, Viktor:* Adsorption of Ag on the Re(10-10) surface.

IMPRS, Kazakhstan, FU/FHI: Prof. Christmann/Prof. Freund

*Schüller, Andreas:* Investigation of interaction processes during grazing incidence ion scattering.

IMPRS, Germany, HU/FHI: Prof. Winter/Prof. Freund

*von Volkmann, Konrad:* Steering of photoinduced surface reactions using optimized femto second laser pulses.

IMPRS, Germany, FU: Prof. Wolf/Prof. Christmann

*Wang, Hui-Feng:* STM investigations of solid/liquid interfaces.

IMPRS, PR China, FHI/FU: Prof. Freund/Prof. Christmann

**Typical schedules of a basic block course: 1 week, 4 lectures each day**

Day 1	
<i>K. Hermann:</i> Surface Crystallography I	<i>M. Heyde:</i> Scanning Probe Microscopy
<i>H.-J. Freund:</i> Adsorption I	<i>R. Schlögl:</i> Principles of Heterogeneous Catalysis
Day 2	
<i>G. Meijer:</i> Advanced Spectroscopy I	<i>H.-J. Freund:</i> Adsorption II
<i>M. Heyde:</i> Scanning Probe Microscopy	<i>Y. Dedkov:</i> Experimental Investigation of Electronic Structure of Solids and Surfaces
Day 3	
<i>K. Hermann:</i> Surface Crystallography II	<i>K. Reuter:</i> Ab Initio Thermodynamics
<i>Y. Dedkov:</i> Experimental Investigation of Electronic Structure of Solids and Surfaces	
Day 4	
<i>K. Reuter:</i> First-Principles Kinetic Monte Carlo	<i>M. Sierka:</i> Theory of Electronic Structure
<i>G. Meijer:</i> Advanced Spectroscopy II	<i>R. Schlögl:</i> Principles of Heterogeneous Catalysis

**Schedule of a block course focussing on an advanced topic:  
synergism between theory and experiment: case studies: 2 hours for each lecture**

Topic	Experiment	Theory
Electron spectroscopy on vanadia surfaces	<i>H. Kühlenbeck (FHI)</i>	<i>K. Hermann (FHI)</i>
SiO <sub>2</sub>	<i>S. Shaikhutdinov (FHI)</i> <i>H. Winter (HU-Berlin)</i>	<i>M. Sierka (HU-Berlin)</i>
Electronic Structure of Carbon Materials	<i>K. Horn (FHI)</i>	<i>J. Carlsson (FHI)</i>
Oxygen on transition metal surfaces	<i>K. Christmann (FU-Berlin)</i>	<i>K. Reuter (FHI)</i>
Transmission Electron Microscopy	<i>M. Lehmann (TU-Berlin)</i>	<i>D. Su (FHI)</i>
Structure of clusters in the gas phase	<i>A. Fielicke (FHI)</i>	<i>J. Döbler (HU-Berlin)</i>
Solid State NMR of zeolites	<i>H. Koller (Uni Münster)</i>	<i>J. Sauer (HU-Berlin)</i>

## **Lectures courses 2008 - 2009:**

### WS 07/08:

"Selected Topics from the Physical Chemistry of Surfaces and Interfaces:  
Heterogeneous Model Catalysis"  
(Prof. Dr. K. Christmann)  
"Experimental and Theoretical Aspects of Surface Physics"  
(Prof. Dr. K. Christmann)  
"Group Theory - an introductory course"  
(Prof. Dr. K. Horn)  
"Metal Oxides and Their Surfaces: Theory of Structure and Electronic Properties"  
(Prof. Dr. K. Hermann)  
"Modern Methods in Heterogeneous Catalysis Research"  
(Prof. Dr. R. Schlögl and Dr. F. Jentoft)  
"Introduction to Surface Science"  
(Prof. Dr. H. Winter)  
"Solid State Physics: Introduction into Surface Physics and time resolved  
Spectroscopy"  
(Prof. Dr. M. Wolf)

### SS 08:

"Physical Chemistry of Surfaces and Interfaces: Introduction and Basics"  
(Prof. Dr. K. Christmann)  
"Experimental and Theoretical Aspects of Surface Physics"  
(Prof. Dr. K. Christmann)  
"Theoretical Material Science - Theoretische Festkörperphysik "  
(Prof. Dr. M. Scheffler)  
"Introduction to Surface Science"  
(Prof. Dr. H. Winter)

### WS 08/09:

"Selected Topics from the Physical Chemistry of Surfaces and Interfaces:  
Interaction of Gases with Solid Surfaces"  
(Prof. Dr. K. Christmann)  
"Experimental and Theoretical Aspects of Surface Physics"  
(Prof. Dr. K. Christmann)  
"Crystallographic Tools for Surface Scientists"  
(Prof. Dr. K. Hermann)  
"Modern Methods in Heterogeneous Catalysis Research"  
(Prof. Dr. R. Schlögl and Dr. A. Trunschke)  
"Nanotechnology – Basics and Applications"  
(Prof. Dr. M. Wolf)

### SS 09:

"Hands-on Tutorial on *Ab Initio* Molecular Simulations: Toward a First-Principles  
Understanding of Materials Properties and Functions"  
(Dr. K. Reuter, Prof. Dr. M. Scheffler)  
"Introduction to Surface Science"  
(Prof. Dr. H. Winter)









**Department of Inorganic Chemistry****Director: Robert Schlögl****Staff scientists:**

Malte Behrens		Dirk Rosenthal
Friederike Jentoft, Habil.	<i>until 30/08/08</i>	Olaf Timpe (FHI Safety Officer)
Axel Knop-Gericke		Detre Teschner
Frank Girgsdies		Annette Trunschke
Bernd Kubias	<i>until 31/05/08</i>	Sabine Wrabetz

Elmar Zeitler (Emeritus), Manfred Baerns (Guest Emeritus)

**Emmy-Noether Groups:**

Christian Hess	+ 2 graduate students	<i>until 29/02/08</i>
Raimund Horn (new)	+ 1 graduate student (UniCat)	
+ 3 post-docs: Michael Geske, Isabella Oprea (UniCat), Ulyana Zavyalova (UniCat)		

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

Kristina Chakarova	<i>until 30/04/08</i>	Katrin Pelzer (maternity leave)
Thomas Hansen	<i>until 30/04/08</i>	Tulio Rocha
Yuri Kolen'ko		Zi-Rong Tang <i>until 31/01/09</i>
Kirill Kovnir	<i>until 31/07/08</i>	Genka Tzolova-Müller
Ed Kunkes		Alberto Villa <i>until 30/09/09</i>
Giulio Lolli	<i>until 14/04/09</i>	Yi-Jun Xu <i>until 31/01/09</i>
Nelli Muratova		Zhang, Wei

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

Rosa Arrigo		Raoul Naumann
Raoul Blume		Lidong Shao
Almudena Celaya Sanfiz		Jean-Philippe Tessonier
Maik Eichelbaum		Di Wang <i>until 30/04/09</i>
Benjamin Frank		Lide Yao
Andreas Furche	<i>until 31/03/08</i>	Aihua Zhang <i>until 14/10/08</i>
Michael Hävecker		Jian Zhang <i>until 31/05/09</i>
Igor Kasatkin	<i>until 11/05/09</i>	Binseng Zhang
Ming Hoong Looi	<i>until 30/04/08</i>	Bo Zhu <i>until 31/10/09</i>

<b>Graduate students:</b>	21	(8 from external funds)
	+ 2	IMPRS (1 <i>until 28/08/09</i> )
	+ 2	UniCat
	+ 6	University of Malaya

<b>Technicians:</b>	6	(+ 3 Service Group Electron Microscopy)
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<b>Trainees:</b>	3	
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**Service Groups:**

Electron Microscopy	2	Hermann Sauer <i>until 31/01/09</i>
		Dangsheng Su
Library	2	Katrin Quetting
		Uta Siebeky



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

**Director: Robert Schlögl**

## **1. General**

## **2. Research concept and synopsis of results**

## **3. Future activities**

## **4. Research highlights**

### **4.1. Copper in C1 chemistry**

- 4.1.1. The nature of active “methanol copper”
- 4.1.2. Understanding the synthesis of Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>)
- 4.1.3. Pd in catalysis

### **4.2. Surface and sub-surface chemistry**

- 4.2.1. Ru in oxidations of CO and of MeOH
- 4.2.2. Silver in selective oxidation
- 4.2.3. Adsorption microcalorimetry

### **4.3. Nanostructured carbon in catalysis**

- 4.3.1. CNT as catalysts for C3 ODH
- 4.3.2. Basic CNT and fluid phase reactions
- 4.3.3. CoMnAlMg systems for CNT synthesis

### **4.4. Selective oxidation**

- 4.4.1. V-SBA 15 systems
- 4.4.2. MoVTe systems
- 4.4.3. Synthesis of binary and ternary model carbide catalysts

### **4.5. Emmy Noether Group „High Temperature Catalysis”**

- 4.5.1 Methane oxidation on Pt
- 4.5.2. Oxidative coupling of methane (OCM) on Li/MgO



## 1. General

The Department of Inorganic Chemistry (AC) finalized its installation in the new building F and is now fully operational including also the outstation at BESSY allowing to conduct complex chemistry in-situ at the synchrotron beamline ISISS. This beamline is now an internationally widely requested research facility. With support from the EU NOE “*IDECAT*” in which the department plays a leading role a total of 17 academic collaborating groups from Europe and from the US and 4 industrial collaborations were supported by the staff from the department, many by multi-week campaigns. Most collaborations led to publications and further collaborative work. With this outreach we are at the limit of the capacity both from beam time allocation and from resources we spend for the collaborative effort.

The department has resumed its activities in building novel equipment for conducting advanced in-situ studies. These include:

- Parameter-controlled autoclaves for synthesis and testing of catalysts featuring in-situ measurements and feedback controls for reactants
- Variable pressure ( $10^{-6}$  mbar-500 mbar) temperature-programmed-desorption from powders including high-pressure pre-reaction treatment
- Transport-optimized in-situ reactor for single-crystalline samples (in collaboration with SWNG Reuter)
- High-temperature adsorption microcalorimeter
- High temperature, high pressure (1300 °C, 40 bar) reactor for measurement of spatial profiles of gas species, surface temperature and gas temperature through a catalyst bed (in collaboration with Emmy Noether group)
- Combined optical diagnostics for MBMS and spatial profile reactor (in collaboration with Emmy Noether group and Berlin COE UniCat)
- Variable pressure (0.1 mbar-1000 mbar) catalytic test reactor in combination with variable pressure in-situ NEXAFS instrument

Some of these developments will be operating at the visit of the Beirat, some will be still under construction.

The department followed the recommendation of the Beirat and changed its attitude towards catalyst testing. The attempt to organize this crucial part of the work through collaboration and paid services that was necessary during the temporary installation of the department is now discontinued. The department operates and develops a range of single-tube and multitubular reactors suiting its needs for catalyst testing. Testing includes now screening of compounds as well as screening of parameter fields of operation. Fluid phase testing is also being developed to allow the use of complex substrates such as components of biomass. In this respect two visits of members of the department to the lab of one of the members of the Beirat were inspiring and shaped the approach to this important aspect of the work of our department.

Several members of the department left in a short period of time after the last meeting of the Beirat. Following the tradition that the department supports the start-up of new groups by letting them take away critical equipment and by discontinuing own research activities in these areas, it became necessary to restructure the research portfolio. Supporting the finalization of respective doctoral theses in collaboration with *Profs. Hess* and *Jentoft* discontinued the activities in zirconium oxide research, in own synthesis of CNT composites and in Mo-based model compounds for ODH. With the completion of the outstation at BESSY it was possible to give away the powder laboratory photoemission instrument that was upgraded with an in-situ RAMAN probe by *Prof. Hess*. The department decided not to engage in novel activities but to concentrate on the existing projects and to explore their relevance in energy research being catalysis to a large extent when it comes to the storage of primary electricity.

The existing activity on the interplay between gas-phase and surface catalysis was strongly augmented by the creation of an Emmy Noether group (*Dr. R. Horn*) that continues now these activities in excellent collaboration with the department. The Emmy Noether group is a main gateway for the participation of the department in the Berlin COE “unifying concepts in catalysis”. Here a concentration on the challenging subject of understanding the mode of operation of the Li-MgO prototype catalyst for methane coupling requires a substantial bundling of resources from the department and from the Emmy Noether group, exceeding

substantially the support granted from the COE. This project enjoys strong collaborations with the MP, CP and TH departments supporting our experiment development and producing theoretical and surface physical experimental boundary observations for the interpretation of the structure and function of high-performing catalysts.

## **2. Research concept and synopsis of results**

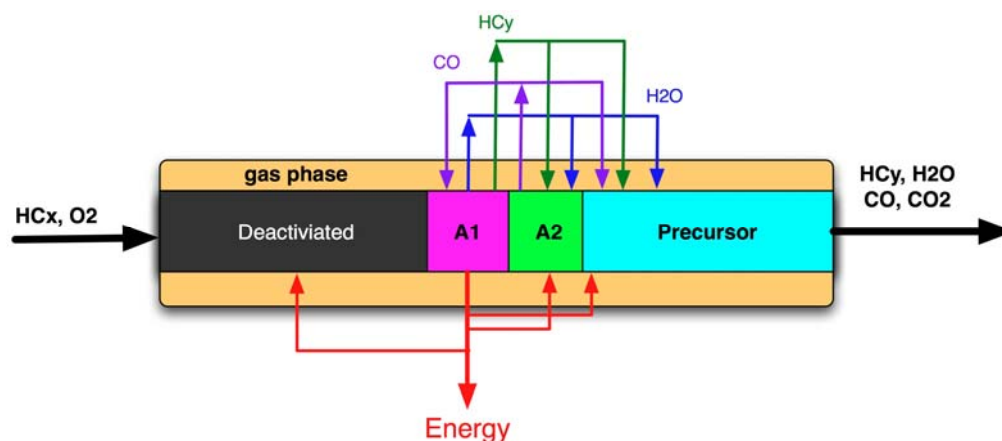
The enormous academic efforts to transform catalysis from its discovery mode to the design mode are still not successful despite the depth of our principal understanding (Nobel prize 2007). The enormous scale of chemical energy storage (20 times the size of all chemical industry) requiring catalysis strongly underlines the even practical need to advance further in our understanding of catalysis.

One strategy addressing this challenge unites the concepts supporting the discovery process in various fields of catalysis. These unified concepts need then to be founded on principles rooting back into physics such that they become accountable by ab-initio theory. The result of such an effort should be a universal concept of a working catalyst. The design phase encompasses then the materialization of such a universal catalyst tailored to its specific function by using a proven toolbox of material science approaches.

This strategy is taken from other areas developing a physical concept into a broad range of applications such as the hard- and software industries. Within this strategy it is of great value that the Berlin COE (UniCat) provides the broader background for the operation of the department. More in depth, the collaboration within the FHI provides interdisciplinary activities for practicing definition and unification of concepts in several classes of reactions.

The AC department sees its role in such a generalized strategy in the discovery and consolidation of the material science of the “dynamical catalyst” as corner stone of the mentioned universal concept. This includes contributions to the synthesis toolbox of catalysis. The department has developed a more genuine perception of the interplay of a dynamical catalyst in its reactor environment for the mesoscopic level shown schematically in Figure 1.

The reactor is a “plug-flow” system exhibiting a solid catalyst and some gas phase performing as example of a selective oxidation reaction. The solid was initially a homogeneous pre-catalyst that transforms in inhomogeneous spatial distribution into a variety of functionally different materials. After some time of initial equilibration (for this reason it is essential to study catalysts not fresh but after some equilibration also by in-situ methods) a distribution of species may be found as sketched in Figure 1. In technical reactors the formation of a so-called “hot spot” is a practical evidence for the zoning of materials.



**Figure 1: Mesoscopic model of the chemical system formed between a catalyst and its reactor environment. The most relevant feedback mechanisms are indicated.**

The combined action of excess heat, reactants and water will have caused decomposition of the active phase into a mix of thermodynamically stable phases in the zone of the deactivated catalyst. There one finds evidence for “phase cooperation” as remnant of the active phase. The active phase seen by the input stream is first a material exhibiting a redox state enabling the target reaction to be performed (A1). This zone is followed by a different active phase (A2) with a lower redox state performing unwanted reactions due to the strong drop in oxygen potential and due to the feedback of the more reducing chemical potential of the product onto the precursor material. In the prototype example this may be a C-C bond cleavage reaction or the addition of water to olefins both representing consecutive reactions leading to CO and hydrogen that scavenges all oxygen and



thus prevent further consecutive reactions at a lower temperature level of the product over the still unactivated pre-catalyst.

With time on stream the A1 zone travels through the catalyst bed driven by the formation of stable deactivation products. This shifts also the temperature “hot spot” through the reactor. The products at a rising temperature level are essential to activate the pre-catalyst allowing thus for the understanding that initial equilibration either takes a long time or can be controlled by adding reducing species such as organic solvents or ligand residues during preparation. In this picture the wanted catalyst is only formed through a cascade of solid state reactions transforming the pre-catalyst into the unwanted reduced form A2 and from there into the wanted active phase A1. It is obvious that the design of such a sequence of transformation is still a substantial challenge for catalysis. Similar diagrams can be constructed for other reaction types, including metal catalysts where the phase diversity arises from surface and sub-surface compound formation of a nominally single element active phase. Examples of this nanoscopic rather than macroscopic phase zoning can be found in this report (Cu/Ag, Ru<sub>x</sub>O<sub>y</sub>).

The zoning depicted in Figure 1 depends on the interplay of several kinetic process chains of reactant transformations and of solid-state dynamical responses. The feedback loops indicated in Figure 1 give the scientific justification as to why catalyst studies have to be performed in-situ and outside the “pressure gap” being a “local chemical potential gap”. For practical in-situ experiments it is imperative to ensure that the conditions of a catalyst study respect the zoning and do not drive the active system quickly through all the zones leaving behind during observation the stable deactivated state as study object. For this reason the in-situ experiments are only valid when spectroscopy and catalysis are recorded simultaneously as defined in the work programme of the department.

A prototypical study highlighting the effects of macroscopic zoning is the study of CPO of methane over Pt catalysts conducted in the Emmy Noether group. The use of a reactor allowing experimental verification of gradients of chemical potential through a catalyst bed has evidenced in this case the positive effect of zoning in the oxidation potential. What effects this has on the state of the catalyst being

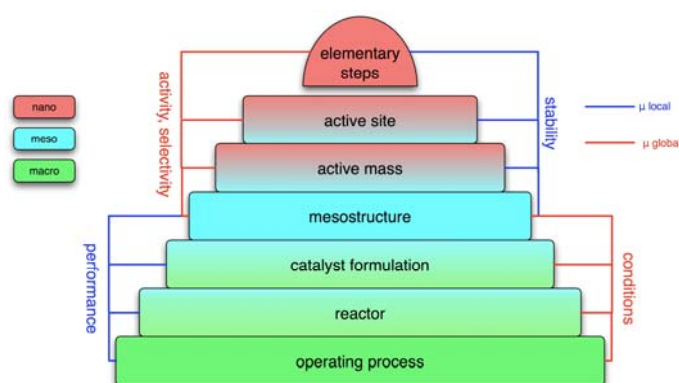
active in the two zones is under investigation. It is planned to study other reactions in this reactor, provided that a suitable form of catalyst preparation can be found.

The pre-catalyst from Figure 1 is synthesized such that it can adapt its surface structure to the chemical potential under operation within boundaries defined by the bulk structure. The potential is given by the adsorption properties of the active surface, the operation conditions and the transport properties of the catalyst environment and may thus deviate significantly from the potential calculated from the thermodynamics of the reaction conditions. One critical element in this essential adaptation process is the solid-state kinetics of surface transformations explaining the enigmatic influences of catalyst synthesis controlling the nanostructure and thus the meta-stability of the precursor. The other element is the effectiveness of the feedback control system provided by the gradients in reactant composition and in energy over the catalyst bed onto the dynamics of the catalyst material. This effectiveness is determined by the surface chemistry of the catalyst and by the transport properties of the total system on various scales of time and space.

These two elements are keys to understanding of the origin of gaps between surface science and high performance catalysis. The transformation of a surface into an active form is not a uniquely determined process but depends on the boundary conditions in its extent and even in its qualitative result. This means that under different conditions (e.g. low pressure, high pressure, or dry and in steam) different results will be obtained of the dynamic transformation of an identical precursor. Under conditions of low chemical potential the resulting structures may be metastable, as strong kinetic hindrances freeze structures of only partial adaptation. In this picture partly forcefully conducted debates about the nature of active catalysts find their natural explanations. Examples of such debates within the field of activity of the department are the discussion about the active state in ruthenium during total and selective oxidation and the nature of the active state of Cu during methanol synthesis.

The department makes an attempt to observe the multi-scale nature of catalysis in its practical studies in order not to be captured by the complexity of the catalyst

transformation pathways. This justifies the multiple methodical approaches developed over the years and requires a highly collaborative and integrated conduct of the projects. An impression about the multi-scale nature of catalysis as seen by the department is given in Figure 2. The existence of two couplers between the dimensions being the global and the local chemical potential render the in-situ observation mandatory for meaningful catalyst characterisation. The department understands “in-situ” as the simultaneous detection of structural and functional properties under conditions that result in qualitatively the same kinetics



**Figure 2. Hierarchy of catalysis science; the colours indicate the gross dimension. At the level of meso-structuring where we most lack analytical methods both couplers between the dimensions intersect being the chemical potential of the reactor (global) and at the active site (local).**

as under practical operation conditions. This can be verified by studying a series of catalysts with different performance in practical conditions; under in-situ conditions the ranking between the samples has to prevail.

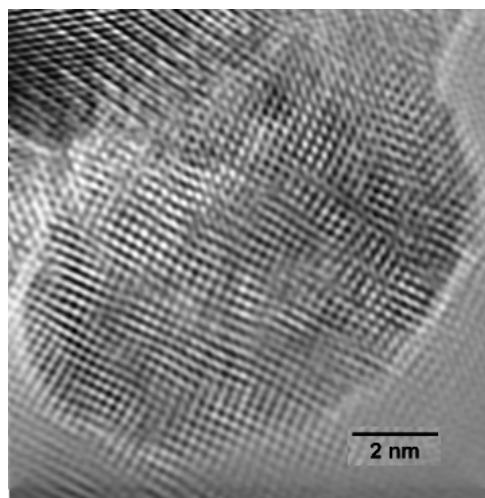
Three independent factors control the kinetics of activation and deactivation of the active phase. These are:

- The thermodynamic properties of the bulk *phase* including its stability
- The solid state *kinetics* of its response to the local chemical potential given by the material nanostructuring
- The choice of *operating conditions* of the reaction

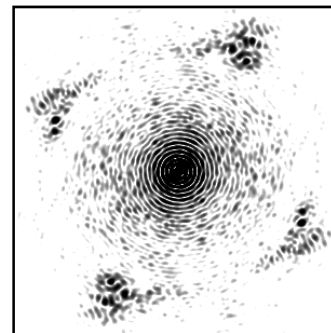
The active phase representing the terminating structure of the bulk catalyst (or the supported material) as thin overlayers is a mixture of site-isolating components with inter-dispersed active sites. These are considered as clusters of atoms in this overlayer much in the way as suggested long ago by Taylor in his “checkerboard model” of an active catalyst. The formation of this checkerboard surface is understood as “dynamical” response of the catalyst to the combined action of the

overall chemical potential and its local variation through the feedback loops. The dynamical response frequently does not modify the bulk material. It creates an inhomogeneous structure (A1, A2 in Figure 1) reflecting the local variation of conditions in a catalyst reactor. Such a response is different from a phase transformation as occurring during structural deactivation, following one overall gradient in chemical potential.

The active sites themselves are also not static but are adaptive in their electronic and chemical structure allowing thus for complex and selective transformations of



**Figure 3:**  
Multiple dislocations in a nanoparticle of  $t$ -ZrO<sub>2</sub> cause mosaicity clearly seen in the split reflections of the power spectrum. The resulting distorted surface exposes multiple under-coordinated sites suitable as active sites in isomerisation catalysis.



reactant molecules. In this way it becomes possible that a catalyst can activate a stable molecule and does not re-activate the resulting product being less stable than its precursor. The site- isolating matrix must provide the necessary stability for the active site clusters to allow for their facile regeneration in the catalytic cycle. This precludes the notion that well-ordered translational symmetric surfaces should be highly active and selective sites but rather calls for “molecular” entities as active sites exhibiting the necessary structural flexibility for minimizing the activation barriers in their adaptive function. A prototypical representation of an unexpected active phase in a refractory oxide is depicted in Figure 3.

The department has developed this lead model of an active catalyst from the results obtained over the last years and uses it now to focus the activities within each of the projects. The overall target is to support or correct this lead model and to provide at first multiple qualitative supporting evidences for the model. In particular, the microscopic chemical realization of the lead model in terms of

generation and site isolation of active sites in various systems will be a key activity driving projects and instrumentation development.

The department engages in method development, which allows providing in further steps quantitative information on the catalyst dynamics suitable to be treated with kinetic and ab-initio theoretical tools. A prototypical project is the study (*D. Teschner, P. Sautet*) of sub-surface carbon in palladium catalysts controlling their hydrogenation selectivity. In this project extensive exchange of our ideas with the results of the *CP department* (*S. Schauermaann, Sh. Shaikudtinov*) was instrumental and helped shaping our refined views on the overall dynamics of the system.

A central element in the overall strategy is mastering the synthesis of catalysts. In recognition of the multiple requests from the Beirat to develop this often neglected crucial part of catalysis science, the department has acquired a solid yet limited base of synthetic protocols chosen to produce well-characterized materials. Catalyst synthesis is now an integral part of all projects and no longer left to a “synthesis group”. Cross-fertilization occurs between the specific synthesis needs in the different projects.

The synthesis of high performing catalysts is a sequence of completely kinetically controlled reactions many occurring without notion such as ageing of precipitates or restructuring during washing and drying. The nature of such processes can only be described if the synthesis batch size is large enough to allow application of in-situ probes for process analysis and to exclude the detrimental effect of reactor walls on synthesis kinetics. These boundary conditions led to the selection of synthesis scales performed in the department. They are not the most economical and are not suitable for rapid discovery but they guarantee reproducibility and analytical control. Examples of the merits of these efforts are the understanding in the Cu system and the generation of a family of single-phase M1 MoVTe catalysts with different nanostructures. The progress in scaling the synthesis of V-SBA 15 model catalysts for the Berlin SFB 546 (project poly-B) allows now a multi-group effort in characterizing different aspects of C3 ODH and eventually even leads to an improved performance of this class of partial oxidation catalysts.

### 3. Future activities

The department obtained substantial insights into the material dynamics of heterogeneous catalysts behaving at their surfaces rather like molecular entities than as rigid bodies. The department was able to start tracing the underlying control mechanisms operating on different scales of time and space. Such a form of catalysis science qualifies as a prototypical example of the emerging field of “systems chemistry”. The department does not wish to repackage its research but sees its approach at the forefront of chemical research despite of the “old-fashioned” study problems of large-scale chemical transformations.

The department intends to continue the exploration and deepening of the lead model of the dynamical catalyst as described above. The portfolio of reactions is adequate to arrive at generic conclusions about the mode of operation of a catalyst. The application horizon will shift to issues of chemical energy storage. Here the control of the redox chemistry of di-oxygen is a central challenge, being exactly the same problem as studied in the department since quite some time. A possible deepening of the MPG-wide research network “*enerchem II*” that is coordinated by the department will emphasize some facets of research already conducted. In particular, the carbon project would benefit from the extension, as electrochemistry with carbon both in the context of water splitting and of battery electrodes will be studied. Here we benefit from the electrochemical expertise brought to us from the PC department that houses its electrochemistry activity in the AC department. Cheap nanocarbon as catalyst support is of growing interest in biomass conversion reactions involving hydrothermal synthesis reactions. This will be studied in the *PIRE* consortium and also in the UniCat context with two students of *BIG NSE* co-supervised with *P. Strasser* from TUB.

The department has started this year the work in the Seventh Framework EU Programm *Technotubes*. Aim of the investigations is the optimisation of catalyst performance by in situ surface analysis of the catalyst during the pretreatment and the nanotube nucleation step.

With respect to technology transfer the department has always conducted some industrial collaborations. They serve as challenging test cases for the validity of the results through a successful scale-up of catalyst concepts by the industrial

partner developed in the department from fundamental insight. This cannot be done within the scope of the MPG research. In addition, the resulting materials and test results from pilot-plant and full plant trials that would not be available to academic labs are most valuable input for further research. The department actively engages in relationships with industrial catalyst manufacturers (Süd Chemie, BASF) to stabilize its access to technical catalysis. Different forms of collaborations are being practiced. With Süd Chemie a long-term formal relation within the framework of the “*catlab*” project is under development. With BASF the *unciat* platform is used as well as bilateral research projects. Additional industrial collaborations feature the specialized in-situ analytical capabilities of the department.

#### 4. Research highlights

This section describes selected results providing some support for the general concept described in section 2. The information provided at the homepage ([www.fhi-berlin.mpg.de](http://www.fhi-berlin.mpg.de)), the poster abstracts, the department brochure (latest edition available at the Beirut meeting) and the publication record give a more complete insight into the research of the department. The following table lists the projects with their target systems. The project names emerge from their history and do not reflect their present research portfolio.

Project title	Leader	Key Elements	Reactions studied
C1 Chemistry	M. Behrens	Cu, Pd, Ga	MeOH synthesis CO <sub>2</sub> hydrogenation C <sub>2</sub> H <sub>2</sub> hydrogenation
Surface and sub-surface chemistry	A. Knop-Gericke	Cu, Ag, Au, Ru,	C <sub>2</sub> H <sub>4</sub> oxidation CH <sub>3</sub> OH oxidation CO oxidation HCl oxidation
Nanostructured carbons	D. Su	C; N,B,P modified Supported (Li, Pd, Au, Ru, Fe, Ni, Mo)	Battery electrodes Alcohol (sugar) transformations Ammonia splitting Water splitting CNT synthesis
Selective oxidation	A. Trunschke	V-SBA 15, CNT, Mo,VX,Y mixed oxides, carbides, phosphates	C3 oxidation ODH C2, C3, C4

A number of long-standing academic collaborations augment the research portfolio. The department actively contributes to the Berlin research networks within the SFB 546 (transition metal aggregates) and the COE UniCat. Within the MPG the department critically contributes to the research network *enerchem*.

Larger external projects are the “Pd project” encompassing groups in Austria ( *B. Klötzer, M. Rupprechter*) and the US (*D. Zemlianov*), the “*intermetallics*” project conducted with the MPI CPFS (Dresden) (*J. Grin, M. Armbrüster*), the contribution of *carboscale* (with *M. Muhler* and *W. Wirth*) to the national competence network *INNOCNT* and a *PIRE* project on renewable energies conducted with a consortium from the US led by *J. Dumesic* and *A. Datye*. Within the framework of the EU-NOE *IDECAT* and our franco-italian (*G. Centi, F. Garin*) collaboration (*ELCASS*) the department pioneered together with the TU Berlin the awarding of 2 European Doctoral Diplomas emphasizing the multi-national character of the degree.

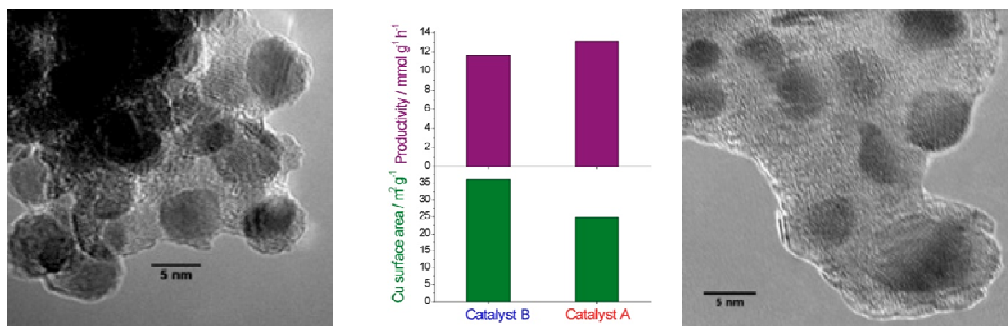
## **4.1. Copper in C1 chemistry**

### **4.1.1. The nature of active “methanol copper”**

The methanol synthesis catalyst based upon  $\text{Cu/ZnO/Al}_2\text{O}_3$  is a long-standing study object both in the literature and also in the department. The important effect of the microstructure of the  $\text{ZnO/Al}_2\text{O}_3$  component as well as the surprisingly large adjustability of the intrinsic activity of Cu (surface-normalized methanol productivity) was shown by comparing two highly active  $\text{Cu/ZnO/Al}_2\text{O}_3$  samples (Fig. 4) [1]. One system was prepared using a novel continuous method (catalyst A), while the other one was prepared according to the conventional co-precipitation and ageing process (catalyst B). Careful TEM analysis revealed that the Cu phases were very similar in both samples concerning the spherical particle shape and their size. The microstructure of the oxide component was clearly different: ZnO was present as discrete and crystalline particles in case of catalyst B, but as an amorphous and continuous oxide matrix in case of catalyst A. The encapsulation of Cu particles within the oxide material resulting from the novel synthesis was significantly more pronounced (surface:interface area ratio of Cu particles ca. 50:50) than for the conventional system (ca. 65:35) The productivity



of the less-accessible system was higher due to a ca. 50 % higher intrinsic activity of Cu in catalyst A.



**Figure 4: Mesostucture of a novel type of oxide-embedded Cu nanoparticles (A) and of a conventional diluted system (B) in relation to their unexpected catalytic performances in MeOH synthesis.**

We believe that this is the consequence of the enlarged metal-oxide interface contact, creating and stabilizing a non-equilibrated state of Cu, which is favorable for catalysis. Structural investigations showed a slight expansion of the Cu lattice parameter for the intrinsically more active sample by Rietveld refinement of XRD data, which might be caused by lattice strain, epitaxial stress or dissolution of foreign atom in the Cu lattice. Preliminary results have shown the applicability of line profile analyses of neutron diffraction data for further investigation of the structural properties of intrinsically highly active Cu [2].

#### 4.1.2. Understanding the synthesis of Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>)

A comprehensive model was elaborated for the traditional technical synthesis with the aim to rationalize the parameters of all unit operations. Previously the process

was studied only phenomenologically and optimized by empirical procedures. It was now found that a hierarchical two-step meso- and nano-structuring of the catalyst precursor occurs during precipitate ageing and thermal decomposition of the first carbonate precursor [3]. Zincian malachite,  $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$ , was identified as the for the technical synthesis relevant precursor phase leading to highly active catalysts. One key property of this phase its evolution into a needle-like morphology with a needle thickness of only a few nanometers upon secondary recrystallization during ageing. The morphology pre-determines the porosity of the final catalyst through its decomposition kinetics during calcination. A second critical property is a Cu:Zn elemental ratio approaching unity which leads to an effective isolation of the individual Cu active phase nanoparticles by ZnO nanostructures being formed upon mild calcination followed by careful reduction. The Cu:Zn ratio of zincian malachite can be estimated practically through analysis of structural data of the precursor. The shift of a characteristic XRD reflection was explained by a ligand field effect due to the different coordination requirements of the Jahn-Teller ion  $\text{Cu}^{2+}$  ( $d^9$ ) and the  $d^{10}$  ion  $\text{Zn}^{2+}$  in the common cationic lattice [4]. A clear structure-function correlation was established between the XRD structure of the precursor and the performance of the final catalyst in high-pressure MeOH synthesis.

The choice of parameters of the technical preparation route was partly optimized through unintended control of the two key properties of the precursor phase. This can now be performed much faster and to a greater extent with physical lead properties in hand. As consequence it occurs that the synthesis parameter space has to be re-explored when other target precursors are synthesized. Such systems are hydrotalcite-like materials [5] or amorphous basic carbonates [1]. Without careful re-determination of the synthesis parameters any comparison about the performance of different precursor compounds is not valid. This has not been done in the past as the correlations between morphology and composition of the precursor to the kinetics of catalyst activation was not known.

### 4.1.3. Pd in Catalysis

Metallic Pd is a versatile catalyst and is employed in many important processes. The successful work in the Pd project in the last years was focused on hydrogenation reactions on Pd-X model catalysts (X = C, Zn, Ga). The sub-surface chemistry of Pd was identified to determine the selectivity of alkyne hydrogenation [6]. Multiple effects of sub-surface species on the electronic structure of the surface and its adsorption properties are responsible for this feedback loop. In general, sub-surface chemistry is switched on during high-performance operation unintentionally through the high chemical potential of reactants (sub-surface carbon [7]), or through *in-situ* alloy formation involving support species (PdZn, CuZn). In an intended way the modification of active Pd can be done by direct synthesis [8,9] of intermetallic compounds (PdGa) withstanding without segregation the chemical potential of operation. The current goal of the Pd project is to combine the ideas developed on basis of the Pd-X models with the synthetic concepts successfully applied in the Cu project (see above) in order to prepare highly active Pd-based catalysts. These catalysts exploit the design of electronic structures of materials and could after successful aqueous-phase synthesis be used practically, illustrating the contributions of the department to the toolbox of catalyst design.

The precursor-based synthesis concept is similar to the successful preparation of Cu/ZnO catalysts (see above) and comprises co-precipitation of small particles of a precursors phase with Pd, Ga (and the support species) in a common cationic lattice. Nanostructuring of the individual particles will then be done through subsequent thermal treatment. The final formation of Pd-Ga intermetallic compounds should occur through catalytic reduction of the oxides utilizing spill-over effects of the nanostructured Pd component. First experiments were performed using a hydrotalcite-like precursor of the general composition  $(M1^{II}, M2^{II})_{1-x} M3^{III}_x (OH)_2 (CO_3)_{x/2} \cdot m H_2O$  with  $M1^{II} = Pd^{2+}$ ,  $M2^{II} = Mg^{2+}$  and  $M3^{III} = Ga^{3+}$ . Such precursors successfully yield catalytically active and selective Pd<sub>2</sub>Ga particles supported on Ga<sub>2</sub>O<sub>3</sub>/MgO.

- [1] M. Behrens, A. Furche, I. Kasatkin, A. Trunschke, W. Busser, M. Muhler, B. Kniep, R. Fischer, R. Schlögl, *Chem. Eur. J.*, submitted.
- [2] M. Behrens et al., *BENSC Experimental Reports 2008*, Proposals CHE-01-2202 & CHE-01-2357.
- [3] M. Behrens, *J. Catal.* 267 (2009) 24.
- [4] M. Behrens, F. Girgsdies, A. Trunschke, R. Schlögl, *Eur. J. Inorg. Chem.* 10 (2009) 1347.
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- [7] D. Teschner, Z. Révay, J. Borsodi, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Milroy, S. D. Jackson, D. Torres, P. Sautet, *Angew. Chem. Int. Ed.* 47 (2008) 9274-9278.
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- [9] J. Osswald, R. Giedigkeit, R. E. Jentoft, M. Armbrüster, F. Girgsdies, K. Kovnir, T. Ressler, Y. Grin, R. Schlögl, *J. Catal.* 258 (2008) 210.

## 4.2 Surface and sub-surface chemistry

### 4.2.1. Ru in oxidations of CO and of MeOH

The formation of oxygen species relevant for oxidation reactions over Ru and Ag catalysts was investigated by different techniques. The formation of subsurface oxygen plays an important role in the oxidation of methanol over Cu and in the epoxidation of ethane over silver as our previous in-situ work has clearly shown. The aim now is to show that the formation of subsurface oxygen is a more common phenomenon, which is realized also in other metals under selective oxidation conditions. The highly exothermic CO oxidation over  $\text{RuO}_x$  was revisited with a flow reactor experiment for overall activity data and by in situ XRD to clarify the role of the bulk phase of the system.

Commercial  $\text{RuO}_2$ , the starting material is always not single phase  $\text{RuO}_2$  as seen by XRD or EDX. Metallic Ru can be found as “impurity” even in XRD. Therefore commercial  $\text{RuO}_2$  was re-oxidized at 1023 K. This produces single crystals in the  $\mu\text{m}$  range evidenced by XRD and EBSD. These single crystals exhibit in contrast to the expected habit (four pronounced lateral surfaces) eight pronounced lateral surfaces. This may be caused by a reconstruction of the  $\{100\}$  surfaces into a  $c(2 \times 2)$  structure and of the  $\{110\}$  surfaces into microfaceted  $c(2 \times 2)-(100)$  surfaces. These  $\text{RuO}_2$  crystals are initially inactive in CO oxidation under ambient pressure flow conditions. The samples activate during an induction period of more than 24 h either in net-oxidizing or net-reducing conditions. Under net-oxidizing conditions kinetic oscillations occur as shown in Figure 5 right. The apical surfaces are strongly faceted but still smooth after becoming active. After

activation under net-reducing conditions the apical faces of the crystals are roughened. In both cases the sample is still RuO<sub>2</sub> by bulk-sensitive XRD but the rough faces are reduced (From EDX point analyses of morphologies seen in Figure 5 right) Under net-oxidizing conditions the sample bulk stays RuO<sub>2</sub> in all cases. In net-reducing conditions the phase evolves either into defective oxide or into metal plus sub-surface oxygen depending on the sample temperature (or synonymously on the heat of reaction).

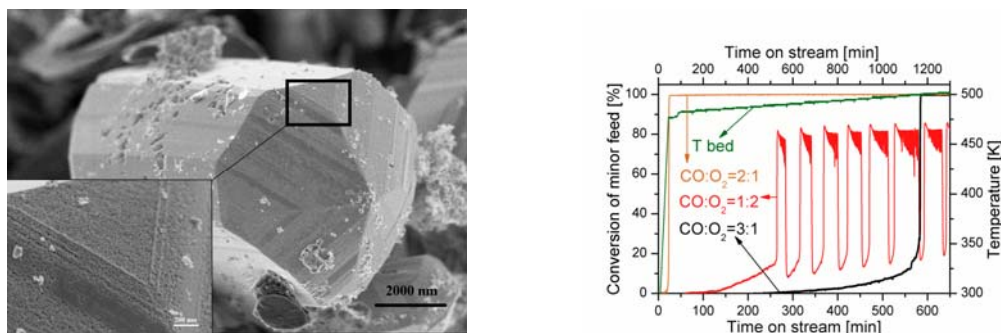
The large data set under atmospheric reaction conditions showed that heat and mass transport controls the phase evolution. The heated debate in the literature about the nature of the active phase is revolving around boundary conditions: the most active phase is metal plus sub-surface oxygen, followed by defective oxide and by pure metal. The frequently observed co-existence of phases is caused by the slow dynamic responses of the well-ordered Ru-O system to the local chemical potential and explains the apparently conflicting results in the literature.

In contrast to CO oxidation, the identification of possible reaction pathways for CH<sub>2</sub>O production from CH<sub>3</sub>OH is more complex. The present study of CH<sub>3</sub>OH oxidation on model Ru(0001), Ru(10-10) and polycrystalline Ru catalyst interrogates with in-situ photoemission the catalytically active states under different reaction conditions.

Ru 3d and O 1s core level spectra, measured with photon energies of 450eV and 650eV, respectively, were used as fingerprints for the dynamic response of the catalyst surface to changes in temperature and chemical potential realized by molecular mixing ratios. The gas phase products were monitored by mass spectrometry as a measure of the catalytic activity. The investigations were carried out in the pressure range of 10<sup>-2</sup> to 10<sup>-1</sup> mbar using different CH<sub>3</sub>OH:O<sub>2</sub> molecular mixing ratios and catalyst temperatures.

Our experiments reveal that the reaction pathways are identical on the (0001), (10-10) and polycrystalline Ru surface supporting a nano-structured catalytically active state without long-range order (structure insensitivity). This state was identified as a non-stoichiometric oxygen-doped metal Ru<sub>x</sub>O<sub>y</sub>. It is formed by interaction with the reactants in the gas phase independently of the initially present material be it oxide or metal.

Both activity and selectivity are very sensitive to the  $\text{CH}_3\text{OH}:\text{O}_2$  mixing ratio at a given temperature. Three different  $\text{CH}_3\text{OH}$  oxidation pathways, partial oxidation  $\text{CO}+\text{H}_2+\text{H}_2\text{O}$  (a) and  $\text{CH}_2\text{O}+\text{H}_2\text{O}$  (b) for ratios of 2.3 and 1.5, and full oxidation to  $\text{CO}_2+\text{H}_2\text{O}$  (c) at a ratio of 0.75 were found to be exclusively determined by the amount of accumulated oxygen (the  $y$  parameter in the  $\text{Ru}_x\text{O}_y$  formula)



**Figure 5:  $\text{RuO}_2$  in CO oxidation:** Left, SEM: One of the particles rarely observed with one rough lateral facet to be seen in the magnified micrograph. Right: Comparison of consecutive reaction experiments with varying feed composition, the temperature program is indicated.

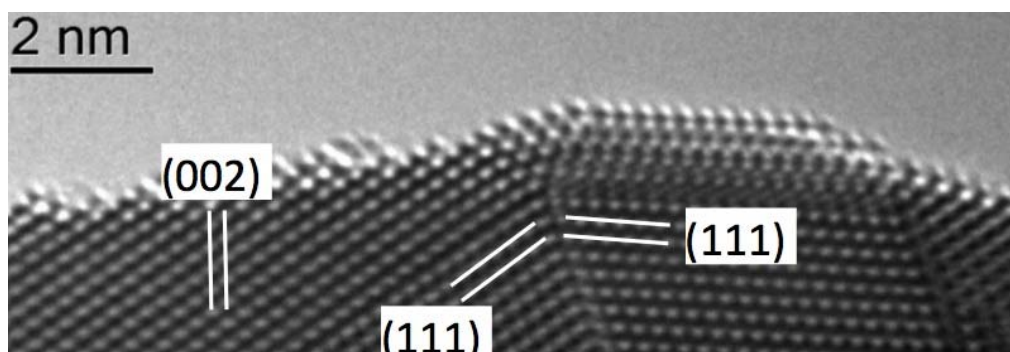
controlling the interaction of the catalyst surface with the reactants  $\text{CH}_3\text{OH}$  and  $\text{O}_2$ . From a quantitative structure-function correlation it occurs that the pure oxide phase  $\text{RuO}_2$  frequently advertised as the most active state is inactive in all 3 reaction pathways under all conditions used here. The dramatic changes in the selectivity relating to relatively small differences in the chemical state of  $\text{Ru}_x\text{O}_y$  demonstrate the critical relevance of the dynamic response of the catalyst to changes in the surrounding chemical potential as generalized in Figure 1. It is assumed that the variation in the  $y$  parameter changes the nature of the surface-adsorbed oxygen species between electrophilic and nucleophilic reactivity as evidenced in the Ag-O system.

#### 4.2.2. Silver in selective oxidation

The silver catalyzed partial oxidation of methanol and ethylene are two important catalytic reactions in the chemical industry [1,2]. Over the last 30 years, a wealth of information about mechanistic details of these reactions has been obtained and different oxygen surface species have been identified and assigned as active sites

[2,3]. However, recent experimental results and calculations have pointed out that this picture might be oversimplified and the role of different oxygen species as spectators or active site is not clear [4]. The complexity of the surface termination of such a simple object as a silver nanoparticle can be observed from Figure 6. This image is a result of the novel aberration-corrected TEM becoming operational throughout the last 6 month at the department. Obtaining such images without beam-damage artefacts is still a major challenge and cannot be considered as “analytical” technique. It is obvious that such a surface can host a range of oxygen atomic adsorbates with quite variable interactions to the metal.

In situ photoemission spectroscopy revealed the existence of four different atomic oxygen species for reference Ag foils under 0.5 mbar O<sub>2</sub> as shown in Figure 7. Their relative abundance was found to depend not only on the temperature, as can be seen in Figure 7, but also on the sample history and gas phase atmosphere. This

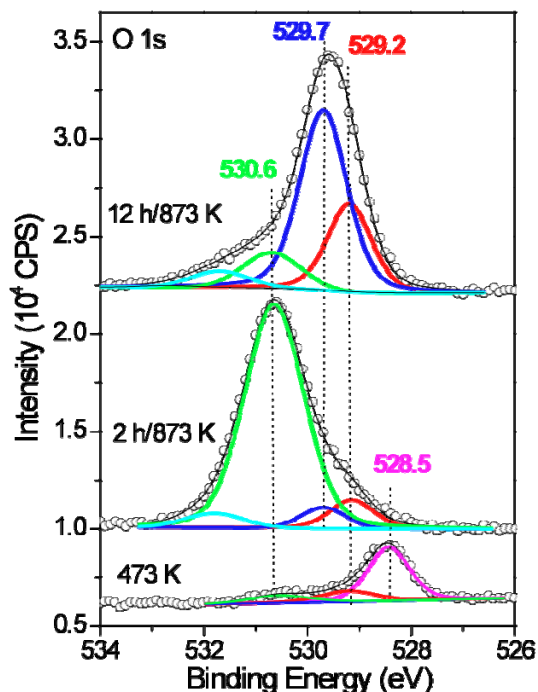


***Figure 6: Aberration-corrected HRTEM image of an Ag surface from a silver nanoparticle. The co-existence of translational terminations and highly defective surface patches on the same surface can clearly be seen. The blurred contrast of the disordered patches can be attributed to strongly bound atomic oxygen.***

clearly indicates the dynamic character of the Ag-O system under reaction conditions and explains the large number of apparently conflicting reports about oxygen species in the Ag-O system. Figure 6 provides an impression about the ease at which local restructuring may occur and hence “visualizes” the dynamic character of the system.

The different chemical nature of these oxygen species arises from the dissimilar bonding with the Ag host as it is evidenced by the binding energies, by the

formation of ionic Ag and also the by the temperature dependence of their relative abundance.



**Figure 7:** *in situ* O1s core-level spectra for Ag foil at 0.5 mbar O<sub>2</sub> and different temperatures, at 473 K (bottom spectra), at 873 K for 2 h (middle spectra) and after 12 h at 873 K (top spectra).

For different oxidation reactions using Ag foils and micrometer sized Ag powders, similar oxygen species were found, but with different concentrations in each case. Oxygen species around 530.7 eV are present for both methanol and ethylene

oxidations. However, while at 500 K under ethylene epoxidation, these species are localized in the surface and respond to changes in the gas phase, they are dispersed in the bulk at 873 K under methanol oxidation conditions, being less sensitive to changes in the gas phase. Moreover, during ethylene oxidation, the species with 529.2 eV binding energy are much more abundant than those emitting at 529.7 eV. On the other hand, for the methanol oxidation, the species at 529.2 eV are very scarce, while the species at 529.7 eV are more evident and exhibit a structure-function correlation with both activity and product ratio, suggesting their role as active species in this reaction. Experiments with improved gas analytics are planned to quantitatively correlate the activity and selectivity of both reactions with the oxygen species identified by *in situ* XPS.

The Ag-Cu alloy, recently proposed as an improved catalyst for ethylene epoxidation [5], was also investigated by a combination of first-principles calculations with *in situ* photoelectron spectroscopy [6]. We studied how the composition and structure of the catalyst surface is affected by the temperature



and partial pressure of the reagents. The formation of a thin Cu-O surface oxide occurred under reaction conditions while the surface alloy was found to be unstable. Several possible surface structures were identified, among which the surface is likely to dynamically evolve under reaction conditions. In agreement with the literature the beneficial effect of the presence of a thin layer of oxidized copper was clearly found; the addition of the typical co-catalyst chlorine immediately and irreversibly destroyed the positive effect of the Cu species.

#### **4.2.3. Adsorption microcalorimetry**

Adsorption microcalorimetry is a direct method to determine number, strength and energy distribution of the adsorption sites on a catalyst. It allows for measuring the differential heats evolved when known amounts of gas probe molecules are adsorbed on the catalyst surface. The evolved heat is related to the energy of the bonds formed between the adsorbed species and the adsorbent and hence to the nature of the bonds and to the chemical reactivity of the surface. The data obtained of substantial value for comparing theoretical and experimental hypotheses about reaction pathways. For this reason the method was broadly employed in several projects of the department and yielded a surprising spread of energetic data for the same molecule on different surfaces, some of which are given in the Table.

As an example for the non-intuitive results of calorimetry, an activation study of Pt-doped H-mordenite (Pt/HM) is used being relevant as a solid acid catalyst for the isomerization of light alkanes [7]. To establish correlations between the surface sites and catalytic properties we studied (i) *n*-butane adsorption by microcalorimetry at 313K, (ii) CO adsorption by FTIR spectroscopy at RT, and (iii) catalytic activity in the isomerization of *n*-butane at 623 K. From Figure 8a and 8b we can conclude that preparations of Pt/HM with high platinum dispersion are highly active for *n*-butane isomerization only when activated properly.

**Selected calorimetric measurements on supported metal oxide and mixed metal oxides .**

Probe molecule	Catalyst / Activation / Catalytic activity	T <sub>adsorption</sub> [K]	q <sub>initial</sub> <sup>+</sup> [kJ/mol]
<i>n</i> -butane	0.5wt%Pt/H-Mordenite / H <sub>2</sub> reduced at 648 K /active	313	350
<i>n</i> -butane	0.5wt%Pt/H-Mordenite / dehydr. at 723 K / less active	313	42
<i>n</i> -butane	3.5wt% VO <sub>x</sub> -Al <sub>2</sub> O <sub>3</sub> / H <sub>2</sub> reduced at 773 K /active	313	63
<i>n</i> -butane	Θ Al <sub>2</sub> O <sub>3</sub> / H <sub>2</sub> reduced at 773 K /non-active	313	35
propane	10 wt% V <sub>x</sub> O <sub>y</sub> -SBA15 / dehydrated at 373 K / active	313	45 80 160
propane	3 wt% V <sub>x</sub> O <sub>y</sub> -SBA15 / dehydrated at 373 K / active	313	45
propane	SBA15 / dehydrated at 373 K / non-active	313	32
propane	hydrothermal synth. – M1 /dehydr. at 423 K /active, 58*	313	71
propane	precipitation – M1 /dehydrated at 423 K /active , 43*	313	56
propane	SHWVT ** – M1 / dehydrated at 423 K / active, 5*	313	64
CO <sub>2</sub>	CNFox functionalized by NH <sub>3</sub> at 873 K	313	150
	673 K		50
	473 K		90
CO <sub>2</sub>	Fe-CNT / dehydrated at 373 K	313	272
	FeIO-XT 24PS-CT / dehydrated at 373 K		191
O <sub>2</sub> ***	precipitation – M1 / H <sub>2</sub> activated at 653 K	473	218
	precipitation – M1 / propane activated at 653 K		257
O <sub>2</sub> ***	8wt%V <sub>x</sub> O <sub>y</sub> -SBA15 / dehydrated at 673 K	473	248

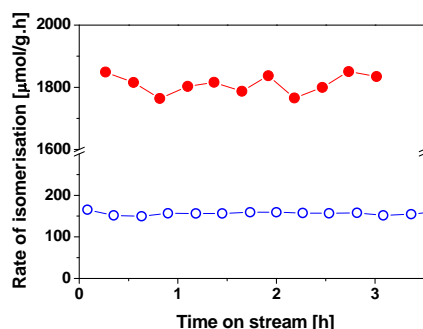
<sup>+</sup> We have adopted the calorimetric sign criterion (positive energetic quantity for an exothermic process).

\* partial oxidation of propane (POP); Selectivity to acrylic acid [mol-%]

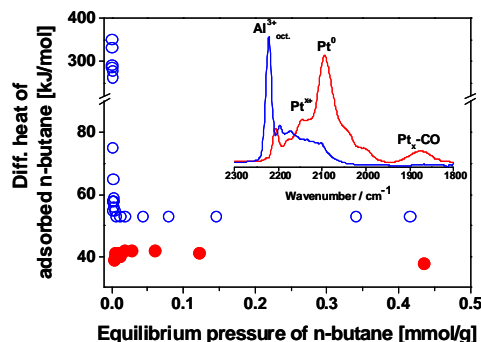
\*\* superheated-water vapor treatment (SHWVT)

\*\*\* cooperation with Instituto de Química Física "Rocasolano", CSIC, Madrid (Spain)

The active state of Pt/HM is characterized by Brønsted-acidic bridging OH groups, by a small amount of Lewis acid sites (Al<sup>3+</sup>oct., extraframework alumina), by small metallic platinum particles, and interestingly by an overall weak interaction of the surface acid sites with *n*-butane.



**Figure 8a:** *n*-Butane isomerization in a flow of 15 kPa *n*-butane in H<sub>2</sub> on a fully H<sub>2</sub>-reduced Pt/HM (red) and not completely H<sub>2</sub>-reduced Pt/HM (blue) at 623 K.



**Figure 8b:** Differential heats of *n*-butane adsorption at 313 K on almost fully H<sub>2</sub>-reduced Pt/HM (red) and not completed H<sub>2</sub>-reduced Pt/HM (blue).

Inset: IR spectra of CO adsorption at RT of both samples.

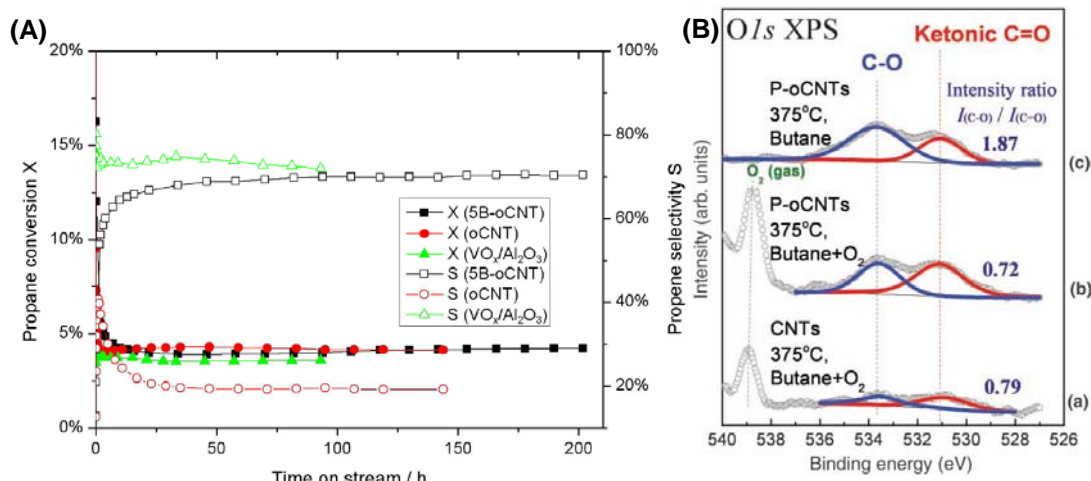
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### 4.3. Nanostructured Carbon in Catalysis

#### 4.3.1. CNT as catalysts for C3 ODH

In the past years, the research work on gas phase reactions using CNTs as catalysts moved from the oxidative dehydrogenation (ODH) reaction of ethylbenzene [1-5] to the more challenging activation of lower alkanes [6-9], where the selectivity issue plays an important role. Without further surface modification, nanocarbons are active, but poor catalysts for the activation of the lower hydrocarbons due to the total oxidation of the substrate and the consecutive combustion of the alkene [6]. The surface modification of CNTs with  $P_2O_5$  and  $B_2O_3$  has been performed to increase the alkene selectivity [6, 7]. The activation of *n*-butane, propane, and ethane over these new materials provides alkene yields comparable to supported vanadia catalysts. Using a low  $O_2$ /alkane ratio of 0.5–1 at 673 K, the modified CNT catalyst maintains a high activity, i.e., suffers neither oxidation nor coking, for a period as long as up to 200 h time-on stream, whereas the selectivity at almost iso-conversion increases from 20% (oCNTs) up to 70% (5 wt%  $B_2O_3$ -oCNTs and  $VO_x/Al_2O_3$ ) (Fig. 9A) [7, 8]. The CNTs can resist the surface modification and a wide range of ODH reaction conditions without structural damage. The initial evolution of activity is determined by the decomposition of labile functional groups (carboxylic acid and anhydride, lactone), and their replacement by high-temperature stable ketones and quinones. *In-situ* generated diketonic C=O groups mildly catalyze the selective ODH, and apparently mimic the function of vanadyl oxygen in vanadia catalysts. The reaction intermediates were investigated by an *in-situ* XPS study (Fig. 9B). During ODH of *n*-butane, the intensity ratio  $I_{C-O}/I_{C=O}$  of C–O single bonds and

C=O double bonds on the carbon surface is almost the same for pristine and P<sub>2</sub>O<sub>5</sub> modified CNTs at 0.75±0.05, but drastically increases (1.87) if oxygen is removed from the feed gas. This finding indicates that diketonic C=O groups are a critical ingredient of the active sites whereas C–O groups constitute inactive intermediates or adsorbates [6].



**Figure 9** (A) ODH of propane over oCNTs, 5 wt% B<sub>2</sub>O<sub>3</sub>-oCNTs, and VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>; C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub>/He = 1:1:48, 673 K; (B) In-situ O1s XP spectra of catalysts during ODH of n-butane taken at 648 K: (a) CNTs: n-C<sub>4</sub>H<sub>8</sub>/O<sub>2</sub> = 1:1, 0.25 mbar; (b) 5 wt% P<sub>2</sub>O<sub>5</sub>-oCNTs, n-C<sub>4</sub>H<sub>8</sub>/O<sub>2</sub> = 1:1, 0.25 mbar; (c) 5 wt% P<sub>2</sub>O<sub>5</sub>-oCNTs, n-C<sub>4</sub>H<sub>8</sub>, 0.125 mbar.

This finding is in excellent agreement with a model study using a pre-designed aromatic molecule with diketonic functions that was performed within the *enerchem* collaboration with K. Müllen. The catalytic activity in ethylbenzene ODH of this solid system representing “pure active sites” was about 40 times higher than of the best [5] heterogeneous catalyst.

Temperature-programmed oxidation proves both the high thermal stability of the composites and their enhanced resistance against O<sub>2</sub> as compared to the pristine CNTs. B<sub>2</sub>O<sub>3</sub> as electron attracting promoter hinders the adsorption of O<sub>2</sub> and blocks unselective active domains. With <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> in the gas phase, the formation of mixed labeled oxygen is only observed for the non-modified CNTs, its intermediates being most likely the origin of direct alkane combustion and low alkene selectivity. Besides the interaction of the hydrocarbons with the *oxidized* surface also the adsorption on the *reduced* surface is detrimental for the alkene selectivity [7, 8]. Again the surface modified CNTs show superior performance

over the non-modified samples [8, 9]. In both cases,  $C_3H_8$  once adsorbed on the reduced surface inevitably yields  $CO_x$  by interaction with  $O_2$ , however, the surface modification with  $B_2O_3$  and  $P_2O_5$  here drastically reduces the amount of hydrocarbon adsorbed. Consequently, for the non-modified CNTs, the  $C_3H_6$  yield is the highest under  $O_2$ -rich reaction conditions. In the cyclic mode, for all the samples the amount of  $C_3H_6$  formed during one catalysis cycle is almost the same, indicating that the surface modification affects solely the non-selective active sites on the carbon catalyst.

The studies provide an interesting material alternative to oxide catalysts and exhibit interesting thermal properties. In a collaborative effort with groups from chemical engineering an attempt will be made to design other reactor concepts for partial oxidation in order to interrogate the influence of the omni-present plug-flow reactor concept on catalyst performance. In any case the CNT family provides the material for studying selective oxidation with the strict exclusion of lattice oxygen and outside of the “Mars-van Krevelen” kinetic concept.

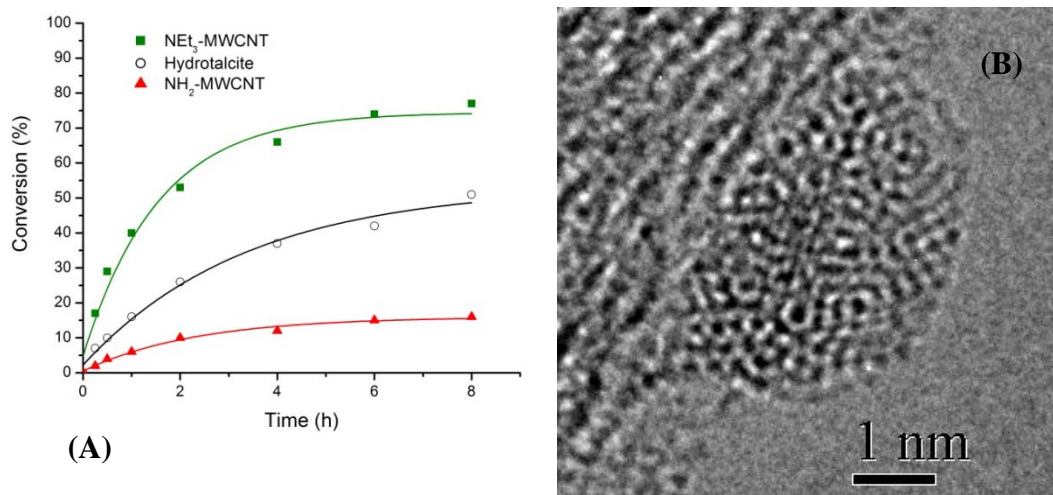
#### **4.3.2. Basic CNT and fluid phase reactions**

Heteroatom functionalization of nanotubes, i.e., by oxygen or nitrogen, can control the hydrophilic/hydrophobic character as well as the acid-base properties. Two different nitrogen functionalization routes were explored: wet chemistry and gas phase post-treatment with ammonia. For the former, we employed organic chemistry reactions to graft the desired groups on the surface of the CNTs [10]. With this technique, we are aiming for a single-site design of the catalyst. For the latter, carbon nanostructures are treated at high temperature (200–600 °C) with ammonia [11].

The grafting of amino groups on oxidized CNTs may suffer from the co-existence of acidic oxygen-containing groups and basic amino groups on the surface, which can significantly decrease the basic character of the sample. We therefore developed a novel synthetic route to graft the desired molecules on surface defects of pristine CNTs, directly via C-C coupling. C-H bonds located at defects (vacancies, terminations) are activated by *n*-butyllithium to form surface

carbanions. A bromoamine, i.e., 2-diethylaminoethylbromide, is then added for electrophilic attack of the CNTs. A C-C bond between the CNT and the functional group is created, thus leading to grafted triethylamino groups [10]. This synthesis procedure allows the grafting of a high concentration of groups ( $1 \text{ mmol g}^{-1}$ ), homogeneously distributed on both the internal and external surfaces with remarkable thermal stability (60% of the groups are stable up to  $570^\circ\text{C}$ ). When dispersed in water, the sample increases the pH to 10.3.

It was shown in the 1990s that carbon materials can be “doped” with nitrogen by simple treatment with gaseous ammonia. We explored this route to insert nitrogen in vapor grown carbon nanofibers (VGCNFs). High nitrogen concentrations in the VGCNFs sample can only be achieved after pre-treatment with nitric acid. At the low temperatures employed ( $200\text{--}600^\circ\text{C}$ ),  $\text{NH}_3$  hardly reacts with non-functionalized carbon. However, when oxygen is present on the surface, nitrogen is inserted on the surface by amination and amidation reactions. We found that the nature of the nitrogen-containing functional groups and the ratio between different species depend on the reaction temperature. This technique therefore allows controlling the surface acid-base properties of VGCNFs via functionalization [11]. When used as a support for catalytically active metal nanoparticles, the local modification of the carbon electronic structure induced by the functionalization



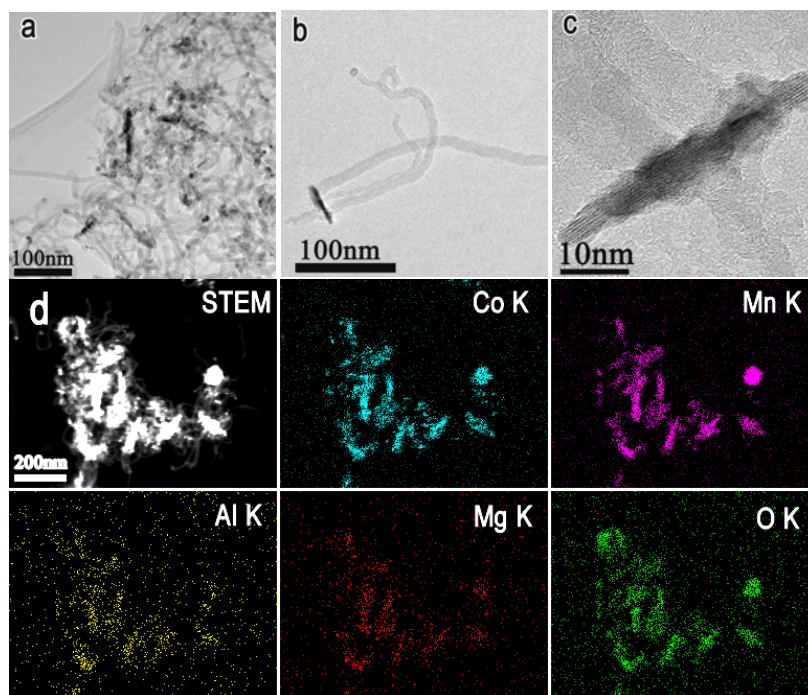
**Figure 10.** (A) Catalytic performance of N-CNTs synthesized by grafting using the electrophilic attack route (■) and the oxidation/amidation route (▲). (B) Cs-corrected HRTEM image of a Pd particle on a N-VGCNF.

leads to a stronger metal-support interaction. This results in a more homogenous distribution of metal particles and to the stabilization of non-equilibrated and hence supposed-to-be more active metal species as shown in Figure 10 B [12]. The N-CNTs catalysts synthesized by grafting were tested in the transesterification of glyceryl tributyrate with methanol (Figure 10A), as a model reaction for base-catalyzed biomass transformations [13]. The catalytic tests show a rapid deactivation of the sample prepared via oxidation/amidation due to the leaching of the amino groups. In contrast, the catalyst prepared via the electrophilic attack route exhibits a higher activity than hydrotalcite, which is a reference catalyst for this reaction, or than N-CNTs synthesized by gas-phase procedures lacking many sites of high basicity. The grafting of amino groups onto CNTs is a suitable method to obtain active and stable basic catalysts for application in liquid phase reactions. Only a slight deactivation was detected after 10 runs, due to the leaching of a small amount of the anchored amines (4%) and the inevitable loss of catalyst during the recycling test in the batch reactor [13]. A series of Pd@N-VGCFs catalysts was tested in the oxidation of benzyl alcohol to benzaldehyde. The results indicate that the presence of N hetero-cyclic moieties on the surface of CNFs is beneficial for improving the wetting of the metal and thus the formation of “raft” metal particles (see Figure 10B) exhibiting many non-equilibrium sites with respect to (111)-terminated Pd particles often found on conventional carbon-based catalysts.

#### **4.3.3. CoMnAlMg systems for CNT synthesis**

Although the CNT synthesis field has been extremely active over the past 15 years, research is ongoing to develop catalysts with higher activity, stability and selectivity towards CNTs. In multi-metal systems, the active centers in CoMnAlMg catalysts lead to a 10 fold higher CNT yield than catalysts typically reported in the literature. It is speculated that an electronic factor should improve the CNT yield; we considered alternatively the in-situ nano-structuring of the active phase through components of the catalyst mixture. The study is conducted in collaboration with the group of *M. Muhler* (Bochum) taking care about the complementing microkinetic analysis.

CoMnAlMg mixed oxides were prepared by co-precipitation using the nitrate precursors, followed by drying and calcination. XRD and TEM showed that after calcination, Co atoms are dispersed in mixed oxide particles with a spinel structure.



**Figure 11.** TEM images (a-c) and elemental mapping (d) of the catalyst after 6 s on stream at 485°C. The data provide an example of the analytical capabilities at the meso scale of the department.

Catalyst grains of 250-355  $\mu\text{m}$  in diameter were exposed to a  $\text{C}_2\text{H}_4/\text{H}_2$  mixture at 650°C as well as at 485°C for a short times (between 6 s and 10 min) in order to investigate the growth mechanism of the CNTs on a macro- and on a microscopic level. For both reaction temperatures, the catalyst grains follow the expanding universe mechanism: the CNT growth on the surface and in the bulk of the porous material leads to its exponential fragmentation into smaller particles. This particular mechanism leads, after synthesis, to grains made of entangled CNTs. On a microscopic level, the CNTs follow the tip growth mechanism when the reaction is performed at 650°C. Cobalt atoms are reduced and sinter to form particles of ca. 10 nm in diameter which then catalyze the CNT synthesis. The Co dispersion in the initial mixed oxide leads to Co particles with a narrow size distribution and therefore to CNTs with homogeneous size and structure. Sintering of the Co atoms was not observed at 485°C. In this case, CNTs grow



directly from the mixed oxide particles, following a root growth mechanism (Figure 11). The data clearly indicate the beneficial effect of this complex catalyst not to be caused by a single microscopic effect (alloying of Co) but through the in-situ structuring at the mesoscopic scale of a single-species catalyst (Co metal) brought into the right form and place through the interaction of the catalyst with its reactants.

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## 4.4. Selective oxidation

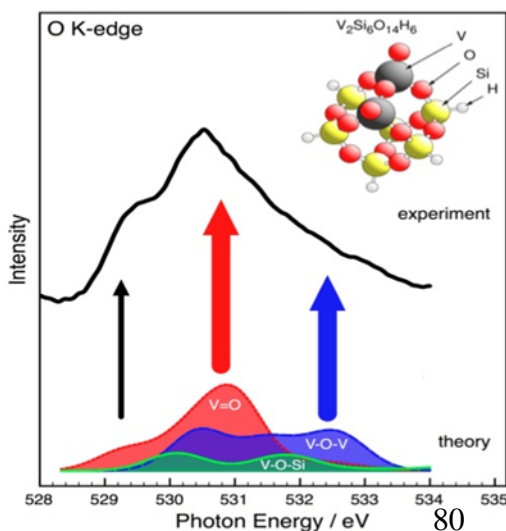
### 4.4.1. V-SBA 15 systems

Highly dispersed vanadium oxide supported on mesoporous silica (SBA-15) is used as model system to investigate the effect of the degree of aggregation of vanadium oxo-species on the reactivity in oxidative dehydrogenation of propane. The model catalysts are prepared via a multistep ion exchange synthesis [1]. Compared to impregnation techniques, the ion exchange procedure allows better control of vanadia dispersion and provides homogeneous, well-defined materials. Since the quality of SBA-15 is critical with respect to stability of the hexagonal pore structure during subsequent calcination of the supported vanadium oxide at 823 K, the SBA-15 synthesis [2] has been optimized resulting in a reproducible and robust procedure achieving batch sizes of approximately 25 g [3].

V/SBA-15 catalysts with varying vanadia loading were prepared and characterized by small angle X-ray diffraction, N<sub>2</sub> adsorption, electron microscopy, UV-vis, Raman, and infrared spectroscopy. The adsorption of propane was studied by microcalorimetry. The number of adsorbed propane molecules per surface area increases with increasing vanadium content indicating that propane is also adsorbed on surface sites associated with vanadium species. The differential heat of adsorption of propane on V/SBA-15 dehydrated in vacuum at 373 K is approximately 45 kJ·mol<sup>-1</sup>, which is only slightly higher than the heat of adsorption of propane determined on SBA-15 [4]. The differential heat at low surface coverage increases significantly (170 kJ·mol<sup>-1</sup>) after dehydration in vacuum at 673 K due to stronger interaction of propane with coordinatively unsaturated vanadium species. The quantitative determination of the abundance of hydroxyl groups shows that under dehydration conditions an excess of hydroxyl groups (e.g. about 10 OH but 2 V groups per nm<sup>2</sup>) over the vanadia species remains on the surface allowing concluding that despite of the “dehydrated” vanadia groups some hydroxyl species may play a role in the reaction pathway.

A kinetic study in a fixed bed reactor revealed that the oxidative dehydrogenation of propane on highly dispersed vanadium oxide supported on SBA-15 (0.7 V/nm<sup>2</sup>) is described by a simple consecutive mechanism with negligible contributions of propane combustion [4]. Further kinetic studies are necessary to understand the effect of V<sub>x</sub>O<sub>y</sub> cluster size on the catalytic properties.

It is noteworthy that UV-vis, Raman, and NEXAFS experiments are differently sensitive to structural characteristics of supported vanadium oxide [3]. The degree of aggregation of vanadium oxo-species on the silica surface was studied by



**Figure 12: Comparison of experimental O K-edge in-situ NEXAFS (0.5 mbar oxygen, 723 K) and theoretical absorption bands from model structures. The black arrow designates contributions from V<sub>2</sub>O<sub>5</sub>-like structures, whereas the coloured arrows indicate the absorption bands from terminal (red) and bridging (blue) oxygen atoms in monomeric and oligomeric species.**

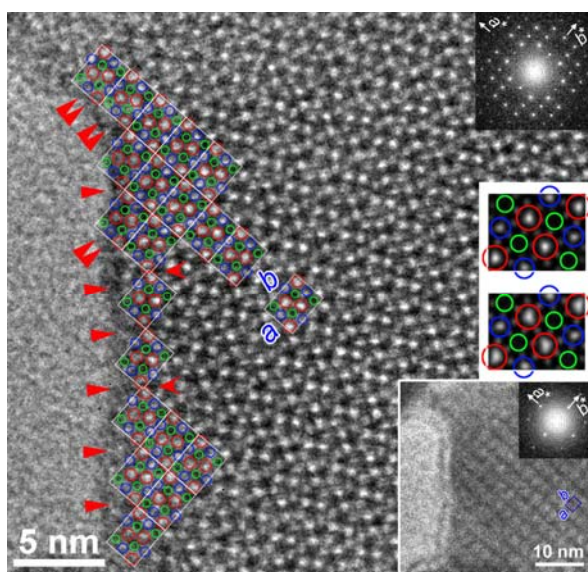
combining *in-situ* X-ray absorption fine structure (NEXAFS) measurements at the oxygen K-edge with density-functional theory (DFT) calculations on oxygen core excitations in vanadia-silica cluster models. A characteristic result that was persistent over several families of synthetic reproductions is shown in Figure 12. The comparison of theoretical and experimental NEXAFS spectra resulting from an intense collaboration with *K. Hermann* from the *TH department* provides evidence that dispersed vanadium oxo-species even in the highest dilution ( $0.7 \text{ V/nm}^2$ ) are present not only as monomeric, but also as poly-oxo clusters on the surface of SBA-15 [5]. This mixed connectivity prevails over higher loadings with a gradual intergrowth of vanadium oxide nanocrystals until transformation into  $\text{V}_2\text{O}_5$  occurs at loadings around 10 wt% vanadium in excellent agreement with literature studies based on RAMAN and UV spectroscopies.

#### **4.4.2. MoVTe systems**

Ethane, propane, and *n*-butane are converted with high efficiency into oxygenates over complex crystalline bulk catalysts containing vanadium as primary framework component. Correlations between structural characteristics, surface termination and catalytic properties in selective oxidation of propane to acrylic acid have been studied over phase-pure  $\text{MoVTenbO}_x$  model catalysts consisting of an orthorhombic bronze-like phase denominated as M1 (ICSD 55097). The catalysts were prepared by hydrothermal synthesis in batch sizes of approximately 10 g without further product purification by chemical treatment. The synthesis conditions have been optimized regarding temperature, time, composition and concentration of the starting solutions [6]. The chemical composition of M1 was varied resulting in homogeneous, isostructural materials within the now known phase width of the M1 structure with different metal site occupancies for all four metal components as shown by EXAFS [7]. It is found that the structure is quite sensitive to the V-content but tolerates larger variations in the other constituents namely Mo. The bulk compositional differences are reflected in the variation of the lattice parameters and in the chemical composition at the surface showing a good correlation between the concentrations of the metals in the crystalline bulk as analyzed by EDX and ICP-OES and in the near surface region (information

depth 0.8 nm) as measured by surface-sensitive synchrotron-XPS. The slopes of the bulk-surface compositional correlations are different from unity, which is indicative of a surface stoichiometry that is different from the crystallographic stoichiometry of the M1 unit cell (Figure 13).

*In-situ* XPS experiments revealed an enhanced mobility of Te especially in presence of water vapor [8]. The surface termination of the rod-like M1 crystals is anisotropic with respect to chemical composition and abundance of structural motives implying crystal plane specificity (structure sensitivity) of the selective oxidation of propane. The role of the (001) crystallographic plane (see Figure 13),



**Figure 13.** HR-TEM image of the M1 phase along the  $\langle 001 \rangle$  direction near Scherzer focus illustrating the termination of M1; inset bottom: image taken far from Scherzer focus visualizing the M1 unit cells; inset top: Fast Fourier Transform (FFT); insets center: simulated images (conditioned at a thickness of 13.2 nm and  $\Delta f = -10$  nm) using crystallographic models with (top) and without (bottom) Te in the heptagonal channels (red); hexagonal channels are indicated in blue and pentagonal motives are indicated in green.

which is the basal plane of the cylindrical M1 particles, was addressed by preparing a model catalyst preferentially exposing this surface. The specific rate of formation of acrylic acid on the model catalyst was found to be similar to that on the phase-pure M1 reference material, indicating that the (001) plane of the M1 crystal structure did not have better catalytic properties compared with the lateral surface of the cylindrical M1 particles in propane oxidation [9]. Excitation-energy-dependent valence band spectra of M1 MoVTaNb oxide clearly reveal a substantial covalent character of the metal-oxygen bonds in M1 under reaction conditions [10]. It is proposed that surface restructuring (see Figure 13 terminating layer perpendicular to (001)) and possible formation of M-Te linkages leading to heteropoly oxometalate clusters may provoke spatial isolation of vanadium-containing active sites embedded in an insulating matrix on the surface

of the semiconductor M1. In contrast to other crystalline phases, such as the tetragonal  $\text{Mo}_5\text{O}_{14}$ -type structure, the orthorhombic M1 phase seems to fulfill the critical catalyst requirement to segregate only as 2-D structure at reaction temperature and under the chemical potential of all reactants. We envisage a terminating V/Te ternary layer containing the active sites, that energetically stabilizes the M1 crystals and prevents their decomposition into more stable constituents such as  $\text{MoO}_3$  being detrimental for selective catalytic performance due to their total oxidation activity. Such a layer structure accounts further for the observed structure insensitivity of the catalytic performance in spite of the pronounced anisotropy of the bulk structure

#### 4.4.3. Synthesis of binary and ternary model carbide catalysts

The use of multi-metal oxides as precursors for carbides is a largely unexplored area of transition metal carbide chemistry. In particular it offers interesting possibilities to produce tailored carbides with enhanced oxidative stability, higher surface areas, and improved catalytic selectivity and performance. Starting from single phase mixed-metal oxide precursors such as  $h\text{-(Mo,V)O}_3$ -type oxides,  $\text{M}_5\text{O}_{14}$ -type structures, ( $\text{M} = \text{Mo, V, Nb}$ ), other oxidic bronzes and polyoxometallate species, a range of binary and ternary transition metal carbides with tunable compositions and nanostructures were synthesized. These oxides were carburized in a temperature-programmed reaction (TPR) according to well established methods and the phase development was followed using *in-situ* powder X-ray diffraction. The catalytic properties of the novel materials are currently explored in non-oxidative and oxidative alkane conversions. Besides possible useful catalytic applications of the resulting carbides, it seems adequate to explore the synthesis and performance of mixed-metal carbides as one realisation of the reduced catalyst species proposed in Figure 1. The inter-conversion between oxide and carbide with its related switching in catalytic function could provide an insight into reaction sequences occurring during selective oxidation under strong gradients in oxygen chemical potential as found in plug-flow reactor geometries.

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#### **4.5. Emmy Noether Group „High Temperature Catalysis”**

The research in the high temperature catalysis project focuses on the catalytic oxidation of methane to valuable intermediates like synthesis gas or ethylene. Depending on the reaction (e.g. methane oxidative coupling to ethylene on Li/MgO or autothermal methane oxidation to synthesis gas on Pt) the catalyst operates at temperatures between 550°C and 1300°C which coined the term “high temperature catalysis”. The research is conducted within the “Emmy Noether Junior Research Group” “High Temperature Catalysis” associated to the Department of Inorganic Chemistry since Juli 2008. Besides funding from the German Research Foundation and from the department, additional funds are provided by the Berlin COE UniCat founded in November 2007 with the Inorganic Chemistry Department being a founding member. The Emmy Noether Group became member in UniCat in December 2008.

High temperature catalytic reactions have in common that the chemical transformations at the catalyst surface are typically very fast leading to a pronounced impact of mass and heat transport on the reaction performance. Furthermore, gas phase reaction channels mediated by free radicals can open up either just because the temperatures are sufficient to overcome the high activation barriers in the gas phase or because the catalyst releases radicals into the gas phase [1]. The research strategy in the high temperature catalysis project is therefore to develop reactor and spectroscopic experiments that allow studying these reactions in situ, i.e. at temperatures up to 1300°C and atmospheric or even elevated pressure. A dedicated high temperature catalysis lab has been established in the Inorganic Chemistry Department equipped with a high temperature/high

pressure reactor for spatial profile measurements, a research grade Raman spectrometer, a molecular beam mass spectrometer and several CW or pulsed laser systems for Raman, Fluorescence and Cavity Ringdown Spectroscopy. The set-up of the laboratory is constantly supported through collaboration and advice offered by the *MP department* through *G. Meijer*.

#### 4.5.1 Methane Oxidation on Pt

Methane oxidation on Pt has been studied by spatial reactor profile measurements and molecular beam mass spectrometry (MBMS) with threshold ionization. For spatial profile measurements Pt nanoparticles were deposited on reticulated  $\alpha$ - $\text{Al}_2\text{O}_3$  foam supports by Microwave Assisted Combustion Synthesis [2]. Gas phase radicals were studied by MBMS in a Pt catalytic wall reactor<sup>3,4</sup>. The species profiles in Fig. 14a at 1.4 bar and the  $\text{O}_2$  profiles at various pressures in Fig. 14b show that methane oxidation proceeds very fast in a narrow oxidation zone right at the catalyst entrance (0-2000 $\mu\text{m}$ ). The oxidation products are  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , CO and  $\text{CO}_2$ . Upon conversion of all gas phase  $\text{O}_2$ , secondary catalytic reactions such as steam reforming and watergas shift take place (2000-20000 $\mu\text{m}$ ).  $\text{CO}_2$  reforming is not observed. Spatial profile measurements from 1.4bar-15bar (Fig. 14b) indicate nearly pressure-independent catalytic performance which we attribute to a zeroth order kinetics caused by blockage of nearly all available catalytic sites. In situ Raman measurements indicate formation of highly defective  $\text{sp}^2$  carbon under reaction conditions. At pressures above 10bar methane gas phase oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  starts becoming important as indicated by pre-catalytic  $\text{O}_2$  conversion (-10000 $\mu\text{m}$ -0 $\mu\text{m}$ ). At very high reaction temperatures (>1150 $^\circ\text{C}$ ) and low surface to volume ratios C2 coupling products such as ethane, ethylene and acetylene are formed [4]. Quantitative in situ measurements of  $\text{CH}_3\cdot$  radicals by MBMS [3] reveal that the C2 products are probably formed in the gas phase driven by heat from exothermic oxidation reactions at the Pt surface. The  $\text{CH}_3\cdot$  radicals react in gas phase radical chain reactions with  $\text{CH}_4$  molecules to  $\text{C}_2\text{H}_6$  as the primary product which is then dehydrogenated to  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  respectively. No evidence for catalytic generation of  $\text{CH}_3\cdot$  radicals was found.

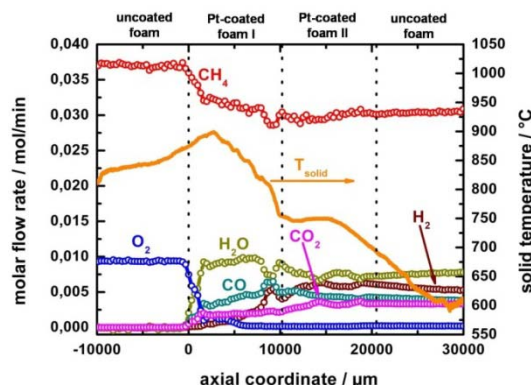


Fig. 14a: Surface temperature and species profiles for autothermal methane oxidation on Pt coated foam catalysts at 1.4bar.

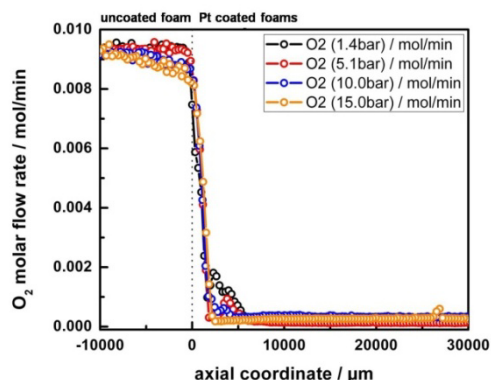


Fig. 14b:  $O_2$  profiles at various pressures from 1.4bar to 15bar indicating zeroth order kinetics and pre-catalytic gas phase chemistry.

#### 4.5.2.Oxidative Coupling of Methane (OCM) on Li/MgO

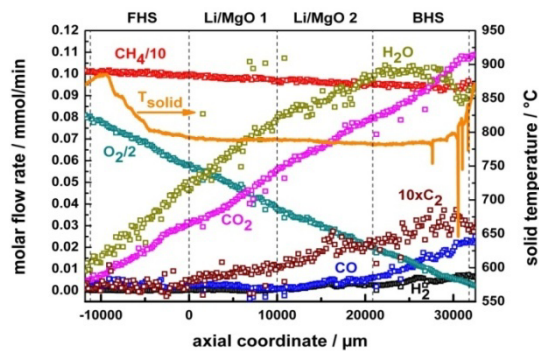
Oxidative coupling of methane to ethylene on Li/MgO is one of the main research subjects within UniCat. Task of the research in the Inorganic Chemistry Department is to help bridging the gap between theory, surface science and model catalysis (area A1) and chemical engineering (area C) by studying the catalyst material chemistry of Li/MgO and by investigating the interaction between surface and gas phase microkinetics and transport phenomena (macrokinetics) and by performing in situ spectroscopy at OCM reaction conditions. To accomplish this goal defect rich Li/MgO catalysts with various Li concentrations (0-40 wt%) were prepared by combustion synthesis. As shown by UV/Vis and fluorescence spectroscopy, the concentration of defects such as low coordinated  $O^{2-}$  ions at terraces, steps, corners and kinks of the MgO nanocrystals increased with increasing Li concentration even though the surface area decreased dramatically. The tool of fluorescence spectroscopy (Figure 15b) can be applied also as in-situ probe to sample dynamical changes during reaction at high-performance conditions. In a close collaboration with the CP department (Drs Nilius, Sterrer, Risse) who study the same system, it is possible to assign the different emission bands to surface and bulk residing defects by comparing our spectra to those obtained from electron injection-induced light emission from model surfaces.

XRD shows that the “as prepared” catalysts consisted of a MgO and a  $Li_2CO_3$  phase. Upon calcination in Ar or  $O_2$  the  $Li_2CO_3$  phase decomposes under  $CO_2$

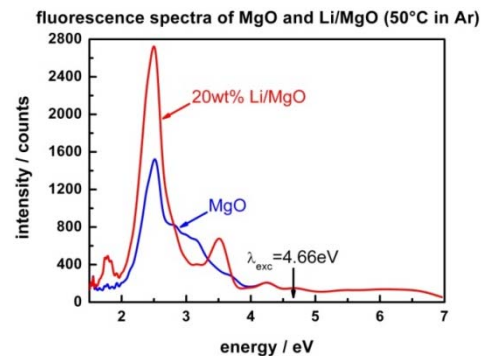


evolution without that an additional Li containing phase was observed by XRD. All catalysts were active for oxidative coupling of methane to ethylene. Without Li doping (pure MgO) the activity is lower than for the Li doped samples but the onset temperature for C<sub>2</sub> formation (~550°C) is the same as with Li doping indicating that the same sites are active for C<sub>2</sub> formation on MgO and Li/MgO. The higher activity of Li/MgO might be attributed to a higher concentration of active sites on Li/MgO compared to pure MgO. Fluorescence spectroscopy (see Figure 15b) with UV excitation seems to be an adequate tool to study defects on MgO and Li/MgO under reaction conditions even though an assignment of the observed fluorescence bands is still missing. The assignment of these bands is work in progress in collaboration with the *CP department* and with the theory group at HU Berlin (*J. Sauer*).

For spatial profiles measurements reticulated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> foam supports were coated by a thin layer (~200nm) of Li/MgO using again combustion synthesis. The profile measurements reveal as shown in Figure 15 a zeroth order methane total oxidation in the gas phase along the entire foam stack consisting of an uncoated front foam, two catalyst coated foams and an uncoated back foam. C<sub>2</sub> formation starts with begin of the catalyst foams but continues also in the uncoated back foam. Further investigation will be required to investigate whether this post-catalytic C<sub>2</sub> formation is due to catalyst induced gas phase chemistry or because some catalytic material was transported with the flow into the uncoated back foam. Based on the results of the profile measurements a reaction cell with molecular beam sampling will be constructed and inserted into the MBMS for radical screening of the gas phase under OCM conditions. Because the MBMS is good for screening but difficult to quantify, Cavity Ringdown Spectroscopy [5] downstream the sampling orifice will be used for radical quantification required as input information for modelling the reaction sequence. As methyl radicals are thought to be key intermediates in OCM the laser system is currently set to 216nm to allow their specific detection and quantification based on the transition  $B(^2A_1') \leftarrow X(^2A_2'')$  [6].



**Fig. 15a:** Species profiles for methane oxidative coupling on Li/MgO coated foams at atmospheric pressure.



**Fig. 15b:** Defect characterization on MgO and Li/MgO by fluorescence spectroscopy.

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*Schlögl, R.:* The role of chemistry in the energy challenge. *ChemSusChem*, accepted (2009).

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*Wrabetz, S., X. Yang, G. Tzolova-Müller, R. Schlögl, and F. C. Jentoft:* Characterization of Catalysts in Their Active State by Adsorption Microcalorimetry: Experimental Design and Application to Sulfated Zirconia. *Journal of Catalysis*, submitted (2009).

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Xia, W., J. H. Bitter, D. S. Su, J. Quian, and M. Muhler: Iron impregnation on the amorphous shell of vapor grown carbon fibers and the catalytic growth of secondary nanofibers. *Diamond & Related Materials* **18**, 1, 13-19 (2009).

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Zavyalova, U., F. Girgsdies, O. Korup, R. Horn, and R. Schlögl: Microwave-Assisted Self-Propagating Combustion Synthesis for Uniform Deposition of Metal Nanoparticles on Ceramic Monoliths. *Journal of Physical Chemistry C*, in press (2009).

Zhang, J., X. Wang, Q. Su, L. Zhi, A. Thomas, X. Feng, D. S. Su, R. Schlögl, and K. Müllen: Metal-Free Phenanthrenequinone Cyclotrimer as an Effective Heterogeneous Catalyst. *Journal of the American Chemical Society* **131**, 32, 11296-11297 (2009).

Zhang, Y., S. Wei, W. Zhang, Y.-J. Xu, S. Liu, D. S. Su, and F.-S. Xiao: Titania Nanocrystals and Adsorptive Nanoporous Polymer Composites: An Enrichment and Degradation System. *ChemSusChem*, accepted (2009).

Zhang, Z., and D. S. Su: Behaviour of TEM metal-grids during in-situ heating experiments. *Ultramicroscopy* **109**, 6, 766-774 (2009).

## **Dissertations**

Arrigo, R.: Nitrogen Functionalization of CNFs and Application in Heterogeneous Catalysis. Technische Universität Berlin 2009.

Geske, M.: Interaction of Surface and Gas Phase Chemistry in the High Temperature Catalytic Methane Oxidation on Platinum. Technische Universität Berlin 2009.

Herbert, R.: Synthesis, Characterization and Catalysis of Nanostructured Vanadia Model Catalysts for Partial Oxidation of Propane. Technische Universität Berlin 2009.

## **Bachelor**

Hermerschmidt, F.: Novel Cu/ZnO catalyst precursors for synthesis of methanol. Freie Universität Berlin 2009.

**Invited Talks of members of the  
Department of Inorganic Chemistry**

**Marc Armbrüster**

- Jan. 2008      "Advanced Processing for Novel Functional Materials" APNFM  
2008, Dresden, Germany  
*Nanoparticulate Pd-Ga Intermetallic Compounds as Highly  
Selective Catalysts for the Semi-Hydrogenation of Acetylene*

**Manfred Baerns**

- Feb. 2009      Advanced Course on Catalysis, IDECAT, Villars-sur-Ollon,  
Switzerland  
*Development of Catalytic Materials for Maximal Performance and  
Their Kinetic Characterizations*

**Malte Behrens**

- July 2009      Symposium "Strukturanalytik in der Katalyse" der Technischen  
Universität München, Munich, Germany  
*Strukturanalytik und konzeptionelle Synthese von  
Realkatalysatoren am Beispiel des Cu/Zn/Al<sub>2</sub>O<sub>3</sub>-Systems*
- July 2009      Annual Meeting Partnership for International Research and  
Education (PIRE): Molecular Engineering for the Conversion of  
Biomass Derived Reactants into Fuels, Chemicals and Materials,  
San Francisco, USA  
*Carbon-supported catalysts for biomass conversion*

**Christian Hess**

- Jan. 2007      Kolloquium, SFB, Berlin, Germany  
*Nanostructured vanadia model catalysts for partial oxidation  
reactions*
- May 2007      Kolloquium Physikalische Chemie, TU Darmstadt, Darmstadt,  
Germany  
*Synthesis, characterization and application of functional  
nanostructured materials for catalysis and sensors*
- Oct. 2007      Kolloquium, Institut für Chemie, Universität Osnabrück,  
Osnabrück, Germany  
*Synthese, Charakterisierung und Anwendung funktionalisierter  
nanostrukturierter Materialien für die Katalyse und Sensorik*

## **Axel Knop-Gericke**

- Sept. 2007      EMRS Fall Meeting, Warszawa, Poland  
*High pressure XPS: a tool for the investigation of heterogeneous catalytic processes*
- Nov. 2007      Sumitomo, Osaka, Japan  
*What do we learn from high pressure XPS in heterogeneous catalysis?*
- Nov. 2007      9th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures, Tokio, Japan  
*Correlation between the Electronic Structure of Working Catalyst Surfaces and the Selectivity of Heterogeneous Catalytic Reactions*
- Feb. 2008      LNLS Users Meeting, Campinas, Brazil  
*High Pressure X-Ray Photoelectron Spectroscopy: A Tool to Bridge the Pressure Gap in Heterogeneous Catalysis*
- March 2008      Rideal Conference, Cambridge, UK  
*The role of subsurface species in heterogeneous catalytic reactions: New insights by high pressure XPS*
- May 2008      Meeting of the Royal Society of Chemistry, Brantigham, UK  
*High-Pressure XPS and in situ XAS in the soft X-ray range*
- Sept. 2008      Marie Curie Early Stage Researcher Training Networks MONET, Aarhus, Denmark  
*Ambient Pressure X-ray Photoelectron Spectroscopy: A new Tool for (Sub) Surface Science*
- July 2009      VIII. International Conference „ Mechanism of Catalytic Reactions”, Novosibirsk, Russia  
*Increased selectivity of Pd based catalysts in alkyne hydrogenation reactions by the modification of their electronic structure*

## **Friederike Jentoft**

- March 2008      Seminar Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, USA  
*Alkane Activation and Conversion on Solid Oxide Catalysts*
- March 2008      University of Oklahoma, Norman, Oklahoma, USA.  
*Alkane Activation and Conversion on Solid Oxide Catalysts*



- May 2008      Second IDECAT Conference on Catalysis: Concepts, Complexity and Diversity in Catalysis, Porquerolles, France  
*Alkane Conversion on Sulfated Zirconia and Zeolite Catalysts*
- May 2008      Institutskolloquium, Institut für Energieverfahrenstechnik und Chemieingenieurwesen, TU Bergakademie Freiberg, Germany  
*Saure Festkörperkatalysatoren: Neue Materialien und zukünftige Herausforderungen*

### **Robert Schlögl**

- April 2007      Dow Chemical Corporation, Midland MI, USA  
*Selective oxidation of small alkane molecules*
- Oct. 2007      Workshop Katalyse/Sensorik, TU Darmstadt, Germany  
*Gibt es Katalysator-Entwicklung, die auf Verständnis basiert?*
- Oct. 2007      Workshop on Ambient Pressure Photoelectron Spectroscopy, Berkeley, CA, USA  
*High pressure photoemission in heterogeneous catalysis*
- Oct. 2007      SFB Symposium Berlin/Bochum: "From clusters to catalysis – transition metal and transition metal oxides", Erkner, Germany  
*V<sub>x</sub>O<sub>y</sub> in selective oxidation: The role of structural complexity*
- Oct. 2007      First International Symposium on Selective Oxidation catalysis: C-H activation via molecular oxygen (SFB 706), Stuttgart-Hohenheim, Germany  
*Dynamics of Heterogeneous Catalysts*
- Nov. 2007      Otto-Warburg-Vorlesung, Universität Bayreuth, Bayreuth, Germany  
*Heterogen-katalytische Oxidationsprozesse: Was wissen wir heute über ihre Selektivität*
- Jan. 2008      Festkolloquium für Professor H.-P. Böhm, Ludwigs-Maximilians Universität-München, München, Germany  
*Kohlenstoff: ein altes Element, ewig jung*
- Jan. 2008      Universität Bremen, Inst. f. Angewandte und Physikalische Chemie, Bremen, Germany  
*Heterogen-katalytische Oxidationsprozesse: was wissen wir heute über ihre Selektivität*
- Feb. 2008      UCSB-MPG Workshop, Lake Arrowhead, CA, USA  
*Copper in C1 Chemistry*

- March 2008 UOP LLC, Des Plaines, Ill., USA  
*“Nanocarbons in heterogeneous catalysis”: FHI activities – an overview*
- April 2008 Max Planck Materials Workshop, Schloss Reisenburg, Würzburg Germany  
*Research Perspectives in Materials Science*
- April 2008 Rundgespräch „Grenzflächenprozesse bei Energiespeicherung und –umwandlung“, Harnackhaus Berlin, Berlin, Germany  
*In-situ-Methoden der Oberflächenchemie*
- May 2008 Delhousie University Halifax, Canada  
*Heterogeneous catalysis as strategy for large scale energy storing*
- May 2008 European Commission, Brussels, Belgium  
*Future prospects of catalysis and the importance for sustainable chemistry*
- May 2008 Inauguration ceremony Cluster of Excellence “UniCat”, Technical University Berlin, Berlin, Germany  
*Katalyse und Oberflächenchemie*
- June 2008 Harvard University, Cambridge, MA, USA  
*High pressure photoemission for in-situ studies on high performing heterogeneous catalysts*
- June 2008 ESF-FWF Conference “Nanotechnology of Sustainable Energy”, Obergurgl, Austria  
*The critical role of heterogeneous catalysis for energy storage and conversion*
- June 2008 Materials Days, Universität Rostock, Rostock, Germany  
*In situ studies of catalyst surfaces*
- July 2008 14th International Congress on Catalysis, Seoul, Korea  
*Dynamics in selective oxidation catalysis*
- Aug. 2008 16th International Conference on Solid Compounds of Transition Elements, Dresden, Germany  
*Pd and intermetallics in heterogeneous catalysis*
- Sept. 2008 Synchrotron Radiation User Meeting, Daresbury Laboratory, Daresbury, United Kingdom  
*High Pressure Photo Emission in Catalysis*

- Sept. 2008 6th International Workshop on LEEM-PEEM, Trieste, Italy  
*High pressure photoemission in catalysis: Still new insights in mature systems?*
- Oct. 2008 Tag der Wirtschaft und Wissenschaft, Humboldt-Gymnasium, Berlin, Germany  
*Katalyse nicht nur im Auto*
- Oct. 2008 Tandem-Vortrag mit P. Albers, ProcessNet Jahrestagung, Karlsruhe, Germany  
*Kohlenstoff als Katalysator / Kohlenstoff als Träger – Unterschiedliche Blicke auf hochdisperse Systeme*
- Oct. 2008 BESAC Workshop „Solving Science and Energy Grand Challenges with Next Generation Photon Sources“, Rockville, Maryland, USA  
*Catalysis and Chemistry*
- Nov. 2008 CBI-Kolloquium, Erlangen, Germany  
*Vanadium oxides in selective oxidation catalysis: dynamics*
- Nov. 2008 3rd Intern. Symposium on Carbon for Catalysis – CarboCat III, FHI-Berlin, Berlin, Germany  
*Nanostructured carbon as heterogeneous catalysts*
- Nov. 2008 International Workshop on Fundamentals of Lithium-based Batteries, Schloss Ringberg, Rottach-Egern, Germany  
*Nanostructured carbon as heterogeneous catalysts*
- Dec. 2008 Nanotechnology International Forum RUSNANOTECH 08, Functional Nanomaterials, Moscow, Russia  
*Nanostructured Oxides as Heterogeneous Catalysts*
- Feb. 2009 IWAM Conference 2009, International Workshop “Frontiers in Materials Science, Ras Al Khaimah, UAE  
*Nanomaterials in heterogeneous catalysis: Cu as case study (Is this an advanced material?)*
- Feb. 2009 Technische Universität Kaiserslautern, Verleihung Steinhöfer-Preis 2008, Kaiserslautern, Germany  
*Heterogene Katalyse: Auf dem Weg zur rationalen Entwicklung*
- March 2009 UniCat Scientific Advisory Board Meeting, Technical University Berlin, Berlin, Germany  
*Hierarchical organized solid catalysts*
- March 2009 TU Denmark, Lyngby, Lyngby, Denmark  
*Pd and its Intermetallics in Heterogeneous Catalysis*

- March 2009 42. Jahrestreffen Deutscher Katalytiker, Weimar, Germany  
*Selectivity in catalytic hydrogenation and oxidation: from concepts to materials?*
- March 2009 ERL Kick Off Workshop, Berlin Adlershof, Berlin, Germany  
*Synchrotron Radiation Experiments for Energy Research*
- March 2009 DPG Symposium (Chemical Reactions on Nanomaterials), TU Dresden, Dresden, Germany  
*Ruthenium oxides as catalysts for CO oxidation: relations between phase and reactivity?*
- April 2009 Argonne National Laboratory, Argonne, Ill., USA  
*Metals as selective catalysts*
- April 2009 IWTFSSC-2, Second International Workshop on Thin Film Silicon Solar Cells, Berlin Adlershof, Berlin, Germany  
*Solar power: what do we do in the dark?*
- May 2009 Catalysis Club Symposium, Univ. of Delaware, Newark, Delaware, USA  
*Simple and complex oxides in selective oxidation reactions*
- May 2009 Catalysis Club Symposium, Univ. of Delaware, Newark, Delaware, USA  
*Selectivity in Oxidation Catalysis*
- May 2009 Joint Meeting of UniCat and Northwestern University, Evanston, USA in Berlin, Germany  
*Material Properties for High Performance Oxidation Catalysts*
- May 2009 Workshop "Catalysis from first principles", University Vienna, Vienna, Austria  
*Simple and complex oxides in selective oxidation catalysis*
- June 2009 Symposium Prof.Güntherodt, University of Basel, Basel, Switzerland  
*Nanostructured carbon as catalyst*
- July 2009 6th World Congress on Oxidation Catalysis, Lille, France  
*Controlled synthesis of vanadia supported on SBA-15 by the use of automated laboratory reactor*
- July 2009 First Chemical Sciences and Society Symposium CS3 „Using the sunlight to address the energy issues – sunlight to power the world“, Kloster Seeon, Germany  
*The role of hydrogen as an energy carrier*

- Aug. 2009      Presentation at discussion meeting, Dow Chemicals, Houston, USA  
*Silver as Catalyst for Ethylene Epoxidation*
- Aug. 2009      Presentation at discussion meeting, Dow Chemicals, Houston, USA  
*Simple and complex oxides for selective oxidation catalysis*
- Aug. 2009      Gordon Research Conferences: Laser Diagnostics In Combustion,  
Waterville Valley, NH, USA  
*Partial oxidation of small hydrocarbons: the role of a catalyst*
- Aug. 2009      CINF Summerschool “Reactivity of nanoparticles for more  
efficient and sustainable energy production”, Sandbjerg Gods,  
Sønderborg, Denmark  
*Synthesis of Cu nanoparticles for improved performance in CI  
Chemistry*
- Aug. 2009      Invited by German Chemical Society Annual Meeting 2009,  
Universität Frankfurt, Frankfurt a. Main, Germany,  
*Welche Materialien braucht die Katalyse?*
- Oct. 2009      ICESS-11 (11th International Conference on Electronic  
Spectroscopy and Structure), Nara, Japan  
*High Pressure Photoemission in Catalysis*

### **Dang Sheng Su**

- Jan. 2008      SFB-Seminar, Bochum, Germany  
*Nano-Scale Characterizations of Catalytic Materials by High  
Resolution Transmission Electron Microscopy*
- June 2008      Seminar at Department of Chemical Engineering (NTNU),  
Trondheim, Norway  
*Carbon-only Catalysis*
- June 2008      Chinese Conference on Electron Microscopy, Yin Chuan, China  
*Nano-Scale Characterization of Catalytic Materials by High  
Resolution Transmission Electron Microscopy*
- July 2008      Forum for Future Technology, Shenyang, China  
*Catalysis for Energy*
- Oct. 2008      Seminar of Institute for Chemical Physics, Dalian, China  
*Catalyzing Oxidation with Carbon Nanotubes*
- Oct. 2008      14th Chinese Conference on Catalysis, Nanjing, China  
*Carbon Catalysis: Potential and Challenges*

- Dec. 2008 2nd CNT Cambridge Symposium, Cambridge, UK  
*CNTs in Catalysis*
- Dec. 2008 CAS Symposium on Interfacial Materials, Shenyang, China  
*Surface and Interface of Catalysts*
- Feb. 2009 NanoCenter, Chinese Academy of Science, Beijing, China  
*Surface Modified Carbon Nanotubes for Oxidative Dehydrogenation Reaction*
- March 2009 Berzelii Centre EXSELENT on Porous Materials, University of Stockholm, Stockholm, Sweden  
*Catalysis by Nanocarbon*
- March 2009 XXIIIrd International Winterschool on Electronic Properties of Novel Materials, Kirchberg in Tirol, Austria  
*Commercial carbon nanotubes as efficient catalysts for alkene synthesis*
- March 2009 XXIIIrd International Winterschool on Electronic Properties of Novel Materials, Kirchberg in Tirol, Austria  
*Commercial Carbon Nanotubes as Efficient Catalysts for Alkene Synthesis*
- April 2009 J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czech Academy of Sciences, Prague, Czech Republic  
*Activation of Butane and Propane by Carbon*
- May 2009 College of Chemistry, Zhong-Shan University, Gaungzhou, China  
*The Surface Structure of Working Catalysts*
- May 2009 15th International Symposium on Intercalated Compounds, Beijing, China  
*TEM and Nanoscience*
- June 2009 1st German – Japanese Joint Symposium on Development and Technology of Carbon Materials, Meitingen, Germany  
*Catalysis by Carbon*
- Oct. 2009 Sino-German Workshop on Designed Materials for Energy Related Catalytic Processes, Dalian, China  
*Alkane Activation by Carbon*
- Oct. 2009 12th National Conference on Catalysis of Young Scientists, Jin Hua, China  
*Metal-free catalysis: present and future*

Nov. 2009     1st International Green Energy Nanocarbon Conference, Chonju, South Korea  
*Nanostructured Carbon and Carbon Composite for Electrochemical Energy Storage*

Nov. 2009     FTSE FIChemE Annual Conference on Advances in Functional Nanomaterials, Queensland, Australia  
*Nanomaterials for Sustainable Chemistry*

### **Detre Teschner**

Dec. 2008     27th Bessy User Meeting, Berlin, Germany  
*Heterogeneous catalytic hydrogenation: Through the eyes of photons and neutrons*

### **Annette Trunschke**

Sept. 2007     Kolloquium, Leibniz-Institut für Katalyse e.V., Berlin, Germany  
*Rational Synthesis of Multi-Metal Oxide Catalysts*

Oct. 2008     LSAC group meeting; Laboratory for the Science and Application of Catalysis, Berkeley, CA, USA  
*New look at the active surface of nanostructured molybdenum-vanadium oxides for selective oxidation of propane to acrylic acid*

### **Alberto Villa**

June 2009     Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), Strasbourg, FRANCE  
*Au-Pd alloy for liquid phase oxidation*









**Staff Scientists:**

Dr. M. Heyde	
Dr. H. Kuhlenbeck	(Habilitation)
Dr. N. Nilius	(Habilitation)
Dr. T. Risse	(Habilitation)
Dr. S. Schauermann	
Dr. S. K. Shaikhutdinov	
Dr. M. Sterrer	
Dr. T. Schmidt	<i>from Jan. 01, 2008</i>
Dr. K. Watanabe	<i>until Nov. 01, 2009</i>

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

Dr. Hiroko Ariga	Prof. Dietrich Menzel
Dr. Oleksandr Bondarchuk	Dr. Anastassia Pavlovska
Dr. Esther Carrasco Burgos	Dr. Zhihui Qin
Dr. Janaina Fernandes Gomes	Prof. Karl-Heinz Rieder
Dr. José Manuel Flores Camacho	Dr. Aditya Savara
Dr. Lars Heinke	Dr. Xiang Shao
Dr. Ki Hyun Kim	Dr. John Uhlrich
Dr. Daniel Löffler	

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

Dr. Heather Abbott	<i>AvH Fellow</i>	Prof. S. Ted Oyama	<i>AvH Awardee</i>
Prof. Ernst Bauer	<i>AvH Awardee</i>	Prof. Gianfranco Pacchioni	<i>AvH Awardee</i>
Dr. Matthew Brown	<i>AvH Fellow</i>	Prof. Martin Schmal	<i>AvH Awardee</i>
Prof. Cynthia Friend	<i>AvH Awardee</i>	Dr. Violeta Simić-Milošević	
Prof. Elio Giamello	<i>AvH Awardee</i>	Prof. Sundal Song	
Dr. Xiao Lin	<i>AvH Fellow</i>	Dr. Dario Stacchiola	<i>AvH Fellow</i>
Prof. Robert Madix	<i>AvH Awardee</i>		

**Graduate Students:** 23 (3 IMPRS students, 5 students paid from external funds)

1 Internship

1 Trainee

**Technicians:** 9

**Associated Research Group:** Phil Woodruff (group leader)

1 student

1 postdoc

**PP&B Group:** H. Junkes (group leader)

1 Trainee

4 Technicians

**Crystal Preparation Laboratory:** 2 Technicians

*AvH= Alexander von Humboldt Foundation*



## Recent Developments in the Department of Chemical Physics

Director: H.-J. Freund

### General Remarks

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

Dr. Niklas Nilius finished his habilitation in Physics in July 2009 at the Humboldt University Berlin.

Since January 2008 Dr. Thomas Schmidt was made group leader of the *Spectro-Microscopy* group (*SMART*) within the CP Department.

A new technical staff member, Marcel Springer, has joined the *Spectro-Microscopy* group effective February 01, 2008.

Dr. Kazuo Watanabe left the group effective November 01, 2009, to accept a postdoctoral associate position at Oak Ridge National Laboratory. The group *Photo-Induced Processes* will be discontinued after the student has finished his thesis.

The CP Department is hosting (during PC construction period) the *Second Harmonic Generation and Raman Spectroscopy* group associated with the PC Department to set up joined (CP and PC) TERS experiments on molecules on nanoparticles.

Among the postdoctoral associates in the group, Dr. Dario Stacchiola left to become Assistant Professor at Michigan Technology University, Department of Chemistry, and Dr. Zhihui Qin left to become Associate Professor at Wuhan Institute of Physics and Mathematics (WIPM) of the Chinese Academy of Sciences.

For a number of years Prof. Dietrich Menzel has been very successfully associated with the CP Department (*Photon-Induced Processes* Group) on a part time arrangement. This has been crucial for the performance of the group, and will be continued. A similar arrangement has now been set up for Prof. Karl-Heinz Rieder, effective August 2009, to be associated with the *Atomic Force Microscopy* group.

## Honors and Awards:

### *Hans-Joachim Freund*

- Chairman of the University Council, University Erlangen-Nürnberg (Dec. 2007).
- V. N. Ipatieff Lecture Award, Northwestern University, Center for Catalysis and Surface Science (March 2008).
- Invitational Lecture Series, UOP Honeywell, USA (March 2008).
- Hassel Lecture of the Norwegian Chemical Society (May 2008).
- Honorary Visiting Professorships at University of Science and Technology of China, Hefei, China (2008), and University of Birmingham, Birmingham, UK (2007 and 2008).
- Member of the German Academy of Sciences Leopoldina, Halle, (April 2009).

### *Ki Hyun Kim:*

- Student Award in DIET XII (The Twelfth International Workshop on Desorption Induced by Electronic Transitions, April 2009).

### *Wiebke Ludwig:*

- Poster Award 2009, Meeting of the *Deutsche Bunsengesellschaft*, Spring 2009.

### *Thomas Risse:*

- Nernst-Haber-Bodenstein Award 2008 of the *Deutsche Bunsengesellschaft für Physikalische Chemie*.

### *Tobias Schalow:*

- Otto-Hahn-Medal 2007 for „Untersuchungen der Struktur und Reaktivität von getragenen Pd-Nanoteilchen bei Oxidationsreaktionen“.

### *Swetlana Schauerermann:*

- Fellowship of the Robert Bosch Foundation-Excellence and Leadership Program Fast Track (2008-2010).

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

### *Hans-Joachim Freund*

- Member of the Scientific Advisory Board of Institute for Molecules and Materials (IMM) Nijmegen, The Netherlands (April 2008).
- Member of the International Advisory Board of the Nanoscience Center, University of Jyväskylä (May 2008).
- Member, Board of the Cluster of Excellence “Unifying Concepts in Catalysis” (UniCat), Berlin (Nov. 2008).
- Member of the Committee for European Research Policy associated with the Hochschulrektorenkonferenz (March 2009).

- Member of the Scientific Council of the Helmholtz-Zentrum Berlin für Materialien und Energien (April 2009).
- Member, International Advisory Board of “ChemCatChem” (April 2009).
- Presentations at Schools: “Katalyse: Was ist das?”  
Hedwig-Bollhagen-Gymnasium, Velten 2008.  
Strittmatter-Gymnasium, Gransee 2009.

*Thomas Risse*

- Vice-Chairman of the COST action D41 “Inorganic Oxides: Surfaces and Interfaces” (Jan. 2008).

*Thomas Schmidt*

- Member of the BESSY-II User Committee (2008).

The following events have been organized by the department.

- Annual meeting of the COST action D41 (Oct. 2007).
- Visit of Research Fellows of the Alexander von Humboldt Foundation (April 2008).
- Visit of University Students from Erlangen University (Prof. Th. Fauster, Sept. 2008).
- Winterschool “Methods to Characterize Oxide Surfaces” (Feb. 2009).
- Joint Meeting of the UniCat Researchers and the Catalysis Center of the Northwestern University, Evanston, USA (May 2009).
- Joint Meeting of German Science Foundation funded Indian and Chinese Researchers (July 2009).
- Visit of pupils (Strittmatter Gymnasium Gransee, July 2009).

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

1. Spectroscopy  
*Helmut Kühlenbeck*
2. Structure and Reactivity  
*Shamil Shaikhutdinov*
3. Atomic Force Microscopy  
*Markus Heyde*
4. Scanning Probe Spectroscopy  
*Niklas Nilius*
5. Magnetic Resonance  
*Thomas Risse*

6. Catalysis/Laser Spectroscopy  
*Martin Sterrer*
7. Molecular Beam  
*Swetlana Schauermann*
8. Photon-Induced Processes  
*Kazuo Watanabe (until 10/09)*
9. Spectro-Microscopy (SMART)  
*Thomas Schmidt*

Associated Research Group: Scanned-energy Mode Photoelectron Diffraction  
*Phil Woodruff*, University of Warwick,  
Coventry, U.K.

In the Department of Chemical Physics we have continued to concentrate in the last two years on structure and reactivity studies on oxide surfaces and ultra thin films, electronic structure, and adsorption on metal and oxide nanoparticles and instrumentation developments. The Department has also participated in a number of projects funded from outside sources which are listed below.

A particular project involved the acquisition of “Cluster of Excellence” (CoE), “Unifying Concepts in Catalysis” (UniCat) funded by the DFG. The Department of Chemical Physics was deeply involved in the planning and the final proposal. The department represents the institute in the Board of the CoE.

Further collaborations involve:

Collaboration N. Nilius: DFG, SPP 1234  
“Quantum transport at the molecular scale”

Collaboration H.-J. Freund, Th. Risse, N. Nilius:  
ESF COST Action D41  
“Inorganic Oxides: Surfaces and Interfaces“

Collaboration H.-J. Freund, N. Nilius, Th. Risse, M. Heyde:  
Center of Excellence, UniCat, Teilprojekt A1,  
“Bridging Model Systems to Real Catalysis: Methane Activation on  
Li Doped MgO“



Collaboration Th. Risse:  
Center of Excellence, UniCat, Teilprojekt B3,  
“Towards an Atomistic Understanding of MoCo Containing  
Molybdoenzymes“

Collaboration H.-J. Freund, S. K. Shaikhutdinov:  
*SFB 546 Struktur, Dynamik und Reaktivität von  
Übergangsmetalloxid-Aggregaten*, Teilprojekt B1  
„Struktur-Reaktivitäts-Beziehung von Vanadiumoxid-Aggregaten auf  
geordneten Übergangsmetalloxidoberflächen“

Collaboration H.-J. Freund, H. Kuhlenbeck:  
*SFB 546 Struktur, Dynamik und Reaktivität von  
Übergangsmetalloxid-Aggregaten*, Teilprojekt C1  
„Elektronenstruktur und Adsorptionsverhalten von geordneten  
Vanadium-, Molybdän- und Nioboxidoberflächen“ (2007)  
"Theoretical Modelling of XPS and NEXAFS spectra" (2008-2009)

Collaboration D. P. Woodruff (Warwick), J. Sauer:  
*SFB 546 Struktur, Dynamik und Reaktivität von Übergangs-  
metalloxid-Aggregaten*, Teilprojekt C8  
„Structure determination of VO<sub>x</sub> surfaces, thin films and interfaces  
based on scanned-energy mode photoelectron diffraction“

Collaboration H.-J. Freund, G. Centi (Messina):  
Network of Excellence, E.U.  
„Integrated Design of Catalytic Nanomaterials for a Sustainable  
Production (IDECAT)“

Collaboration H.-J. Freund, M. Asscher (Jerusalem):  
G.I.F.  
„Dynamics of Electronic Processes in Confined Environment“

Collaboration H.-J. Freund, E. Umbach (Würzburg):  
BMBF-BESSY „SMART- ein hochauflösendes Elektronen-Spektro-  
Mikroskop für die Oberflächenforschung“

Further collaborations include:

Collaboration with Brazil: H.-J. Freund and M. Schmal, Universidade Federal do  
Rio de Janeiro (UFRJ), Rio de Janeiro.

Collaboration H.-J. Freund with a partner group in China: W. Huang, University  
of Science and Technology of China, Chinese Academy of Sciences, Hefei,  
China.

Collaboration with Finland: H.-J. Freund, N. Nilius and H. Häkkinen,  
Nanoscience Center, University of Jyväskylä, Finland.

Collaboration on solid-liquid interfacial STM: H.-J. Freund and K. Wandelt, Institute of Physical and Theoretical Chemistry, University of Bonn, Bonn, Germany.

Collaboration with Hungary: H.-J. Freund and F. Solymosi, University of Szeged, Academy of Sciences, Szeged.

Collaboration with Italy: H.-J. Freund and E. Giamello, IFM, Università degli studi di Torino, Torino. H.-J. Freund and G. Pacchioni, Università degli Studi Milano-Bicocca, Milano. N. Nilius and S. Valeri, Università de Modena, Modena.

Collaboration with Japan: H.-J. Freund and K. Asakura, Catalysis Research Center, Hokkaido University, Sapporo. S. Schauermaun, M. Wilde, and K. Fukutani, The University of Tokyo, Tokyo.

Collaboration with Mexico: H.-J. Freund, M. Heyde and A. Köster, Centro de Investigacion y de Estudios Avanzados, San Pedro Zacatenco.

Collaboration with Poland: M. Heyde and M. Nowicki, Institute of Experimental Physics, University of Wroclaw, Wroclaw.

Collaboration with Spain: S. Schauermaun and K.M. Neymann, University of Barcelona, Barcelona.

Collaboration with the UK: S. Shaikhutdinov and M. Bowker, A. Carley, P. Davies, D. Edwards, School of Chemistry, Cardiff University, Cardiff.

Collaboration with the USA: H.-J. Freund and P.S. Bagus, University of North Texas, Denton. S. Schauermaun and C.T. Campbell, Washington University, Seattle. H.-J. Freund and J.C. Hemminger, School of Physical Sciences, University of California. Th. Risse and W. Hubbell, Jules Stein Eye Institute, School of Medicine, UCLA, Los Angeles. S. Schauermaun and R.J. Madix, Harvard University, Cambridge. Freund, M. Heyde and S.T. Oyama, Virginia Polytechnic Institute and State University, Blacksburg. H.-J. Freund and P.C. Stair, Northwestern University, Evanston.

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

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

- A systematic study of 1-dimensional and 2-dimensional Au clusters supported on alumina and magnesia ultra thin films has been carried out using scanning probe imaging and spectroscopy in collaboration with Joachim Sauer's (Phys. Rev. Lett. (2007)), Gianfranco Pacchioni's (Phys. Rev. Lett. (2008)) and Hannu Häkkinen's (Phys. Rev. Lett. (2009)) groups.

- The concept of tailoring the electronic properties of oxide surfaces and oxide film-metal interfaces has been substantiated by STM experiments on Pd, Au and Fe incorporation, and on Li doping of ultra thin silica films (Phys. Rev. Lett. (2008), Phys. Rev. Lett. (2009))
- In connection with our efforts within UniCat, molecular adsorption of tailor made (Prof. Blechert's group, TU Berlin) organic molecules on Au and oxide surfaces, as a prelude to the study of adsorption of the same molecules on supported clusters in order to modify cluster-support interaction, has been studied using STM imaging.
- With respect to the study of model systems for methane activation, which is a central theme within UniCat, successful attempts have been made to prepare thick Li doped MgO films. Characterization of the doped film properties using fluorescence studies with the photon STM and ESR spectroscopy are in progress.
- The development of atomic resolution AFM at cryogenic temperatures has been pushed forward by resolving atomically the top layers of alumina films with unprecedented quality and performing force microscopy on MgO film surfaces (Appl. Phys. Lett. (2007), New. J. Phys. (2009)).
- It has been possible to detect the adsorption site of single Au atoms on alumina via atomically resolved AFM images, and also to image color center defects on MgO(100).
- In collaboration with Joachim Sauer's groups we have been able to generate unique structure-spectroscopy-reactivity correlations for vanadia-on-ceria-monolayer model systems, in particular with respect to oxidative methanol dehydrogenation to formaldehyde. Monomeric and

polymeric  $V_xO_y$  species on ceria have been imaged and their vibrational and photoelectron spectra have been assigned. This has led to a reassignment of vibrational data in the catalytic literature and explain the observed strong influence of the support for this reaction (Angew. Chem. (2009)).

- As a reference system for oxidative methanol dehydrogenation the initial steps of the molecules adsorption and reaction has been studied on  $V_2O_3(0001)$  and  $V_2O_5(001)$  films. A correlation between defect abundance and methoxy formation was firmly established and correlated with theoretical studies in Joachim Sauer's group (within the SFB 546) (Angew. Chem. (2008)).
- Also within the SFB 546 collaboration, after many unsuccessful attempts, a strategy has been developed to grow mixed metal-titania films on  $TiO_2(110)$  singly crystal substrates.
- By investigating the system  $Pt/Fe_3O_4(111)$  a unique SMSI state has been discovered where a  $FeO(111)$  film migrates onto the Pt nanoparticles. Both, the overgrowing oxide film and the  $Fe_3O_4(111)$  substrate were imaged with atomic resolution. This SMSI state exhibits the very interesting property of enhanced activity towards CO-oxidation if the reaction is performed under atmospheric conditions which raises the general question whether ultrathin oxide films could be designed to enhance chemical activity. The experiments are carried out within a high pressure cell, using gas chromatographic detection. The SMSI state deactivates by a dewetting of the  $FeO$  film (Catal. Lett. (2007), J. Catal. (2009)).

- The structure of the  $\text{Fe}_3\text{O}_4(111)$  surface is being investigated using the LEEM option of the SMART I (see for SMART II below) microscope, with its unique lateral resolution of 2.6 nm.
- Progress has been made in identifying and localizing adsorbed hydrogen on and in Pd nanoparticles supported on  $\text{Fe}_3\text{O}_4(111)$ . Resonant-Nuclear-Reaction Analysis (r-NRA), (in collaboration with M. Wilde and K. Fukutani, The University of Tokyo), has been used to identify and quantify subsurface hydrogen and correlate its presence with olefin hydrogenation (Phys. Rev. B 2007), Angew. Chem. (2008), J. Phys. Chem. (2008)).
- In collaboration with Charlie Campbell a micro-calorimeter has been built to study adsorption enthalpies of CO on  $\text{Fe}_3\text{O}_4(111)$  supported Pd nanoparticles as a function of particle size. Interesting and unexpected behaviour has been found as a function of particle size.
- Along with incorporating the SMART activity into the department, an analysis of the PEEM performance of the SMART I instrument has led to the conclusion, that it is necessary to replace the magnetic  $\Omega$ -filter by an electrostatic analogous instrument which allows to keep the high voltage of the electron beam as it leaves the beam splitter. This is best done by setting up a new instrument, called SMART II, for which funds have been acquired from the General Administration of the Max Planck Society.
- Photon assisted processes on supported Ag nanoparticles in comparison with Ag(111) single crystal surfaces have been investigated using techniques such as mass-selected time-of-flight and resonance enhanced multiphoton ionization (Phys. Rev. Lett. (2007), Phys. Rev. Lett. (2008), JACS (2008)). Photodesorption cross-sections as a function of photon-energy and particle size reveal new mechanistic aspects of the photo

desorption process and its dynamics (energy partitioning). When femtosecond excitation is applied very strong changes (orders of magnitude) in cross-sections have been observed but not yet understood.

- Water adsorption on MgO(100) has been studied from submonolayer coverage to multilayer ice coverage using IRAS and SFG with respect to dissociation and its influence on metal (i.e. Au) nanocluster formation.
- A new research direction aims at a molecular-level understanding of wet catalyst impregnation. A solid-liquid STM-SFG system has been planned and is being tested. A thin FeO(111) film on Pt(111) has been imaged in the liquid. PdCl<sub>2</sub> was used to deposit Pd and the clusters formed after calcination have been imaged in air.
- EPR signals from alkali and alkali earth deposits on MgO films have been recorded and assigned (Chem. Phys. Lett. (2008)). These results are important towards our understanding of paramagnetic species involved in methane activation over Li/MgO within the UniCat activity.
- The W-band EPR system has been fully assembled and novel concepts to operate the resonator have been developed. The instrument has been tested to provide monolayer sensitivity.
- Protein adsorption on lipid bilayers as well as various lipid bilayer phases using spin-labelling techniques are being studied intensely using EPR. To access protein adsorption on metal surfaces, new resonator assemblies are being developed. In parallel, studies began to develop addressable protein switches by controlling the external electric field.

## Progress Reports

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

### Spectroscopy Group

Many studies in the past two years dealt with ordered  $V_2O_3(0001)$  and  $V_2O_5(001)$  layers grown on Au(111). Adsorption/reaction studies were in the foreground of the investigations with a certain focus put onto microscopic details of the reactivity of the surfaces. An upcoming topic is the preparation of  $TiO_2(110)$  layers doped with molybdenum and vanadium for reaction and adsorption studies. These studies were performed in the framework of the Sonderforschungsbereich 546 of the Deutsche Forschungsgemeinschaft.

#### *Methanol adsorption on $V_2O_3(0001)$ and $V_2O_5(001)$*

Methanol adsorption experiments were performed for  $V_2O_5(001)$  and  $V_2O_3(0001)$ , focussing on the role of surface oxygen atoms and the hydroxyl groups resulting from methoxy and formaldehyde formation. In the case of both substrates, non-defective oxygen-terminated surfaces are inactive for reactive methanol adsorption; only molecular adsorption occurs. If surface oxygen atoms are removed then on both substrates already at 100 K methoxy is formed which is transformed into formaldehyde at temperatures between 450 and 600 K. Using different experimental (STM, IRAS, TDS, XPS, NEXAFS) and theoretical methods (DFT, kinetic modelling) it could be shown that the hydroxyl groups produced in the course of the methoxy formation play a decisive role. In the case of the  $V_2O_3(0001)$  surface the hydrogen atoms bind to vanadyl groups and form water upon annealing. This removes vanadyl oxygen atoms from the surface, thus forming additional sites for methoxy formation. Herewith more hydrogen are produced which again form water and so on. This self limiting chain reaction doubles the density of sites reactive for methoxy formation. At higher temperature hydroxyl groups steer the selectivity for formaldehyde formation in that nearly all hydrogen atoms produced during formaldehyde formation react with methoxy to

produce methane in addition to formaldehyde. Additional hydrogen atoms on the surface shift the selectivity towards more methane.

For the  $V_2O_5(001)$  surface the role of the hydrogen atoms is somewhat different. In this case there is a high probability for hydrogen+methoxy→methanol recombination which occurs already below room temperature and leads to the removal of methoxy groups from the surface at temperatures below the formaldehyde formation temperature. The only way for the methoxy groups to survive up to the temperature where formaldehyde production is possible ( $>450$  K) is the removal of hydrogen atoms by water formation which competes with methanol formation for surface hydrogen atoms. With a kinetic model the time dependence of the methoxy concentration on the surface could be well reproduced.

#### *Molybdenum and vanadium doped $TiO_2(110)$ layers on $TiO_2(110)$*

These investigations aim at learning about the properties of a supported model catalysts ( $MoO_x/TiO_2$  and  $VO_x/TiO_2$ ) with respect to the mixing of the components, the oxidation states of the dopant ions, and their reactivity. Up to now preparation recipes could be developed and characterization studies were performed. After many tries to grow ordered layers of regular  $TiO_2$  on different platinum and gold surfaces (which were chosen because of their chemical inertness) finally single crystalline  $TiO_2(110)$  was chosen as substrate for the growth of the mixed oxides. These are produced by co-deposition of titanium with molybdenum or vanadium in an oxygen atmosphere. Molybdenum forms an ordered mixed bulk phase with  $TiO_2$  with molybdenum in a 4+ oxidation state. On the surface also 5+ and 6+ oxidation states are found. In the case of vanadium doped  $TiO_2(110)$  additional stabilization is required due to the fast vanadium diffusion into the bulk upon annealing. This can be prohibited by a diffusion barrier consisting of a  $W+TiO_2$  mixed oxide layer. Whether this layer can also block diffusion of reduced titanium atoms is currently studied. If this is the case this may help to produce a  $TiO_2(110)$  surface with a low defect density.



### *Theoretical modelling of XPS and NEXAFS spectra*

In co-operation with Paul Bagus and co-workers, spectroscopic details of XPS and X-ray absorption spectra of oxides were studied. Calculations were performed by Paul Bagus and co-workers and we took care of the experimental part. For the case of  $\text{V}_2\text{O}_5(001)$  the V2p X-ray absorption branching ratios were calculated using the Russell-Saunders coupling scheme in order to get a qualitative understanding of the previously not theoretically modelled experimental spectrum and for the case of  $\text{CeO}_2(111)$  Ce4s and 5s XPS spectra were calculated with a rigorous parameter-free theoretical approach showing that the usually used model which explains the fine structure of the Ce XPS peaks in terms of  $\text{O}2\text{p} \rightarrow \text{Ce}4\text{f}$  charge-transfer states with different Ce4f occupations is by far too simple in that charge reorganization within the Ce atoms also plays a significant role.

### Structure and Reactivity

During the last years the group has focused on the study of: (i) the role of oxide support dimension on the gold/ceria interaction; (ii) atomic structure and reactivity of ceria-supported vanadia clusters in methanol oxidation; (iii) structural and catalytic properties of iron oxide supported Pt particles in CO oxidation. To carry out the reactivity studies at realistic pressure conditions, we have built a “high-pressure” cell inside an UHV chamber that allowed us to monitor reaction kinetics by gas-chromatography and to perform structural characterizations of model catalysts ex situ.

### *Interaction of gold with cerium oxide supports*

Chemical reactions on gold surfaces have received much attention owing to the unusual catalytic properties of highly dispersed gold. Among the reaction mechanisms proposed in the literature, there are some involving positively charged (“cationic”) Au species supported on reducible oxides, in particular on ceria. Moreover, nano-crystalline ceria (“nano-ceria”) as a support was reported to remarkably increase the activity of gold as compared to conventional ceria supports. In order to rationalise these effects we performed a comparative study of

morphology, electronic structure and CO adsorption of gold supported on well-ordered CeO<sub>2</sub>(111) films and CeO<sub>x</sub> nanoparticles.

Ceria films were prepared on Ru(0001) using the new recipe that significantly improved quality of the films. Ceria nanoparticles were grown on ultra-thin SiO<sub>2</sub>/Mo(112) films using water (ice) assisted deposition. The ceria nanoparticles (~3-5 nm in diameter) possess significant amounts of Ce in the 3+ oxidation state (up to 60%), i.e. in contrast to CeO<sub>2</sub>(111) films (<5%).

The results showed that partially charged Au<sup>δ+</sup> species are formed by deposition at low temperatures (~ 100 K) and low coverages on both ceria supports. The formation of Au<sup>δ+</sup> on CeO<sub>2</sub>(111) films is kinetically limited and is attributed to the interaction of the gold ad-atoms with defects. In variance to extended ceria surfaces, where only metallic Au nanoparticles were observed at 300 K, the “cationic” gold species were formed in abundance on nano-CeO<sub>x</sub> and exhibited enhanced thermal stability. Nano-ceria as a support stabilizes small Au clusters, which may even be incorporated into the ceria nanoparticles at elevated temperatures. These structural effects may be relevant to the enhanced reactivity of Au/nano-ceria as reported in the literature.

#### *Linking structure and reactivity of vanadia/ceria catalysts in methanol oxidation*

The reactivity of vanadia “monolayer” catalysts in oxidative dehydrogenation reactions has been shown to depend strongly on the oxide support, with reducible oxides exhibiting much higher activity as compared to irreducible oxides. To elucidate the support effects, we studied vanadia clusters deposited onto CeO<sub>2</sub>(111) films in comparison to alumina and silica films previously studied in the group.

Using a combination of STM, IRAS, and PES with synchrotron radiation, we unambiguously demonstrate the formation of monomeric, O=V<sup>5+</sup>-O<sub>3</sub> species on the CeO<sub>2</sub>(111) surface at low vanadia loadings. A direct relationship between the vibrational properties and the nuclearity of vanadia species (monomeric vs polymeric), as observed by STM and IRAS, allows one to link the structure of vanadia surface species and the Raman/IR characterization of real catalysts in a

more definitive manner. The results show that ceria surfaces stabilize small vanadia species, such as monomers and trimers, in a 5+ oxidation state accompanied by reduction of the ceria surface. These experimental results are fully supported by DFT calculations performed by the group of Prof. Sauer at HU (Berlin).

TPD spectra of methanol on our model systems revealed two, vanadia-related peaks for formaldehyde production. The species of low nuclearity revealed reactivities at much lower temperatures as compared to polymeric structures, which in turn show strong similarities to reactivity of vanadia nanoparticles formed on alumina and silica from the onset. It is concluded that strong support effects reported in the literature for the real catalysts are related to the stabilization of small vanadia (5+) clusters and the reduction of the oxide support.

*Promotional effect of strong metal-support interaction on CO oxidation over Pt supported on iron oxides*

Platinum supported on the reducible oxides often exhibits the so-called strong metal-support interaction (SMSI) via encapsulation of the Pt particles by a thin oxide layer stemming from the support. We studied the morphology and thermal stability of Pt particles deposited on Fe<sub>3</sub>O<sub>4</sub>(111) films by STM and TPD of CO. The combined results provided strong evidence for the encapsulation of Pt particles upon vacuum annealing at elevated temperatures by a thin iron oxide film that is a FeO(111) monolayer in nature. Unexpectedly, reactivity studies at atmospheric pressure revealed that the Pt particles, that underwent encapsulation prior to the reaction, showed higher CO oxidation rates as compared to the clean Pt particles.

To gain a deeper understanding of the role of the FeO films on reactivity of Pt, we studied CO oxidation on a clean Pt(111) single crystal and iron oxide films grown on Pt(111) at different CO:O<sub>2</sub> ratios (between 1:5 and 5:1) and partial pressures up to 60 mbar at 400-450 K. It is found that monolayer FeO(111) films are much more active than clean Pt(111) and nm-thick Fe<sub>3</sub>O<sub>4</sub> (111) films at all reaction conditions studied, thus indicating that the enhanced reactivity is intimately connected to the atomic structure of ultra-thin FeO(111) films. The

reaction rate at 450 K exhibited first order for O<sub>2</sub> and non-monotonously depended on CO pressure.

Post-characterization of the catalysts revealed that in an O<sub>2</sub>-rich ambient the FeOx films were enriched with oxygen while maintaining the long range order. We propose that the reaction proceeds through the formation of a well-ordered, oxygen-rich FeOx ( $1 < x < 2$ ) film that reacts with CO through the redox mechanism. In CO-rich ambient, the reaction is accompanied with dewetting that deactivates the catalyst.

These findings strongly indicate that encapsulation of Pt particles by ultra-thin oxide films may even have promotional effects, at least in oxidation reactions. Since adsorbed species on ultra-thin oxide films supported on metallic substrates may, under certain conditions, induce electron transfer through the film onto the adsorbate (as recently demonstrated), it is conceivable, that such electron transfer in turn induces reactivity between molecules, ultimately resulting in restructuring of the ultra-thin oxide film and unexpected reactivity.

#### Atomic Force Microscopy

Frequency modulation dynamic force microscopy (FM-DFM) is well-suited for atomic scale studies of wide band gap materials like oxide films or bulk single crystals.

#### *Atomic structure of the thin alumina on NiAl(110) and its antiphase domain boundaries*

A comprehensive atomic scale study of antiphase domain boundaries within the alumina on NiAl(110) has been conducted. Images show in detail the surface unit cell, both types of antiphase domain boundaries (zigzagged, straight) and lateral displacements within these types of boundaries. Due to the loss of translational symmetry at the boundary, structures of even increased complexity are revealed. Lateral models for these local arrangements have been created on the basis of adjusted unit cell structures. The before mentioned contrast matches the topmost oxygen layer even with respect to topographic height, which adds the third dimension to the analysis. With this the antiphase domain boundaries are shown

to be shallow depressions. New symmetry aspects have been found in the topography of these boundaries. The local structure of the film surface shows evidence of substrate influence in its topography and the domain boundary network shows indications that its growth behavior is affected by this interaction in its very details beyond sheer appearance. Presented results can be linked to the relation between growth and structure of an emerging class of structurally related ultrathin alumina films.

#### *Imaging of individual ad-atoms on oxide surfaces*

In further studies we have employed this contrast to determine adsorption sites of gold species on this oxide surface. Sites of the metal adsorbates are characterized with respect to lateral position and chemical identity. The method allows the determination of adsorption sites with substrate site precision in principle for any imageable adsorbed species. Considering the capabilities of FM-DFM on bulk insulators this will enable single ad-atom studies on oxides with spatial resolution equivalent to or even surpassing that of scanning tunneling microscopy (STM). An important feature of the FM-DFM contrast is the clear chemical identification of the imaged surface species without which the adsorption site could not be named. Results point to shallow depressions in the structure as preferred locations for gold ad-species. The adsorption sites are not found on positions identified by earlier theoretical work.

#### *Atomic resolution on a metal single crystal*

Furthermore, we have obtained atomically resolved FM-DFM images with our tuning fork setup on an Ag(001) surface. The necessity of well chosen tip-surface interaction parameters is demonstrated. A narrow parameter range makes atomically resolved FM-DFM images scarce. The capability of our setup to measure frequency shift and simultaneously tunneling current gives insight into different tip trajectories and possible contrast formation mechanisms in FM-DFM and STM. Here, one explanation is related to local variations in the decaying signals which may originate from different density of states contributions to tip-sample force and tunneling current.

#### *Work function measurements of thin oxide films on metals - MgO on Ag(001)*

Also work function shift measurements of thin oxide films on metals have been performed. It is a key parameter for charging of adsorbates with high electron affinity on these systems. For the first time, experimental data for the work function shift of Ag(001) induced by 1, 3, and 8 monolayers of MgO were measured in situ by three independent scanning probe techniques. These three techniques have been applied on the same surface area with the same tip configuration, rendering the different approaches directly comparable. Furthermore, the results compare well with density functional theory calculations. The measurements are performed using a dual-mode FM-DFM/STM working in ultrahigh vacuum at low temperature (5 K). The methods to detect the work function shift are based on Kelvin probe force microscopy measuring the contact potential difference,  $I(z)$  curves and field emission resonances.

#### *Characterization of color centers on MgO(001) films - charge states and dynamics*

A detailed understanding of surface defects is highly desirable e.g. to clarify their role as active sites in catalysis. Here localized defects on the surface of MgO films deposited on Ag(001) are investigated. Since the electronic structure of color centers depends on their local position, spectroscopic signals are highly convoluted and often difficult to disentangle. In this study we aimed to obtain morphological and spectroscopic information on single color centers at a microscopic level with FM-DFM in ultrahigh vacuum and at low temperature.

This scientific approach opens up the way to analyze the local morphological nature of these defects on thin films as well as on thick bulk oxide systems. The charge state and the position of these defects are locally characterized and manipulated by interactions with the probing tip. The main future goal is to capture the dynamics of atomic scale processes in FM-DFM. The dynamics of these defects in connection with the charge state is in the focus of the current study. Comparison with cluster calculations should corroborate the assignment of the defects to singly, doubly or uncharged color centers as well as the understanding of their dynamical behavior. Theoretical work is performed by with

Gianfranco Pacchioni and Andreas M. Köster. From these calculations the relative stabilities of different defect sites could be estimated. A direct comparison to the corresponding experiments is possible. A major goal of the theoretical studies would be the investigation of the dynamics of neutral and charged color centers on MgO films with different coordination, i.e. terraces, steps and kinks. This will be accomplished by the calculation of activation barriers and the corresponding intrinsic reaction coordinate for the defect migrations. These results can be compared with experimentally measured diffusion coefficients.

### Scanning Probe Spectroscopy

The *Scanning Probe Spectroscopy (SPS)* group has focused its activities on a topographic and spectroscopic characterization of oxide thin-films and individual adatoms, molecules and metal aggregates bound to their surface. The main experimental tool is scanning tunneling microscopy combined with a number of spectroscopic techniques. Light emission spectroscopy with the STM is employed to probe the local optical properties of oxide surfaces. Thereby, electrons are injected from the STM tip into a nanometer sized sample region and the emitted radiation is collected with a CCD detector. Local electronic properties are investigated with STM conductance spectroscopy, being applied to oxide defects, single adsorbates as well as metal particles. The group runs three low-temperature STM setups, each equipped with special spectroscopic facilities. The research activities of the last two years can be divided into three main topics:

#### *Tailoring electronic and adsorption properties of thin oxide films*

Wide gap oxide materials are often chemically inert and interact with adsorbates only via defects and low-coordinated lattice sites. This unspecific adsorption behavior has been modified by inserting artificial binding sites into the surface or by tuning global oxide properties to alter certain binding parameters. Both approaches were realized on a two-layer silica film grown on Mo(112), which is chemically inert in its pristine form. Due to a porous structure, the films offers sub-surface binding sites that can be loaded with small-sized metal atoms, e.g. Li and Pd atoms. The inserted species are now able to anchor adsorbates on the oxide

surface. The adhesion strength hereby results from the interplay between a covalent contribution induced by the anchor site and a repulsive one exerted by the electron density at the oxide surface. The anchoring mechanism has been demonstrated for single Au, Ag and Fe adatoms, which are unable to bind to the silica/Mo(112) film in absence of the sub-surface species.

In the second approach, the silica properties were systematically altered to make the thin film attractive for electronegative adsorbates only. For this purpose, the silica-Mo interface was doped with Li atoms, which ionize upon adsorption and create a strong positive surface dipole. The resulting work function decline promotes electron transfer from the Mo support into suitable adsorbates, which become charged and develop new electrostatic and polaronic interaction schemes with the oxide surface. The anionic species do strongly bind to the oxide film, although their neutral counterparts are unstable. This concept has been demonstrated for a Li-doped silica/Mo(112) film, which is capable to stabilize Au adatoms and clusters even when no surface defects are available.

Li-doping has been studied for MgO/Mo(001) as well, aiming for a better understanding of the unique catalytic properties of this system in the oxidative coupling of methane. The Li insertion into the oxide matrix results in a pronounced red-shift of an exciton-mediated photon-emission line of the MgO, suggesting the formation of Li-related defect levels in the oxide band gap. For comparable doping experiments, recipes for the preparation of epitaxial CaO and Li<sub>2</sub>O films have been developed as well.

#### *Investigating quantization effects and optical properties of single metal clusters*

The electronic properties of metal particles undergo dramatic changes when the number of atoms is reduced below a few hundred and the bulk band structure breaks into a set of quantized states. This metal-to-non-metal transition is hardly observed with non-local spectroscopic techniques due to the size and shape distribution of particles in an ensemble, but can be accessed with STM conductance spectroscopy. Discrete electronic states, arising from the delocalization of the Au 6s electrons, have been observed for Au aggregates on alumina and magnesia thin films. The quantum nature of these states was



determined from maps of the electron density probability via conductance imaging. In linear Au clusters containing 2 to 7 atoms, the energy levels show the symmetry and dispersion relation of quantum well states in a 1D box potential. In monolayer Au islands, on the other hand, the orbitals reproduce the eigenstates of a free-electron gas confined in a 2D parabolic potential. A comparison with DFT calculations revealed a higher electron count in the quantum well states of oxide-supported clusters than expected for charge-neutral ones, indicating an electron transfer from the metal support into the ad-clusters.

Employing light emission spectroscopy with the STM, the optical properties of single alkaline earth (Ca, Mg) and noble-metal particles (Au) have been probed on MgO thin films. In all three examples, the emission is governed by plasmon modes in the particle electron gas, excited by inelastic electron tunneling across the STM junction. Due to the higher electron density and the absence of *d*-states, the emission lines are blue-shifted in the alkaline-earth with respect to the Au particles. For all particle types, a distinct fine-structure occurs in the emission spectra, which suggests a discrete plasmon excitation mechanism. It is traced back to the presence of quantized transport channels in a double-barrier STM junction consisting of a vacuum and an oxide gap.

#### *Exploring the interaction of molecules with oxide-supported nanoparticles*

Catalytic activity of a metal-oxide system is often restricted to the presence of nano-sized metal clusters. As ultra-small aggregates are subject to constant diffusion and aggregation processes in a reactive environment, suitable ways for readjusting the particle dispersion needs to be established. In cooperation with the Chemistry Department at the TU Berlin, sulfur-containing benzene derivatives have been tested in their ability to dissolve Au atoms from large particles and redistribute them on the surface. Hereby, a single molecular transporter was found to bind two Au atoms that are removed from the host cluster. As a consequence, the mean particle size decreases, which is a first step towards a controlled re-dispersion of the cluster material.

## Magnetic Resonance

The magnetic resonance group has worked on three different topics. The first topic is embedded into the center of excellence “Unifying Concepts in Catalysis” and focuses on an atomistic understanding methane activation using Li doped MgO films. The second project focuses on the installation of an ultrahigh vacuum compatible high-field electron paramagnetic resonance (EPR) experiment operating at 95 GHz. Finally, the group has made efforts towards a characterization of proteins on surfaces using a technique called site directed spin labeling.

### *Li doped MgO/ defects on MgO*

The aim of this project is to establish a suitable model system which can be used for an atomistic characterization. EPR spectroscopy is particularly important since the key species involved in the mechanism of methane activation on this catalyst are radical species, namely suboxide ( $\text{O}^\cdot$ ) anions and methyl radicals and EPR was key to provide experimental evidence for these species.

First, we have investigated the interaction of Li metal with MgO(001) surface by depositing Li metal at low temperature on 20 ML thick MgO(001) films grown on Mo(100) surfaces. At low temperature (40 K) it is possible to stabilize a certain fraction of the deposited Li as individual metal atoms. These atoms are characterized by a doublet ground state and show up in the EPR by a characteristic quartet of lines. The splitting of the two Zeeman levels of the ground state into four pairs originates in the hyperfine interaction of the unpaired electron with the underlying nuclear spin of the Li atoms. Based on an analysis of angular dependent spectra it is possible to prove that these atoms are located on the terrace of the MgO islands. The majority of the deposited Li forms small metal clusters which can be observed by STM. With respect to the mechanism of methane activation it is thought that substitutional doping of Mg with Li creates suboxide ( $\text{O}^\cdot$ ) anions, because of the lack of one electron introduced by the Li doping. Various preparation methods were tried to dope MgO with Li. However, up until now no indications were found for the presence of suboxide anions after the preparation of these films.

After deposition of small amounts of Li metal there are no indications for an ionization of Li atoms and a corresponding capture of the electron in appropriate sites of the MgO lattice. This is in contrast to the deposition of additional Mg metal onto a freshly prepared MgO film. In case Mg is deposited at low temperatures onto the MgO surface a new EPR line occurs which can be attributed to the presence of scavenged unpaired electrons- usually called color centers- on suitable surface sites. The properties of these sites are rather similar to the paramagnetic color centers prepared by electron bombardment which have been characterized before. However, the location of these sites are different. While the majority of color centers prepared by electron bombardment are located at the edges of the MgO islands and are created by electron stimulated desorption of oxygen from the lattice, the trapping sites of the excess electrons produced by additive Mg coloring have to be trapped on preexisting sites such as reversed corners.

The paramagnetic color centers are interesting sites in view of the mechanism of methane activation, because it is possible to transform them readily into suboxide anions by reaction of the color centers with  $\text{N}_2\text{O}$ . This reaction can be monitored by EPR proving the transformation of paramagnetic color centers into suboxide anions. Initial experiments on the surface chemistry the suboxide anions show that there is some reactivity of the paramagnetic site with methane which currently investigated in detail.

#### *W-band EPR machine*

The group has build up a high field (95 GHz) EPR machine operating under UHV conditions and combines this technique with STM and IR to allow for a comprehensive characterization of the surfaces. Increasing the operating frequency by a factor of ten offers an enhanced spectral resolution and has the prospects for an improved sensitivity. To adapt the high field spectrometer to UHV conditions it is not possible to use a monomodal resonator due to the size requirements imposed by a wavelength of about 3 mm. Instead we decided to use a Fabry-Perot resonator. Here, the single crystal metal surface in UHV serves as the planar mirror of the Fabry-Perot resonator while the concave mirror is located

in fine vacuum and sealed against the UHV by a 100  $\mu\text{m}$  thick quartz window. Long term stability of the resonator structure has turned out to be a serious issue particularly for a cooled sample. It was necessary to redesign the feedback and control system to keep the cavity on resonance for the required period of time. To this end it is important to notice that relative length changes between the mirrors of 500 nm will cause a detuning of the resonator. For the given setup this renders temperature fluctuations of about 0.1 K detrimental. Since a stabilization of the room temperature to this degree is not feasible we have decided to actively manipulate the length of the outer Ti tube using a Peltier element controlled by the automatic frequency control of the microwave bridge. This design allows for an active stabilization of the resonator structure as long as no major length changes occur. In practice one has to wait about 2-3 hours after cooling the cryostat before it is feasible to start a measurement. After this initial period the system can be stabilized for long term acquisition of EPR spectra.

Deposition of Di-tert-butyl nitroxide (DTBN) - a stable radical - on a thin MgO(100) film under UHV conditions has shown that the setup has submonolayer sensitivity. Currently, first investigations on paramagnetic surface centers on MgO(100) are under way.

#### *Proteins on surfaces*

In the past the group has shown that site directed spin labeling combined with an EPR spectroscopic characterization of the proteins allows to gain insight into the structure and dynamics of proteins on planar surfaces. One of the aims of the previous studies was to relate the information on the structure with physical and chemical properties of surfaces. To this end we have used T4 lysozyme (T4L) a small globular enzyme. We have shown that the interaction of T4L with model membranes containing DOPC lipids is very weak and causes no structural changes while mixed PC/PS bilayers cause a significant change in the adsorption behavior. To understand this behavior it is important to understand the properties of the lipid bilayers such as the phase behavior in more detail. This is currently pursued. A second line of research develops the methodology to allow a characterization of structural changes of proteins in the presence of an external

electric field. The idea is to gain atomistic understanding of structural changes which can be used to create addressable protein switches. The investigation of proteins on appropriately modified metal surface is challenging for EPR spectroscopy and requires suitable resonator structures. We are currently developing such a resonator which has the required sensitivity to allow for a characterization of proteins on metal surfaces. Along the same lines we started to work on membrane proteins of the bacteriorhodopsin family which are known to show conformational changes upon light (bacteriorhodopsin) or electric field (sensory rhodopsin).

### Catalysis/Laser Spectroscopy

In the last two years we have in part continued our investigations of adsorption and catalytic reactions on metal single crystals and oxide-supported metal clusters using linear (polarization-modulation IRAS) and non-linear (sum-frequency generation, SFG) in-situ vibrational spectroscopies in high-pressure environment. In addition, the design and set-up of in-situ experiments for the investigation of metal precipitation from a liquid (aqueous) phase onto the surface of single-crystalline oxide thin films has advanced. As a connection between the newly introduced researches on solid-liquid interfaces with our previous studies on clean oxide surfaces in vacuum or gas environment we have started to investigate the modification of oxide surfaces with relevant gases such as H<sub>2</sub>O or CO<sub>2</sub> at elevated pressure and the influence of surface modification on the properties of vapor-deposited metal clusters.

#### *In-situ studies at high pressures*

High coverage CO adsorption structures ( $\theta > 0.5$ ) on Pt(111) were investigated in a wide pressure (UHV to 1 bar) and temperature (150 K to 400 K) range with both PM-IRAS and SFG. In contrast to previous high pressure studies we could show that under certain conditions a CO super structure exhibiting two on-top CO bands rather than a single one can be stabilized. Whether this vibrational signature can be attributed to the domain-wall or the Moiré models described in the literature is currently under discussion.

The unique capability of PM-IRAS to obtain in-situ surface vibrational data and kinetic information from a catalytic reaction at the same time was applied to study CO oxidation over FeO(111)/Pt(111) (in collaboration with the *Structure and Reactivity group*, S. Shaikhutdinov). It could be shown that a decrease in reaction rate correlates with the appearance of an IR signal of CO adsorbed on Pt(111). Therefore, catalyst deactivation could unambiguously be related to dewetting of the FeO film and formation of FeO<sub>x</sub> particles.

#### *Hydroxylation of MgO(001)*

Adsorption of water on the surface of MgO(001)/Ag(001) thin films of different thickness (2-20 ML) was studied extensively from UHV to mbar pressure conditions using IRAS, SFG, XPS and TDS (a) in order to obtain information about the MgO film thickness dependence of H<sub>2</sub>O physisorption and chemisorption (hydroxylation), (b) to elucidate the interaction between the first and subsequently adsorbed water layers, and (c) to study the influence of surface hydroxylation on the properties of deposited metal clusters.

The monolayer H<sub>2</sub>O super structure on MgO(001) could be shown to be preserved even in the limit of 2 ML thin MgO films providing evidence that H<sub>2</sub>O physisorption is not affected by the presence of the underlying metal substrate. SFG spectroscopy was used to probe exclusively the interaction between the first H<sub>2</sub>O monolayer on MgO(001) and multilayer ice since this method is almost insensitive to bulk ice. The results show that there is significant H-bond interaction between the first and the second H<sub>2</sub>O layer, in contrast to conclusions from previous molecular dynamics simulations.

In contrast to H<sub>2</sub>O physisorption, hydroxylation of MgO(001) thin films strongly depends on MgO film thickness. The threshold hydroxylation pressure as determined from XPS and IR spectroscopy was found to decrease by three orders of magnitude (from 10<sup>-3</sup> mbar H<sub>2</sub>O to 10<sup>-6</sup> mbar H<sub>2</sub>O) when the MgO layer thickness is decreased from 20 ML to 2 ML. The assignment of the vibrational features as well as the structure of the hydroxylated MgO(001) surface are subject of a collaboration with the Theory group of Prof. J. Sauer, Humboldt University, Berlin. The influence of MgO surface hydroxylation on the properties of

deposited metal clusters has been studied and compared with those on a clean oxide surface for vapor-deposited gold particles. TDS and IR experiments using CO as a probe revealed that gold particles deposited on the hydroxylated MgO surface exhibit a higher abundance and thermal stability of low coordinated sites. This suggests stronger binding of Au to its nucleation site on the hydroxylated MgO surface leading to the stabilization of small Au clusters.

#### *Solid-liquid interfaces*

With this new research direction we are aiming at a molecular-level understanding of the different stages of catalyst preparation, i.e. precipitation of metals from a solution onto an oxide support, washing, drying, calcination, and reduction. The main in-situ experimental methods applied are solid-liquid STM and solid-liquid SFG. In order to combine these methods with the samples used in the experiments appropriate transfer systems and sample cells needed to be designed and constructed that allow for clean sample transfer between UHV and liquid environment.

In the first stage of this project, the transfer system for in-situ STM experiments has been completed. Initial UHV-to-liquid transfer experiments were carried out with a Ag(001) single crystal. As a next step, a thin FeO(111) film was prepared on Pt(111). The Moiré super structure of this very well known UHV model surface could be imaged in both air and neutral aqueous solution. As a first proof of principle for this new set-up, Pd was deposited from a PdCl<sub>2</sub> containing aqueous solution onto the FeO(111) surface and the resulting Pd clusters were imaged in air.

#### Molecular Beam

The activities of the molecular beam group focused on two main projects: (1) establishing the correlations between the structure of the model catalysts and their catalytic activity in chemical reactions and (2) development of a new single crystal adsorption microcalorimeter operating under UHV conditions for measuring heats of adsorption and reaction on the oxide-supported model catalysts.

### *Cis- and trans-2-butene conversions with hydrogen on Pd/Fe<sub>3</sub>O<sub>4</sub>/Pt(111)*

In this project we continue exploring the microscopic mechanisms of olefin conversions with hydrogen on nano-sized supported Pd clusters. Particularly, we focus on investigation of the processes related to dissociative hydrogen adsorption and diffusion into the subsurface region of Pd nanoparticles and their influence on the activity and selectivity toward competing *cis-trans* isomerization and hydrogenation pathways. Previously, we have shown that olefins can effectively decompose on the catalyst surface creating a large variety of molecularly adsorbed and/or partly dehydrogenated hydrocarbon species, which exact stoichiometry depends on the reaction temperature. These species were recognized to critically influence the catalytic properties of the Pd nanoparticles. For example, co-adsorbed strongly dehydrogenated carbonaceous deposits were shown to induce a sustained hydrogenation activity of *cis*-2-butene, which is otherwise not possible on the C-free Pd particles. However, the exact role that those carbon species play in the promotion of the persistent hydrogenation activity remained unknown. In the last two years we established that these effects are closely connected to the processes of dissociative hydrogen adsorption and its diffusion into the subsurface region of Pd nanoparticles.

First, by applying  $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$  nuclear reaction analysis (NRA) for hydrogen depth profiling (in collaboration with Prof. Fukutani, Tokyo University) to separately monitor the surface-adsorbed and volume-absorbed hydrogen atoms in combination with transient molecular beam experiments, we provided for the first time a direct experimental proof that the hydrogenation reaction pathway requires the presence of subsurface hydrogen species. The crucial role of carbon in maintaining the hydrogenation activity under the steady state reaction conditions was ascribed to facilitation of activated hydrogen diffusion from the surface into the subsurface region of Pd particles. This hypothesis was recently confirmed by the DFT calculations carried out in collaboration with Prof. K.M. Neyman (University of Barcelona, Spain). Here, the presence of carbon species was shown to nearly eliminate activation barriers for subsurface hydrogen diffusion, resulting in facilitation of the diffusion rate by about three orders of magnitude under our



experimental conditions. Carbon-induced elongation of the Pd-Pd interatomic distances in the atomically flexible nanoclusters, creating larger surface openings for hydrogen penetration into subsurface, was recognized to be the main reason for such pronounced reduction of the diffusion barrier.

Secondly, to address the kinetics of dissociative hydrogen adsorption and its subsurface diffusion as well as the abundance of both hydrogen species on a quantitative level, we performed pulsed molecular beam experiments on  $\text{H}_2 + \text{D}_2$  exchange (in collaboration with R.J. Madix, Harvard University, USA). In these experiments, the concentrations of atomic deuterium species in both surface and subsurface states under the isothermal reaction conditions were probed by applying short pulses of hydrogen, which reacts with deuterium to form HD. The intensity of the hydrogen beam was chosen to be about 100 times smaller than the deuterium flux to prevent any noticeable perturbation of the steady state deuterium concentrations by reaction with hydrogen. The amplitude and the time evolution of the HD formation rate allow to draw conclusions on the abundance of both species and on the rate of subsurface deuterium/hydrogen diffusion under the particular reaction conditions. The first results indicate that all hydrogen-related processes strongly depend on the presence and stoichiometry of co-adsorbed olefin species. Thus, strong inhibition of dissociative  $\text{D}_2$  adsorption in presence of *cis*-2-butene as compared to the clean Pd surface was observed, even under the conditions when the amount of dosed  $\text{D}_2$  exceeded the olefin flux by nearly three orders of magnitude.

Complementary, we carried out a series of pulsed molecular beam experiments, where the activity and the selectivity of the model catalyst toward *cis-trans* isomerization and hydrogenation of *cis*-2-butene was compared under the steady state reaction conditions and in the transient regime on the Pd-particles pre-saturated with deuterium. Here, the reaction conditions such as the reactant pressures and their ratios as well as the reaction temperature were varied in a large range. This approach allows us to obtain detailed information on the rate-determining steps and deduce the particular reaction conditions, at which transition to hydrogen-deficient conditions occurs. Formal reaction orders in the

*cis*-2-butene and deuterium pressure both under the steady state conditions and on the surface saturated with deuterium were determined. The temperature dependence of the *cis-trans* isomerization and hydrogenation reaction rates indicates that higher activation energies are required for the hydrogenation pathway and implies that different rate limiting steps are involved in the competing reactions.

*Heats of adsorption of carbon monoxide on Pd/Fe<sub>3</sub>O<sub>4</sub>/Pt(111) model catalysts by single-crystal adsorption microcalorimetry: particle size dependence*

Establishing the correlation between the energetics of adsorbate-surface interaction and the structural properties of a catalyst is an important fundamental issue and an essential prerequisite for understanding the realistic catalytic processes. Traditional experimental techniques for probing the energetics of adsorption, such as e.g. thermal desorption spectroscopy, provide reliable results only for reversible adsorption systems and cannot be correctly applied for processes including dissociation, clustering, diffusion into the bulk or reaction with co-adsorbates. These restrictions can be overcome by using a direct calorimetric measurement of the heat of adsorption. For this purpose we designed and set up a new UHV single crystal calorimetry experiment based on the method previously developed by D.A. King and C.T Campbell (in collaboration with C.T. Campbell, Washington University, Seattle, USA). The method relies on the measurement of temperature rise upon adsorption of gaseous molecules on the ultrathin (1-10  $\mu\text{m}$ ) single crystals, which is realized by application of a piezoelectric detector and an independent laser-based energy calibration. The new experimental set-up allows the calorimetric measurements in a wide temperature region ranging from 100 to 400 K and application of a broad range of adsorbates including both light and heavy gaseous molecules. The test measurements of adsorption heats of CO and benzene on Pt(111) were carried out at 100 and 300 K. The detector sensitivities of about 1-2 V/ $\mu\text{J}$  are found with a noise limited resolution of about  $\sim 15$  nJ. The detection limit of the calorimeter for CO adsorption on clean Pt(111) was estimated to be  $1.5 \times 10^{12}$  molecules $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  corresponding to less than 0,1% of the monolayer coverage. We obtained the absolute accuracy in energy to within a few percent. In the following, we applied

a newly developed microcalorimetry set up to determine the adsorption heats of carbon monoxide on Pd nanoparticles of different sizes supported on a well-defined  $\text{Fe}_3\text{O}_4/\text{Pt}(111)$  film. Particularly, we systematically varied the Pd cluster size in the range of  $\sim 100$  to 5000 Pd atoms to address the energetics of CO interaction with the nanoparticles of different dimensions. As a reference for the CO interaction with an extended surface, the adsorption heats were also determined on Pd(111). The first calorimetric measurements revealed a decrease of the initial heat of CO adsorption on the smallest Pd nanoparticles by about  $15 \text{ kJ}\cdot\text{mol}^{-1}$  as compared to the larger Pd clusters and the extended single crystal surface, the result, which was predicted theoretically but to date was not confirmed experimentally.

#### Photon-Induced Processes

The activities of the group are focused on the quantitative understanding of the plasmon excitation and the particle-size effects of photochemistry on supported metal nanoparticles. The electronic structures, the optical properties, and the catalytic properties of metal nanoparticles strongly depend on the particle's size and morphology. Especially, the excitation of the surface plasmon of metal nanoparticles (Mie plasmon) may have tremendous influences on photochemistry at their surfaces. The group has reported that plasmon excitation of silver nanoparticles leads to hyperthermal chaotic photodesorption of Xe atoms by direct electronic interaction and that it enhances photoreactions of adsorbed NO molecules. The questions to be asked here are how and why the photochemical activity changes with the particle size. For this purpose the group has conducted systematic photochemical experiments as a function of particle size as well as photon energy. Photochemistry on flat bulk metal surfaces has been also studied as the reference of an infinite size. Experimental methods used include mass selected time-of-flight (MS-TOF) measurement, resonance enhanced multiphoton ionization (REMPI), and temperature programmed desorption (TPD).

### *NO/Ag NPs: size dependence of photochemistry*

Size controlled silver nanoparticles (Ag NPs, mean diameter 3 – 12 nm) deposited on thin alumina films on NiAl(110) have been used for the studies of the size and the plasmonic effects on surface photochemistry, as they possess the (1,0)-mode plasmon resonance at  $\sim 3.6$  eV. Nitric oxide (NO) molecules were used as the probe molecules as their photochemistry on silver surfaces have been relatively well established; the photodesorption mechanism of NO on metal surfaces has been explained in terms the MGR/Antoniewicz model in which desorption proceeds via a transient negative ion (TNI) state ( $\sim 2.5$  eV for NO dimer on Ag(111)) created by the attachment of a hot electron from the substrate to the adsorbate. However, a new reaction channel has been found by the group as mentioned below.

NO molecules dosed on silver surfaces at low temperatures below 77 K form adsorbed dimers. When heated these dimers dissociate into NO molecules or decompose into  $\text{N}_2\text{O}$  and O. It has been found that the temperatures of TPD peaks arising from these reactions decrease with decreasing mean size of Ag NPs. Furthermore, the peak temperature shift was found to scale to the inverse of the particle radius ( $1/R$ ). This indicates that the interaction between the NO dimers and the Ag NPs decreases with  $1/R$ , probably due to the reduction of dispersion forces with decreasing size.

A  $1/R$  dependence was also found in the photodesorption cross section (PCS) of the NO dimers on the Ag NPs. By irradiation from a nanosecond laser at photon energies of 2.3 and 4.7 eV, the PCS increased with  $1/R$  from the value at Ag(111). This scaling is attributable to the increase of the surface flux of photogenerated hot electrons exciting the adsorbates with the surface to volume ratio: ( $S/V$ ) is proportional to  $1/R$ . At 3.5 eV in  $p$  polarization, i.e., on the plasmon resonance, the PCS increased much more steeply and reached a maximum  $\sim 1.7 \times 10^{-16} \text{ cm}^2$  (43 times enhancement compared to Ag(111)) for 5 nm diameter, particles, followed by a sharp decline. The volcano-like behavior is attributable to the interplay of the size-dependences of the plasmon decay channels and the plasmon oscillator strength.

On the other hand, the translational temperature ( $T_t$ ) measured by the MS-TOF method of NO photodesorbed from the Ag NPs was almost constant at  $\sim 700$  K for all the investigated particle sizes at 2.3 and 3.5 eV in  $p$  polarization. This suggests that the plasmon excitation does not change the photodesorption dynamics of NO, though it does enhance the photoexcitation probability. At 4.7 eV, however, a linear increase of  $T_t$  with  $1/R$  was observed for particles smaller than 6 nm in diameter. At this photon energy, electrons in the d-band can be excited. Thus, the increase may be explained by an increasing contribution of the attachment of photo-holes from the d-band, which may be localized at the surfaces of Ag NPs to desorption.

#### *State-resolved studies of photodesorption of NO from Ag NPs*

REMPI measurements have been conducted to investigate the energy partitioning into not only the translational but also the rovibronic degrees of freedom in photodesorption dynamics of NO. A strong positive correlation between the translational temperature and the rotational energy was found, which can be explained by the impulsive model. However, little changes with the particle size in translational, rotational, and vibrational temperatures were found at 2.3 and 3.5 eV. This corroborates that the photodesorption dynamics of NO is not sensitive to the particle size and also the plasmon excitation at these photon energies. Only at 4.7 eV, significant increases in translational, rotational, and vibrational temperatures were found for the smallest Ag NPs ( $\sim 4$  nm). This result is consistent with the MS-TOF measurements mentioned above, indicating that different mechanisms of photoexcitation and photodesorption are operative at this photon energy.

Photodesorption of NO from Ag(111) and from Ag NPs induced by femtosecond (fs) laser pulses (3.1 eV, 80 fs) were also studied. The PCS at Ag(111) did not change significantly between nanosecond (ns) and fs laser pulses for laser fluences up to  $2 \text{ mJ/cm}^2$ . However, the PCS measured for NO on the Ag NPs was found to be about 500 times larger than that for Ag(111) under fs laser irradiation. Also, the  $T_t$  of NO photodesorbed with fs pulses increased with the laser fluence. These peculiarities can be due to an anomalous rise of electronic temperatures

within the Ag NPs confined on the thin alumina film. More theoretical and experimental investigations will be required to elucidate these phenomena

#### *Photochemical N<sub>2</sub> formation from NO dimers on Ag(111)*

The group has found a new photoreaction channel of the NO dimer adsorbed on Ag(111); irradiation of 2.3 – 4.7-eV photons produces N<sub>2</sub> directly from (NO)<sub>2</sub>/Ag(111) by the concerted scission of the two N-O bonds in O-N-N-O, which is adsorbed in the cis form with the N-ends on the surface. The N<sub>2</sub> formed via this channel desorbs with a very high translational temperature (5700 K) due to a strong acceleration by the steep Pauli repulsive part of the physisorption well of N<sub>2</sub> on Ag(111). In the gas phase NO dimer, such a path has not been found. This can be regarded as a photochemical reduction of adsorbed NO.

#### Spectro-Microscopy (SMART)

The group studies the growth of thin oxide films and characterizes the chemical and structural inhomogeneities. Furthermore, the chemical and structural properties of individual metal nanoparticles grown on this support are in our interest. The systems have been investigated with the SMART microscope (SpectroMicroscope with Aberration correction for many Relevant Techniques), which has been built up within a collaboration.

#### *SMART-Project*

The spectromicroscope SMART combines x-ray photoemission electron spectroscopy with a low energy electron microscopy (LEEM). The direct (i.e. non-scanning) and therefore fast imaging method enables the *in-situ* and *real-time* observation of surface processes like film growth, oxidation or annealing by using photo-emitted or reflected electrons. An aberration corrector improves the lateral resolution down to 2.6 nm, which is twice as good as the best uncorrected LEEM system. The Omega-type imaging energy analyzer together with a high flux density beamline at BESSY-II allows photo-electron spectroscopy from selected nanometer sized surface areas. Together with the diffraction mode this instrument obtains comprehensive information about e.g. morphology, structure, chemical distribution or work function of selected objects of only a few nanometers in size.

In the last two years the installation at the new high flux-density beamline UE49 at BESSY-II has been finished. As a new routine the x-ray illumination spot on the sample surface was directly observed with the SMART which results in a fast focusing of an about 10  $\mu\text{m}$  small, high intense x-ray spot. Additional to the instrumental optimizations, the scientific projects of the collaborating partner Universität Würzburg were completed: i) surface faceting induced by the organic growth of PTCDA molecule on a vicinal Ag(111) surface and ii) the study of the formation of CdSe quantum dots.

A new instrument with an improved performance – called SMART-II – is currently under construction in our department and will substitute the first version on long term. The aim of the new instrument is a routine operation with easy handling at a high lateral resolution better than 2 nm in LEEM and 5 nm in PEEM.

#### *Growth and structure of $\text{Fe}_3\text{O}_4$ thin films on Pt(111)*

The preparation of FeO and  $\text{Fe}_3\text{O}_4$  thin films on a Pt(111) surface has been observed *in-situ* and *in real-time* by microscopy and LEED. The influence of the different parameters like deposition rate, oxygen exposure or oxidation temperature on the structure, the morphology and the surface termination has been studied. The morphology of the  $\text{Fe}_3\text{O}_4$  films shows in LEEM terraces a few hundreds of nanometers wide. Furthermore, we found an unknown Moiré like pattern with a lateral periodicity of about 60 nm and 6-fold symmetry, aligned along the atomic rows of the substrate. This pattern can be explained by a periodic height modulation in the oxide film due to a strain, induced by the underlying Pt(111) substrate.

The known but not fully understood  $p(2\times 2)$  reconstruction of the  $\text{Fe}_3\text{O}_4$  film surface has been investigated by local LEED and LEEM. By dark-field imaging we found two types of reconstruction domains, each having the same three-fold symmetry but rotated by  $180^\circ$  to each other. One type of domain is dominant and covers between 70 and 95 % of the surface, depending on the oxidation temperature. The domain size and shape correlates with the substrate morphology like atomic steps and step bunches.

The structure and the surface termination have been studied by local LEED-IV, whereas contributions of the different domains could be disentangled. We found that the preparation – e.g. the final annealing of the prepared oxide film – influences significantly the structure and morphology of the film.

#### Scanned-energy mode photoelectron diffraction

This activity is based on a collaboration with Phil Woodruff at the University of Warwick that originally involved Alex Bradshaw in the Surface Physics Department. Christine Lamont at the University of Huddersfield also contributes to the activity. A postdoctoral researcher based at the FHI is funded through SFB 546 of the DFG, while a research student is jointly funded by CP and AC. Scanned-energy mode photoelectron diffraction (PhD) is a novel synchrotron-radiation- based method to determine quantitatively the local structure at surfaces in an element-specific and chemical-state-specific fashion. While the group continues to exploit this method to investigate the structure of increasingly complex small molecules (recently measurements have been made on furan, tartaric acid and the nucleotide bases, cytosine and uracil) on metal surfaces, the focus of the FHI-based component of the collaboration is on transition metal oxide surfaces. During the last 2 years this aspect of the work has continued to focus on ultra-thin epitaxial films of  $V_2O_3$  (most recently grown on Au(111)), with some continuing interest in adsorbates on  $TiO_2(110)$ . At the time of writing a new project to study V adsorption on epitaxial  $CeO_2(111)$  is also being initiated to link to other work in the CP department. The work on  $V_2O_3$  grown on Au(111), for which one obtains high-quality films as judged by sharp LEED patterns, exploits prior characterisation work by the Electron Spectroscopy and Synchrotron Radiation group within CP on the preparation and reactivity of the resulting (0001) surface. We have conducted extensive investigations of a range of adsorbate molecules on this surface, but the results have not always proved conclusive. The as-prepared surface shows a very low activity for adsorption but this can be enhanced by low-energy electron bombardment that is believed to remove terminal oxygen atoms from surface vanadyl species, exposing the more reactive V atoms. So far the PhD results do not fully support this interpretation.



Our investigation of surface hydroxyl species on this surface, produced both by reaction with molecular water or by adsorption of atomic hydrogen, show that it is the O atoms in the outermost bulk layer, and not the vanadyl O atoms, that are hydroxylated. The PhD results indicate any coverage of hydroxylated vanadyl O atoms must be very low. This somewhat surprising result has gained some support from theoretical results obtained within the Theory Department by Klaus Hermann and colleagues, who find the energetics of these alternative processes are too similar to distinguish convincingly. The results of this collaborative study were published in 2008. The local structure of hydroxyl species on  $\text{TiO}_2(110)$  has also been investigated, again using atomic hydrogen adsorption to overcome the need to create surface defects (bridging oxygen vacancies) to achieve reaction with molecular water. As expected, the surface bridging O atoms are hydroxylated, but the PhD analysis, currently being completed, will provide quantitative information on the chemisorption bondlengths. A study of the interaction of glycine with  $\text{TiO}_2(110)$  shows that a deprotonated glycinate, and not zwitterionic glycine, is the surface species produced, and this bonds to the surface in a bidentate fashion through the two carboxylate O atoms.

#### PP&B (Personal Computers, Realtime & Image Processing)

Based on the data network infrastructure, provided by the Joint Network Center (GNZ), the PP&B group is responsible for the installation and maintenance of the desktop systems (including laptops), workstations, telephone system and the electronic building control system.

The technical consulting service supports scientists of the institute in the configuration, modification, acquisition, and adaption of computer equipment to the experiments (in close cooperation with the service group for electronics). Since the last meeting the group is developing a general purpose acquisition system (iMess) based on SOAP which can be used by all experimental groups in the future. The deployment of this software is planned for 2010.

Several server systems perform services for data storage, mail, web, printing, number crunching and databases for different document archives. A new

computer cluster ('xfhix' with 248 cores) was granted by the BAR (Beratender Ausschuss für Rechnersysteme) beginning this year and was successfully installed in spring 2009. This system superseded the old system ('fhix') dating to the end of 2005 and is in heavy use by different users of all departments. The centralized storage system was expanded to 50 Tbyte within the last two years. The video conference system is now located in a larger room in building S and is now accepted well.

The group is housed in building S which has not been renovated so far and there are technical obstacles concerning the placement of some server and storage systems.

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## **Master Theses**

*Gonchar, A.*: Properties of Point Defects on Single Crystalline MgO(100) Films. Southern Federal University, Rostov/Don, Russia 2008.

*Sperling, F.*: Ansteuerung des Strahlrohrs im BESSY-SMART Projekt unter Verwendung von EPICS und VxWorks. Technische Fachhochschule Berlin 2008.

## **2009**

*Bagus, P.S., C.J. Nelin, E.I Ilton, M. Baron, H. Abbott, E. Primorac, H. Kühlenbeck, S. Shaikhutdinov, and H.-J. Freund*: The complex core level spectra of CeO<sub>2</sub>: An analysis in terms of atomic and charge transfer effects. Physical Review Letters, submitted (2009).

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*Angewandte Chemie International Edition* **48**, 3695-3698 (2009).

- Formaldehydbildung auf den Vanadiumoxidoberflächen on  $V_2O_3(001)$  und  $V_2O_5(001)$ : Wie bildet sich der stabile Methoxy-Zwischenzustand?

*Angewandte Chemie* **121**, 3750-3753 (2009).

*Heyde, M., G.H. Simon, and T. König: Study of thin oxide films with NC-AFM: Atomically resolved imaging and beyond. In: S. Morita, F.J. Giessibl, R. Wiesendanger (Eds.), Noncontact Atomic Force Microscopy. Springer-Verlag 2009, in press.*

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*Lizzit, S., G. Zampieri, K.L. Kostov, G. Tyuliev, R. Larciprete, L. Petaccia, B. Naydenov, and D. Menzel:* Charge transfer from core-excited argon adsorbed on clean and hydrogenated Si(100): ultrashort timescale and energetic structure.

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*Lizzit, S., Y. Zhang, K.L. Kostov, L. Petaccia, A. Baraldi, D. Menzel, and K. Reuter:* O- and H-induced surface core level shifts on Ru(0001): prevalence of the additivity rule.

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*Ludwig, W., B., Brandt, A. Savara, R.J. Madix, S. Schauermann, and H.-J. Freund:* Kinetic study on the conversion of cis-2-butene with deuterium on a Pd/Fe<sub>3</sub>O<sub>4</sub> model catalyst.

Physical Chemistry Chemical Physics, submitted (2009).

*Martinez, U., J.-F. Jerratsch, N. Nilius, L. Giordano, G. Pacchioni, and H.-J. Freund:* Tailoring the interaction strength between gold particles and silica thin films via work function control.

Physical Review Letters **103**, 056801-1-4 (2009).

- Modifying the adsorption properties of silica thin films via work function control.

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Physical Review Letters, submitted (2009).

*Simon, G. H., T. König, M. Heyde, and H.-J. Freund:* Imaging individual adatoms on oxide surfaces.

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- Realization of an atomic sieve: Silica on Mo(112). Surface Science **603**, 1145-1149 (2009).

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## **Habilitation**

*Nilius, N.:* Oxide Surfaces and their Adsorption Characteristics Investigated by Scanning Tunneling Microscopy. Humboldt-Universität zu Berlin 2009.

## **Doctoral Theses**

*Kim, Ki Hyun:* Enhancement of Photoinduced Processes on Supported Ag Nanoparticles Compared to a Flat Ag Surface. Freie Universität Berlin 2009.

*Guimond, S.:* Vanadium and Molybdenum Oxide Thin Films on Au(111): Growth and Surface Characterization. Humboldt-Universität zu Berlin 2009.

### **Diploma Thesis**

*Müller, M.:* Implementierung eines Hardware Abstraction Layers zur Steuerung einer hochauflösenden 14Bit CCD-Kamera am Berlin Elektronensynchrotron (BESSY). FB VI (Informatik und Medien) Beuth Hochschule für Technik Berlin (ehemals Technische Fachhochschule Berlin) 2009.

### **Master Thesis**

*Dowler, R.:* The Testing and Design of an STM and Transfer System for the Characterization of Surfaces at the Solid-liquid Interface. The University of Auckland, New Zealand 2009.



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

### Hans-Joachim Freund

- Nov. 2007      Centenary Lecture Tour, University of Southampton, Southampton, UK  
*Models for heterogeneous catalysts at the atomic scale*
- GDCh Vortrag, Karlsruher Chemische Gesellschaft, Karlsruhe, Germany  
*Atome und Cluster auf Oxidoberflächen: Atomare Einblicke in die Katalyse*
- Feb. 2008      Kuwait University, Kuwait City, Kuwait  
*1. Nanoparticles on oxide surfaces an atomic view*  
*2. Reactions on model systems for heterogeneous catalysts*
- March 2008      APS March Meeting “Fundamental Issues in Catalysis”, New Orleans, USA  
*Gold atoms, chains and islands on oxide films: looking at orbitals and counting electrons*
- March 2008      V. N. Ipatieff Lectureship 1, Northwestern University, Chicago, USA  
*1. Metal atoms, clusters, and nanoparticles on oxide supports*  
*2. Ultra-thin film oxides: Materials with tailored properties*  
*3. Optical properties and photochemistry of nanoparticles*
- March 2008      Invitational Lecture Series at UOP Technical Community Organization Honeywell Technology, Des Plaines, USA  
*Supported metal clusters as model for heterogeneous catalysts at the atomic scale*
- March 2008      Seminar Argonne National Laboratory, Argonne, USA  
*Ultra-thin Oxide Films as Designable Model Catalysts*
- April 2008      Francisco Zaera's Arthur W. Adamson Award for Distinguished Service in the Advancement of Surface Chemistry, ACS Spring Meeting, New Orleans, USA  
*Interaction and reaction of hydrocarbons with supported nanoparticles*
- April 2008      George A. Olah Award in Hydrocarbon or Petroleum Chemistry: Symposium in Honor of Israel E. Wachs, ACS Spring Meeting, New Orleans, USA  
*Model studies on bulk vanadia surfaces and on supported vanadia nanoscale systems*

- April 2008      Physikkolloquium, Universität Ilmenau, Ilmenau, Germany  
*Metallatome und Nanoteilchen auf dünnen Oxidfilmen: Systeme mit einstellbaren Eigenschaften*
- April 2008      Physikalisches Institut Köln, Köln, Germany  
*Metal atoms and clusters on thin oxide films: Systems with designable properties*
- May 2008        Festveranstaltung aus Anlass des 60. Geburtstages von E. Umbach, Karlsruhe, Germany  
*Atomare Einblicke in die Katalyse*
- May 2008        “Catalysis for Society”, Cracow, Poland  
*Metal atoms and clusters as model systems with designable properties*
- May 2008        CERC3 Workshop “Surface Chemistry of Nanomaterials”, Vienna, Austria  
*From atoms to nanoparticles on oxide supports: An atomic view at structure-chemistry relations*
- May 2008        Hassel Lecture, Oslo, Norway  
*1. Metal atoms and clusters on thin oxide films: Systems with designable properties*  
*2. Chemistry on supported nanoparticles: Model studies*
- May 2008        Universität Hannover, GDCh-Vortrag, Hannover, Germany  
*Atome und Cluster auf Oxidoberflächen: Atomare Einblicke in die Katalyse*
- May 2008        Symposium in honour of Wyn Roberts, Cardiff, UK  
*Ultra-thin oxide films as designable model catalyst system*
- May 2008        11. Steinheimer Gespräche des Fonds für den Hochschullehrer-nachwuchs, Frankfurt am Main, Germany  
*Der wissenschaftliche Forschungsrat: Ein neues Instrument europäischer Forschungsförderung*
- June 2008        4th International Conference on X-rays and Related Techniques in Research and Industry (ICXRI 2008), Kota Kinabalu, Sabah, Malaysia  
*Hydrogen on and in nanoparticles: Key to catalytic activity*

- June 2008 Seminar, Department of Chemistry, Universiti Kebangsaan Malaysia Research and Industry (ICXRI 2008), Kuala Lumpur, Malaysia  
*Metal atoms and clusters on thin oxide films: Systems with designable properties*
- June 2008 NATO ARW “Self-Organization of Molecular Systems in Micro-, Nano, and Macro-Dimensions: From Water to Nanoparticles, to Nanotubes, to DNA and Proteins”, Kiev, Ukraine  
*Nanoparticles as models for heterogeneous catalysts: An atomic view*
- July 2008 3. Workshop on Nanoscale Physics and Devices, Yunnan University, Kunming, China  
*From atoms to clusters: Models for heterogeneous catalysts*
- July 2008 Catalysis Summit, Sapporo, Japan  
*Basic research in catalysis to sustain energy supply for the future*
- July 2008 International Symposium on Creation and Control of Advanced Selective Catalysis as Celebration of the 50th Anniversary of Catalysis Society in Japan, Kyoto, Japan  
*An atomic view of model catalysts*
- July 2008 Catalysis as the Pivotal Technology for the Future Society , COEX Convention Center, 14th International Congress on Catalysis, Seoul, Korea  
*Metal atoms and clusters as model systems with designable properties: Model systems for catalysis*
- July 2008 Lecture, University of Science and Technology of Hefei, Hefei, China  
*From metal atoms and clusters to nanoparticles on oxide surfaces: Model systems for heterogeneous catalysis*
- July 2008 ECOS-25, Liverpool, UK  
*Nanoparticles as models for heterogeneous catalysts: An atomic view*
- Aug. 2008 Grand Challenge for Catalysis Workshop, Santa Barbara, USA  
*From supported atoms to nanoclusters: Surface chemistry at the nanoscale*
- Aug. 2008 Annual Scientific Meeting, Center for Catalysis and Surface Science, Northwestern University, Evanston, USA  
*From atoms to nanoparticles supported on oxide surfaces*

- Aug. 2008 Seminar Talk, Department of Chem. Engin., University of Wisconsin, Madison, USA  
*Catalytic chemistry on and in nanoparticles: Oxide supported model systems*
- Sept. 2008 “Free, coordinated and supported clusters: Bridging experiment and theory” Conacyt – DFG Workshop, Mexico-City, Mexico  
*Metal atoms and clusters on oxide surfaces*
- Sept. 2008 6th German-Brazilian Workshop, Titi-See, Neustadt, Germany  
*Surfaces of functional materials at the atomic level: Catalysis, a case study*
- Sept. 2008 Gallei Workshop, BASF Katalysetag, Ludwigshafen, Germany  
*Surface Science Models in Catalysis: An View at the Atomic Level*
- Oct. 2008 AVS 55th International Symposium, Boston, USA  
*Reactivity studies on oxide supported metal nanoparticles*
- Dec. 2008 2nd Forum of the AvH International Advisory Board, Berlin, Germany  
*Strategies to win the best: German approaches in international perspectives, The European perspective: A report from the ERC*
- Dec. 2008 Helmut Schwarz Birthday Symposium, GDCh, Stiftung Kloster Eberbach, Eltville, Germany  
*Metal atoms and clusters on oxide surfaces: Surface science quo vadis?*
- Jan. 2009 Universite Libre de Bruxelles: Outstanding PhD formation day, Bruxelles, Switzerland  
*Heterogeneous catalysis and nanostructures*
- Jan. 2009 Paul Scherrer Institut, Villingen, Switzerland  
*Metal nanoparticles on oxide Surfaces: Models for heterogeneous catalysts at the atomic level*
- Jan. 2009 25th Annual Meeting of the Swiss User Group Surfaces and Interfaces, Fribourg, Switzerland  
*Surfaces of functional materials at the atomic level: Catalysis, a case study*
- Feb. 2009 Max Planck-University of British Columbia Workshop, MPI for Solid State Research, Stuttgart, Germany  
*Supported metal and oxide nanoclusters: From electronic structure to reactivity*

- Feb. 2009 COST Winter School “Methods to Characterize Oxide Surfaces”, Berlin, Germany  
*Photoemission and related techniques*
- March 2009 Model Systems for Heterogeneous Catalysis, WPI-AIMR 2009 Annual Workshop, Miyagi, Japan  
*From Atoms to Nanoparticles on Oxide Surfaces*
- March 2009 22nd Symposium on Surface Science (3S), St. Moritz, Switzerland  
*Methanol Oxidation over Vanadia: A Combined STM, TDS, XPS, IRAS Study*
- March 2009 ACS Symposium “The Convergence Between Theory and Experiment in Surface Chemistry and Heterogeneous Catalysis”, Salt Lake City, USA  
*From adsorbed atoms to supported clusters: Experiments vs. theory*
- March 2009 CATL Symposium, Salt Lake City, USA  
*Reactivity studies on oxide supported metal nanoparticles*
- May 2009 Ehrenkolloquium Klaus Heinz, Universität Erlangen, Erlangen, Germany  
*Heterogeneous catalysis and nanostructures*
- May 2009 Bunsentagung, Köln, Germany  
*Engineering materials surfaces at the atomic level: Catalysis as a case study*
- June 2009 Lecture at Rijksuniversiteit Groningen, Nijmegen, The Netherlands  
*Engineering surfaces at the atomic level*
- June 2009 inGAP-NANOCAT Summer School: "Nano designed-catalysts: from molecules to industrial processes", Trondheim, Norway  
*Models for heterogeneous catalysts: Supported nanoparticles at the atomic scale*
- July 2009 Surface Physics Lecture Series, State Key Lab for Surface Physics, Institute of Physics, Beijing, China  
*Engineering surfaces at the atomic level*
- Aug. 2009 CINF Summer School 2009, Sandberg Gods (Estate), Sønderborg, Denmark  
*Reactivity of oxide supported nanoparticles at the atomic scale*
- Sept. 2009 ChinaNANO 2009, Peking, China  
*Au nanostructures and their interaction with molecules*

- Sept. 2009      Conference “Nanostructures at Surfaces - Spectroscopy at the Atomic and Molecular Scale”, Monte Verità, Switzerland  
*Oxide supported nanoparticles and its reaction to reactivity*
- Oct. 2009      11th International Conference on Electronic Spectroscopy and Structure (ICESS11), Nara, Japan  
*Effects of plasmon excitation on photodesorption of small molecules from supported silver nanoparticles*
- Oct. 2009      ECASIA, Antalya, Turkey  
*The electronic structure of the nanoparticle-oxide interface*

### **Markus Heyde**

- May 2008      EMPA - Swiss Federal Laboratories for Materials Research, Dübendorf, Switzerland  
*Atomically resolved imaging on thin oxide films by dynamic force microscopy and beyond*
- Nov. 2008      Universität Osnabrück, Osnabrück, Germany  
*Frequency modulated dynamic force microscopy studies on thin oxide films*
- Dec. 2008      Department of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, Japan  
*Dual mode frequency modulated dynamic force and scanning tunneling microscopy: Basic concept, experimental design, signal electronics, atomic resolution*
- April 2009      University College London, Materials Simulation Laboratory, London, UK  
*Detailed frequency modulation dynamic force microscopy studies on oxide films*
- May 2009      Innovations for High Performance Microelectronics (IHP), Leibniz-Institut, Frankfurt/Oder  
*Atomic force microscopy studies on oxide films*

### **Niklas Nilius**

- Jan. 2008      Humboldt Universität zu Berlin, Arbeitsgruppe Grenzflächen und dünne Schichten, Berlin, Germany  
*Adsorptionsverhalten dünner Oxidefilme*

- Jan. 2008      University of Modena, Department of Physics, Modena, Italy  
*Adsorption of metal atoms on thin oxide films*
- March 2008    University of Milano, Department of Materials Science, Milano, Italy  
*Au chains self-assembled on alumina thin films*
- May 2008      Humboldt Universität zu Berlin, Berlin, Germany  
*Elektronische Eigenschaften linearer Atomketten auf metallischen und oxidischen Substraten (Habilitation-Colloquium)*
- Feb. 2009      University of Modena, Department of Physics, Modena, Italy  
*Photon-emission spectroscopy at the nanometer scale*

### **Thomas Risse**

- Dec. 2007      Institut für Physik, Universität Bielefeld, Germany  
*ESR Spektroskopie an wohl definierten planaren Oberflächen: von Atomen im Ultrahochvakuum zu Proteinen unter physiologischen Bedingungen*
- Feb. 2008      DPG Jahrestagung, Berlin, Germany  
*Molecular adsorption on bimetallic particles supported on well defined oxide surfaces*
- June 2008      FU-Berlin, Berlin, Germany  
*Tuning the properties of Au atoms and clusters supported on MgO(001)-films*
- June 2008      Universität Bonn, Bonn, Germany  
*Wege zur Modifikation von oxidgeträgerten Metallpartikeln: von Punktdefekten zu bimetallic Systemen*
- Sept. 2008     Workshop on modern magnetic resonance techniques, MPI-Polymerforschung, Barsinghausen, Germany  
*EPR spectroscopy on well defined planar surfaces: From ultrahigh vacuum to physiological conditions*
- Oct. 2008      AVS annual meeting 2008, Boston, USA  
*Tuning the properties of Metals on Oxides: Au on MgO(001)-films a case study*
- Dec. 2008      Università Milano Bicocca, Milano, Italy  
*An atomistic view on heterogeneous catalysis using well defined model systems*

- June 2008      Universität Bielefeld, Bielefeld, Germany  
*Structure and dynamics of proteins at well defined surfaces as characterized by EPR spectroscopy*
- July 2009      TU Munich, Munich, Germany  
*Atomistic characterization of model catalysts: From ultrahigh vacuum to physiological conditions*
- Sept. 2009      EFEP conference, Antwerp, Belgium  
*Tuning the properties of single crystalline MgO(100) surfaces by point defects*

### **Swetlana Schauer mann**

- April 2008      Surface Science Seminar, Tulane University, New Orleans, USA  
*Molecular beam experiments on supported model catalysts*
- May 2008      CERC3 Young Chemists' Workshop "Surface Chemistry of Nanomaterials", Vienna, Austria  
*Carbonaceous deposits critically control selectivity in olefin conversions.*
- Nov. 2008      Surface Science Seminar, University of Tokyo, Tokyo, Japan  
*Molecular beam experiments on supported model catalysts*
- Jan. 2009      International Workshop on Oxide Surfaces (IWOX) VI, Schladming, Austria  
*Hydrocarbon conversions on oxide supported model catalysts*
- May 2009      IDECAT Conference on Catalysis, Porquerolles, France  
*Hydrocarbon conversions on oxide supported model catalysts*
- May 2009      Institute of Physical and Theoretical Chemistry, University of Bonn, Germany  
*Selectivity in hydrocarbon conversions on supported model catalysts*

### **Shamil Shaikhutdinov**

- Oct. 2007      Pacific North National Laboratory, Richland, USA  
*Towards understanding structure-reactivity relationships in catalysis: Model studies*
- Dec. 2007      NSoS International Workshop, Linz, Austria  
*Iron oxide films: Twenty years after*



- March 2008 Rideal Conference, Cambridge, UK  
*Oxide supported model catalysts: Model studies*
- April 2008 IMPRS Lectures, Technical University, Berlin, Germany  
*Growth of thin silica films on metals*
- Aug. 2009 ECOSS 26, Parma, Italy  
*Oxide surfaces: Thin films vs nanoparticles*

### **Thomas Schmidt**

- Feb. 2008 Frühjahrstagung der Deutschen Physikalischen Gesellschaft, Berlin, Germany  
*SMART – Spectromicroscopy with aberration correction for high resolution surface characterization*
- June 2008 SRI 2008 Meeting, Saskatoon, Kanada  
*1. SMART – an aberration corrected photoemission electron microscope for surface characterization on nanometer scale*  
*2. Organic thin film growth studied by photoemission electron microscopy*
- Nov. 2008 International Symposium on Surface Science and Nanotechnology (ISSS-5), Tokyo, Japan  
*SMART – using an aberration corrected photoemission electron microscope as a nano-analytic tool*

### **Martin Sterrer**

- April 2008 COST-Workshop Paris, France  
*Modification of MgO(100) films at high pressures*
- July 2009 8<sup>th</sup> International Conference “Mechanisms of Catalytic Reactions”, Novosibirsk, Russia  
*Surface science models in heterogeneous catalysis – A view at the atomic level*

### **Kazuo Watanabe**

- Feb. 2008 Farkas Symposium on Photochemistry in Organized Media, Bokek, Israel  
*Surface photochemistry on nanosized metal particles*

- April 2008     International Max Planck Research School Block Course,  
Technische Universität Berlin, Berlin, Germany  
*Plasmons and photochemistry on supported metal nanoparticles*
- July 2008     CINSaT – Kolloquium, Kassel Universität, Kassel, Germany  
*Effects of plasmon excitation on photodesorption of NO and Xe  
from supported Ag nanoparticles*
- Nov. 2008     Nanoscale Science Department Seminar, Max Planck Institute for  
Solid State Research, Stuttgart, Germany  
*Size and plasmonic effects in photochemistry on metal  
nanoparticles*
- Nov. 2008     Department of Chemistry, Faculty of Science, Kyoto University,  
Kyoto, Japan  
*Size and plasmonic effects in photochemistry at metal  
nanoparticles*
- Nov. 2008     Cluster Research Laboratory, Faculty of Science, Genesis Research  
Institute, Chiba, Japan  
*Size and plasmonic effects in thermal and photochemistry on metal  
nanoparticles*
- Dec. 2008     Surface Chemistry Laboratory, RIKEN, Saitama, Japan  
*Size and plasmonic effects in photoinduced reactions on supported  
metal nanoparticles*
- April 2009     DIET XII, The Twelfth International Workshop on Desorption  
Induced by Electronic Transitions, Pine Mountain, Georgia, USA  
*Size and plasmonic effects in photodesorption of NO from  
supported silver nanoparticles*
- June 2009     Special WPI-Joint Seminar, Tohoku University, Sendai, Japan  
*Plasmonic effects in photodesorption of NO from supported silver  
nanoparticles - nanoplasmonic photocatalysts for solar energy  
conversion -*

#### **D. Phil Woodruff**

- May 2008     New Light Source Project Condensed Matter Workshop,  
Rutherford Appleton Laboratory, Didcot, UK  
*VUV photoemission from solids: fast and slow*

- June 2008      Structure, Assembly and Reactivity of Molecules at Surfaces, RSC  
Solid Surfaces Group Meeting, London, UK  
*Getting quantitative local structural information on molecular  
adsorbates*
- Sept. 2008      PendryFest: a Fest for Sir John Pendry, FRS, London, UK  
*Photoelectron diffraction – ‘internal LEED’ for local surface  
structure determination*
- Feb. 2009      Seminar by RSC: Chemistry Department, University of Warwick,  
Warwick, UK  
*Getting quantitative local structural information for molecules on  
surfaces*
- July 2009      Lise-Meitner-Kolloquium,      Helmholtz-Zentrum      Berlin      für  
Materialien und Energie GmbH, Berlin, Germany  
*Understanding atomic-scale structural effects at surfaces*







**Staff scientists (as of November 2009):**

Knut Asmis	(Habilitation)	Karsten Horn	(Habilitation)
Uwe Becker	(Habilitation)	Jochen Küpper	
Horst Conrad	(Habilitation)	Adela Marian	(EU/AvH Fellow)
André Fielicke		Bas van de Meerakker	
Bretislav Friedrich	(Habilitation)	Melanie Schnell	(Liebig Fellow)
Gert von Helden		Wieland Schöllkopf	

**Guest scientists, staying for at least six months:**

Markus Braune		Jonathan T. Lyon	(AvH Fellow)
Yuriy Dedkov		Jesus Martinez Blanco	
Thalia Deniozou		Jens Riedel	
Daniel Goebbert		Axel Reinköster	
Daniel Harding		Gabriele Santambrogio	(AvH Fellow)
Ling Jiang	(AvH Fellow)	Bum Suk Zhao	(AvH Fellow)
Sanja Korica			

**Scientists (temporary) paid from external funds:**

Ad van der Avoird (AvH Awardee)	University of Nijmegen, The Netherlands
Phil Bunker	National Research Council of Canada, Ottawa, Canada
Wolfgang Jäger (AvH Awardee)	University of Alberta, Edmonton, Canada
Hitoshi Odashima	Meiji University, Kawasaki, Japan
Lokesh Tribedi	Tata Institute of Fundamental Research, Mumbai, India
Boris Sartakov	Russia Academy of Science, Moscow, Russia
Yunjie Xu	University of Alberta, Edmonton, Canada

<b>Graduate students:</b>	18
<b>Diploma student:</b>	10
<b>Technicians:</b>	8





## **Recent Developments in the Department of Molecular Physics**

**Director: Gerard Meijer**

### **General remarks**

Since the last visit of the Fachbeirat, there have been some changes among the scientific staff members of the department:

- Dr. Knut R. Asmis has been promoted to a permanent staff member.
- Dr. Hendrick L. Bethlem received an ERC Starting Grant and accepted a permanent position (“Universitair Docent”) at the Free University of Amsterdam, The Netherlands, in January 2008.
- Dr. Steven Hoekstra, post-doc since May 2005 and group leader since early 2008, accepted a tenure-track Assistant Professor position at the KVI in Groningen, The Netherlands, starting November 2009.
- Dr. Andreas Osterwalder received a “Foerderprofessur des Schweizerischen Nationalfonds”, or SNSF Professorship, at the EPFL, Switzerland, where he moved to in May 2009.
- Dr. Wieland Schöllkopf has been promoted to a permanent staff member and as the scientist in charge of the infrared free electron laser (IR-FEL) project at the FHI.

The ongoing research projects are described below in four different sections. The first section deals with “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. Highlights during the last two years have been the measurement of the far-infrared spectra of neutral gold clusters in the gas phase and the study of the microhydration of ions, i.e., the study of the dependence of the geometric and electronic structure of ions on the degree of hydration and on temperature. An important experimental development is that we have been able to catch mass-selected biomolecular ions in superfluid He-droplets, yielding interesting possibilities for future investigations. The IR spectroscopic experiments are still largely performed at the Free Electron Laser for Infrared eXperiments (FELIX) facility, at the FOM Institute for Plasmaphysics

“Rijnhuizen” in Nieuwegein, The Netherlands. Complementary studies to those at the FELIX facility are performed with table-top IR laser systems that have been installed at the FHI. A detailed presentation of the progress in this research area is given on the posters MP 1 through MP 5. During the last Fachbeirat meeting, the proposed installation of a dedicated IR-FEL on the FHI campus was discussed. Following the positive advice of the Fachbeirat, we have submitted this proposal to the MPG in early 2008 and this project has been granted in the summer of that year. The present status, planning and perspectives of the FHI IR-FEL project are outlined on poster MP 21.

A large experimental effort is devoted to research under the theme of “Cold Molecules”. The aim of these research projects is to develop experimental schemes to achieve full control over both the internal and external degrees of freedom of neutral molecules, and to exploit these schemes in investigations of the properties of (samples of) cold molecules. In various experiments, time-varying electric fields are used to slow down and trap neutral polar molecules. Alternative methods to produce samples of cold molecules as well as a variety of schemes to achieve further cooling or increased number densities of trapped samples of molecules are actively being pursued. Highlights of this research have been the quantification of trap loss due to nonadiabatic transitions, the successful operation of the 2<sup>nd</sup> generation “molecular synchrotron”, the demonstration of spatial separation of conformers of biomolecules, and the demonstration of the deceleration and trapping of neutral molecules on a chip. The progress in this research area, together with a description of future research plans, is presented on the posters MP 6 through MP 17.

Apart from these research activities that were introduced at the FHI with the appointment of Gerard Meijer, the ongoing research activity originating from the former department of surface science is described in the sections on “VUV and soft X-ray photo-ionization studies” and on “Electronic structure of surfaces and interfaces”. Highlights of this research have been the analysis of entanglement in the photo-ionization of homonuclear diatomic molecules and the study of the band structure of graphene grown on silicon carbide. This research is presented in more detail on the posters MP 18 through MP 20.

## **I. Molecular physics studies with infrared radiation**

FELIX is ideally suited for a large variety of experiments in gas-phase molecular physics. On the one hand this is due to the available wavelength tuning range, extending from 2.5 to 250  $\mu\text{m}$  and thereby covering the full “molecular fingerprint” region, and the possibility of user-controlled wavelength scanning. The feature that really distinguishes FELIX from other lasers for applications in this research area is that it has 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.

In some experiments, FELIX is 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, FELIX 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 now dissociate by evaporating off small atomic or molecular fragments. Very tightly bound species, however, will undergo thermionic emission, i.e. they choose to evaporate off an electron instead. The resulting charged species can be easily detected, and monitoring them as a function of wavelength yields information on the IR spectrum of the neutral molecule.

The light output of FELIX comes in macropulses of 5  $\mu\text{s}$  duration at a repetition rate of 10 Hz. Each macropulse contains micropulses that are 300 fs to 5 ps long and that are spaced by 1 ns. The bandwidth is Fourier transform limited, implying a typical spectral resolution of several  $\text{cm}^{-1}$  at a central frequency of  $1000\text{ cm}^{-1}$ . FELIX is therefore mainly restricted to studies in which a 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 FELIX induced change in ion signal.

Since the end of 2007, the Free Electron Laser for IntraCavity Experiments (FELICE) has also become operational at the FOM-Institute. Together with the “in-house” user-group at the FOM-Institute, we have designed and installed a molecular beam machine as an integral part of FELICE. In a first test experiment, we have used this machine to study the IR resonance enhanced multi photon ionization and fragmentation of C<sub>60</sub>; with up to a few Joules of tunable IR light circulating inside the cavity extremely efficient pumping of vibrational energy – up to more than 100 eV – appeared to be possible in these molecules. We have also performed first experiments on far-IR multiple photon ionization of metal clusters with FELICE. One future application will be IR multiple photon electron detachment from anionic clusters as a means to obtain their vibrational spectra.

To be able to perform preparatory and complementary experiments to those performed at the FELIX facility, we have set up different table-top laser systems at the FHI. These systems are either based on a Nd:YAG pumped IR optical parametric oscillator and amplifier (IR OPO/OPA), or on a tunable dye laser in combination with non-linear frequency mixing techniques. These systems can produce light pulses of ~ 5 ns, and are currently used to cover the region between 3 and 5  $\mu\text{m}$ . Although the energy per pulse of these laser systems is only limited to a few mJ, their superior bandwidth down to 0.05  $\text{cm}^{-1}$  compensates for this in many experiments. To extend the available wavelengths further into the infrared, we are also experimenting with the production of pulsed mid-IR laser radiation via stimulated backward Raman scattering in crystalline para-hydrogen at 4 K.

#### *Infrared excitation of gas-phase molecules and clusters (Gert von Helden)*

The experimental study of the structure and dynamics of small and medium sized biological molecules remains an important focus of our research. The experiments are performed in the gas phase where solvent molecules are explicitly absent; they can be added one by one, however, thus allowing to disentangle intra- and

intermolecular interactions. A high degree of control over the species to be investigated is achieved by investigating mass/charge selected ionic molecules. Over the last years, we have pioneered methods to characterize those molecules via IR multiple photon dissociation (IR-MPD) spectroscopy and we have applied this technique to a variety of small and larger peptides and proteins. For smaller species, the experimental results can be compared directly to the outcome of calculations. In case of larger species, the experimental spectra have to be compared to those of molecules with known structures. As reference materials, we investigated peptides that presumably have a beta sheet secondary structure as well as species with helical structures. For the latter ones, we investigated polymers of the amino-acid alanine, as these molecules likely have a propensity for helix formation. There is an active collaboration with the theory department to support and interpret the experimental data.

Frequently, however, the amount of information that can be obtained from the spectra is limited by the fact that the molecules under investigation are at room temperature. In addition, the IR-MPD process is inherently non-linear, causing spectral broadenings and shifts. As a remedy, initially cold species can be investigated, however the limitations imposed by the IR-MPD process remain. As a new approach, we developed a machine that allows the investigation of sustained cold species by embedding them in liquid helium droplets. Single photon infrared absorption spectra can then in principle be recorded via monitoring the evaporation of helium atoms from the droplet. In our set-up, the droplets are generated by a pulsed valve, operated at cryogenic temperatures. The superfluid droplets then traverse an ion trap, filled with mass selected ions. Upon impact of a droplet on an ion, the ion can be embedded into the droplet and because of the high kinetic energy of the droplet (a result of its high mass), the doped droplet can leave the trap and be further investigated. In the summer of 2009 the first ever signal of mass selected ions in helium droplets could be obtained using this approach. At the moment, characterization of the doped droplets is in progress and first spectroscopic experiments are planned immediately after that.

In our research, we focus on the investigation of the structures of metal clusters and complexes with small molecules in the gas phase using vibrational spectroscopy. These studies aim to obtain fundamental insights in the effects of geometric and electronic structure on reactivity, resulting in a detailed local picture of reactions on well-defined metal sites.

We have pursued our studies on strongly bound clusters using far-IR photodissociation spectroscopy and extended it to transition metals relevant in catalytic applications. Although in many cases the rare gas atoms bound to the cluster just act as messenger of the IR absorption, we found for cationic cobalt clusters a pronounced influence of the attached argon atoms on the vibrational spectra. Detailed DFT based investigations (Karsten Reuter, theory department) allowed us to explain the strong interaction between cobalt clusters and Ar atoms. For rhodium clusters, the comparison of experimental and calculated vibrational spectra suggests the clusters to have mainly close-packed structures, in contrast to recent predictions of a cubic growth mechanism. This finding highlights the importance of including some exact exchange contributions in the DFT calculations, via hybrid functionals, for the description of clusters of late transition metals (collaboration with Tiffany Walsh, University of Warwick, and Stuart Mackenzie, University of Oxford, UK).

One of the highlights of our research has been the determination of the far-infrared spectra of neutral gold clusters in the gas phase (size range from 3 to 20 atoms) from which their structure, and in particular the transition from planar to three-dimensional structures, can be deduced. We expect to obtain a more detailed understanding of the effects of anharmonicities and internal temperature on the vibrational spectra from Molecular Dynamics simulations performed in the FHI theory department by Luca M. Ghiringhelli.

In collaboration with Peter Lievens (University of Leuven, Belgium) we have extended the studies on transition metal doped silicon clusters and also obtained information of the structures of pure cationic and neutral Si clusters.

A second area of research has been the study of adsorbates on the surface of transition metal clusters. Together with David M. Rayner (NRC Ottawa, Canada) we have now obtained a general picture on the interaction of CO with transition metal clusters. This shows many parallels with the chemistry of CO on extended surfaces, including the transition from dissociative to molecular binding or the preference for higher CO coordination sites for the *4d* and *5d* metals. In joint efforts with Frank de Groot and Bert Weckhuysen (University of Utrecht, The Netherlands) to study fundamentals of hydrogenation reactions, we focussed on the hydrogen binding to clusters of *3d* transition metals and identified, for instance, molecular H<sub>2</sub> binding on small nickel clusters, which can be seen as model for a precursor state to dissociation. First effects of the reaction temperature on hydrogen binding have been revealed by vibrational spectroscopy as well.

The studies on metal clusters are part of our activities within the Cluster of Excellence (CoE) “Unifying Concepts in Catalysis” coordinated by the TU Berlin. As a second contribution to this CoE we have started the investigation of magnesium oxide clusters, which will be studied by vibrational spectroscopy and anion photoelectron spectroscopy. For the latter experiments, a velocity map imaging set-up has just become operational; with this set-up, we have recently obtained first high-resolution photoelectron spectra of small gold clusters anions.

#### *Vibrational spectroscopy of gas-phase ions (Knut Asmis)*

Gas-phase vibrational spectroscopy is arguably one of the most direct and generally applicable experimental approaches to the structural investigation of complex gas-phase ions currently available. In the past two years we have extended our particular implementation of this technique, namely mass-selective infrared photodissociation spectroscopy combined with a temperature controllable ring electrode ion trap, to measure IR spectra of ions at variable temperature (10-300 K) and in a wide range of the IR spectrum (100-4000 cm<sup>-1</sup>). As tunable and intense IR light sources we use FELIX as well as a table-top OPO/OPA laser system, the latter which, combined with a novel multipass cell setup, now also

allows us to measure IR multiple photon dissociation spectra. Complimentary single-photon vibrational predissociation spectra are measured of the corresponding ion-messenger atom complexes.

The central focus of our research has shifted towards characterizing the microhydration of ions, that is, the dependence of geometric and electronic structure of ions on the degree of hydration and on temperature. Recent studies included the characterization of  $\text{NO}_3^-(\text{H}_2\text{O})_{1-6}$ ,  $\text{HCO}_3^-(\text{H}_2\text{O})_{1-12}$ ,  $^-\text{OOC}-(\text{CH}_2)_6\text{COO}^-(\text{H}_2\text{O})_{0-16}$  and  $\text{Mg}^{2+}\text{NO}_3^-(\text{H}_2\text{O})_{1-7}$ . The atmospherically relevant nitrate and bicarbonate anions, measured in collaboration with the Neumark group (UC Berkeley, CA, USA), both prefer surface solvation, in contrast to the previously studied sulfate dianions. The suberate dianion shows evidence for a structural change around  $n=13$ . At this point more favorable hydrogen bonding drives the initially quasi-linear dicarboxylate anion into assuming a bent, higher energy conformation. Particularly intriguing are the microhydrated magnesium nitrate cations. The first four water molecules sequentially hydrate the Mg dication, leading to an exceptionally stable  $\text{NO}_3^-\cdot\text{Mg}^{2+}(\text{H}_2\text{O})_4$  species. Currently, we are looking for evidence of the solvent-separated ion pair, which is predicted to appear around  $n=8$  and is characterized by strongly red-shifted O-H stretching frequencies.

As part of the DFG Collaborative Research Center 546 “Structure, Reactivity and Dynamics of Transition Metal Oxide Aggregates” we continued the experiments on metal oxide clusters, aimed at gaining a molecular level understanding of their structure-reactivity relationship and ultimately unravelling the adsorbate/active site/support interaction important in heterogeneous catalysis. Following the detailed structural characterization of vanadium oxide ions up to  $\text{V}_8\text{O}_{20}^{+/-}$ , aided by calculations from the Sauer group (HU Berlin), we studied cluster ions of typical support materials ( $\text{Si}_x\text{O}_y^+$ ,  $\text{Al}_x\text{O}_y^+$ ,  $\text{Ce}_x\text{O}_y^+$ ). Particularly noteworthy were the results on aluminium oxide cations, which revealed a previously unknown, very stable conical structural motif, as well as the first IR spectra for gas-phase ceria cations, which provide a crucial experimental benchmark for testing the accuracy of DFT calculations when applied to lanthanoids. Currently, we are constructing a novel, cryogenically cooled dual laser vaporization source targeted



at producing supported metal oxide ion / neutral metal oxide complexes. As part of our collaboration with the Lievens group (Leuven, Belgium), and using the technology developed in the Fielicke group, we have extended our accessible spectral range down to  $100\text{ cm}^{-1}$ , demonstrated by measuring the IR spectrum of  $\text{Au}_6\text{Y}^+\cdot\text{Ar}$ , which exhibits a pair of characteristics bands at 181 and  $121\text{ cm}^{-1}$ .

Our third project involves the study of molecular cluster ions. The protonated ammonia dimer is a prototypical system exhibiting strong hydrogen bonding, in which the proton is shared equally by two monomer units. This unusual binding motif leads to a characteristically red-shifted, markedly anharmonic antisymmetric stretching vibration involving the central proton. We located the fundamental transition at  $374\text{ cm}^{-1}$  and assigned it aided by multidimensional quantum dynamical calculations based on a 6D model Hamiltonian performed in the Kühn group (Rostock, Germany). More recently, we looked at carbon sulfide cluster anions together with the Sanov group (University of Arizona, Tucson, AZ, USA). The temperature-dependent IR spectra convincingly show, that at 10 K the weakly bound  $\text{CS}_2^-\cdot\text{CS}_2$  dimer is predominantly present, while at higher temperatures population is transferred very efficiently to the covalently bound  $\text{C}_2\text{S}_4^-$  anion, which represents the dominant absorbing species at 300 K.

## II. Cold 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. We have been exploring and exploiting the possibility of slowing down and trapping neutral molecules by the use of time-varying inhomogeneous electric fields. It is well known that beams of molecules with an electric dipole moment, i.e. with an internal anisotropic charge distribution, can be deflected and focused with static inhomogeneous electric fields. This approach has been extensively and successfully used in the field of atomic and molecular beams ever since the Stern and Rabi era. However, this manipulation exclusively involved the transverse motion of the molecules. It was only in 1999, that we experimentally demonstrated that appropriately designed arrays of electric fields

in a so-called “Stark decelerator” can also be used to influence and control the longitudinal (forward) velocity of the molecules in a beam, *e.g.* to decelerate a beam of neutral polar molecules. Since then, the ability to produce focused packets of state-selected accelerated or decelerated molecules has made a whole variety of new experiments possible.

Since the first demonstration of the Stark decelerator, we have experimentally investigated its operation characteristics in great detail. We have demonstrated the possibility to guide molecules on overtones of the frequency with which the electric fields are switched, and we have studied the coupling of the transverse motion to the longitudinal motion in the decelerator. Together this has enabled us to reach a complete, experimentally verified description of the complex three-dimensional motion of the molecules through the decelerator. The decelerated beams of molecules have subsequently been loaded into a variety of traps. In these traps, electric fields are used to keep the molecules confined in a region of space where they can be studied in complete isolation from the (room temperature) environment. In our first experiments of this kind, we demonstrated trapping of ammonia molecules in a quadrupole electrostatic trap, but we have demonstrated trapping in more versatile geometries as well. Apart from ammonia, we have also demonstrated the deceleration and trapping of OH radicals as well as of metastable NH and CO molecules. The long interaction time afforded by the trap has been exploited to measure the radiative lifetime of metastable states and to study optical pumping of the trapped molecules by blackbody radiation, for instance.

For many applications, deceleration and trapping of polar molecules in “high-field-seeking” states is required, if only because the lowest energy level of any molecule is high-field seeking. Manipulation of molecules in high-field-seeking states is generally required if one aims to get full control over heavy diatomic molecules or over large (bio-) molecules. We have shown that the concept of alternating gradient (AG) focusing – commonly used in charged particle physics – can be applied to polar molecules when using electrostatic dipole lenses, and AG deceleration of molecules in high-field-seeking states has thus been demonstrated.

To trap molecules in high-field-seeking states various AC electric traps have been developed.

As already hinted at in the last report to the Fachbeirat, we have stopped our studies on the buffergas cooling and magnetic trapping of molecules after the student working on this project (Michael Stoll) had successfully completed his PhD thesis. We had started on this project in 2004 in collaboration with Achim Peters, junior-professor at the HU Berlin at that time, who set up a cryogenic cell with the magnetic trap and the associated optical detection systems for this in our laboratory. We tested and characterized the experimental set-up by trapping of Cr atoms and identified CrH and MnH (with strong optical transitions and with 5 and 6  $\mu_B$  magnetic moment in their electronic ground state, respectively) as good candidate molecules for magnetic trapping in this apparatus. In collaboration with Tim Steimle (University of Arizona, Tempe, AZ, USA) we investigated these molecules spectroscopically, and accurately determined the Zeeman shifts of the relevant energy levels. We then demonstrated buffergas cooling and magnetic trapping of both CrH and MnH, and we determined the trapping time as a function of the buffergas pressure and as a function of the depth of the magnetic trap. With a maximum number of about  $10^6$  trapped molecules and with trapping times on the order of 100-200 ms even for these rather ideal molecules, however, we have come to the conclusion that the general applicability of the combination of buffer gas cooling of molecules with magnetic trapping is substantially curtailed at the moment; for most of our future applications, the Stark deceleration method appears to be better suited. In 2008, Achim Peters obtained a permanent professor position at the HU Berlin, and he will use the setup for other experiments over there.

*Trapping of neutral polar molecules (Steven Hoekstra / Bas van de Meerakker)*

In the last few years our group has focussed mainly on the Stark deceleration and electrostatic trapping of ground-state OH radicals. The long-term goal of these experiments is to achieve densities of trapped molecules that are high enough to experimentally study (and manipulate) the interactions between the molecules in

the trap. For this, the molecular densities that have been obtained thus far need to be further increased. Already in 2001, a promising scheme has been proposed to accumulate multiple packets of ground-state NH molecules from successive cycles of the experiment in a *magnetic* trap. Last year we have experimentally demonstrated the Stark deceleration and electrostatic trapping of metastable NH molecules, a last prerequisite for the experimental realization of this accumulation scheme. The interaction of cold molecules with strong magnetic fields has been explored by retro-reflecting a slow beam of OH radicals from rare-earth permanent magnets.

When magnetic fields are used instead of electric fields to trap Stark-decelerated molecules, the final deceleration stages can be decoupled from the trapping potential itself, and can therefore be optimized independently. It also becomes possible to magnetically trap molecules in a state that is not disturbed by electrostatic fields; this is the basis of the aforementioned trap-reloading scheme for NH molecules that we are now actively pursuing. For this, we have implemented an electromagnetic trap for the Stark-decelerated molecules by running a large current through two copper coils in anti-Helmholtz configuration. Special electrodes have been developed that bring the slow molecules from the exit of the decelerator to the trap center with minimal losses. We could demonstrate the magnetic trapping of metastable NH molecules using this trap. We have furthermore characterized the transfer of the metastable molecules to the electronic ground state, an essential step for the reloading scheme.

To improve the number of magnetically trapped molecules and to improve the trapping time we have developed a second magnetic trap, composed of permanent magnets. Using this trap we have succeeded in magnetically trapping OH radicals. We are currently trying to demonstrate the accumulation of multiple packets of Stark-decelerated NH molecules in this trap. Besides higher densities we would like to achieve longer trapping times (up to a minute), for which we might need a cooled trap in the future.

In this newly started research group, our efforts are focused on crossed beam scattering experiments using Stark-decelerated beams. Compared to conventional molecular beams, Stark-decelerated beams offer tunability of the velocity, a narrow velocity spread, and a quantum state purity that approaches 100%. In 2006, we have demonstrated in a proof-of-principle experiment the feasibility of crossed beam scattering using Stark-decelerated beams, although the scattering signals were limited by the rather low number densities of decelerated molecules. In the last three years, we have constructed a 2.6 meter long and state-of-the-art Stark decelerator apparatus that is now fully operational in our laboratory. This decelerator is designed to produce molecular beams with a superior number density using the so-called  $s = 3$  operation mode. This mode of operation eliminates the loss of molecules due to unstable trajectories that is present in Stark decelerators of earlier designs. The improved performance of this operation mode has been verified experimentally using a beam of OH radicals. Currently, this new apparatus is used to scatter a Stark-decelerated beam of OH radicals with Ar atoms, and to measure the state-to-state scattering cross sections for a vast number of inelastic channels. The collision energy is varied from 70 to 1000  $\text{cm}^{-1}$ , and the behavior of the cross sections around the energetic thresholds is accurately determined. A second identical Stark decelerator is currently under construction, and will be placed orthogonally to the existing decelerator. Once completed, this will allow us to study collisions between completely state-selected molecules at collision energies between 1  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  with an energy resolution of better than 1  $\text{cm}^{-1}$ . The scattering between OH radicals and NO radicals, the first bi-molecular system that is planned, will be investigated first by colliding a beam of hexapole state-selected NO radicals with the Stark-decelerated OH radicals. For this, a compact hexapole state selector has been developed with which an intense molecular beam of state-selected NO ( $X^2\Pi_{1/2}$ ,  $J = 1/2$ ,  $f$ ) radicals has been produced. This crossed-beam project is part of the ESF collaborative project (EuroQUAM) on “Collisions of Cold Polar Molecules” (CoPoMol; 2007-2010).

A molecular storage ring, loaded from a Stark decelerator beamline, offers interesting prospects for scattering studies as well. To fully exploit the possibilities offered by ring structures, it is imperative that the molecules remain in a bunch as they revolve around the ring. During the last years, a molecular synchrotron consisting of two half rings with a small vacuum gap has been developed in our department. The broken symmetry of the ring allows for bunching of the packet to prevent spreading out in the ring, and allows for the storage of multiple packets of molecules simultaneously. The number of packets that can be stored, and the efficiency of the bunching process, depends on the number of individual segments in the ring. We are currently testing a new synchrotron consisting of 40 straight hexapoles that has become operational beginning of this year. Thus far we have been able to demonstrate the improved performance of this ring and to store packets of ammonia molecules for up to 150 round trips. The future vision is to use the synchrotron to store 20 packets of molecules going clockwise and 20 packets going anti-clockwise. These packets will repeatedly interact at well defined times and positions, i.e., a low-energy neutral-molecule collider as the ultimate replica of high-energy charged-particle colliders.

*Manipulating the motion of large molecules (Jochen Küpper)*

Over the last two years we have further explored the possibilities to manipulate the motion of large molecules, for which all states are high-field seeking at the practically relevant electric field strengths. We have set up and demonstrated the deflection, alternating gradient focusing, and AG deceleration of prototypical large and complex molecules. These experiments employing strong inhomogeneous electric fields are the neutral-molecule analogs of well-known “classical” experiments, namely, the Stern-Gerlach deflector, the quadrupole mass spectrometer, and the linear accelerator (LINAC), respectively.

We have used two setups, the electric deflector and the AG focuser, to spatially separate the individual structural isomers of the prototypical complex molecule 3-aminophenol and have compared the performance characteristics of these setups.

Using the AG focuser, we have investigated the dynamic focusing scheme in more detail, i.e., we have investigated the possibility to improve the selectivity by changing the duty-cycle in the high-voltage time-sequence and derived an approximate analytical and more detailed numerical description of the process. We have also investigated, numerically and experimentally, the quantum state-selectivity of the two setups. In a third experiment, we have decelerated benzonitrile using the AG decelerator.

We are currently setting up an improved AG focuser experiment in which we will experimentally investigate the focusing process on an individual-quantum-state level. We plan to use the new setup to improve the separation of different structural isomers of complex molecules, as well as to separate individual clusters from the size and isomer distribution present in a cluster beam.

In collaboration with the group of Henrik Stapelfeldt at the University of Aarhus, Denmark, we have investigated the manipulation of the rotational motion of quantum-state-selected samples. We have set up an electric deflector in Aarhus in order to prepare quantum-state-selected samples for laser-induced alignment experiments. We have demonstrated unprecedented degrees of laser-induced alignment and mixed-field orientation of iodobenzene and three-dimensional orientation of 2,6-difluoro-iodobenzene.

In upcoming experiments we will investigate the structural and dynamical properties of such complex molecules using quantum-state and isomer-selected, aligned or oriented samples. In a project jointly headed by us and Henry Chapman (CFEL, Hamburg) we will perform diffractive X-ray imaging of aligned gas-phase molecules using the LINAC coherent light source (LCLS) at the Stanford Linear Accelerator Center (SLAC). We have been granted beam time for this in the first *user-assisted-commissioning* period in December 2009.

One main project during the last two years has been the quantitative study of losses due to nonadiabatic transitions of electrostatically trapped ammonia molecules. Nonadiabatic transitions are known to be major loss channels for atoms in magnetic traps, but had thus far not been experimentally reported upon for trapped molecules. For this, we developed and implemented a DC electric trap with a non-zero trap minimum, e.g., the electric equivalent of the magnetic Ioffe-Pritchard trap. In such a trapping configuration, losses due to nonadiabatic transitions are suppressed. Furthermore, we designed the trap geometry such that a second trapping configuration with zero electric field in the center can be generated where nonadiabatic transitions can occur. By comparison of the trap lifetimes of ammonia molecules for the two trap configurations, the time constants for losses due to nonadiabatic transitions can be determined directly. Nonadiabatic transitions are seen to dominate the overall loss rate even for the present samples that are at relatively high temperatures of 30 mK. It was also found that the importance of trap losses due to nonadiabatic transitions depends very critically on the detailed energy level structure of the molecule under consideration. It is anticipated that losses due to nonadiabatic transitions in electric fields are omnipresent in ongoing experiments on cold molecules.

Central to our research remains the manipulation of the motion of polar molecules using microwave radiation. We recently developed a microwave setup that allows us to transversely focus polar molecules. A near-resonant standing microwave field ( $TE_{11n}$  mode) is generated in a cylindrically symmetric copper resonator, which is located behind the decelerator. Due to the special shape of the microwave mode, polar molecules experience a focusing force in transverse direction. Depending on the sign of the detuning of the microwave frequency from the molecular transition frequency, molecules in either the low-field-seeking or in the high-field-seeking states can be focused.

In a next step, we will exchange the cylindrically symmetric copper resonator by a Fabry-Pérot type microwave resonator. Besides its very open design, this setup will allow us to not only focus the molecules, but also to decelerate and trap them.



Since the force exerted on a polar molecule in such a microwave trap largely depends on the detuning of the cavity frequency from the molecular transition frequency, microwave radiation is especially suited since very small detunings to molecular transitions are possible. This can lead to a linearization of the Stark energy, so that strong interaction energies can be achieved and even molecules with a quadratic Stark effect can be trapped efficiently.

In a new project, we are developing and implementing a crossed-beam optical dipole trap. Such an optical trap allows not only trapping of polar molecules in high-field-seeking states but also of nonpolar molecules, since the trapping force depends on the polarizability of the species and not on the dipole moment. With such a trap, sympathetic cooling of an ensemble of trapped polar molecules with a cloud of trapped ultracold atoms might also become possible.

#### *Micro-structured devices to manipulate molecules (Horst Conrad)*

In this project we aim to manipulate and control polar molecules using electric field gradients produced by micro-structured electrodes. The ultimate goal is to produce a variety of molecule manipulation tools, including lenses, mirrors, guides, decelerators, storage rings and traps, all integrated on a chip.

By miniaturizing electrode geometries high electric fields, and even higher electric field gradients, can be produced using modest voltages. Since a few years, we have been experimenting with a micro-structured electrode array to guide and to decelerate polar molecules on a chip. Rather than working with switched fields, as in the normal decelerators, sinusoidal waveforms are applied to the electrodes such as to generate an array of travelling potential wells above the planar substrate with the array of micro-structured electrodes. We load molecules into these potential wells directly from a pulsed supersonic beam; upon arrival above the chip, the molecules are confined in tubular electric field traps approximately 20 micrometers in diameter, centered 25 micrometers above the chip, that move along with the molecular beam at a velocity of several hundred meters per second. An array of these miniaturized moving traps is brought to a standstill over a

distance of only a few centimeters. After a certain holding time, the molecules are accelerated off the chip again for detection.

Just before the last meeting of the Fachbeirat, we had already successfully demonstrated the guiding of metastable CO molecules at a constant velocity above this micro-structured electrode array. Shortly after that, we also managed to demonstrate gentle deceleration of the molecules above the chip, but we observed an unexpectedly large loss of molecules with increasing deceleration. In the course of last year we realized that in the low electric field region near the center of the traps, molecules are lost due to nonadiabatic transitions to non-trappable degenerate states. In magnetic traps for atoms on a chip, this hole at the center of the trap is commonly plugged by adding a homogeneous magnetic field. An offset magnetic field could also be added in the present setup. For molecules in electric traps, however, there often exists the alternative solution to simply select an isotopologue with a favourable hyperfine level structure such that there is no degeneracy between trappable and non-trappable states in zero electric field. The most abundant CO isotopologue,  $^{12}\text{C}^{16}\text{O}$ , has no hyperfine structure and the low-field-seeking  $M_Q = -1$  level of the  $a^3\Pi_1$  ( $v'=0, J'=1$ ) state is degenerate with the  $M = 0$  level in zero electric field, making this species susceptible to nonadiabatic transitions. In  $^{13}\text{C}^{16}\text{O}$ , however, the coupling of the nuclear spin of the  $^{13}\text{C}$  nucleus with the orbital angular momentum results in a lifting of this degeneracy; the low-field-seeking levels never come closer to the non-trappable level than 53 MHz in any electric field, effectively preventing nonadiabatic transitions from occurring. Therefore, by simply switching from  $^{12}\text{CO}$  to  $^{13}\text{CO}$  these losses were completely eliminated and confinement of molecules in static traps on a chip could be successfully demonstrated. The loading and detection methodology that we have developed is applicable to a wide variety of polar molecules – provided appropriate measures are taken to avoid nonadiabatic transitions – enabling the creation of a gas-phase molecular laboratory on a chip.

This work is part of an FP7 EU-funded project (STREP) on “Nano-optics for molecules on chips” (2008-2011), with the reverse acronym CHIMONO.

A project aimed at demonstrating the production of cold neutral molecules via deceleration and photodetachment of negative ions was started in 2006 and showed promising preliminary results by the end of 2007. Ions are much more sensitive to electric fields than neutrals, and the deceleration was therefore expected to be much simpler. At the end of the deceleration, the negative ions were neutralized by near-threshold laser-photodetachment to obtain the neutrals at the same velocities. In the present setup, however, the deceleration of the negative ions to low velocities was hampered by the presence of large densities of positive and negative ions. As a result, the ions moved in a dense cloud with an overall charge of zero, shielding each other from the deceleration potentials. Attempts to filter this “plasma” and extract the negative ions alone were unsuccessful. It was realized that the chosen source (hot filament electron source, combined with a pulsed supersonic expansion) was not ideal for this experiment. In view of the upcoming move by Andreas Osterwalder to the EPFL, Switzerland, it was decided to postpone continuation of this project in the summer of 2008; Andreas will set up an extended and improved version of this method that should eliminate the core difficulties encountered here at his new laboratory in Lausanne.

We then focused, as a side-project, on the demonstration of an improved velocity-filter (using an electrostatic hexapole bent in a half circle, i.e. one half of the 1<sup>st</sup> generation molecular synchrotron) to extract polar molecules from a thermal sample, and, in particular, on the development and implementation of a new type of Stark decelerator in which a moveable 3D electrostatic trap is generated. The key idea in the latter experiment is to use continuously varying deceleration fields instead of the switched fields that are generally employed in Stark deceleration. The method draws on the experience gained with the Stark decelerator on the chip, which is here “only” extended to three dimensions and scaled up in size by a factor hundred. The two main challenges in this setup were in the mechanical construction and in the electronics required to generate the high-voltage sine waves (20 kV peak-to-peak) with a frequency tunable between 30 kHz and dc. For a proof-of-principle experiment, the frequency range was chosen to only go down

to 10 kHz in order to simplify the electronics. With this setup we have recently been able to successfully demonstrate deceleration of metastable CO molecules from about 300 m/s to 150 m/s. The excellent signal-to-noise ratio in the first measurements and the relatively easy control of the setup fully confirm our expectations that this kind of Stark decelerator bears a very high potential for all future applications of cold polar molecules.

*Interactions of molecules with fields (Bretislav Friedrich)*

Collisions of molecules in electric, magnetic, or radiative fields are nearly ubiquitous in nature as well as in the laboratory. Molecules colliding in the Earth's atmosphere or in interstellar space are commonly subjected to magnetic and radiative fields; in the laboratory, collisions in fields appear with particular prominence in stereodynamics, coherent control, and molecular trapping and cooling. Molecular collisions in fields have been the subject of a number of theoretical studies. However, analytic models of such collisions are scarce and limited to the collision regime near the Wigner limit. Recently, we have developed an analytic model of state-to-state rotationally inelastic collisions of atoms with molecules in fields, applicable at thermal and hyperthermal collision energies. The model, based on Fraunhofer scattering of matter waves, is inherently quantum and makes it possible to separate dynamical and geometric effects in collisions.

Another important ongoing line of research is the theoretical study of the spectroscopy of molecules in electric, magnetic, or radiative fields. Directional states of molecules are at the core of all methods to manipulate molecular trajectories. This is because only in directional states are the body-fixed multipole moments "available" in the laboratory frame where they can be acted upon by space-fixed fields. In the case of polar molecules, the body-fixed permanent dipole moment is put to such a full use in the laboratory by creating oriented states characterized by as complete a projection of the body-fixed dipole moment on the space-fixed axis as the uncertainty principle allows. In order to achieve a high degree of orientation, one had to rely on special properties of particular

molecules. This has been done away with by the development of techniques that combine a static electric field with a nonresonant radiative field. The combined fields give rise to an amplification effect that occurs for any polar molecule, as only an anisotropic polarizability, along with a permanent dipole moment, is required. This is always available in polar molecules. Thus, for a number of molecules in their rotational ground state, a very weak static electric field can convert second-order alignment by a laser into a strong first-order orientation that projects about 90% of the body-fixed dipole moment on the static field direction. If the polar molecule is also paramagnetic, combined static electric and magnetic fields yield similar amplification effects. Oriented states have a unique spectroscopic behavior, due to their *sui generis* energy level patterns and modified Hönl-London factors. Our effort is directed towards identifying oriented states among the eigenstates of molecules in the combined fields and finding their spectroscopic signature.

#### *Sympathetic cooling of molecules (Adela Marian / Wieland Schöllkopf)*

The goal of this experiment is to use a dense, ultracold sample of magnetically trapped rubidium atoms to increase the phase-space density of a trapped molecular sample. Our first step was to show that a magnetic trap for atoms can be spatially overlapped with an AC electric trap. Additionally, we have experimentally verified that the magnetically trapped atoms are not perturbed by the AC electric fields needed for trapping molecules. Because AC electric trapping of neutral atoms proved to be a research project worth pursuing in its own right, we carried out detailed studies of the dynamics in an AC trap for rubidium and are currently testing a new AC trap with a larger trap depth. The second step was to design and test a compact ultrahigh-vacuum molecular-beam machine that can accommodate all the spatial and vacuum requirements imposed by the existing atom apparatus. Subsequently, a new kind of Stark decelerator has been developed especially for this project and in conjunction with the new vacuum system. The electrodes of this 100 stage decelerator are 0.6 mm diameter tantalum wires, resulting in a total length of the decelerator of 110 mm,

approximately 10 times smaller than a conventional Stark decelerator with the same number of electrode pairs. Next, we plan on using the packets of slow molecules produced by such a wire decelerator for collision experiments with magnetically trapped rubidium. This project is part of the ESF collaborative project (EuroQUAM) on “Collisions of cold polar molecules” (2007-2010).

*Atom optics and quantum reflection of molecular beams (Wieland Schöllkopf)*

In this project we perform optical experiments with atomic and molecular beams including diffraction from a reflection grating and focusing by a concave mirror. The experiments are carried out with a molecular beam apparatus of high angular resolution ( $\sim 100 \mu\text{rad}$ ), originally built at the Max-Planck-Institut für Strömungsforschung. The apparatus allows to resolve small angle diffraction of atom beams reflected at near grazing incidence from a microstructured surface grating (periodicity of several micron). Typically, helium atom beams are used because of their relatively large mean de Broglie wavelength of a few Ångström and their narrow velocity distribution.

In recent experiments we have investigated *quantum reflection*, which is the underlying mechanism for coherent reflection at near grazing incidence. In quantum reflection a wave packet is reflected at the attractive van der Waals branch of the atom-surface interaction. Quantum reflection takes place tens of nanometers above the actual surface. As equi-potential surfaces at such distances are smooth even if the actual surface is not, coherent reflection is achieved even for microscopically rough surfaces. Quantum reflection is effective only when the normal component of the atom wave-vector is very small. By fitting the observed reflectivity data with a numerical model we determined the  $C_3$ -coefficient of the atom-surface van der Waals interaction for various surfaces.

The probability of quantum reflection depends only on the normal component of the wave-vector. However, for somewhat larger normal components, where the quantum reflection efficiency tapers off, the total reflectivity is found to depend on the parallel component as well. We attribute this behaviour to classical reflection from the repulsive branch of the surface potential. In this regime a

universal behaviour has been observed which is independent of the details of the actual surface sample: for a given normal component the reflectivity increases with increasing parallel component. Still, we expect the total reflectivity in this regime to scale with the surface roughness. This is why we plan to try out a graphene surface (in collaboration with the group of Karsten Horn); as it is highly regular and smooth a large classical reflectivity can be expected.

In another experiment we have applied quantum reflection from a concave surface to focus a helium atom beam in one dimension. The surface is a commercial cylindrical quartz mirror with a radius of curvature of 78 m. At near grazing incidence, where a reflectivity of several percent is achieved, the focal length is only tens of cm because it scales as the sine of the grazing angle. The smallest width of the focus that has been achieved is 1.8  $\mu\text{m}$ , essentially limited by spherical aberration.

In another line of experiments a beam of methylfluoride molecules is scattered off a microstructured surface grating. When a positive voltage is applied to every second grating stripe and a negative voltage to every other second stripe, a strong static electric field is created above the surface. In the direction normal to the surface the field decays exponentially. Therefore, polar molecules in low-field-seeking states approaching the surface are repelled. We have observed the resulting specular reflection, i.e. the electric field forms a mirror for polar molecules. As the equi-potential surfaces are corrugated, diffraction peaks are expected in addition to the specular reflection. We expect to observe the diffraction pattern with an improved microstructure grating that has recently been fabricated for this experiment.

### **III. VUV and soft X-ray photo-ionization studies (Uwe Becker)**

During the last two years, our research program has concentrated on two topics, namely (i) the analysis of coherence and entanglement in the photo-ionization of homonuclear diatomic molecules, and (ii) the study of nonlinear multi-photon processes by angle-resolved electron spectroscopy using the Free Electron Laser in Hamburg (FLASH) as photon excitation source.

In the first project we succeeded in the analysis of electron entanglement in ordinary space, an effort extending the corresponding studies in quantum optics, which employed spin-like variables for entanglement only. Because position and momentum are continuous variables, which can have any arbitrary eigenvalue, we had to introduce corresponding dichotomic variables for a Bell type analysis instead. These are the complementary sets of variables *gerade* ( $g$ ) and *ungerade* ( $u$ ), representing bipolar positions, and *backward* ( $b$ ) and *forward* ( $f$ ), representing dichotomic momentum directions “out of” and “in to” the molecule regarding the direction of the emitted electron. The two sets of variables are eigenstates of the parity and momentum operator, respectively. The complementary systems parity and momentum offer the possibility of a Bell type entanglement analysis analogous to the corresponding spin-based experiments. A Bell type analysis requires the determination of correlations of a particular variable between the entangled particles, which have to be measured in coincidence. Entirely correlated events correspond in our case to entirely localized, and entirely uncorrelated events to entirely delocalized positions, which is an alternative description to be either in the *gerade* or *ungerade* symmetry eigenstate. Apart from these two extreme situations that correspond to a relative phase of  $\pm\pi/2$  and  $0$  ( $2\pi$ ) between the two eigenvalues of the variable position “left” and “right” there is, however, a continuum of other phases that may be realized. In order to observe the continuous phase change between these two complementary systems by coincidence experiments one has to employ momentum eigenvalues differing in size regarding *forward* and *backward* emission. This is in case of the undisturbed eigenvalues  $f$  and  $b$ , however, unfortunately not given. Their entanglement is a property, which is in principle hidden from any outside observation and has hence no physical reality. However, in two particular cases nature offers a window into the hidden world of entanglement in ordinary space. This is the regime of intra-molecular scattering associated with photoelectron emission and the occurrence of Doppler induced energy shifts of electrons emitted during dissociation. In both cases the momentum eigenvalues  $f$  and  $b$  differ in size, making a Bell type analysis of entanglement possible. We succeeded in both cases, proving that the individual eigenvalues of the variable position have indeed no physical reality for



a pair of two or more completely entangled particles, such as two emitted electrons or one emitted electron and one remaining fragment ion, as in our case.

In the second project we used angle-resolved photoelectron spectroscopy at the FLASH facility to study the nonlinear multi-photon processes emerging in the photo-ionization of atoms, molecules and clusters as a function of photon intensity. As reported already last time, sequential processes dominate the two-photon double photo-ionization once the required photon energy for this process is exceeded. This time we concentrated more on the angular distributions of the corresponding photoelectrons, which are characterized by an additional asymmetry parameter  $\beta_4$ . Briefly, our experiments showed an unexpected behavior of this asymmetry parameter  $\beta_4$  in the energy region of a Cooper minimum. Although the occurrence of such a minimum of the partial photo-ionization cross section is basically a radial effect of the wavefunction of the outgoing photoelectron, our data show distinct differences of the  $\beta_4$ -behavior upon the angular momentum coupling of the electrons in the remaining ion. This is a clear indication of a coupling dependency of the anisotropic final state interactions of the outgoing photoelectron. Theory predicts even more dramatic effects in this direction, which we plan to study in the forthcoming beamtime period at FLASH. Regarding the intensity distribution between the one- and the two-photon induced peaks in the photoelectron spectrum, different theoretical models predict very different intensity distributions depending on the role of dynamical screening. Strong screening should give rise to increasing continuous photoelectron intensity between the two photoelectron peaks caused by the direct or the sequential process. So far, our data provide only weak evidence for the existence of such a screening effect. However, we plan to search for this interesting phenomenon at more appropriate photon energies during future beam time periods at FLASH.

#### **IV. Electronic structure of surfaces and interfaces (Karsten Horn)**

The investigation of the properties of graphene, the single layer of hexagonally coordinated carbon atoms, has been at the focus of research in our group.

Graphene is one of the most interesting materials in solid state physics, on account of its unique electronic structure (“massless Dirac Fermions”), constituting the ultimate 2-dimensional material. Since its experimental “discovery” about five years ago, a veritable rush has ensued to characterize this material and to use it in various applications. Surface science methods have been most important for an elucidation of various aspects of graphene’s physical and chemical properties. We have investigated the band structure of graphene grown on silicon carbide as a monolayer and in multilayers, both as a pristine material and under different conditions of doping, using angle-resolved photoemission in collaboration with groups in Berkeley and the University of Erlangen. These studies have been central to an understanding of the band structure of graphene, in particular near the so-called Dirac point, and have received widespread attention in the community. A considerable amount of work has been devoted to the question whether a gap opens up at the Dirac crossing point of the linearly dispersing bands. This controversial point has been clarified – from our point of view – through the study of symmetry-related intensity changes, showing that any gap opening must be well below 100 meV. Other studies have addressed the morphology of graphene on silicon carbide using LEEM and STM; these have been used in the optimization of growth processes leading to “wafer”-like quality of graphene films grown under atmospheric pressure. More recently, we have added graphene grown on metal surfaces to our scope of experiments. Graphene on ferromagnetic substrates is of great interest for a possible use as spin-filtering devices in spin field-effect transistors. We are also currently involved in a program of studies related to a functionalization of graphene through hydrogen and other adsorbates, as well as intercalation of metals between the substrate and the graphene layer, with a view to studying the effect of charge transfer and the transition from a  $sp^2$ - to a  $sp^3$ -bonded situation in the carbon network. Other projects in the group concern STM studies of possible novel procedures for graphene growth using coronene, a seven-membered benzene ring molecule.

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### **Doctoral Theses:**

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*Stoll, M.:* Buffer-gas cooling and magnetic trapping of CrH and MnH molecules. Humboldt Universität zu Berlin 2008.

*Wohlfart, K.:* Alternating-gradient focusing and deceleration of large molecules. Freie Universität Berlin 2008.

### **Diploma Theses:**

*Grätz, F.:* Alternating gradient - Abbremsung von Benzonitril. Freie Universität Berlin 2008.

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*Kirste, M.:* Das elektrostatische Analogon einer Ioffe-Pritchard-Falle. Freie Universität Berlin 2008.

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### **Doctoral Theses:**

*Heiner, C.E.:* A molecular synchrotron. University of Nijmegen, The Netherlands 2009.

*Gilijamse, J.J.:* Experiments with Stark-decelerated and trapped molecules. University of Nijmegen, The Netherlands 2009.

*Gruene, P.:* Structure and reactivity of metal and semiconductor clusters in the gas phase. Technische Universität Berlin 2009.

### **Diploma Theses:**

*Bergmann, R.:* Aufbau und Charakterisierung einer Multipasszelle zur schwingungsspektroskopischen Untersuchung hydratisierter Ionen. Freie Universität Berlin 2009.

*Bertsche, B.:* Ein Geschwindigkeitsfilter für polare neutrale Moleküle. Freie Universität Berlin 2009.

*Braun, T.:* Entwicklung und Charakterisierung einer Elektronenlinse für abbildende Photoelektronenspektroskopie. Freie Universität Berlin 2009.

*Schewe, H.C.:* Focusing of helium atoms by reflection from a concave surface. Freie Universität Berlin 2009.



**Invited Talks of members of the  
Department of Molecular Physics**

**Knut Asmis**

- May 2008      107. Hauptversammlung der Deutschen Bunsen-Gesellschaft für  
Physikalische Chemie, Saarbrücken, Germany  
*Probing stepwise ion solvation by gas phase vibrational  
spectroscopy*
- Sept. 2008      Findungssymposium - W2 Professur Spektroskopie & Katalyse,  
Leibniz Institut für Katalyse der Universität Rostock, Rostock,  
Germany  
*Clusterspektroskopie & Katalyse: Welchen Beitrag können Gas-  
phasenuntersuchungen leisten?*
- Sept. 2008      Gordon Research Conference on Molecular and Ionic Clusters,  
Aussois, France  
*Ion hydration: new developments in and insights from gas phase  
vibrational spectroscopy*
- Oct. 2008      4<sup>th</sup> International Conference on Laser Probing, Nagoya, Japan  
*Structure characterization of gas phase clusters with infrared free  
electron laser radiation*
- June 2009      433. WE-Heraeus-Seminar “Anions; from the lab to the stars”, Bad  
Honnef, Germany  
*Vibrational spectroscopy of microhydrated negative ions*
- July 2009      XII<sup>th</sup> Dynamics of Molecular Collisions Meeting, Snowbird, UT,  
USA  
*Dudley Herschbach Medal Winner: Daniel M. Neumark*
- Oct. 2009      Physical Chemistry Seminar, University of Basel, Basel,  
Switzerland  
*Vibrational spectroscopy of microhydrated ions: about solvent-  
separated ion pairs and solvent-induced conformational changes*

**Uwe Becker**

- Nov. 2007      SFB 450 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Tunneling-induced entanglement of electrons in molecular double-  
slit experiments*

- Jan. 2008      The US-Africa Advanced Studies Institute, Cairo University, Cairo, Egypt  
*Tunneling-induced entanglement of electrons in molecular double-slit experiments*
- Jan. 2008      Gordon Research Conference on Photoions, Photoionization & Photodetachment, Il Ciocco, Italy  
*Electron correlation and entanglement in scattering and photo-ionization*
- Feb. 2008      Molecular Physics Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Coherence and entanglement in photoelectron spectroscopy*
- April 2008      Allgemeines Physikalisches Kolloquium der Universität Münster, Münster, Germany  
*Tunnelinduzierte Kohärenz mit Verschränkung von Photoelektronen*
- May 2008      15th Central European Workshop on Quantum Optics, CEWQO 08, Belgrade, Serbia  
*Electron entanglement through tunneling-induced coherence between two emitter-sites*
- June 2008      International Workshop on Photoionization, Uppsala, Sweden  
*Electron tunneling studied by core-hole clock-based Doppler electron-spectroscopy*
- June 2008      21<sup>st</sup> International Conference on X-Ray and Inner-Shell Processes, Paris, France  
*Mirror-symmetry induced entanglement in real and momentum space*
- July 2008      40<sup>th</sup> EGAS Conference, Graz, Austria  
*Multi-photon ionization and excitation of the rare gases by free electron laser radiation*
- Aug. 2008      International Workshop on Time-Resolved X-Ray Dynamics, Dresden, Germany  
*Nonlinear and time-resolved spectroscopy of atoms and molecules*
- Sept. 2008      11<sup>th</sup> International Conference on Multiphoton Processes, Heidelberg, Germany  
*Search for a coexistence regime of simultaneous and sequential processes in multi-photon ionization*



- Oct. 2008 Workshop on Ultraviolet Technology and Applications, WUTA08, Frascati, Italy  
*Entanglement in space-time: “Suddenly this overview, big question-small questions”*
- Nov. 2008 International Workshop on Atomic Physics, Dresden, Germany  
*Study of entanglement of continuous variables by photoinduced processes*
- Nov. 2008 Theoretical Chemistry Colloquium, Free University of Berlin, Berlin, Germany  
*Entanglement of continuous variables in molecular photoionization experiments*
- March 2009 Seminar, Max Planck Institute for Quantum Optics, Garching, Germany  
*Evidence for a violation of Bell’s inequality in a localization based EPR experiment*
- June 2009 Seminar, Institute of Optics and Quantum Optics, University of Jena, Jena, Germany  
*A realisation of Einstein’s original proposal to prove the completeness of quantum mechanics*
- July 2009 The Fourth International Symposium on Atomic Cluster Collisions, ISACC 2009, Ann Arbor, MI, USA  
*Direct observation of fullerene plasmon oscillations in momentum space*
- July 2009 International Symposium on (e<sup>2</sup>e), DPI and Related Topics, University of Kentucky, Lexington, KY, USA  
*Evidence for violation of Bell’s inequality in localization based EPR-experiments*
- Aug. 2009 Free Electron Laser Conference, Liverpool, UK  
*Evidence for position based electron entanglement from dissociating O<sub>2</sub> molecules*

### **André Fielicke**

- March 2008 Frühjahrstagung der Deutschen Physikalischen Gesellschaft, Darmstadt, Germany  
*Vibrational spectroscopy of isolated metal clusters with a free electron laser*

- Aug. 2008      Chemistry Colloquium, University of Cambridge, Cambridge, UK  
*Vibrational spectroscopy of isolated metal cluster complexes with a free electron laser*
- Oct. 2008      Seminar, Helmholtz Centre Berlin for Materials and Energy, Berlin, Germany  
*Vibrational spectroscopy of isolated metal cluster complexes with a free electron laser*
- Oct. 2008      Seminar, University of Utrecht, Dept. of Inorganic Chemistry and Catalysis, Utrecht, The Netherlands  
*Vibrational spectroscopy of isolated metal cluster complexes with a free electron laser*
- Feb. 2009      Kolloquium, Institut für Chemie, Humboldt-Universität zu Berlin, Berlin, Germany  
*Vibrational spectroscopy of isolated metal cluster complexes with a free electron laser*
- June 2009      GDCh Kolloquium, Universität Ulm, Ulm, Germany  
*Gas-phase metal cluster complexes: surface chemistry en miniature*

#### **Bretislav Friedrich**

- May 2008      Kolloquium, Freie Universität Berlin, Berlin, Germany  
*Manipulation of molecules by nonresonant fields*
- July 2008      Invited Lecture, Freie Universität Berlin, Berlin, Germany  
*Emigration and immigration: homage to a second life*
- July 2008      6<sup>th</sup> Congress of the International Society for Theoretical Chemical Physics, Vancouver, Canada  
*Molecules in electric fields: eigenstates, collisions, motions*

#### **Philipp Grüne**

- Sept. 2007      Clustertreffen 2007, Berlin, Germany  
*Fern-Infrarotspektroskopie von Metallclustern in der Gasphase*

#### **Steven Hoekstra**

- Feb. 2008      Diavolezza meeting, Diavolezza, Switzerland  
*Lifetime measurements of trapped molecules and NH reloading*

- May 2009 Seminar, KVI, Groningen, The Netherlands  
*Cold neutral molecules probing fundamental physics*
- June 2009 Hot Topic Talk, Free Radicals Conference, Savonlinna, Finland  
*Magnetic and electrostatic trapping of neutral polar molecules*

### **Gert von Helden**

- Jan. 2008 Physics@FOM, Veldhoven, The Netherlands  
*Infrared spectroscopy of biomolecules in the gas-phase*
- April 2008 International Conference on Isolated Biomolecules and Biomolecular Interactions, Valladolid, Spain  
*IR Spectroscopy on cyclic peptides in the gas phase*
- Aug. 2008 ACS National Meeting, Philadelphia, USA  
*Structures of peptides and proteins in the gas phase probed by IR spectroscopy*
- Sept. 2008 Jahrestagung der Deutschen Gesellschaft für Biophysik, Berlin  
*Infrared spectroscopy on gas-phase peptides and proteins*
- June 2009 XXIII International Symposium on Molecular Beams, Dalian, China  
*Catching mass selected biomolecular ions in liquid helium droplets*
- June 2009 Hands-on Tutorial on *Ab Initio* Molecular Simulations, Fritz-Haber-Institut, Berlin, Germany  
*Fingerprinting molecules: vibrational spectroscopy, experiment and theory*

### **Karsten Horn**

- Nov. 2007 Seminar, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany  
*Graphene: electronic structure of an intriguing material*
- April 2008 Physics Colloquium, Technical University of Cottbus, Cottbus, Germany  
*Electronic structure of carbon materials*
- April 2008 Kolloquium, Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany  
*Graphen – masselose Dirac-Fermionen und deren Eigenschaften*

- May 2008      3<sup>rd</sup> Euroschool on Complex Metallic Alloys, Ljubljana, Slovenia  
*Electronic structure of complex metallic alloys*
- June 2008      International Symposium for the Planning of Experiments on the  
Spanish Synchrotron source ALBA, Madrid, Spain  
*Case studies in electronic structure investigations*
- June 2008      8<sup>th</sup> International Workshop on Photoionization (IWP 08), Sättra  
Brunn, Sweden  
*Electronic structure of graphene revealed by electron spectroscopy*
- Sept. 2008      Symposium on Carbon-based Materials, Kloster Banz, Germany  
*Electronic structure of graphene investigated by photoelectron  
spectroscopy*
- Oct. 2008      Symposium on Frontiers in Complex Materials, Zagreb, Croatia  
*Electronic structure of complex metallic alloys*
- Jan. 2009      Physics Colloquium, University of Mainz, Mainz, Germany  
*Electronic structure of graphene revealed by photoelectron  
spectroscopy*
- May 2009      Kolloquium, Hochschule Weingarten-Ravensburg, Germany  
*Graphen; Struktur und Physikalische Eigenschaften*
- May 2009      Kolloquium, Naturwissenschaftliche Fakultät, Universität  
Erlangen-Nürnberg, Germany  
*Die seltsame Welt der Quasikristalle*
- May 2009      Kolloquium, Naturwissenschaftliche Fakultät, Technische  
Universität Ilmenau, Germany  
*Aperiodische Kristalle - ein Blick auf die elektronische Struktur*
- May 2009      Kolloquium Technische Physik, Technische Universität Ilmenau,  
Germany  
*Graphen – Struktur und Physikalische Eigenschaften*
- June 2009      Spring Meeting of the European Materials Research Society,  
Strasbourg, France  
*Electronic structure of graphene revealed by electron spectroscopy*
- Sept. 2009      10<sup>th</sup> International Conference on Atomically Controlled Surfaces,  
Interfaces and Nanostructures, ACSIN-10, Granada, Spain  
*Graphene – electronic structure of a model 2D solid*

- Oct. 2009      International Conference on Solid State Devices and Materials  
SSDM, Sendai, Japan  
*Growth and electronic structure of epitaxial graphene on silicon  
carbide*
- Nov. 2009      International Conference on Magnetism, Superconductivity and  
Phase Transitions in Novel and Complex Materials, Kolkata, India  
*Electronic structure of graphene*

### **Jochen Küpper**

- July 2007      Chemistry Seminar, University of Alberta, Edmonton, Alberta,  
Canada  
*Stark deceleration of polar molecules – from small to large*
- Aug. 2007      Exploratory workshop on Coherent Control of Ultracold Molecular  
Systems”, University of British Columbia, Vancouver, BC, Canada  
*Stark deceleration of polar molecules – from small to large*
- Nov. 2007      SFB 450 Seminar, Free University of Berlin, Berlin, Germany  
*Spatially separating individual conformers of neutral molecules*
- May 2008      107. Hauptversammlung der Deutschen Bunsen-Gesellschaft für  
Physikalische Chemie, Saarbrücken, Germany  
*A selector for structural isomers of neutral molecules*
- June 2008      Physics Colloquium, Free University of Berlin, Germany  
*Selektion, Fokussierung und Abbremsung großer Moleküle*
- Nov. 2008      LCLS/SSRL Annual User’s Meeting and Workshops, Menlo Park,  
CA, USA  
*Coherent diffractive imaging of oriented molecules in the gas  
phase*
- Nov. 2008      International Workshop on Single Particle Imaging at the European  
XFEL, Uppsala, Sweden  
*Coherent diffractive imaging of conformer selected and oriented  
(bio)molecules*
- Feb. 2009      Kolloquium Physikalische Chemie, Universität Basel, Basel,  
Switzerland  
*Manipulating the motion of large molecules: translations,  
rotations, and quantum-state selection*
- March 2009      1<sup>st</sup> LCLS AMO Users’ meeting, Stanford Linear Accelerator  
Center, Menlo Park, CA, USA  
*Diffractive imaging of gas-phase molecules*

- April 2009 Faraday Discussions 142: Cold and Ultracold Molecules, Durham, UK  
*Manipulating the motion of large neutral molecules*
- April 2009 Kolloquium, Eduard-Zintl-Institut, Technische Universität Darmstadt, Germany  
*Manipulating the motion of large molecules: translations, rotations, and conformer selection*
- May 2009 108. Hauptversammlung der Deutschen Bunsen-Gesellschaft für Physikalische Chemie, Köln, Germany  
*Manipulating the motion of large molecules: translation, rotation, and conformer selection*
- June 2009 GDCh Kolloquium, Universität Regensburg, Regensburg, Germany  
*Manipulating the motion of large molecules: information from the molecular frame*
- July 2009 2<sup>nd</sup> Conference on Attosecond Physics, Manhattan, KS, USA  
*Manipulating the motion of large molecules - quantum-state and conformer selection, alignment and orientation: towards diffractive imaging of gas-phase molecules*

### **Adela Marian**

- Feb. 2008 Diavolezza meeting, Diavolezza, Switzerland  
*An ac electric trap for neutral atoms*
- April 2008 EuroQUAM Inauguration Conference on Cold Quantum Matter, Barcelona, Spain  
*AC electric trapping of neutral atoms*
- April 2009 EuroQUAM Satellite Meeting on Cold and Ultracold Molecules, Durham, UK  
*Towards sympathetic cooling of molecules with ultracold atoms*

### **Samuel Meek**

- Sept. 2009 Physics Colloquium, University of Oklahoma, Norman, OK, USA  
*Guiding, decelerating, and trapping polar molecules on a chip*

## **Bas van de Meerakker**

- Feb. 2008      Colloquium, Sandia National Laboratories, Livermore, CA, USA  
*Deceleration and trapping of neutral polar molecules*
- Feb. 2008      Colloquium, JILA, Boulder, CO, USA  
*Deceleration and trapping of neutral polar molecules*
- May 2008      SFB 450 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Deceleration and trapping of neutral polar molecules*
- Aug. 2008      MOLEC XVII, St. Petersburg, Russia  
*Crossed beam collision experiments with Stark-decelerated beams*
- Oct. 2008      Stereodynamics 2008, Dalian, China  
*Crossed beam collision experiments with Stark-decelerated beams*
- April 2009      Faraday Discussions 142: Cold and Ultracold Molecules, Durham, UK  
*Collision experiments with Stark-decelerated beams*
- May 2009      DAMOP 2009, Charlottesville, VA, USA  
*Experiments with Stark-decelerated beams and trapped molecules*
- June 2009      Colloquium, Laboratoire Aimé Cotton, Orsay, France  
*Taming molecular beams*
- July 2009      Colloquium, University of Freiburg, Freiburg, Germany  
*Taming molecular beams*

## **Gerard Meijer**

- Nov. 2007      GdCh Kolloquium, University of Würzburg, Würzburg, Germany  
*Deceleration and trapping of neutral polar molecules*
- Nov. 2007      Seminar, Center for Ultracold Atoms, Harvard/MIT, Cambridge, MA, USA  
*Deceleration and trapping of neutral polar molecules*
- Nov. 2007      Seminar, Steacie Institute for Molecular Sciences, NRC, Ottawa, Canada  
*Deceleration and trapping of neutral polar molecules*
- Jan. 2008      16<sup>th</sup> Symposium on Atomic and Surface Physics and Related Topics, SASP 2008, Les Diablerets, Switzerland  
*Deceleration and trapping of neutral polar molecules*

- March 2008 ESF-FWF Conference on Quantum Optics: From Photons and Atoms to Molecules and Solid State Systems, Obergurgl, Austria  
*Deceleration and trapping of neutral polar molecules*
- March 2008 APS Spring meeting, Focus session on Photophysics of Cold Molecules, New Orleans, LA, USA  
*Molecular collision studies with Stark-decelerated beams*
- March 2008 Physics Colloquium, University of Groningen, Groningen, The Netherlands  
*Cold molecules*
- April 2008 EuroQUAM Inauguration Conference on Cold Quantum Matter, Barcelona, Spain  
*Molecular collision studies with Stark-decelerated beams*
- June 2008 Colloquium, Max Planck Institute for Nuclear Physics, Heidelberg, Germany  
*Taming molecular beams*
- Sept. 2008 Gordon Research Conference on Molecular and Ionic Clusters, Aussois, France  
*Taming molecular beams*
- Sept. 2008 The 8<sup>th</sup> IAMS retreat, Yi-Lan, Taiwan  
*Taming molecular beams*
- Sept. 2008 Seminar, National Institute of Information and Communications Technology, Tokyo, Japan  
*Deceleration and trapping of neutral polar molecules*
- Oct. 2008 Physics Colloquium, Tokyo University, Tokyo, Japan  
*Deceleration and trapping of neutral polar molecules*
- Oct. 2008 Physics Colloquium, Toyama University, Toyama, Japan  
*Deceleration and trapping of neutral polar molecules*
- Oct. 2008 Seminar, Genesis Research Institute, Ichikawa, Chiba, Japan  
*Deceleration and trapping of neutral polar molecules*
- Oct. 2008 Norman Hascoe Distinguished Lecture, University of Connecticut, Dept. of Physics, Storrs, Connecticut, USA  
*Taming molecular beams*
- Oct. 2008 92<sup>nd</sup> annual meeting of the Optical Society of America, Frontiers in Optics 2008 & Laser Science XXIV, Rochester, New York, USA  
*Manipulating polar molecules: traps, synchrotrons and chips*



- Jan. 2009      Colloquium, University of Southampton, Dept. of Physics and Astronomy, Southampton, United Kingdom  
*Taming molecular beams*
- May 2009      Durham Lectures 2009, Public Lecture, University of Durham, Durham, UK  
*Cold molecules*
- May 2009      Durham Lectures 2009, Physics Lecture, University of Durham, Durham, UK  
*A molecular laboratory on a chip*
- May 2009      Durham Lectures 2009, Chemistry Lecture, University of Durham, Durham, UK  
*Infrared spectroscopic characterization of gas-phase clusters and cluster-adsorbate complexes*
- May 2009      Symposium on Interfaces in Molecular Systems, The Fritz Haber Center for Molecular Dynamics, Kibbutz Tzuba, Israel  
*A molecular laboratory on a chip*
- June 2009      XXIII International Symposium on Molecular Beams, Dalian, China  
*Taming molecular beams: towards a molecular laboratory on a chip*
- June 2009      Colloquium, Helmholtz Centre Berlin for Materials and Energy, Berlin, Germany  
*Accelerator physics with neutral molecules*
- June 2009      European Graduate College on Quantum Interference and Applications, Berlin, Germany  
*Taming molecular beams; towards a molecular laboratory on a chip*
- July 2009      Chemistry & Biochemistry Seminar, Arizona State University, Tempe, Arizona, USA  
*Towards a molecular laboratory on a chip*
- July 2009      Colorado Cold Molecule (CoCoMo) workshop, JILA, University of Colorado, Boulder, CO, USA  
*Taming molecular beams; towards a molecular laboratory on a chip*
- July 2009      XXVI International Conference on Photonic, Electronic, and Atomic Collisions, Kalamazoo, MI, USA  
*Taming molecular beams; towards a molecular laboratory on a chip*

- Aug. 2009     18<sup>th</sup> International Mass Spectrometry Conference, Bremen, Germany  
*Taming molecular beams*
- Sept. 2009     Seminar, Cluster of Excellence on Quantum Engineering and Space-Time Research (QUEST), Braunschweig, Germany  
*Stark-deceleration of molecules*
- Oct. 2009     Summerschool of the Center for Functional Nano-Materials, Karlsruhe, Germany  
*Infrared spectroscopic characterization of gas-phase clusters*
- Oct. 2009     Asilomar Conference on Mass Spectrometry, Asilomar, CA, USA  
*Infrared spectroscopic characterization of metal clusters, metal-oxides and cluster-adsorbate complexes*
- Nov. 2009     Kolloquium, Nordrhein-Westfälische Akademie der Wissenschaften und der Künste, Düsseldorf, Germany  
*Moleküle in Zeitlupe*

#### **Andreas Osterwalder**

- Jan. 2008     Seminar, SNF Bern, Switzerland  
*Cold neutral molecules - novel production schemes and application to reactive scattering studies*
- May 2008     Kolloquium, Technische Universität Berlin, Berlin, Germany  
*Kalte Atome und Moleküle*

#### **Ludwig Scharfenberg**

- Feb. 2008     Diavolezza meeting, Diavolezza, Switzerland  
*Towards scattering experiments with Stark-decelerated molecular beams*

#### **Wieland Schöllkopf**

- Nov. 2007     International Workshop on Atomic Physics, Dresden, Germany  
*Trapping of Rb atoms by AC electric fields*
- Feb. 2008     Seminar, Physikalisches Institut der Universität Heidelberg, Heidelberg, Germany  
*Diffraction of molecular beams from a microstructured quantum-reflection grating*

- Dec. 2008      Quantum Optics & Laser Science Seminar, Imperial College,  
London, UK  
*Experiments with an AC electric trap for Rb atoms and with He  
atom beams*
- Jan. 2009      Seminar, Helmholtz Centre Berlin for Materials and Energy,  
Berlin, Germany  
*The IR-FEL project at the Fritz-Haber-Institut in Berlin*

### **Bum Suk Zhao**

- May 2008      Seminar, Department of Chemistry, Seoul National University,  
Seoul, Korea  
*Controlling translational motions of neutral molecules and atoms  
without using internal state transition*
- Oct. 2008      Seminar, Department of Materials Science and Engineering,  
Gwangju Institute of Science and Technology, Gwangju, Korea  
*Quantum reflection of helium atom beams from a microstructured  
grating and a concave mirror*
- Nov. 2008      Seminar, Department of Physics and Astronomy, Seoul National  
University, Seoul, Korea  
*Quantum reflection of helium atom beams from a microstructured  
grating and a concave mirror*
- May 2009      Seminar, Department of Chemistry, Korea Advanced Institute of  
Science and Technology, Daejeon, Korea  
*Coherent reflection and focusing of He atom beams from rough  
surfaces at near-grazing incidence*
- May 2009      Seminar, Department of Physics, Korea University, Seoul, Korea  
*Coherent reflection and focusing of He atom beams from rough  
surfaces at near-grazing incidence*
- June 2009      Seminar, Department of Physics, Pohang University of Science and  
Technology, Pohang, Kyungbuk, Korea  
*Coherent reflection and focusing of He atom beams from rough  
surfaces at near-grazing incidence*

### **Peter Zieger**

- Feb. 2008      Diavolezza meeting, Diavolezza, Switzerland  
*Production, deceleration and electrostatic trapping of metastable  
NH molecule*







**Staff scientists:**

Markus Eiswirth		
Christian Frischkorn	(Habilitation)	from 09/2008
Leonhard Grill	(Habilitation)	from 07/2009
Alexander Mikhailov		
Bruno Pettinger	50% appointment until 04/2011	
Julia Stähler		from 04/2009
Gerhard Ertl (Emeritus)		

**Guest scientists, staying for at least six months:**

Sebastian Hagen  
 Jesus Martinez  
 Yasuaki Kobayashi  
 Carlos Villagomez Ojeda  
 Peter Plath  
 Sonja Sauerbrei  
 Nicola Scott  
 Zefeng Ren  
 Simon Wall  
 Peter West

**Scientists (temporary) paid from external funds:**

Rocio Cortes	<i>AvH Fellowship</i>
Makoto Ima	<i>VW- Fellowship</i>
Marcel Krenz	<i>Sfb 450</i>
Oliver Rudzick	<i>Sfb 555</i>
Toru Shimada	<i>AvH Fellowship</i>
Tatsno Yanagita	<i>VW- Fellowship</i>

<b>Graduate students:</b>	<b>12</b>	(1 IMPRS student, 5 from external funds)
<b>Diploma students:</b>	<b>2</b>	
<b>Trainees:</b>	<b>1</b>	
<b>Technicians:</b>	<b>5</b>	





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

**Director: Martin Wolf**

1. General
  - 1.1 Current activities at the FHI and FU Berlin
  - 1.2 Planning of the Department of Physical Chemistry
2. Projects
  - 2.1 Ultrafast Dynamics in Solids and at Interfaces**
    - 2.1.1 Dynamics of Interfacial Electron Transfer
    - 2.1.2 Photoinduced Dynamics in Correlated Materials
    - 2.1.3 Ultrafast Optical Spectroscopy of Low-energy Excitations
  - 2.2 Molecular Processes at Surfaces**
    - 2.3.1 Nanoscience with Functional Molecules
    - 2.3.2 Tip Enhanced Raman Spectroscopy
    - 2.3.3 Photoinduced Surface Reactions and Vibrational Spectroscopy
  - 2.3 Complex Dynamics**
    - 2.3.1 Spatiotemporal Self-Organization
    - 2.3.2 Complex Systems
3. Research projects funded from outside resources
4. Publications of the Department of Physical Chemistry
5. Invited talks of members of the department



## 1. General

The Department of Physical Chemistry is currently in a transition period. In connection with the appointment of a new director in 2008 and substantial changes in the infrastructure, a restructuring of the department and the development of new scientific activities are planned for the next 2-3 years. This report is split into two parts: First, a brief summary of the ‘status quo’ at the FHI and the Freie Universität Berlin is given followed by an overview of the future research directions of the department. The second part reports about the existing projects at the FHI, and those at the FU Berlin which will be transferred to the FHI. These projects are also documented in the poster abstracts.

### 1.1 Current activities at the FHI and FU Berlin

Due to the renovation of the historical Building A the members of the department are currently located at several sites of the FHI campus and at the FU Berlin. The departments of Inorganic Chemistry, Molecular Physics and Chemical Physics have generously provided space to relocate existing equipment and to setup new experiments in the lab area dedicated to the future Free Electron Laser at the FHI. With the completion of Building A in 2010 the projects from the FU Berlin will be transferred to the FHI. Currently the planning for a new building with special infrastructure for laser experiments is performed; the construction of this building shall be finished until the end of 2011.

At the FHI a new research group is currently set up by *Julia Stähler*, which will focus on ultrafast electron dynamics and correlation effects at interfaces using time- and angle-resolved photoemission spectroscopy. Furthermore, three groups are active, which have started their research under the former director, Prof. G. Ertl. The groups of *Markus Eiswirth* and *Alexander Mikhailov* study complex dynamics in chemical systems, in particular, nonequilibrium pattern formation in electrochemical systems and problems of nanobiology and active soft matter. The technique of tip-enhanced Raman spectroscopy is developed by the group of *Bruno Pettinger* to study individual molecules and nanostructures under UHV conditions.

The research group of *Martin Wolf* is still located at the FU Berlin and focuses on electron dynamics in correlated materials and adsorbate overlayers, molecular switches at surfaces, THz time-domain and vibrational spectroscopy as well as photoinduced surface reactions. In the last two years several younger scientists received offers for university professorships: *Luca Perfetti* and *Uwe Bovensiepen* accepted offers from the Ecole Polytechnique Palaiseau and University of Essen-Duisburg, respectively. Also *Petra Tegeder* will continue her research on molecular switches on a W2-position at the FU Berlin.

In this context only some of the current activities at the FU will be transferred to the FHI: The scanning tunneling microscopy group, which is headed by *Leonhard Grill*, will focus on functional molecules on surfaces and their controlled manipulation by tunneling electrons, electric fields, chemical forces and light. Also the growth of controlled architectures from weakly bound supramolecular and covalently bound macromolecular nanostructures will be studied. The activities on photoinduced surface reactions (headed by *Christian Frischkorn*) will be developed further aiming towards control of reactions by light. *Tobias Kampfrath* (currently at AMOLF) will join the department in March 2010 and will set up a new group to study the dynamics of solid state materials by time-resolved optical spectroscopy and intense THz fields. In addition, several other research groups may be created in the next years. The final organizational structure of the department will consist of approximately ten small research groups headed by a junior or staff scientist.

## **1.2 Planning of the Department of Physical Chemistry**

The research of the Department of Physical Chemistry will be focussed on the dynamics of elementary processes at surfaces and interfaces and in solids. A key goal is to develop a microscopic understanding of electronic interactions and correlations as well as of photoinduced reactions and molecular processes at a single molecule level. On the one hand the dynamics of such processes will be studied by ultrafast spectroscopy directly on the relevant time scales. Hereby a broad spectrum of laser-based techniques allows analyzing the dynamics of electron transfer processes and vibrational degrees of freedom at adsorbate

covered surfaces, the dynamics of electronic excitations and scattering processes in solids, and the mechanisms of optically induced phase changes in highly correlated materials. On the other hand molecular processes at surfaces will be studied on a single molecule level and employing various schemes of optical excitations. This includes also studies of photo-induced surface reactions. Scanning probe microscopy (in part combined with optical excitation) allows imaging, manipulation and spectroscopy as well as inducing and probing of chemical processes of individual molecules. For the preparation and characterization of these systems various surface science methods are employed. Further activities of the department in the field of complex dynamics of chemical systems focus on problems of nanobiology and electrochemistry. Here, theoretical studies of reactive soft matter, individual molecular machines and networks of interacting molecular machines are performed, complemented by the studies of nonequilibrium pattern formation in electrochemical systems and general aspects of chemical kinetics.

In the next few years research at the Department of Physical Chemistry will be structured into three areas:

- Ultrafast Dynamics in Solids and at Interfaces
- Molecular Processes at Surfaces
- Complex Dynamics

In the following, some key goals and general research directions of these areas are discussed. A more detailed account of the current projects and their future planning is given in part 2.1 - 2.3.

*Ultrafast Dynamics in Solids and at Interfaces:* Research in this area aims towards the understanding of electronic correlations, interactions and scattering processes in solids and at interfaces and will be pursued in several directions:

(i) Some of the most fascinating problems in solid state physics like superconductivity or metal-insulator transitions arise from electron correlation effects and coupling between electronic and other degrees of freedom of a material (e.g. lattice, orbital or spin excitations). Such electron correlation effects are particularly strong in low-dimensional systems like layered materials or quasi

one-dimensional systems. Direct time-resolved studies of the ultrafast dynamics of such highly correlated materials open a new dimension, which yields information complementary to conventional frequency domain spectroscopy or transport measurements. For example, photoexcitation can drive a material into different regions of a phase diagram, which are not accessible under equilibrium conditions. Furthermore, the coupling strength of collective modes to different states of the electronic band structure as well as their damping can be studied directly in the time domain. In particular, the dynamics of the opening and closing of electronic gaps at the Fermi level provides fundamental information about the mechanisms of photoinduced phase transitions.

Studies of the ultrafast dynamics of low-dimensional correlated systems will therefore be a key topic of research of the department. As time-resolved photoemission spectroscopy provides the most direct access to electronic structure, several experimental setups will be developed including high-harmonic generation (HHG) of VUV laser pulses at high repetition rates (10-100 kHz). The latter approach opens also the possibility to extend such studies into the attosecond time domain. These time-resolved studies will be complemented by high-resolution photoemission experiments at the corresponding photon energies using laboratory or synchrotron light sources.

(ii) Another important aspect in such studies of non-equilibrium dynamics of solids is how selectively the system is excited and brought out of equilibrium. As many fundamental excitation energies in solids (e.g. phonons, magnons) are in the range of several meV to a few 100 meV, excitation and optical spectroscopy of solids in the (far to near) infrared regime can most directly address such low-energy transitions. For example, resonant pumping of IR-active phonon modes provides a selective way of excitation, which is fundamentally different from the response to a hot carrier distribution created by absorption of visible or UV photons. So far most time-resolved studies of solids have been restricted to the latter regime, i.e. to excitation energies much larger than the fundamental gaps or collective modes. A key goal is therefore, to develop schemes to selectively excite low frequency modes using the electrical (or magnetic) field of intense THz or IR pulses and to analyze the response of the material with appropriate spectroscopic

(THz, optical or photoemission) techniques. These studies will be complemented by THz absorption and emission spectroscopy (see 2.1.3).

(iii) Electron dynamics at surfaces and at interfaces will be another direction of research. Interfaces (like molecule-metal or molecule-oxide) allow studying fundamental processes like interfacial electron transfer, carrier localization or electron solvation processes, which are of relevance for surface chemistry, organic photovoltaic and electrochemistry. The well established technique of time- and angle-resolved two-photon-photoemission (2PPE) will be developed further to obtain state-of-the art ( $<20$  fs) time resolution with tuneable laser pulses combined with parallel momentum detection. Furthermore fundamental studies of the photoemission process will be performed, for example, by using phase-stabilized laser pulses to study the role of the carrier-envelope phase in nonlinear photoemission at surfaces.

(iv) Further activities in this area will depend on the future hiring of research group leaders. For example, time-resolved nonlinear optics could be applied as a highly interface- and symmetry-sensitive spectroscopy to study carrier or spin dynamics at interfaces of materials with anisotropic electronic or antiferromagnetic properties. Adding spin-resolved detection to time-resolved photoemission spectroscopy would provide access to the dynamics of spin-orbit interactions and spin-dependent scattering processes at surfaces.

*Molecular Processes at Surfaces:* The second major research area of the department is devoted to studies of elementary processes of molecules at surfaces using scanning probe techniques as well as to studies of photoinduced surface reactions. One of the long-term goals is to combine these approaches to study light induced processes on individual nanostructures. A further goal is to induce and control surface reactions by light via appropriate excitation schemes.

(i) Scanning tunneling microscopy at low temperatures opens fascinating possibilities for the study of molecular processes as it allows on the one hand to induce chemical processes or intramolecular changes via manipulation (by tunneling electrons, electric fields, chemical forces or light) at the single molecule level in a controlled way. On the other hand, the induced changes (and thus the molecular

function) can be analyzed in detail by imaging and spectroscopic characterization before and afterwards, even with respect to the atomic scale environment. Furthermore, the controlled growth of supra- and macromolecular nanostructures from functional building blocks on different surfaces is a key topic in the research activities, because it allows to assemble molecules in a specific, pre-defined architecture. Depending on the chemical structure of the molecules, various intermolecular interactions – from weak van der Waals to strong covalent forces – are used for the molecular coupling. In the next years, the activities will be extended to the growth of heterogeneous, covalently bound, nanostructures that include molecular units with a specific function. By using molecular wires as connection between the functional building blocks, the possibility of charge transfer/transport through such an architecture will be explored. Such systems could open the way towards functional molecular circuits at the atomic scale, the central issue in the field of Molecular Electronics.

(ii) Combining scanning probe microscopy with optical spectroscopy allows both topographic imaging as well as spectroscopic investigation of individual nanostructures or molecules without limitations from inhomogeneous broadening. Tip-enhanced Raman spectroscopy (TERS) exhibits such spatial resolution on the nanometer scale and allows the identification and characterization of molecular adsorbates by vibrational (Raman) spectroscopy. The current TERS activities of the department will be further developed to study individual Raman active molecules on single crystal and nanostructured surfaces prepared under UHV conditions. This will be done in cooperation with the Department of Chemical Physics (Prof. Freund). A long term goal is the combination of TERS (or local optical excitation) with low-temperature STM, which would combine the potential of atom manipulation with several means of spatial resolved optical/tunneling spectroscopy. Application of TERS to liquid-solid interfaces including electrochemical potential control could also be an attractive route.

(iii) Controlling chemical reactions by light is a longstanding dream of laser-chemistry, whereby, bond-selectivity competes with rapid vibrational energy redistribution (IVR). However, using amplitude- and phase-shaped femtosecond laser pulses optimum control of chemical reactions can be achieved for molecules



in the gas phase or in solution. Transfer of such concepts to femtochemistry at metal surfaces is hindered by rapid dephasing and energy dissipation processes. Two routes to achieve light induced control over surface reactions will be investigated: One approach will combine optimum control of gas phase reactions in a flow reactor (to generate e.g. radicals) with surface femtochemistry on a catalyst in direct contact with the gas phase. The target of control could be either optimization of branching ratios (selectivity) or the reaction yield. Another route is based on resonant IR pumping of vibrational modes which are strongly coupled to the reaction coordinate and will employ intense femtosecond IR pulses in conjunction with visible or UV excitation of hot substrate electrons. The goal is to explore the reactivity and dynamics of vibrationally ‘hot’ adsorbates, which are resonantly heated by IR excitation. Such studies will be first performed using laser based IR sources in the lab (exciting high frequency vibrational modes), but will be later extended to experiments at the infrared free electron laser of the FHI to address also excitation of low-frequency (external) modes.

*Complex Dynamics:* Studies of complex dynamics in chemical systems continue a tradition of research on nonlinear dynamics and spatiotemporal pattern formation established by its former director, Prof. G. Ertl. In the next years, two main research directions will be pursued:

(i) The first aims on the understanding of complex nanoscale dynamics in biological systems and, specifically, in single-molecule protein machines. Modeling of slow conformational relaxation processes in proteins and of ligand-induced mechano-chemical motions in such macromolecules will be performed. Furthermore, complex self-organized collective dynamics in biochemical networks will be studied. This theoretical research may have important practical applications, with single-molecule machines providing the basis of a new nanotechnology generation. Using low-temperature STM, elementary molecular interactions and self-assembly of molecular architectures in two dimensions can be also studied experimentally as described above. These links, joining experimental and theoretical investigations within the department, shall be explored.

(ii) The second activity includes experimental and theoretical investigations of spatiotemporal self-organization in electrochemical processes. Additionally, general aspects of chemical kinetics are analyzed. In the future mechanistic studies of electrochemical processes, which are relevant for applications in fuel cells and for energy conversion, shall be extended and will be studied in cooperation with the Department of Inorganic Chemistry (Prof. Schlögl).

The proposed activities of the department will depend in part on the future hiring of staff scientists and can become only fully operational after the new building is available. This will strongly enhance the cross links between different projects and allow to operate the laser infrastructure under optimum conditions.

## 2. Projects

### 2.1 Ultrafast Dynamics in Solids and at Interfaces

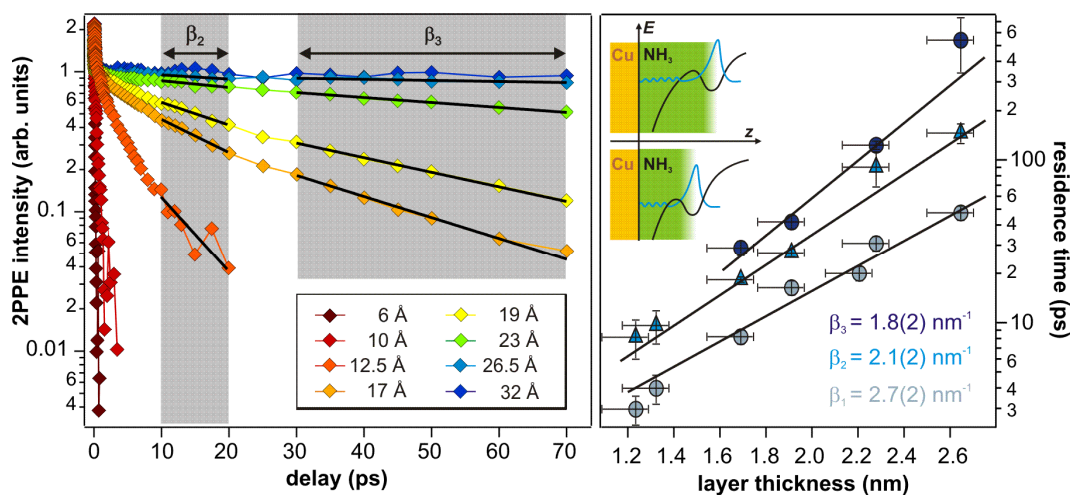
Electronic correlation and interactions are at the heart of solid state physics and chemical bonding. In dissipative systems with many degrees of freedom (like solids and surfaces) time-resolved spectroscopy can provide unique information about the interaction between different subsystems (e.g. electronic and nuclear degrees of freedom), which cannot be obtained from frequency domain spectroscopy. The study of the non-equilibrium, ultrafast dynamics in solids and at interfaces allows therefore to gain fundamental insights into elementary processes like electron transfer and localization, electron-phonon coupling and energy relaxation.

#### 2.1.1. Dynamics of Interfacial Electron Transfer

Electron dynamics at molecule-metal interfaces is of key relevance for a variety of application e.g. organic light emitting devices, nanoscale molecular electronic devices or organic solar cells. The investigation of interfacial electron dynamics requires access to energy and momentum distribution of a non-equilibrium electron population and a temporal resolution of femtoseconds, i.e. on the timescale where electronic excitations occur and relax. Femtosecond time- and angle-resolved two-photon photoelectron (2PPE) spectroscopy grants insight into the occupied and unoccupied electronic band structure at surfaces. Thereby, a first laser pulse (*pump*) creates a non-equilibrium electron population and a second, time-delayed pulse (*probe*), monitors the subsequent electron dynamics by photoexcitation of the transient electron distribution above the vacuum level.

So far, the group of *Julia Stähler* (and coworkers at the FU Berlin) has focussed on electron transfer (ET), localization, and relaxation dynamics at polar molecule-metal interfaces. These systems are particularly interesting, as excess electrons in polar environments such as ice or ammonia localize and stabilize (solvate) by rearrangement of the surrounding molecules. Systematic studies of the influence of the substrate's electronic band structure, the adsorbate's structure and morphology, solvation site, temperature, coverage, and solvent unveil the fundamental electron dynamics occurring at such interfaces: Metal electrons are photoexcited to unoccupied metal states and are injected into the adlayer via the

adsorbate's conduction band. The excited electrons localize at favorable sites and are stabilized by reorientations of the adjacent molecules. Concurrently, they decay back to the metal substrate, as it offers a continuum of unoccupied states. The process of electron solvation leads to a decreasing electronic coupling between the excess electron and the substrate states. This competition of electron back transfer and solvation facilitates the study of heterogeneous electron transfer as a function of coupling strength. For amorphous ice-metal interfaces, the electron transfer is initially dominated by the substrate's electronic surface band structure. With increasing solvation, a transient barrier evolves at the interface that increasingly screens the electrons from the substrate and that determines the excess electron residence time [1].



**Fig. 1.** Left: Electron population traces for amorphous NH<sub>3</sub>/Cu(111) for various layer thicknesses. The residence time increases with increasing coverage. Right: The excess electron residence time rises exponentially with layer thickness due to a decreasing wave function overlap with the substrate as illustrated by the inset. The inverse range parameters  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  correspond to three “snapshots” of electron solvation at early (<3 ps), intermediate (10-20 ps), and late time delays (30-70 ps) [2].

For amorphous NH<sub>3</sub>/Cu(111) interfaces, two species of solvated electrons were found, one exhibiting electron dynamics on femtosecond, the other one on picosecond timescales [2]. A similar transition between ET regimes was observed as for water ice. Using Xenon overlayers to test the influence on the electron binding energy, the solvation site (bulk versus surface) could be determined [3]. For NH<sub>3</sub>/Cu(111) interfaces, the excess electron is bound at the ammonia/vacuum

interface and its distance to the metal substrate can thus be varied in a systematic way. Key results are displayed in Fig 1. The analysis of the exponential dependence of the tunneling rate on the layer thickness indicated a transient evolution of tunneling barrier (see Fig. 1 right) [2]. For thicker layers the weak coupling limit is reached, where the electron transfer is mediated by thermally activated rearrangement of the solvent. Upon crystallization, the electron dynamics slow down significantly both for D<sub>2</sub>O and NH<sub>3</sub>, as the electrons reside for *minutes* in the adlayer. After the ultrafast formation their energetic stabilization spans up to 17 orders of magnitude in time. Their high degree of screening is achieved by localization at orientational defects at the adsorbate-vacuum interface [4].

Currently, the group develops a new setup for 2PPE spectroscopy at the FHI that will have a significantly improved time resolution due to shorter laser pulse durations, higher pulse energies for high density excitations, and parallel detection of the electron momentum due to a hemispherical analyser equipped with a 2D-CCD camera. The regeneratively amplified fs-laser system (35 fs, 250 kHz) will pump both, a collinear and a non-collinear optical parametric amplifier (OPA/NOPA) which will provide independently tuneable light from 460-760 nm. In particular the NOPA, which delivers <20 fs laser pulses, will enable the observation of electronic transitions that have not been accessible for the previous setup. Using this improved experimental design, several new directions will become accessible:

Building on the understanding of the electron dynamics at polar molecule-metal interfaces, chemical reactions with such excess electrons can be studied. In particular, the enormous lifetime of excess electrons in crystalline solvents can be used to initiate electron-driven processes as has been already shown for the dissociation of CFCl<sub>3</sub> on D<sub>2</sub>O/Ru(001) [5]. In addition, we plan to make use of the surface-bound excess electrons on amorphous ammonia layers on Cu(111). The coverage-dependent residence times and the transient presence of the excess electrons at the ammonia-vacuum interface may thus be utilised to trigger electron-induced reactions and study the respective timescales and cross sections.

Another exciting direction is the study the dynamics of strong correlated electron systems at interfaces, which are often related to electron localization phenomena and which can be induced by photodoping. This will be discussed in the subsequent section (2.1.2).

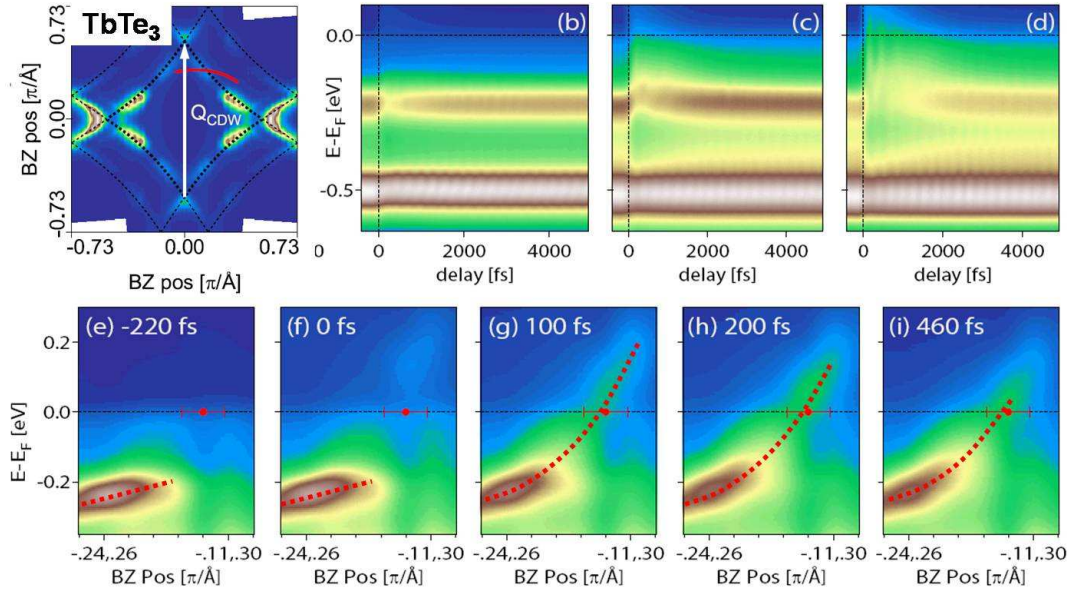
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### 2.1.2 Photoinduced Dynamics in Correlated Materials

One of the basic questions in solid state physics is to understand why a material behaves like an insulator or a metal. Systems with a half-filled band are usually expected to be metallic, however, may undergo a metal-to-insulator transition at low temperatures due to Peierls instabilities or electron correlations. This interplay between electronic and phonon degrees of freedom is of general importance for the understanding of various classes of highly correlated materials like superconductors, charge density wave (CDW) compounds or Mott insulators. Excitation with ultrashort laser pulses may induce a collapse of the respective gaps in the electronic structure via photodoping as well as excitation of collective (vibrational) modes in the material. Time- and angle-resolved photoelectron spectroscopy (trARPES) provides direct access to the dynamics of the electronic structure of such photoexcited materials. In particular both single particle excitations as well as collective modes (e.g. coherent phonons) can be analyzed via the temporal evolution of the spectral function. In contrast to 2PPE spectroscopy typically a UV/VUV laser pulse is used to probe the transient changes of the electron distribution function around the Fermi level (i.e. both the occupied and normally unoccupied electronic states).

In the last few years the photoemission group at the FU Berlin has used femtosecond trARPES to optically excite and probe two model systems, namely the Mott insulator 1T-TaS<sub>2</sub> and the CDW compound TbTe<sub>3</sub>, to investigate the

dynamics of insulator-to-metal transitions directly in the time domain. In TaS<sub>2</sub> photoexcitation by an intense laser pulse leads to an ultrafast transition towards a gapless phase which is accompanied by periodic oscillations of the electronic states (charge density breathing mode), which is lasting for 20 ps without perturbing the insulating phase [1]. The qualitative difference between the oscillatory dynamics of the collective CDW mode and the quasi-instantaneous collapse of the electronic gap followed by a monotonic recovery of the electronic gap prove that TaS<sub>2</sub> is indeed a Mott insulator, which is also supported by DMFT calculations. Moreover it is in clear contrast with the retarded (>100fs) response which is observed for the transient melting of the CDW phase in TbTe<sub>3</sub> [2]. Two coherently excited collective modes are observed in this system; one of them only in the CDW phase at low fluence. The latter is attributed to the CDW amplitude mode, which modulates the spectral function particular strongly at the Fermi surface (see Fig. 2).



**Fig. 2.** Time-resolved photoemission spectroscopy of the CDW compound TbTe<sub>3</sub>. Top: Fermi surface of the CDW phase. The red line shows investigated region of the Brillouin zone (BZ). (b)–(d) Pump-probe spectra recorded for different momentum vectors  $k_{\parallel}$ . Bottom: Snapshots of the electronic structure of TbTe<sub>3</sub> for different time delays after photoexcitation [2]. Note the delayed collapse of the CDW gap after 100 fs and the pronounced oscillations in the spectral function at  $k = k_F$  (panel d) arising from the coupling to the CDW amplitude mode.

Using trARPES allows thus to identify the role of collective vibrations in the transition and to document the highly anisotropic coupling to the electronic system in real time [2]

In the future these studies will be expanded in three directions:

(i) Studies of the photoinduced dynamics of conventional (BCS) and high  $T_c$  superconductors: So far trARPES has been applied to investigate the cuprate superconductor Bi2212, where an ultrafast ( $<50$  fs) electron thermalization and cooling of the electronic temperature on two distinct timescales has been observed. This observation of a bottleneck in the energy flow from the electrons to the lattice suggests that only a minor subset (20%) of all phonon modes contribute to the e-ph coupling with an interaction strength which is strongly anisotropic but weak [3]. Currently these studies are extended to the novel iron pnictides superconductors. A major goal is to investigate the dynamics of superconductors under very weak excitation conditions (i.e. without completely breaking the superconducting state). This will require substantial improvements of the sensitivity of the trARPES experiment.

(ii) The group of *Julia Stähler* plans to drive insulator-to-metal transitions by photodoping *across* the interface between layered Mott insulators and a metallic substrate. Strong electron correlation effects, leading to e.g. insulator-to-metal transitions, are often related to electron localization phenomena. As the charge density is crucial for these phase transitions, they can be either statically induced by chemical doping or pressure variation or dynamically by mode-selective excitation of phonons, lattice heating, and photodoping. However, all studies known to date apply photodoping to bulk materials only. In a new approach photoexcited hot electrons in a metal substrate will be photoinjected from the metal into the upper Hubbard band and induce – if their density is sufficiently large – a collapse of the gap, i.e. the adlayer will become metallic. These experiments will unveil the role of “pure” doping with electrons (or holes) in contrast to the previous experiments with bulk materials where photodoping in fact leads to electron-hole pair (exciton) formation.



(iii) The work on anisotropic CDW compounds will be continued with a systematic study of several  $\text{RTe}_3$  ( $\text{R} = \text{lanthanide}$ ) compounds, some of which exhibit two CDW gaps, which open at different temperatures. Closely related is the problem of Peierls instabilities in quasi-one-dimensional metallic chains, which can be epitaxially grown on semiconductor surfaces. As the current trARPES setup with 6 eV photons (and corresponding low kinetic energies of the photoelectrons) provides only limited access to the full Brillouin zone, a key development would be a VUV source which operates at 9 eV photon energy. First steps in this direction using high-harmonic-generation (HHG) are currently under way.

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### 2.1.3 Ultrafast optical spectroscopy of low-energy excitations

Many elementary excitations in nature occur at transition energies of the order of few meV to several 10 meV, i.e. at frequencies in the terahertz (THz) regime. Examples are quasi-free electrons in plasmas of ionized gases, Cooper pairs in superconductors, excitons in semiconductors or low frequency phonons and external vibrational modes of adsorbates. Electromagnetic pulses with THz frequencies have been proven to be efficient probes of such excitations thanks to their low photon energy (4.1 meV at 1 THz), their large bandwidth (typically more than one octave), and the possibility to detect the transient electric field (rather than intensity) directly in the time domain. In addition, the short pulse duration (typically less than 1 ps) makes it possible to study ultrafast processes.

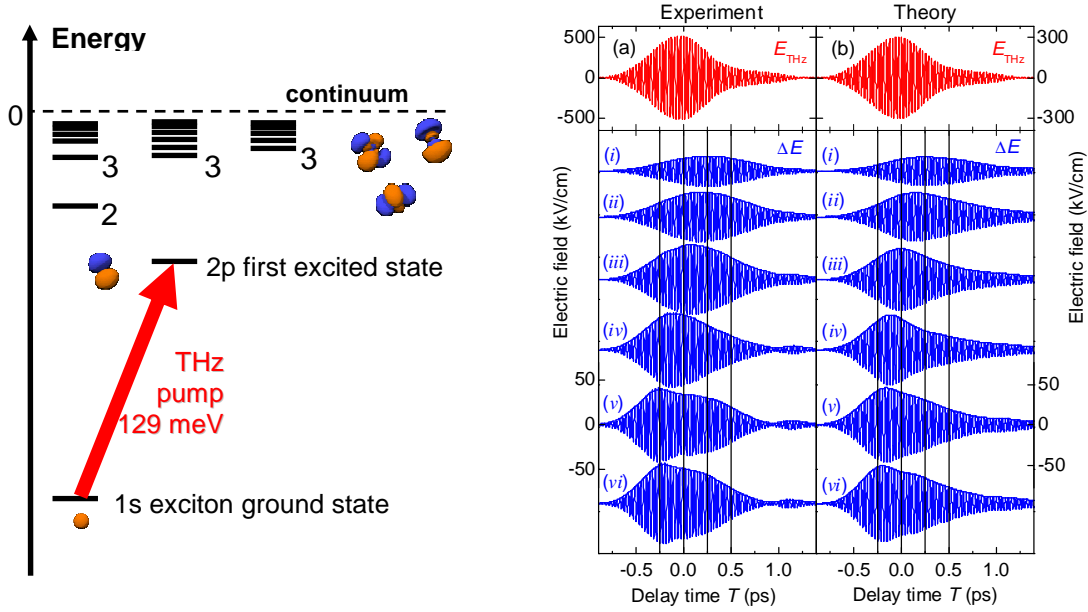
In the last few years the THz group at the FU Berlin (*Tobias Kampfrath* and *Christian Frischkorn*) has implemented THz transmission spectroscopy, whereby the carrier dynamics in a thin sample is triggered by the absorption of a femtosecond laser pulse and, after some delay, probed by a broadband THz pulse. Recently, the mechanism of the far-infrared absorption of carbon-nanotube films has been identified to originate from electronic transitions over the band gap of nanotubes with a small electronic gap of  $\sim 10$  meV [1]. This finding is important

for the understanding of the THz transmittance as a sensitive probe of the doping level of nanotubes. Based on the same pump-probe technique, a new scheme to measure the electronic heat capacity of the high-temperature superconductor BSCCO has been developed. This approach relies on the fact that the energy absorbed from the incident pump laser pulse is first deposited in the electronic system of the solid and allows highly selective heating of the electrons. Currently these studies are extended to various doping levels (critical temperature) in BSCCO. Furthermore, the temperature dependence of optical conductivity of the conducting polymer PEDOT:PSS used in organic photovoltaics has been investigated.

On the other hand THz radiation *generated* by a laser-excited sample can serve as a probe of the sample dynamics. In THz emission experiments with ferromagnetic Fe films the emitted THz radiation was found to be extremely sensitive to the cap material (interface properties) of the Fe film. A detailed analysis shows that the THz radiation reflects the motion of spin-polarized electrons parallel to the two interfaces of the Fe film. This information might be highly relevant for spintronic devices based on the interface-dominated giant magneto-resistance effect.

Future work at the FHI using THz spectroscopy will use this experimental and theoretical know-how to investigate important materials such as high-temperature superconductors, organic materials for photovoltaics, ferroelectrics, and magnetically ordered systems. The experimental setups will be improved to further increase the signal-to-noise ratio and to make reflection measurements possible.

Instead of using THz radiation as a *probe* of electrons, intense THz transients of order MV/cm have been used to coherently control the state of excitons in Cu<sub>2</sub>O [2]. Key results, which demonstrate coherent population transfer from the 1s to the 2p orbitals, are shown in Fig. 3. These results encourage the use of shaped THz pulses to create excitons in any coherent state on demand. From a general perspective this work demonstrates the possibility to employ THz not only as probe of the carrier dynamics, but to resonantly induce non-linear processes in materials (e.g. Rabi cycles) in the THz regime, which can be directly monitored in the time domain via ultra-broadband electro-optic sampling.



**Fig. 3:** Left: Scheme for coherent control of a bound exciton. A cold gas of excitons in  $\text{Cu}_2\text{O}$  is generated by a fs laser pulse and subsequently an intense THz electromagnetic wave (red arrow) resonantly drives the transition from the 1s exciton ground state to the 2p first excited state. Right: (a) Real-time profile of the THz pump pulse (red) and measured reemitted THz fields (blue) for different driving field (0.065–0.5MV/cm). The maximum of the reemitted field shifts to earlier times even develops an oscillatory structure. (b) First-principles microscopic theory, showing for trace (v) a coherent population transfer with an efficiency of up to 80%, followed by two Rabi cycles [2].

In the future this approach will therefore be extended to drive basically various low-energy excitation of a physical system into a nonlinear regime. Highly relevant and fascinating examples are low-energy molecular vibrations or spin waves. Several strategies to generate and optimize intense THz pulses will be investigated. Furthermore we will explore in how far light-management principles from the field of nano-photonics can be implemented into the field of non-linear THz spectroscopy.

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## 2.2 Molecular processes at surfaces

Chemical reactions at surfaces occur via a sequence of elementary steps, which are controlled by interactions on a molecular level. The study of molecular processes at surfaces on a single molecule level can therefore yield important contributions for a microscopic understanding of surface reactions. Inducing surface reactions by light opens a different route compared to thermal activation providing insight into the role of electronically and vibrationally excited states and the dynamics of energy flow between the various degrees of freedom of the system. Studies of molecular processes at surfaces are performed by several groups which employ complementary spectroscopic techniques with high spatial or temporal resolution.

### 2.2.1 Nanoscience with functional molecules

The group of *Leonhard Grill* investigates functional molecules on metal surfaces or on thin insulating films, which allow to decouple the molecules electronically from the substrate. By using scanning tunneling microscopy (STM) at low temperatures below 10 K, single molecules are imaged with sub-molecular resolution and characterized spectroscopically. Furthermore, the STM tip is used for manipulation by using the interatomic forces between tip and molecule, the tunneling electrons or the strong electric field in the junction. Such manipulation experiments allow to induce intramolecular conformational changes or to dislocate molecules or atoms with atomic scale precision in a controlled way.

The research of the group is focussed on the understanding of chemical processes at the single molecule level, molecular “nanomachines” with specific mechanical or electrical functionalities, for instance molecular wheels or switches, respectively, and growth processes of molecular structures and architectures on surfaces. The latter is divided into supramolecular structures with rather weak intermolecular interactions and the bottom-up construction of (covalently bound) molecular nanostructures, the so-called “on-surface synthesis”.

One important class of molecules are molecular switches, which are molecules that exhibit at least two stable states (conformations) with characteristic properties. While these molecules are well studied in solution, the knowledge

about the switching processes on a surface is still very limited. Based on the successful switching of the so-called TBA molecules in our group, we have systematically changed the substrate and added side groups to these molecules. The use of carboxylic acid groups leads to intermolecular hydrogen bonds and characteristic rosette assemblies in which a discrete number of six molecules is connected in a well defined structure. Moreover, the attachment of a methoxy group causes the formation of different close-packed structures on the surface. Interestingly, molecules are only able to switch in some of these structures and only in particular adsorption sites, leading to periodic switching. These results revealed for the first time the importance of the atomic-scale environment, i.e. surrounding molecules and surface atoms, on the switching capability of the molecules.

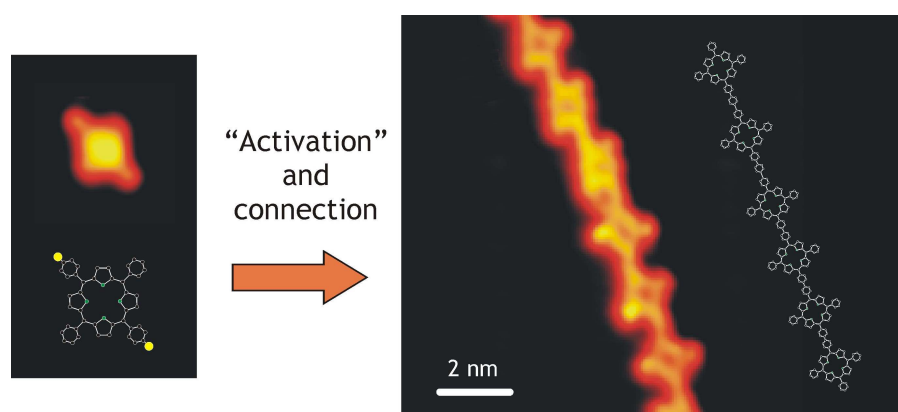


Fig. 4: STM images of a single molecule before (left) and of a molecular chain (right) after the formation of intermolecular covalent bonds by “on-surface-synthesis”. The chemical structures of the initial building block and the chain are indicated [1].

The central research topic of the group of Leonhard Grill is the polymerization of molecules directly on the surface. This so-called “on-surface-synthesis”, which has been developed in the group in the last years, allows the formation of covalent bonds between molecular building blocks on the surface (see Fig. 4). As the dimensions and shape of the resulting macromolecular networks directly reflect the chemical structure of the initial building blocks, we could form different topologies as dimers, chains (see Fig. 4) and networks on gold. In the last year, this method has been extended to another molecule, terfluorene, and the formation of homogeneous conjugated polymers with lengths of more than 100 nm could be

demonstrated. Moreover, the electronic transport has been measured through single molecular wires by pulling them up from a Au(111) surface with the STM tip and thus continuously changing their length up to more than 20 nanometers [2]. This particular manipulation experiment allows the determination of the conductance as a function of the molecular wire length in the junction. The conductance curves show not only an exponential decay, but also characteristic oscillations, as one molecular unit after another is detached from the surface during stretching.

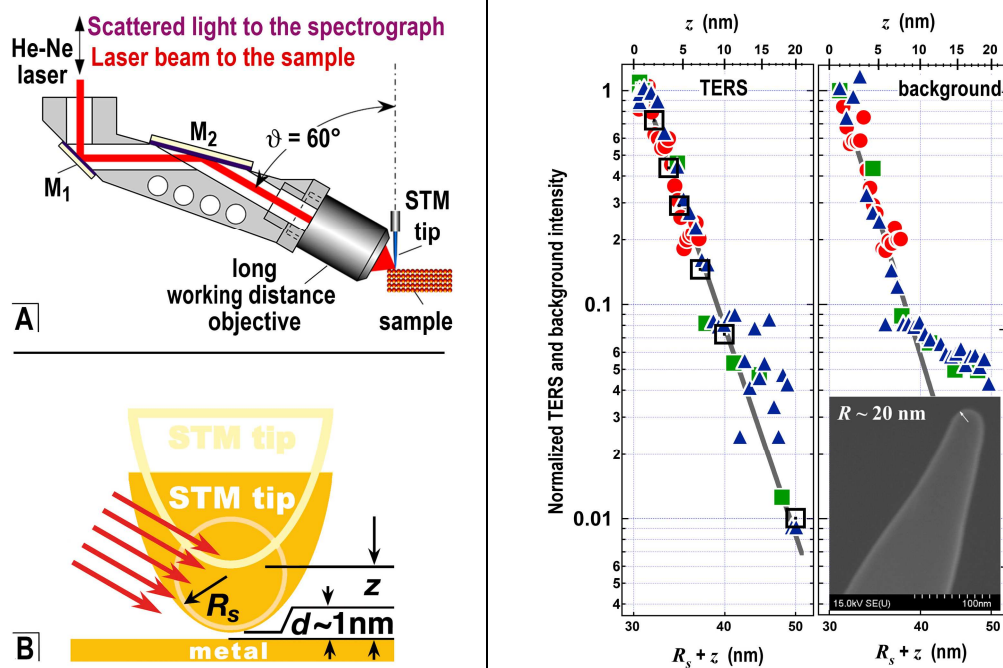
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### 2.2.2 Tip enhanced Raman spectroscopy

There is a growing demand for techniques to topographically and chemically investigate interfaces on a nanometer scale. Tip-enhanced Raman spectroscopy (TERS) has proved to be a powerful tool in this respect as its scanning probe component exhibits spatial resolution on the nanometer scale and its spectroscopic component permits the identification and characterization of adsorbates. This approach has a great potential for application in nanoscience as it provides vibrational spectroscopy with very high sensitivity and nanometer resolution.

The group of *Bruno Pettinger* has transferred the TERS approach to UHV by using a unique concept that places (i) a high numerical aperture parabolic mirror adjustable in between the STM scanner and the sample and (ii) all other necessary optics on a common platform with the STM. In 2007 first promising results have been obtained [1]. However, the first version of this instrument permitted only the proof of principle. Therefore, the current task is to improve the instrument along various lines in order to make UHV-TERS applicable for advanced UHV studies. For example, the optical alignment could not always be maintained, in particular after pumping down and baking out. Consequently, piezo-driven mirrors have been installed permitting a re-alignment of the optical path inside the UHV chamber. In connection with renovation of building A and the movement of the instrument to a laboratory in the Department of Chemical Physics some of the

improvements had to be postponed. A more elaborated task, which is currently under progress, is to add a preparation chamber to the system which allows the preparation and characterization of sample and tip under UHV conditions and the transfer to the TERS/STM unit for vibrational and structural investigations. This includes the preparation of structured interfaces such as nanoclusters on oxide films on a support, a topic that is pursued in cooperation with the Department of Chemical Physics. Currently new experiments are in progress. These include investigations with two-analyte systems in order to determine the spectroscopic properties of individual adsorbates. The measurements will be extended also towards optically non-resonant molecules at single crystal surfaces as well as to individual metal nanoclusters on oxide surfaces.



**Fig. 5:** Scheme for tip-enhanced Raman spectroscopy (ambient conditions). A: Side-illumination approach; B: illuminated STM tip at various distances  $z$ . Minimum distance:  $d \sim 1 \text{ nm}$ .

TER and background intensities for varying distance parameter  $R_s + z$  and different retraction speeds.  $R_s$  is the effective radius of the tip apex (30 nm),  $z$  is the gap width (distance of STM tip to the surface). Inset: SEM image of the STM tip.

The group has also developed different setups for TERS and performed mechanistic investigations. One of the crucial properties of TERS is its tip-sample distance ( $z$ ) dependence (see Fig. 5). The intensities of the Raman lines and the

broad TERS background, decay rapidly with increasing tip-sample distance  $z$ , which is nearly complete within 10 nm withdrawal of the STM tip in the  $z$  direction. A  $\left((R_s + d)/(R_s + z)\right)^{10}$  dependence has been derived from a simple near-field model, where  $R_s$  is the tip radius,  $d$  is the minimum distance ( $\sim 1$  nm) [2]. In addition, the maximum of the broad Lorentzian-shaped TER background is substantially blue shifted in energy with  $z$ . This effect is ascribed to a corresponding blue shift of the energies of localized plasmon modes upon tip retraction.

Another TER study, highlighting the analytical power of TERS, concerns cobalt tetraphenyl-porphyrin (CoTPP) adlayers formed on a Au(111) single crystal [3]. The Raman vibrational fingerprints collected from the nm-sized near-field region just below the STM tip can be correlated with the adsorbate structures seen in the STM images. The TER features of the disordered phase is assigned to CoTPP complexes with CO and/or NO axial ligands, whereas the ordered phase does not show any indication of additional axial complexation of CoTPP.

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### 2.3.3 Photoinduced Surface Reactions and Vibrational Spectroscopy

Surface femtochemistry is initiated by ultrafast laser excitation of an adsorbate-covered metal surface, whereby the non-adiabatic coupling between transiently excited metal electrons and adsorbate vibrational degrees of freedom can efficiently mediate chemical reactions. Due to the ultrafast response of the metal electrons this process can serve as a fast “trigger” of surface reactions. On the other hand, vibrational resonant sum frequency generation (SFG) spectroscopy provides a surface sensitive tool to probe chemical species, with the potential to time-resolve such ultrafast reactive processes.

The group of *Christian Frischkorn* has studied the mechanism of several association and desorption reactions ( $\text{H}+\text{H}\rightarrow\text{H}_2$ ;  $\text{C}+\text{O}\rightarrow\text{CO}$ ;  $\text{H}_2\text{O}$  desorption) on



Ru(0001) induced by excitation with intense fs-laser pulses [1, 2]. It could be demonstrated that the dynamics of the reaction products are determined predominantly by the ground state potential energy surface although the energy is brought into the system via electronic transitions to excited states. For future experiments, the group has setup a pulse shaper and plans to use temporally shaped laser pulses to control branching ratios of femtosecond laserinduced surface reactions. Of particular interest is the coupling of such surface reactions with gas phase species (e.g. radicals), which are generated by photodissociation with appropriately shaped laser pulses. These experiments will be combined with mass spectrometry and SFG spectroscopy to obtain insights into transient reactions products.

In a collaboration with the department of Chemical Physics (within the cluster of excellence UniCat), the group is currently investigating the UV-induced photochemistry of N<sub>2</sub>O and CH<sub>4</sub> on MgO surfaces to elucidate the role excitons and color centers in this photoreaction. In the future these studies will be complemented by the surface photochemistry for the CH<sub>x</sub> radicals in conjunction with femtosecond laser excitation of hot substrate electrons/phonons and vibrational IR-pumping of the C-H stretch bond.

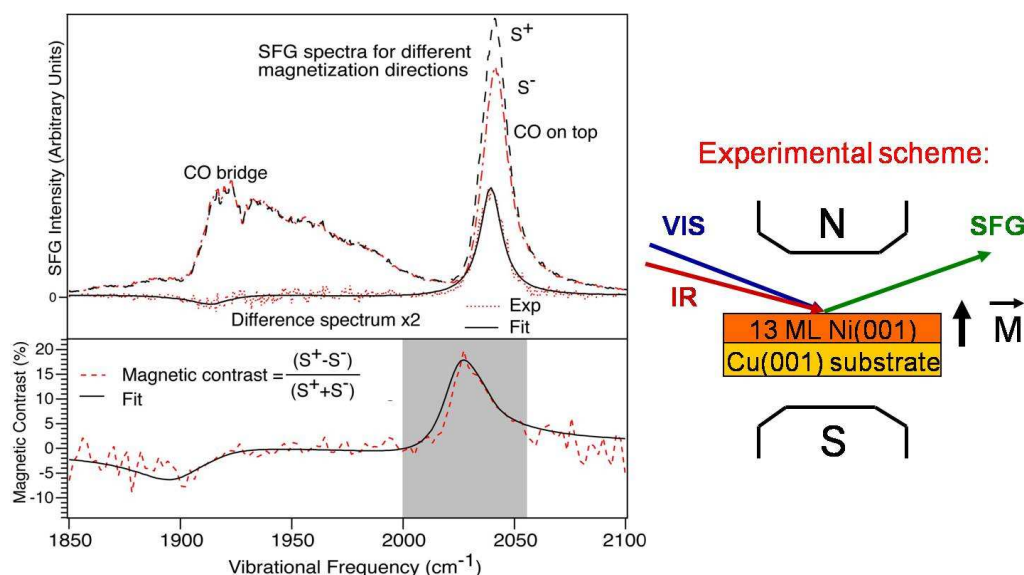


Fig. 6: SFG spectroscopy of CO stretch vibrations on a 13 ML ferromagnetic Ni(001) film for two magnetization directions ( $S^+$  and  $S^-$ ), which exhibit pronounced changes upon magnetization reversal. The lower panel shows the magnetic contrast of the SFG intensities  $S^+$  and  $S^-$ .

The group has also used IR-broadband SFG spectroscopy as a sensitive probe of the coupling between spin and nuclear degrees of freedom at adsorbate-ferromagnetic interfaces, namely CO molecules adsorbed on a thin Ni film. The SFG spectra in Fig. 6 show a significant magnetic contrast at the resonances of the CO stretch vibration. In particular, the magnetic contrast at the resonance of on-top CO species exhibits a temperature dependence which very different from the temperature dependence of the bulk magnetization of the nickel film as observed by magneto-optical Kerr effect and the non-resonant SFG signal. Spin-resolved DFT calculations were performed in collaboration with Theory department (Prof. M. Scheffler). The observed temperature dependence may be attributed to atom and symmetry resolved magnetization densities and their changes under the influence of the coupling of the CO stretch vibration with thermally excited external modes like the frustrated translation and rotation of the CO molecules.

Currently, SFG spectroscopy is also employed to study the vibrational signature of photoinjected electrons in crystalline D<sub>2</sub>O ice layers on a Ru(001) surface. A ‘giant’ increase of the SFG signal is observed (enhancement factor  $10^3$ – $10^4$ ) at a specific resonance energy, which may be attributed to highly polarizable electron-water complexes formed after relaxation of the photoexcited excess electrons.

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## 2.3 Complex Dynamics

Studies of complex dynamics in chemical systems have been performed in two groups which build on the tradition of research on nonlinear dynamics and spatiotemporal pattern formation established in this department by its former director, Prof. G. Ertl.

### 2.3.1 Spatiotemporal Self-Organization

The group of *Markus Eiswirth* has combined theoretical studies with experimental investigations. The attention has been focused on problems of nonequilibrium pattern formation in electrochemical systems. Additionally, general aspects of chemical kinetics and statistical descriptions have been analyzed.

Theoretical investigations of pattern formation using reaction-migration equations were extended to partially insulated ring electrodes; these studies reproduced among other behaviors the saltatory conduction resulting from a pattern induced by the insulated part (so that the mechanism is quite different from classical saltatory conduction in nerve axons). Furthermore, mechanistic studies were carried out in cooperation with H. Varela (Sao Carlos, Brazil) on the oxidation of alcohols on Pt. A mechanism explaining kinetic instabilities in methanol oxidation was developed, it was analyzed using stoichiometric networks, algebraic geometry and numerical simulations.

Experimental studies of spatiotemporal self-organisation in electrochemical systems included a systematic survey of patterns at low conductivity in the electro-oxidation of formic acid on a Pt ring as well as first results with geometries exhibiting close working and counter electrode, which were carried with the same reaction using a Pt ribbon. An understanding of the latter geometry is crucial for modeling industrial applications (e.g. fuel cells).

These mechanistic studies of electrochemical processes will be extended in the future in cooperation with the Department of Inorganic Chemistry (Prof. Robert Schlögl) and also in cooperation with the newly founded Ertl Center for Electrochemistry and Catalysis (Gwangju Institute of Science and Technology, Korea), where Markus Eiswirth has been appointed as a vice director.

Concepts from algebraic geometry (polynomial rings) can be used to analytically determine the stationary states of a chemical reaction network and solve the stability problem. This approach can often lead to complicated expressions which are difficult to analyze. It has been shown that these expressions can be simplified by forming quotient rings from the original polynomial ring in such a way that only the remainders need to be taken into account for the stability analysis. Further studies are needed in order to determine which method would work best for a given mechanism.

The order structures (majorization) can be used to characterize dynamical processes without (or before) specifying any kinetics. Earlier studies were extended to include sinks and sources via weak sub- and supermajorization. This gives a better description, e.g., of bubble size distributions during foam decay. The latter were further characterized by using the Lorenz curves and Renyi dimensions. Future applications may include gas evolution systems and the separation of fluids, but no experiments in this direction have been carried out so far.

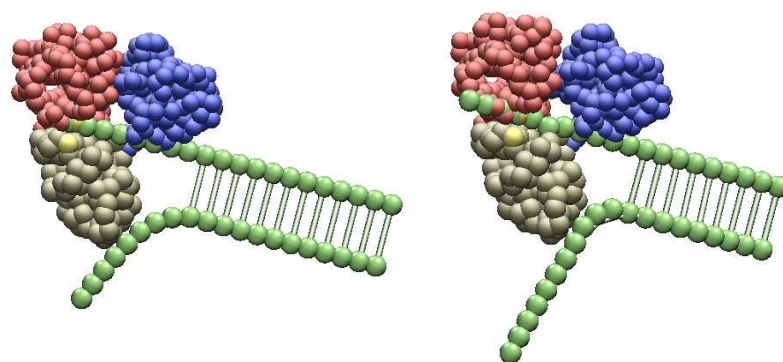
### **2.3.2 Complex Systems**

The group of *Alexander Mikhailov* has completed its transition to new research directions. Theoretical studies of nonequilibrium pattern formation in surface chemical reactions are terminated and attention is focused instead on a class of problems related to nanobiology. Generally, the research on reactive soft matter, individual molecular machines and networks of interacting molecular machines is performed.

Weakly condensed systems, representing soft matter, are characterized by low cohesion and high structural lability. At equilibrium, they show a great variety of structural phase transitions taking place as temperature or other external parameters are changed. Chemical reactions in such systems can interfere with the phase transitions, leading to a wealth of nonequilibrium, stationary or dynamical, structures. Their special property is that such structures can be very small, with the characteristic scales extending to the nanodomain. Nonequilibrium soft matter plays a fundamental role in biological cells and may emerge as the basis of a new

nanotechnology generation. Within the last two years, theoretical investigations of nonequilibrium Langmuir monolayers, biomembranes with active protein inclusions and thin liquid layers with floating molecular machines have been performed in the group. First results of such investigations are summarized in a review article of A. Mikhailov and G. Ertl which has appeared in 2009 in the special issue of *ChemPhysChem*.

At the level of single macromolecules, protein machines provide a spectacular example of nonequilibrium soft matter. In response to the energy supplied to them in the chemical form with individual ATP molecules, such proteins perform ordered internal mechanical motions, cyclically changing their spatial conformations. In molecular motors, such internal motions are used to generate mechanical work. In enzymes, they allow to facilitate catalytic events by bringing together the reacting molecules attached to a protein and by implementing a conformation optimal for the catalytic conversion. These important conformational motions are slow and typically have characteristic timescales of the order of tens of milliseconds. Therefore, they remain well beyond the limit of the modern all-atom molecular dynamics simulations, where only microsecond processes could be so far traced. Thus, coarse-grained descriptions are needed. The use of elastic-network models of proteins allows to speed up computer simulations and to follow slow ligand-induced conformational motions in protein machines.



**Fig. 7** Two snapshots from a simulation of the molecular motor HCV helicase interacting with DNA. The upper protein domains (red, blue) actively translocate along a strand, while the lower domain separates the two DNA strands by repeatedly breaking the base pairs.

Analyzing slow conformational relaxation motions in classical motor proteins (Myosin, Kinesin,  $F_1$ -ATPase), it was found that they proceed along well-defined trajectories, stable against noise and external perturbations, - which is essential for the robust machine operation. As the next step, dynamical elastic-network modeling of whole operation cycles of the molecular motor HCV helicase, splitting the double DNA, has been for the first time performed (see Fig. 7). These investigations are carried out in collaboration with the Osaka University (Prof. T. Yanagida) and the Toronto University (Prof. R. Kapral).

In a cell, protein machines operate in ensembles characterized by complex networks of molecular interactions. Their collective operation resembles that of a factory with many interwoven assembly lines. This factory is however self-organized and, moreover, it can robustly function despite the high noise level and frequent structural perturbations caused by biological mutations. Understanding principal mechanisms of self-organization, control and evolution in dynamical networks of interacting machines is important not only in cell biology, but also for the design of future artificial productions systems which may involve a large number of active nanodevices.

The group participates in an international project devoted to the studies of self-organizing machine networks and collaborates within this project with the groups from the universities of Arizona (Prof. D. Armbruster), Sapporo (Prof. Y. Nishiura), Kyoto (Prof. Y. Kuramoto), ETH Zurich (Prof. D. Helbing) and the Max Planck Institute for Molecular Genetics (Prof. M. Vingron). Investigations are focused on dynamical self-organization in networks of interacting cyclical automata, providing simplified descriptions of real machine networks. Moreover, evolutionary optimization methods are employed to design, in computer simulations, network architectures with the properties of self-correction against errors, allowing such network-based systems to operate at a high level of noise and structural damage.

The group of A. Mikhailov is also involved in an initiative to establish the Berlin Center for Studies of Complex Systems which aims to promote international scientific exchanges and collaborations in this research field.

### 3. Research projects funded from outside resources:

#### Leonhard Grill:

- European research project (ICT FET) “*Alternative routes towards information storage and transport at the atomic and molecular scale*” (single molecule manipulation and spectroscopy with low-temperature STM)

#### Leonhard Grill and Martin Wolf:

- Collaborative Research Center SFB 658 “Elementary Processes of Molecular Switches at Surfaces”, project “*Complex switching units and molecular architectures, studied by scanning tunneling microscopy*” (Nanostructuring, single molecule spectroscopy and manipulation with low-temperature STM)

#### Christian Frischkorn and Martin Wolf:

- Collaborative Research Center SFB 450 “Analysis and Control of Ultrafast Photoinduced Reactions”, project “*Ultrafast Dynamics of Ultrafast Photoinduced Reactions at Surfaces*” (surfaces femtochemistry, vibrational spectroscopy and electron dynamics at adsorbat/metal interfaces)

#### Alexander Mikhailov:

- Collaborative Research Center SFB 555 “Complex Nonlinear Processes”, project “*Self-Organization Phenomena at Active Interfaces*” (nonequilibrium Langmuir monolayers and biomembranes)
- EU Marie Curie Research Training Network “*PATTERNS: Unifying Principles of Nonequilibrium Pattern Formation*” (nonequilibrium pattern formation in soft matter)
- Volkswagen Foundation, international project “*Self-Organizing Networks of Interacting Machines*” (design and analysis of model machine networks)
- DFG Research Training Group (Graduiertenkolleg) “Nonequilibrium Collective Dynamics in Condensed Matter and Biological Systems”, project “*Active Microfluidics Based on Floating Molecular Machines*” (protein machines in thin liquid layers)

**Martin Wolf:**

- DFG Priority Program SPP 1355 “Elementary Processes of Organic Photovoltaics”, project “*Electronic properties of interfaces with conjugated polymers*” (photoelectron spectroscopy and carrier dynamics in polymer based organic films)
- German-Israel Foundation (GIF), cooperation with Prof. Micha Asscher, Hebrew University of Jerusalem, project “*Photochemistry and electron dynamics of oriented molecules within a nano-capacitor*” (photochemistry and charge transfer processes in thin molecular films)



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

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Wolf, M. and P. Tegeder: Reversible molecular switching at a metal surface: A case study of tetra-*tert*-butyl-azobenzene on Au(111). *Surf. Sci.* **603** (10-12), 1506-1517 (2009).

### **Doctoral Theses**

Hagen, Sebastian: Isomerization behavior of photochromic molecules in direct contact with noble metal surfaces – Isomerisierungsverhalten photochromer Moleküle in direktem Kontakt mit Edelmetalloberflächen. Freie Universität Berlin 2009.

Kirchmann, Patrick S.: Ultrafast electron dynamics in low-dimensional materials – Ultraschnelle Elektronendynamik in Niedrig-Dimensionalen Materialien. Freie Universität Berlin 2009.

Prabha, Kaira: Resonance Forcing in Catalytic Surface Reactions – Resonantes Forcen von katalytischen Oberflächenreaktionen. Technische Universität Berlin 2009.

### **Diploma Theses**

Kate, Peter: Photoinduzierte und thermische aktivierte Isomerisation von tetra-*tert*-butyl-Azobenol auf Au(111): Anregungsmechanismus und Reaktionskinetik. Freie Universität Berlin 2009.

Koch, Matthias: Schwingungsspektroskopische Untersuchungen von molekularen Schaltprozessen auf Au(111). Freie Universität Berlin 2009.

Weber, Monika: Terahertz Transmission Spectroscopy of the Organic Polymer: PEDOT:PSS. Freie Universität Berlin 2009.

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

### Markus Eiswirth

- Jan. 2008      Gwangju Institute of Science and Technology (GIST), Gwangju, Korea  
*Chemistry on solid surfaces*
- March 2008    Winterseminar Polydisziplinarität – Struktur der Unordnung, Galtür, Austria  
*Algebraische Geometrie und chemische Kinetik*
- May 2008      University of Sao Paulo, Sao Carlos, Brazil  
*Pattern formation in the electro-oxidation of formic acid on Pt*
- May 2008      Federal University of Sao Carlos, Brazil  
*Waving in the distance*
- May 2008      Ann. SBQ meeting (Sociedade Brasileira de Quimica), Aguas de Lindoia, Brazil  
*Electrochemical pattern formation in constrained geometries*
- June 2009      1<sup>st</sup> RISE symposium (Research Institute for Solar and Sustainable Energy), GIST, Gwangju, Korea  
*Pattern formation on solid surfaces*
- June 2009      Opening ceremony Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju, Korea  
*Chemistry on solid surfaces*
- July 2009      SMB conference, Vancouver, Canada  
*Application of quotient rings for stability analysis in chemical systems*

### Christian Frischkorn

- Feb. 2008      Frühjahrstagung der DPG (Deutschen Physikalischen Gesellschaft), Berlin, Germany  
*Nonadiabatic processes in surface femtochemistry at metals*
- Jan. 2009      SPIE Photonics West 09: International Symposium on Ultrafast Phenomena in Semiconductors and Nanostructure Materials XIII, San Jose, USA  
*Ultrafast changes in the far-infrared conductivity of carbon nanotubes*

- Jan. 2009      Seminar, Stanford University, Stanford, USA  
*Ultrafast dynamics in surface and solid state physics: Coupling between electronic and nuclear degrees of freedom*
- Jan. 2009      Meeting, Terahertz-Initiative Berlin-Brandenburg, PTB  
 (Physikalisch-Technische Bundesanstalt) Berlin, Germany  
*Potenzial zeitaufgelöster THz-Spektroskopie in der Untersuchung ultraschneller Ladungsträgerdynamik in Festkörpern und Gasen*

### **Leonhard Grill**

- May 2008      Fortschrittsbericht auf der Bunsen-Tagung 2008 der Deutschen Bunsen-Gesellschaft für Physikalische Chemie, Saarbrücken, Germany  
*Model systems for molecular nanotechnology studied by STM*
- May 2008      Center for Materials Elaboration and Structural Studies (CEMES) of the CNRS, Toulouse, France  
*Manipulation of single molecules with the STM: Motion, switching and linking*
- July 2008      Institut für Oberflächenchemie und Katalyse, Universität Ulm, Germany  
*Manipulation of single molecules with the STM: Model systems for molecular nanotechnology*
- Sept. 2008      MECNANO workshop, University of Nottingham, UK  
*Controlling the conformation and motion of single molecules by STM manipulation*
- Sept. 2008      Trends in Nanotechnology conference (TNT2008), Oviedo, Spain  
*Manipulation of single molecules with the STM: Towards molecular nanotechnology*
- Nov. 2008      Institut für Physikalische Chemie, Universität Innsbruck, Austria  
*Manipulation von Einzelmolekülen mit dem STM: Modellsysteme für Molekulare Nanotechnologie*
- Nov. 2008      Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität Linz, Austria  
*Model systems for „molecular nanotechnology“ studied by STM*
- Nov. 2008      Institut für Allgemeine Physik, Technische Universität Wien, Austria  
*Wires and switches: Model systems for molecular nanotechnology studied by STM*

- Nov. 2008 Fakultät für Physik, Universität Wien, Austria  
*Manipulation von Einzelmolekülen mit dem STM*
- Nov. 2008 Institut für Experimentalphysik, Technische Universität Graz, Austria  
*Manipulation von Einzelmolekülen mit dem STM: Räder, Drähte und Schalter*
- Nov 2008 Information and Communication Technologies (ICT) conference, Lyon, France  
*Molecular-scale devices and systems*
- July 2009 Nanoscale Science Department, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany  
*Functional molecules studied by STM: Wires and switches*

### **Tobias Kampfrath**

- Jan. 2008 Spin-Dynamics Three-Kings-Meeting of the German Physical Society, Bad Honnef, Germany  
*Terahertz emission from laser-excited ferromagnets*
- July 2008 Institute Colloquium at BESSY, Berlin, Germany  
*Charge and Spin Dynamics Observed by Terahertz Spectroscopy*
- Jan. 2009 Photonics West, San Jose, California, USA  
*Ultrafast far-infrared optics of carbon nanotubes*
- Feb. 2009 8th workshop of the Centre for Ultrahigh Bandwidth Devices for Optical Systems (CUDOS), Lake Crackenback, Australia  
*Ultrafast re-routing and loss of slow light in photonic-crystal waveguides*
- Sept. 2009 Keynote talk at the 34th International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz 2009), Busan, Korea  
*Nonlinear Terahertz Spectroscopy of Magnetically Ordered Solids*

### **Alexander S. Mikhailov**

- Jan. 2008 Seminar, Free University of Brussels (ULB)  
*Nonequilibrium microstructures in reactive soft matter*
- Jan. 2009 Workshop “Active matter”, Institut Poincare, Paris, France  
*Nonlinear elastic dynamics of protein machines*

- Feb. 2008      Workshop “Dynamics and evolution of networks”, University of Palma de Mallorca, Spain  
*Engineering of dynamical networks*
- April 2008     Alexander-von-Humboldt Symposium, Moscow, Russia  
*Nonequilibrium phenomena in the corrosion onset on stainless steels*
- May 2008      Workshop BIONet, Max Planck Institute for Physics of Complex Systems, Dresden, Germany  
*Elastic-network models of protein machines*
- May 2008      School BIONet, Max Planck Institute for Physics of Complex Systems, Dresden, Germany  
*Engineering of dynamical networks*
- Sept. 2008     Conference “Dynamic Days Asia and Pacific”, Nara, Japan  
*Nonlinear elastic dynamics of protein machines*
- Oct. 2008      Seminar, University of Tokyo, Japan  
*Towards active microfluidics: Interface turbulence in thin films with floating molecular machines*
- Oct. 2008      Seminar, University of Tokyo, Japan  
*Networks on the edge of chaos: Global feedback control of network turbulence*
- Feb. 2009      Sapporo Winter School, Hokkaido University, Japan  
*Evolutionary engineering of dynamical networks*
- Feb. 2009      Opening Conference of the Global Center of Excellence, Kyoto University, Japan  
*Physicist’s understanding of molecular machines*
- March 2009     Seminar, Max Planck Institute for Mathematics in Natural Sciences, Leipzig, Germany  
*Evolutionary engineering of dynamical networks*
- April 2009      Lecture, Solvay Institute, Brussels  
*From structure to function: Chemistry in transition*
- April 2009      Lecture, Solvay Institute, Brussels  
*Rich life on catalytic surfaces*
- April 2009      Lecture, Solvay Institute, Brussels  
*Why stainless steel breaks down?*

- May 2009      Lecture, Solvay Institute, Brussels  
*Reactive soft matter: A new challenge*
- May 2009      Lecture, Solvay Institute, Brussels  
*Understanding protein machines*
- July 2009      Colloquium of the Max Planck Institute for Physics of Complex Systems, Dresden, Germany  
*Nonlinear elastic dynamics of protein machines*
- Sept. 2009      Symposium, Hiroshima University, Japan  
*Nonlinear elastic dynamics of protein machines*

### **Bruno Pettinger**

- Oct. 2007      Seminar at INP3 Forschungszentrum Jülich, Germany  
*Tip-enhanced Raman Spectroscopy and Microscopy in UHV: Toward Single Molecule Analysis*
- Jan. 2008      Tip Enhanced Raman and Fluorescence Spectroscopy (TERFS): Challenges and Opportunities, National Physics Laboratory, Teddington, UK  
*Tip-enhanced Raman Spectroscopy and Microscopy in Air and in UHV: Toward Single Molecule Analysis*
- Feb. 2008      DPG Symposium: Vibrational Spectroscopy of Nanolayers with Optical Probes, Berlin, Germany  
*UHV based Tip-enhanced Raman Spectroscopy (TERS): on Adsorbed Molecules*
- May 2008      Department for Chemistry and Biochemistry of the University Bern, Switzerland  
*Tip-enhanced Raman Spectroscopy and Microscopy: Applications in Air and in UHV*
- Sept. 2008      International Society of Electrochemistry 2008, Seville, Spain  
*Tip-enhanced Raman spectroscopy at interfaces*
- Oct. 2008      Institute for Theoretical Chemistry, University of Ulm, Germany  
*Single-Molecule Tip-enhanced Raman Spectroscopy and Microscopy.*
- Nov. 2008      Workshop Electrocatalysis@nanoscale, Leiden, The Netherlands:  
*Surface-enhanced and Tip-enhanced Raman Spectroscopy.*
- May 2009      Institute for Physical Chemistry, University of Wien, Austria,  
*Tip-enhanced Raman Spectroscopy at Interfaces*

- June 2009      Institute for Physics, University of Marburg, Germany  
*Tip-enhanced Ramanspektroskopie an Grenzflächen*
- July 2009      International Conference on Advanced Vibrational Spectroscopy 5,  
 Melbourne, Australia  
*Tip-enhanced Raman spectroscopy: recent developments*
- July 2009      11<sup>th</sup> Fischer-Symposium, Benediktbeuern, Germany  
*Tip-enhanced Raman Spectroscopy of Single Molecules  
 at Interfaces*
- Aug. 2009      Symposium on Nano- & Spectroelectrochemistry, Xiamen, China  
*Tip-enhanced Raman Spectroscopy at Single Molecules*
- Sept. 2009      OSI-VIII, Ischia, Italy  
*Tip-enhanced Raman Spectroscopy and Microscopy of a Few Dye  
 Molecules.*
- Sept. 2009      Nanostructures at Surfaces, 20.-25.Sept. 2009, Ascona, Switzerland  
*Recent Developments in Tip-enhanced Raman Spectroscopy*

#### **Julia Stähler**

- June 2009      Max-Born-Institute, Division A *Clusters and Interfaces*, Berlin,  
 Germany  
*Ultrafast electron transfer and solvation dynamics at polar  
 molecule-metal interfaces*

#### **Martin Wolf**

- Sept. 2007      OSA Meeting & Laser Science XXIII conference, San Jose, USA  
*Time-resolved Photoemission of Correlated Electron Material"*
- Oct. 2007      James Franck Symposium 2007, on "Spectroscopy and Quantum  
 Control of Molecular Systems", Schloss Hohenkammer, Germany  
*Electronic driven conformation changes of molecules at surfaces*
- Dec. 2007      Physikalisches Kolloquium, Universität Erlangen, Germany  
*Electron dynamics in solids and molecular switching at surfaces*
- Dec. 2007      Physikalisches Kolloquium, Universität Rostock, Germany  
*Zeitaufgelöste Elektronendynamik und Femtochemie an Fest-  
 körperoberflächen*



- Feb. 2008      Gordon Research Conference on "Ultrafast Phenomena in Cooperative Systems", Il Ciocco, Italien  
*Time-resolved Photoemission Studies of Correlated Materials*
- Feb. 2008      Farkas Symposium 2008, on "Photochemistry in Organized Media", Ein Bokek, Israel  
*Electron Solvation Dynamics and Photoinduced Molecular Switching at Surfaces*
- March 2008    International Workshop on "Electron Controlled Chemical Lithography", Lissabon, Portugal  
*Electron Induced Molecular Reorganization and Switching at Metal Surfaces*
- April 2008    Physikalisches Kolloquium, Universität Potsdam, Germany  
*Dynamik von Elektronentransfer und molekularen Schaltprozessen an Oberflächen*
- April 2008    235th National Meeting, American Chemical Society (ACS), New Orleans, USA:  
*Ultrafast dynamics of electron transfer and solvation processes at ammonia and water ice/metal interfaces*
- May 2008      International Workshop UltraFast2008, San Sebastian, Spain  
*Time-resolved Photoemission Studies of Correlated Materials*
- June 2008    Physikalisch-Chemisches Kolloquium, Universität Karlsruhe, Germany  
*Dynamik von Elektronentransfer, Solvatisierung und molekularen Schaltprozessen an Adsorbat/Metalloberflächen*
- June 2008    International Workshop on "Nonlinear Optics at Interfaces", Telluride, USA  
*Vibrational Resonant Magneto-Optics and Non-linear Photoemission at Adsorbate/Metal Interfaces*
- June 2008    Conference on Low-Energy Electrodynamics of Solids (LEES08), Whistler, Canada  
*Time-resolved ARPES Studies of Correlated Materials*
- July 2008     6th Conference on "Ultrafast Surface Dynamics", Kloster Banz, Germany  
*Ultrafast Dynamics of Electron Transfer and Solvation Processes at Polar Adsorbate/Metal Interfaces*

- July 2008      European Conference on Surface Science, ECOS-25, Liverpool, UK  
*Dynamics of Interfacial Electron Transfer and Molecular Switching at Metal Surfaces*
- Aug. 2008      Workshop Sfb 616 “Energy dissipation at surfaces”, Bad Honnef, Germany  
*Ultrafast electron dynamics and electron-phonon coupling in metals and highly correlated materials*
- Oct. 2008      Frontiers in Optics Meeting, Optical Society of America (OSA), Rochester, USA  
*Ultrafast dynamics of electron transfer at polar adsorbate/metal interfaces studied with time-resolved photoelectron spectroscopy*
- Nov. 2008      International Workshop on “Time-resolved studies with Synchrotron and FEL Radiation”, Trieste, Italien  
*Time-resolved ARPES Studies of Correlated Materials*
- Nov. 2008      Graduate School „Physics with new coherent radiation sources“, Universität Hamburg, DESY, Germany  
*Ultrafast photoinduced dynamics in solids probed by time-resolved photoemission spectroscopy*
- Dec. 2008      International Workshop on “Nonequilibrium Nanostructures”, Dresden, Germany  
*Ultrafast photoinduced dynamics in solids probed by time-resolved photoemission spectroscopy*
- Dec. 2008      Physikalisch-Chemisches Kolloquium, LMU München, Germany  
*Dynamics of electron transfer and molecular switching processes at surfaces*
- Jan. 2009      WE Heraeus Seminar on „Molecular and Organic Electronics: Bridging the gaps“, Bad Honnef, Germany  
*Dynamics of interfacial electron transfer and photoinduced isomerization at metal surfaces*
- Jan. 2009      3<sup>rd</sup> European XFEL User Meeting, DESY, Hamburg, Germany  
*Photodriven transitions in solids probed by time-resolved ARPES*
- Feb. 2009      MPG-UBC Workshop, MPI-FKF, Stuttgart, Germany  
*Photodriven dynamics of correlated materials probed by time-resolved ARPES*

- March 2009 APS March Meeting 2009, Focus Session on „Structure and Dynamics of Interfacial Water“,Pittsburg, USA  
*Electron solvation dynamics at ice/metal interfaces: Dynamics from femtoseconds to minutes*
- March 2009 DPG Frühjahrstagung 2009, Fachverband Oberflächenphysik, Dresden, Germany  
*Transient electronic structure and insulator-to-metal transitions probed by time-resolved photoemission*
- April 2009 Workshop on Desorption Induced by Electronic Transitions (DIET XII), Callaway Gardens, USA  
*Probing transient electronic structure and lattice modes of photoexcited solids on ultrafast time scales*
- May 2009 Physikalisches Kolloquium Stuttgart, MPI-FKF, Stuttgart , Germany  
*Dynamik von Elektronentransfer-Prozessen an Grenzflächen*
- June 2009 European XFEL-SCS Workshop, Paul-Scherrer-Institut, Villingen, Switzerland  
*Time-Resolved Photoemission Studies of Solids*
- June 2009 Workshop on Surface Science and Heterogeneous Catalysis, Chinese Academy of Science, Dalia, China  
*Dynamics of Electron Transfer and Surface Femtochemistry at Metal Surfaces*
- July 2009 Colloquium, JILA, Boulder, USA  
*Transient electronic structure and insulator-to-metal transitions probed by time-resolved photoemission*
- July 2009 2<sup>nd</sup> International Conference on Attosecond Physics (Atto09), Manhattan, Kansas, USA  
*Overview talk: Ultrafast dynamics in solids and at interfaces*
- Sept. 2009 WE Heraeus Seminar on „Ultrafast x-ray methods for studying transient electronic structure and nuclear dynamics“, Bad Honnef, Germany  
*Introductory talk: Ultrafast dynamics in correlated materials*
- Oct. 2009 11th International Conference on Electronic Spectroscopy and Structure, Nara, Japan  
*Ultrafast dynamics of solids and interfaces analyzed by time-resolved photoelectron spectroscopy*







## Theory Department

**Director: Matthias Scheffler**

### Group leaders:

Volker Blum

Johan Carlsson

Klaus Hermann

(50% head of the Joint Network Center, GNZ, until February 2009)

Sergey Levchenko

(Habilitation)

(AvH Fellow)

Karsten Reuter (Independent Junior Research Group)

(Habilitation)

Alexander M. Bradshaw (IPP Guest Group)

since November 2008

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

Imad Belabbas

Martin Fuchs

Luca Ghiringhelli

Ricardo I. Gómez Abal

Bo Li

Oliver Paz-Borbón

Xinguo Ren

Annabella Selloni

Mina Yoon

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

Arianna Borrelli

Mohammed Bouhassoune

Roberto Car

Javier Carrasco

(Newton International Fellowship of the Royal Society since February 2009)

Matteo Cavalleri

Wei Guo

Felix Hanke

Paula Havu

Hong Jiang

History of Science

Nanoquanta

AvH Awardee

AvH Fellow

AvH Fellow

MMM

Vektra

Nanoquanta

Nanoquanta

Edward Jurkowitz

Feng Liu

Horia Metiu

Angel Rubio

(jointly with E.K.U. Groß)

Aloysius Soon

Alexandre Tkatchenko

Enge Wang

Weitao Yang

History of Science

AvH Awardee

AvH Awardee

AvH Bessel Awardee

AvH Fellow

AvH Fellow

AvH Awardee

AvH Awardee

**Graduate students:** 20

**Diploma students:** 1

### MPG Fellow Group:

E.K.U. Groß (FU Berlin)

Christophe Bersier

Alberto Castro

Kay Dewhurst

Andrea Floris

Sangeeta Sharma

**Graduate students:** 2





## Recent Developments in the Theory Department

Director: Matthias Scheffler

### I. General Remarks

Research in the *Theory Department* focuses on fundamental aspects of the chemical and physical properties of surfaces, interfaces, clusters, and nanostructures. Outstanding results in the last two years include *i)* a new method to account for van der Waals interaction in DFT and Hartree-Fock+MP2, *ii)* new insights into *f*-electron systems (by *GW@LDA+U*) and absorption/emission properties of localized defects (by *GW* corrected LDA geometries and consideration of electron-hole interactions), *iii)* new insights into the dynamics of catalysis at alloy surfaces (where it turns out that the surface is not an alloy) and at vanadia, *iv)* unexpected results for nucleation of water at metal surfaces and proton disorder in bulk ice, as well as *v)* notable advances in code developments.

While “multi-scale modeling from first-principles” has always been a key issue in the department (for example, but not exclusively, in *ab initio* atomistic thermodynamics and in the *ab initio* evaluation of the master equation of statistical mechanics) the various limitations are still obvious; examples are non-adiabatic effects, dissipation, and thermal transport. Work on these topics will remain an important research direction in the years ahead. In addition, we will continue to improve and strengthen “the base”, namely, *ab initio* electronic structure theory describing the chemistry of bond breaking and bond making. Density-functional theory has been very successful for certain binding situations, and in the past we have carefully selected our materials to avoid “problematic” cases, such as systems where strong correlation or van der Waals interactions play a significant role. This is now changing and a considerable amount of work is being put into the development of appropriate concepts, methods, and computer codes for problems that have so far been out of the reach of a reliable first-principles treatment (see Section III for more details).

The collaboration with the University of California Santa Barbara (College of Engineering and College of Mathematical, Life & Physical Sciences) has been

fruitful. Matthias Scheffler is spending about three months per year there, although in the past two years the individual visits were somewhat short, often just 1-2 weeks. The exchange of postdocs and PhD students has turned out to be stimulating and successful.

Some further activities should be mentioned:

- The so-called “UCSB-MPG program” supports joint activities and exchange of students and postdocs between scientists working in Materials Science in the whole MPG and UCSB since 2005. The coordinators are Matthias Scheffler for the MPG and (since 2009) Nicola Spaldin for the UCSB.
- Our Max Planck Partner Group “First-Principles Theory of High-Pressure Oxidation Catalysis” at the Dalian Institute for Chemical Physics (DICP) of the Chinese Academy of Sciences (inauguration was in the summer of 2006) had been visited by the scientific advisory committee in June this year. The summary of their report reads: “We conclude by strongly recommending that the partner group be funded for a new period. We emphasize that such a continued funding will enable the partner group to continue its leading role in the study of first-principle theory of high pressure oxidation catalysis. ...”. At the time of writing this report for the *Fachbeirat* a decision by the Max Planck president had not been announced.
- We are also part of another program involving the DICP: “The Partnership for International Research and Education at the University of California: Electron Chemistry and Catalysis at Interfaces” (PIRE-ECCI). This activity, managed by the UCSB, helps to intensify collaborations through the exchange of graduate students.
- In 2006 Jürgen Renn (Max Planck Institute for the History of Science) and Matthias Scheffler jointly initiated a project on “the history and foundations of quantum physics”. Since 2007 the project enjoys funding from the “*Strategischer Innovationsfonds*” of the MPG President. The kick-off meeting, the international “HQ1 Conference on the History of Quantum Physics”, took place in June 2007 in Berlin. While the theory of quantum physics is in

fact clearly defined (it also forms the basis of the work done in the *Theory Department*), its history is affected by philosophical conflicts. Thus, one has to give consideration to apparent inconsistencies in the notions and perceptions that arose during the development. Such an analysis is complicated by the fact that the number of individuals who contributed to the development and understanding of quantum mechanics is quite large.

At the FHI, Arianna Borrelli and Bretislav Friedrich (*Department of Molecular Physics*) are mainly investigating the evolving role of symmetry arguments in quantum theory. Ed Jurkowitz and Volker Blum concentrate on how quantum mechanics was made quantitative in early atomic, molecular, and condensed matter science, tracing in particular the central contributions of Hartree and Slater to accurate computational techniques for quantum mechanics already in the late 1920's and early 1930's.

- Another project funded by the MPG President's "*Strategischer Innovationsfonds*" is the initiative on "multiscale modeling of condensed matter" (MMM), bringing together 6 Max Planck Institutes (including the FHI *Theory Department* and its *Independent Junior Research Group*). It will run until summer next year but the collaboration and exchange of ideas and codes with the other groups of the MPG will continue.
- Most of the groups previously active in the *Theory Department* were dissolved in the last 12 months, since their leaders have left to take up professorships or senior positions in industry. Subsequently, new groups with new foci have been set up; details are given in Section II. Just two of the already established groups remain, although changes are also imminent here: Karsten Reuter's independent junior research group "First-Principles Statistical Mechanics" (see Section II below as well as his separate report) and Klaus Hermann's group "Cluster Studies on Metal Oxides and Surface Crystallography".

The following Section describes personnel and related matters. Subsequently, Sections III and IV briefly outline some of the work performed in the *Theory De-*

*partment*: Section III summarizes conceptual, methodological, and technical developments, which enable us to study new types of problems and/or improve the accuracy of calculations. In Section IV, the main fields that are studied in the *Theory Department* are outlined and some recent results described.

## II. Personnel and Related Matters

Since the last visit of the *Fachbeirat* in November 2007 several noteworthy developments have taken place with the following scientists receiving offers of prestigious positions:

- **Johan Carlsson** (formerly leading the “Nanoporous Carbon” group) accepted an offer from Accelrys as Senior Scientist and left in November 2008. Since then he is working as consultant at Bayer AG in a project to establish a Molecular Modeling group at “Bayer Technology Services”. The large spectrum of complex problems within this company often requires a combination of methods ranging from electronic structure theory and *ab initio* atomistic thermodynamics to coarse grained methods for determination of structural and dynamic properties of materials.
- **Hong Jiang** accepted an offer from the College of Chemistry at Peking University (Institute for Theoretical and Computational Chemistry) and has been a professor there since June 2009.
- **Karsten Reuter** was offered full professorships by the University of Kiel (Germany), the University of Amsterdam (Netherlands), and the Technical University of Munich (Germany). He accepted the latter offer for a chair in theoretical chemistry, but will stay with us “im Nebenamt” with a 20% appointment for one more year. His plan is to move fully to Munich in summer 2010.
- **Hardy (E.K.U.) Gross** has been a Max Planck Fellow with us since 2006. Recently, he accepted the offer to become a Director at the Max Planck Institute for Microstructure Research in Halle. He has been there since

October of this year, and consequently his Max Planck Fellow status and his group have just ended.

Several new research groups have been established:

- **Sergey Levchenko** (formerly at the University of Pennsylvania) joined the Department in November 2008 and is now leading the Catalysis group. The group's research largely deals with studies done in connection with the DFG funded Cluster of Excellence "Unifying Concepts in Catalysis" (Uni-Cat).
- **Volker Blum** is heading the "*Ab Initio* (Bio)Molecular Simulations" group since April 2009. He is also coordinating, together with Matthias Scheffler, the developments for the new computer code FHI-aims, which in the meantime has become the main workhorse in the department.
- **Patrick Rinke**, who spent two years at UC Santa Barbara on a research fellowship from the German Science Foundation (DFG), returned to the FHI as group leader of the "Many Body Electronic Structure Theory" group at the beginning of November 2009.
- A new research area, "Organic Functional Materials and Molecular Interactions" has been started together with **Mina Yoon** (coming from the DOE Oak Ridge National Laboratory in August 2008) and **Alexandre Tkatchenko** (who had started as an Alexander von Humboldt junior researcher in July 2007). Presently the group is headed by Matthias Scheffler.
- We were able to establish an official connection with **Angel Rubio** (Donostia-San Sebastian, Spain). He plans to stay three months per year in Berlin and is head of the "Theoretical Spectroscopy" group since January 2009.
- **Alex Bradshaw** returned to the FHI in November 2008 after retiring from his post as scientific director of the Max-Planck Institute for Plasma Physics (IPP), where he had been since 1999. He is still a scientific member of the Garching Institute. At the FHI, more precisely at BESSY in Berlin Adlershof, he works with Uwe Hergenhahn and the IPP electron spectroscopy group on experimental studies of photoionization processes in atoms, small

molecules and clusters. He is also interested in surface physics as well as in general questions of energy supply and storage, including the future applications of nuclear fusion.

- **Klaus Hermann** who had been head of the Joint Network Center (GNZ) of the Berlin-Brandenburg Max-Planck Institutions as part-time activity was relieved from his duty on March 1 this year. He is now concentrating in full on his research and on his group “Cluster Studies on Metal Oxides and Surface Crystallography”.
- With some minor restructuring the Joint Network Center (GNZ) of the Berlin-Brandenburg Max-Planck Institutions now has a new (full-time) head, Dipl.-Ing. **Gerd Schnapka** (since March 1, 2009). The responsible Max Planck directors for the GNZ continue to be Martin Vingron (MPI for Molecular Genetics) and Matthias Scheffler.

Members of the *Theory Department* play, or have played, an active role in a *Cluster of Excellence* and in *Collaborative Research Centers* (SFBs) of the *German Research Foundation* (DFG), reflecting the close contacts and collaboration with the Berlin universities and other research institutes. In addition, they take part in various European (EU and ESF) and international programs. The full list of these activities is as follows:

- EU – Network of Excellence (NoE): Nanoscale Quantum Simulations for Nanostructures and Advanced Materials (NANOQUANTA), coordinator: R. Godby; FHI-node leaders: M. Scheffler, A. Schindlmayr, P. Rinke – until May 2008
- EU – Network of Excellence (NoE): Self-Assembled Semiconductor Nanostructures for New Devices in Photonics and Electronics (SANDiE), coordinators: M. Grundmann; P. Kratzer, M. Scheffler – until June 2008
- EU – Network of Excellence (NoE): Integrated Design of Catalytic Nanomaterials for a Sustainable Production (IDECAT), coordinator: G. Centi; R. Schlögl, H.-J. Freund, M. Scheffler – since April 2005

- EU – Integrated Infrastructure Initiative (I3): Distributed European Infrastructure for Supercomputing Applications (DEISA), chair: V. Alessandrini; H. Lederer, M. Scheffler – until April 2008
- EU – DEISA Extreme Computing Initiative (DECI), in Distributed European Infrastructure for Supercomputing Applications (DEISA2), coordinator: S. Heinzel; V. Blum, M. Scheffler – since October 2009
- EU – Integrated Infrastructure Initiative (I3): European Theoretical Spectroscopy Facility (ETSF), coordinator: R. Godby; M. Scheffler – since January 2008
- <sup>(IG)</sup>EU – Marie Curie Host Fellowship for Early Stage Research Training (EST): Molecular Networks at Phase Boundaries (MONET), coordinator: J.N. Andersen; A. Michaelides, K. Reuter, M. Scheffler – since January 2006
- EU – Marie Curie Actions, Human Resources and Mobility:  $\Psi_k$  Training in Computational Nanoscience, chair: P. Dederichs; M. Scheffler – since July 2006
- EU – Marie Curie Actions, Initial Training Network (ITN): Surfaces for Molecular Recognition at the Atomic Level (SMALL), coordinator: J.N. O’Shea, C. Roberts; M. Scheffler – since winter 2009/2010
- ESF – Physical and Engineering Sciences Committee (PESC): Towards Atomistic Materials Design (Psi-k), chair: P. Dederichs; M. Scheffler – until December 2007
- ESF – Physical and Engineering Sciences Committee (PESC): Molecular Simulations in Biosystems and Material Science (SimBioMa), chair: P. Nielaba; M. Scheffler – since May 2006
- DFG – Cluster of Excellence 314: Unifying Concepts in Catalysis (UniCat), coordinator: M. Driess (TUB); M. Scheffler – since November 2007
- DFG – SFB 546: Structure, Dynamics, and Reactivity of Aggregates of Transition Metal Oxides, project C6, spokesperson: J. Sauer; K. Hermann – since August 1999

- <sup>(IG)</sup>DFG – SFB 658: Elementary Processes in Molecular Switches at Surfaces, project C4, spokesperson: M. Wolf; K. Reuter, M. Scheffler – until June 2009
- DFG – SFB 658: Elementary Processes in Molecular Switches at Surfaces, project B3, spokesperson: M. Wolf; K. Hermann – since July 2009
- BMBF – Federal Ministry of Education and Research: Scalable Eigenvalue-Solvers for Petaflop Applications (ELPA), coordinator: H. Lederer (RZG); M. Scheffler, V. Blum – since October 2008
- BMBF – Federal Ministry of Education and Research (“Verbundprojekt”): Virtual Development of Ceramic and Composite Materials with Tailored Transport Properties (VEKTRA), coordinator: S. Lampenscherf (Siemens); M. Scheffler – since June 2007
- NIST Database # 42 Project: Surface Structure Database; K. Hermann, M. Van Hove, P. Watson – since July 1991
- ARC – Australian Research Council, Discovery Project: *Ab initio* Theory in Complex Materials and Surfaces: Prediction and Design of Functional Structures; C. Stampfl, A.J. Freeman, M. Scheffler – until December 2008
- ARC – Australian Research Council, Discovery Project: First-Principles Engineering of Advanced Multicomponent Materials for Clean, Energy Efficient Thermoelectric and Catalytic Technologies; C. Stampfl, A.J. Freeman, M. Scheffler – since January 2009
- <sup>(IG)</sup>IFP – Institut Français du Pétrole, Ph.D. Student Program: Kinetic Monte Carlo Simulations of Gas Solid Reactions and Applications to Hydrotreating Catalysts; K. Reuter, M. Scheffler – until December 2008
- NSF – Partnership for International Research and Education (PIRE): Electron Chemistry and Catalysis, coordinator: A. Wodtke; M. Scheffler – since 2005
- NSF – Partnership for International Research and Education (PIRE): Molecular Engineering for the Conversion of Biomass Derived Reactants to



Fuels, Chemicals, and Materials, coordinator: A. Datye; R. Schlögl, M. Scheffler – since September 2007

- UCSB – University of California, Santa Barbara; College of Engineering and College of Mathematical, Life & Physical Sciences; M. Scheffler

The <sup>(IG)</sup>superscript indicates a collaboration with the *Independent Junior Research Group* of Karsten Reuter.

In the last 8 years we have strongly supported “CECAM”, a high-level European organization devoted to the promotion of fundamental research on advanced computational methods and to their application to important problems in frontier areas of science and engineering. In particular, CECAM organizes scientific workshops and tutorials on computational molecular and materials science. It is financed by European research organizations. The Max Planck Society became a member in 2008. Since 2008 the CECAM headquarters is at the EPFL Lausanne, and “CECAM nodes” have been established in several member states. In Germany there is one node, “cecam-MM1P.de”, directed by Thomas Frauenheim (University Bremen), Björn Winkler (University Frankfurt/Main) and Matthias Scheffler. It focuses on multi-scale modeling from first principles (MM1P) with emphasis on methods and applications to materials and biophysics. The MPG in Halle with Hardy Gross will join this node in winter 2009/10. It is expected that other CECAM nodes may be founded in Germany next year, e.g. one on “soft matter” in Mainz.

In the field *ab initio* calculations of complex processes in materials CECAM has informal contacts to Psi-k.org. This is the umbrella organization for the electronic-structure community in Europe and beyond; Matthias Scheffler is one of its directors. Psi-k.org, for example, organizes the big  $\Psi_k$ -conference every 5 years (one of the international key meetings in the field, attracting more than 600 participants). The next one is scheduled for September 2010 in Berlin – a welcome challenge for the FHI *Theory Department*, the conference organizer.

Scientists of the *Theory Department* were involved in various services to the surface science and electronic-structure communities worldwide. For example, they lecture at the *Free University* and the *Technical University Berlin* as well as at the

*International Max Planck Research School.* They organized or co-organized conferences on topics in surface science and biophysics, and coordinated several international workshops and summer schools on methods for electronic-structure calculations, impacting upon the careers of numerous students of theoretical surface science. This list includes:

- UCSB-MPG Workshop on “Inorganic Materials for Energy Conversion, Storage, and Conservation”, February 20-22, 2008, Lake Arrowhead, California, USA; organizers: T. Cheetham (University of Cambridge, UK), J. Maier (MPI for Solid State Research, Stuttgart, Germany), R. Seshadri (University of California Santa Barbara, USA), and M. Scheffler
- Symposium on “Exact-Exchange and Hybrid Functionals Meet Quasiparticle Energy Calculations, February 28-29, 2008, at DPG Spring Meeting, Berlin, Germany; organizers: P. Rinke and M. Scheffler
- DPG Spring Meeting, Condensed Matter Section, February 25-29, 2008, TU Berlin, Germany; M. Scheffler (as Chair of the Surface Science Division until March 2008)
- Marie-Curie  $\Psi_k$  Training Summer School on “Modern Concepts for treating and Analyzing Surfaces and Nanoscale Materials”, May 12-16, 2008, Sant Feliu de Guíxols, Spain; organizers: K. Fichthorn (Pennsylvania State University, USA) and M. Scheffler
- 13th ETSF/Nanoquanta Conference “Theoretical Spectroscopy and Quantum Transport”, September 23-27, 2008, Pugnochiuso, Italy; organizers: F. Sottile (LSI, Ecole Polytechnique, Palaiseau, France), V. Olevano (CNRS, Institut NEEL, Grenoble, France), P. Rinke, G.-M. Rignanese (Unité PCPM, Louvain-la-Neuve, Belgium), J.J. Rehr (University of Washington, Seattle, USA), and L. Wirtz (IEMN / ISEN, Villeneuve d'Ascq Cedex, France)
- IWOM<sup>3</sup> 2009 – International Workshop on “Multiscale Materials Modeling”, March 10-13, 2009, Berlin, Germany; organizers: K. Kremer (MPI for Polymer Research, Mainz) and M. Scheffler

- Symposium on “*Ab Initio* Approaches to Excitations in Condensed Matter”, March 26-27, 2009, at DPG Spring Meeting, Dresden, Germany; organizers: C. Ambrosch-Draxl (University of Leoben, Austria) and M. Scheffler
- Symposium on “Chemical Reactions on Nanomaterials: Progress from In-Situ Experimental Studies and Theoretical Investigations”, March 26, 2009, at DPG Spring Meeting, Dresden, Germany; organizers: R. Denecke (University of Leipzig), K. Reuter, and A. Stierle (MPI for Metal Research, Stuttgart)
- Workshop on “Catalysis from First Principles”, May 25-28, 2009, Vienna, Austria; organizers: J. Hafner (University of Vienna, Austria), J. Nørskov (Technical University of Denmark, Lyngby), and M. Scheffler
- Hands-on Tutorial on “*Ab Initio* Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions”, June 22 - July 1, 2009, Berlin, Germany; organizers: V. Blum, K. Reuter, and M. Scheffler
- 14th ETSF Workshop on Electronic Excitations: “Ab-initio Tools for the Characterization of Nanostructures”, September 14-19, 2009, Evora, Portugal; organizers: L. Wirtz (CNRS-IEMN and University of Lille, France), G.-M. Rignanese (Université Catholique de Louvain, Belgium), M. Marques (CNRS-LPMCN and University of Lyon 1, France), V. Olevano (CNRS Institut Neel, Grenoble, France), F. Sottile (Ecole Polytechnique, Palaiseau, France), and P. Rinke
- KITP long program on “Excitations in Condensed Matter: From Basic Concepts to Real Materials”, October 5 - December 18, 2009, KITP, Santa Barbara, USA; coordinators: C. Ambrosch-Draxl (University of Leoben, Austria), K. Burke (University of California, Irvine, USA), R. Car (Princeton University, USA), and M. Scheffler
- Conference “From Basic Concepts to Real Materials”, November 2 - November 6, 2009, KITP, Santa Barbara, USA; organizers: C. Ambrosch-Draxl (University of Leoben, Austria) and M. Scheffler

### III. New Concepts, Methods, and Techniques

#### III.1 The Atom-Centered Numeric Basis-Set Code “FHI-aims”

Two years ago we introduced the beta version of a new code “FHI *ab initio* molecular simulations (aims)”, which treats the all-electron problem of DFT, Hartree-Fock+MP2, RPA,  $G_0W_0$  without significant numerical approximations. Thanks to the chosen basis set, its efficiency is similar to or better than plane-wave pseudopotential codes, while the accuracy is on par with, e.g. full-potential LAPW. The official version of the code was released in 2009 and was successfully employed at the “Hands-On Tutorial on *Ab Initio* Molecular Simulations” (Berlin, June 22 - July 1, 2009) with more than 90 participants.

The primary new developments since 2007 include the addition of numerous density functionals beyond standard LDA and GGA, i.e., hybrids and exact exchange plus the random phase approximation (RPA) for correlation (Stefan Gutzeit, Mariana Rossi, Volker Blum, Xinguo Ren, and Sergey Levchenko)

Also van der Waals interactions have been added to the code. This includes a post-processing version of the Langreth-Lundqvist functional which is based on a code from Claudia Ambrosch-Draxl’s group as well as the DFT and MP2 variants of the parameter-free  $C_6/R^6$  approach discussed in Section III.3 below. (Mina Yoon and Alexandre Tkatchenko)

Major infrastructure improvements include molecular dynamics with standard and recent thermostats and the functionality to extract vibrational spectra including anharmonic effects. (Mariana Rossi, Felix Hanke, Luca Ghiringhelli, and Volker Blum)

Work on a scalar relativistic implementation beyond the present, “scaled ZORA” based formalism is ongoing. In addition, spin-orbit coupling can now be treated as a perturbative post-processing step. (Paula Havu, Volker Blum, Matthias Gramzow<sup>(IG)</sup>, and Karsten Reuter<sup>(IG)</sup>)

Finally, major performance improvements of FHI-aims have been geared towards massively parallel platforms such as IBM’s BlueGene architecture – with regard to both large-scale electronic structure problems (Au/Pt surface reconstructions) and mid-sized, long-running molecular dynamics simulations. We highlight here

especially the development of a robust, conventional solver for Hermitean, generalized eigenvalue problems that overcomes the known performance obstacles of the standard Scalapack implementation. For example, this solver presently provides scalability up to 8192 CPU cores on the BlueGene for a 1000-atom benchmark example. Work on further improvements to this solver is ongoing and now linked to a larger BMBF-funded project, ELPA. (Volker Blum, Paula Havu, Ville Havu, and Rainer Johanni)

### **III.2 Further Improvements in the Stockholm-Berlin (StoBe) Cluster Code**

The StoBe (Stockholm-Berlin code) program package, developed in collaboration with L. G. M. Pettersson (University of Stockholm) for the calculation of chemical/ physical properties of large molecules and clusters (including electronic excitations) has been further extended. Recent improvements have been added due to local needs in specific applications as well as by requests from the world-wide StoBe user community. They include

- the implementation of an efficient transition state search based on the nudged-elastic-band (NEB) and climbing-image methods (together with Matthias Gruber);
- further improvements in the evaluation of electronic core excitations for the interpretation of experimental X-ray photoemission (XPS) and absorption (XAS) spectra. New core localization schemes facilitate the identification of core holes in large systems and can speed up convergence (together with Lars Pettersson);
- the trust-region SCF method [JCP 123 (2005) 074103] to improve convergence of the electronic density in large systems. At present, the implementation is in its testing phase but first results are encouraging (together with Lars Pettersson).

The StoBe software is available for MS Windows® 2000/ XP and Linux/Unix systems and is distributed by the Fritz Haber Institute. (Klaus Hermann)

### III.3 Practical and Accurate Treatment of van der Waals Interactions in DFT and Hartree-Fock+MP2

Non-covalent interactions, of which van der Waals (vdW) interactions are an important special case, are essential aspects of many problems in chemistry and biophysics. However, for density-functional theory vdW interactions are lacking in the local-density, gradient-corrected, as well as conventional hybrid exchange-correlation functionals. Hartree-Fock plus Møller-Plesset perturbation theory (MP2) is able to describe vdW interactions but its accuracy is often not sufficient.

Our approach starts from the widely employed Ansatz that adds the leading interatomic vdW term via pair-wise atom-atom interactions to the internuclear energy term. The novel feature is that the dispersion coefficients and vdW radii are determined from first-principles (ground-state electron density). The approach can be linked to gradient-corrected density functionals (e.g. PBE+vdW) and hybrids. It can also be used to correct MP2: MP2+ $\Delta$ vdW. The accuracy achieved is noticeably higher than that of any other DFT+dispersion scheme and recent functionals. In particular, the MP2+ $\Delta$ vdW method achieves accuracy comparable to the computationally much more expensive CCSD(T) method for a wide variety of non-covalent systems. Still, also in our approach some deficiencies remain. These are the *ad hoc*-introduced damping function (to eliminate the divergence of the  $R^{-6}$  terms at short internuclear distance) and the lack of screening of dispersion coefficients in bulk metals. (Alexandre Tkatchenko)

While PBE+vdW provides a good geometry, for the energetics and electronic structure such efficient geometry optimization should (in some cases) be followed by a PBE-hybrid+vdW calculation. (Alexandre Tkatchenko; work done in collaboration with Noa Marom and Leeor Kronik (Weizmann Institute, Israel))

### III.4 Many-Body Perturbation Theory for (Supposedly) Strongly Correlated Materials

The term “strongly correlated” typically refers to situations in which a single-particle description and first-order perturbation theory for the self-energy fail to describe the electronic properties. However, the literature on this issue appears more

confusing than helpful.  $f$ -electron systems, e.g. lanthanides and their oxides, are key examples of “strongly correlated” materials.

We have developed an all-electron LAPW based approach (starting from the WIEN code) to evaluate the electron self-energy in the  $G_0W_0$  approximation. Through the screened Coulomb interaction  $W$  the approach captures the screening among itinerant electrons while at the same time treating exchange at the exact-exchange level. The latter should account for a large part of the interactions among localized  $f$ -electrons. To overcome the pathologies of LDA for  $f$ -electron systems, we apply  $GW$  as correction to LDA+ $U$ , where the parameter  $U$  is determined by means of constrained DFT calculations. An application of the approach to lanthanide oxides is discussed in Section IV.3b below. (Hong Jiang, Ricardo Gómez-Abal, and Patrick Rinke)

### III.5 The Random Phase Approximation for Treating Correlations in Exact-Exchange DFT

The local-density and generalized gradient approximations to DFT, although tremendously successful in electronic structure calculations, suffer, amongst others things, from severe self-interaction errors and the absence of long-range van der Waals (vdW) interactions. These deficiencies can lead to *qualitative failures*, as exemplified by the adsorption of certain molecules at metal surfaces whose bonding mechanism involves donation/back-donation. For example, for CO adsorption on (111) surfaces of Cu, Rh, and Pt LDA and GGA predict the wrong adsorption site. This and the renewed interest in vdW interactions are tied to the more fundamental quest of finding an improved electronic structure method, that combines accuracy and tractability. The linkage of “exact exchange” with a correlation energy based on the renormalized (screened) Coulomb potential (the random phase approximation, RPA) that is finite for metallic systems represents a promising avenue. We have therefore implemented this approach in the electronic structure code FHI-aims. Our RPA calculations are performed as a post-correction to either a self-consistent DFT or Hartree-Fock (HF) ground state calculation.

(Xinguo Ren and Patrick Rinke)

### **III.6 Reduced Density-Matrix-Functional Theory for Strongly Correlated Solids**

In the Max Planck Fellow group of Hardy Gross, reduced density matrix functional theory (RDMFT) was further developed to tackle strongly correlated solids such as Mott insulators. This was achieved with a novel functional, the “power functional”, which involves a fractional power of the density-matrix operator. With this functional, the fundamental gaps of transition metal oxides were found in good agreement with experiment, also for cases like FeO which are very hard to capture with any flavor of DFT. As there exists no single-particle eigenvalue equation in RDMFT, a long-standing challenge has been the calculation of the quasi-particle spectrum within RDMFT. As a first step in this direction, a new technique to determine the density of states within RDMFT was developed. Again, the results for transition metal oxides (as well as other materials) turned out to be in excellent agreement with experiment. (Sangeeta Sharma, J. Kay Dewhurst, Nektarios N. Lathiotakis, Florian Eich, Miguel A. Marques, and Hardy (E.K.U.) Gross)

## **IV. Applications – Some Highlights**

### **IV.1 Metals**

#### **IV.1a Accurate Surface Energies of the 4d Transition Metal Series**

The surface energies of low index surfaces of 4d transition metals (from Y to Ag) have been calculated with carefully determined error bars addressing, for the first time, the accuracy of the exchange-correlation functional. This is achieved by comparing a variety of gradient-corrected and hybrid functionals, as well as exact exchange plus RPA for correlation and, for selected systems, also coupled cluster (CCSD(T)) studies. The previous understanding of trends is confirmed. The achieved accuracy is better than that of experimentally deduced surface energies. (Aloysius Soon, Martin Fuchs, and Bo Li)



#### **IV.1b Large-Scale Reconstructions of Late 5d's**

In contrast to the 4d's, the fcc (100) surfaces of the late 5d's (Ir, Pt, Au) undergo large-scale reconstructions. With FHI-aims running on IBM's massively parallel BlueGene computer we were able to treat large unit cells (e.g. 786 Au atoms) and analyzed the energetics and reconstruction mechanism of the “(5 x N)” type quasihexagonal reconstructions of these metals. The current literature claims a significant difference between the experimental reconstruction energies of Pt (*in vacuo* by CO titration calorimetry) and Au (in an electrochemical environment), as well as a significant difference between the (5 x 1) based theoretical reconstruction energy of Pt(100) and experiment. Our calculations (DFT-LDA and PBE) indicate that the theoretical reconstruction energies of Au and Pt are in fact very similar if the *full* reconstruction is taken into account, and that the DFT reconstruction energy of Pt agrees remarkably well with the latest experimental reassessment. (Paula Havu, Ville Havu, and Volker Blum)

#### **IV.1c Quantum Interference at the Twist Boundary in Graphene**

In collaboration with Oleg Pankratov (University Erlangen) the Max Planck Fellow group of Hardy Gross applied standard density-functional techniques to elucidate some of the novel properties of topical materials like graphene; a condition for the decoupling of the graphene layers was derived and it was shown that even for the smallest possible commensurate rotation of two graphene layers the decoupling is effectively perfect. (Sangeeta Sharma and Sam Shallcross)

### **IV.2 Semiconductors**

#### **IV.2a Materials Parameters of Group-III Nitrides**

Knowledge of materials parameters is crucial for semiconductor device modeling. For group-III-nitrides (here AlN, GaN, and InN) such parameters are not well known because for some of these materials it is nearly impossible (so far) to grow good bulk samples. Strain is always present in group-III-nitride devices. It is significant and noticeably influences the light absorption and emission. We used the  $G_0W_0$  approximation as well as the HSE hybrid functional to overcome the band-

gap problem. Our  $G_0W_0$  and HSE results agree closely but differ from the LDA/GGA ones, in particular, for the band-gap related deformation potentials. For the regime around the experimental lattice parameters, we determined a complete and consistent set of deformation potentials. (Ricardo I. Gómez-Abal, Qimin Yan, Chris Van de Walle, and Patrick Rinke)

#### **IV2.b Sources of Electrical Conductivity in $\text{SnO}_2$**

$\text{SnO}_2$  is widely used as a transparent conductor and sensor material, and it is the active coating in heat reflective glass which became common in modern architecture. Furthermore, wide-band-gap oxides, such as  $\text{SnO}_2$ , hold great promise for applications as semiconductors but progress has been impeded by the lack of control over conductivity. Ambipolar doping would enable an entire additional range of devices, including optical detectors and light emitters. Using density functional theory, we could show that the conventional attribution of  $n$ -type conductivity to intrinsic point defects is incorrect. Unintentional incorporation of hydrogen provides a consistent explanation of experimental observations. Most importantly, we find that  $\text{SnO}_2$  offers excellent prospects for  $p$ -type doping by incorporation of In or other group-IIIA acceptors on the Sn site. (Abhishek Singh, Anderson Janotti, and Chris Van de Walle)

#### **IV.2c Structural, Magnetic, and Electronic Properties of $\text{Co}_2\text{MnSi}(001)/\text{MgO}$ Heterostructures**

Tunneling magnetoresistance (TMR) devices, consisting of two ferromagnetic electrodes separated by a tunneling barrier, have been subject to intense research. This is, e.g. motivated by the search for better nonvolatile magnetic random access memories. We studied the structural stability and magnetic and electronic properties of  $\text{Co}_2\text{MnSi}(001)/\text{MgO}$  heterostructures. Employing *ab initio* atomistic thermodynamics, it is found that the Co or MnSi planes of bulk-terminated  $\text{Co}_2\text{MnSi}$  form stable interfaces, while pure Si or pure Mn termination requires nonequilibrium conditions. Except for the pure Mn interface, the half-metallic property of bulk  $\text{Co}_2\text{MnSi}$  is disrupted by interface bands. Even so, at homogene-

ous Mn or Co interfaces these bands contribute little to the minority-spin conductance through an MgO barrier, and hence such terminations could perform strongly in TMR devices. (Björn Hülse and Peter Kratzer)

### IV.3 Oxides

#### IV.3a The Oxygen Vacancy in MgO

Metal oxides are often treated by DFT-LDA/GGA, although they can be considered as borderline towards strongly correlated materials. Subsequently, defects (in the bulk and at the surface) are not described reliably. The anion vacancy in bulk MgO (also called F- or color center) is a – maybe even “the” – classical intrinsic point defect in compound insulators. Still the absorption and emission spectrum is not understood, in particular why the charged and neutral defects,  $F^+$  and  $F^0$ , absorb light at practically identical energies. Combining DFT-LDA calculations of the potential-energy surface (PES) in different charge states with many-body perturbation theory in the  $G_0W_0$  approach, we find that the many-body corrections are significant (the change in absorption and emission energies is 1 eV or larger). Going one step further in the hierarchy of many-body perturbation theory, i.e., solving the Bethe-Salpeter equation, we find that the electron-hole interaction, that is not contained on the level of the  $G_0W_0$  approach, is also significant and gives additional correction of the order of 0.7 eV. (Patrick Rinke)

#### IV.3b Electronic Structure of the Lanthanide Oxide Series

In the lanthanide-oxide series (from  $\text{La}_2\text{O}_3$  to  $\text{Lu}_2\text{O}_3$ ) the number of  $f$ -electrons contributed by each rare earth atom increases from 0 to 14. The simultaneous presence of strongly localized and itinerant states and the interactions between them requires a many-body description that is free of spurious self-interaction errors and treats localized and itinerant states on the same footing. Our  $G_0W_0@LDA+U$  calculations (cf. Section III.4 above) reproduce the main features found for the optical experimental band gaps. The relative position of the occupied and unoccupied  $f$ -states explains the observed variation in the measured band

gaps and confirms the experimental conjecture derived from phenomenological arguments. The good agreement between our results and available experimental data therefore challenges the classification of these materials as strongly correlated. (Hong Jiang, Ricardo Gómez-Abal, and Patrick Rinke)

#### **IV.3c Structural Analysis of Silica-Supported Vanadia**

Monomeric  $\text{VO}_x$  centers are widely assumed to actuate the catalysis of silica-supported vanadia. However, the experimental identification of these centers is not unambiguous because vibrational spectroscopy cannot safely discriminate between monomeric  $\text{VO}_x$  and polymeric  $\text{V}_x\text{O}_y$  species. Oxygen core excitations in vanadia-silica model clusters have been calculated applying the StoBe DFT cluster code. Comparing the results with X-ray absorption fine structure (NEXAFS) measurements of vanadia model catalysts supported by SBA-15 silica allows to identify structural details of the vanadia species beyond vibrational analyses. The detailed results on various oxygen centers can explain the asymmetric shape of the experimental peak and suggest very strongly that a mixture of monomeric and polymeric vanadia species exist at the SBA-15 support in contrast to the conventional view. (Matteo Cavalleri and Klaus Hermann)

#### **IV.3d Surface Energy and Surface Proton Order of Ice Ih: The Ice Surface is “Superchilled”**

We all know that ice becomes slippery down to some 20-40 K below its bulk melting point. Less is known, however, about the surface of ice at lower temperatures such as those experienced by ice crystals in the upper atmosphere. Through a series of DFT, force field, and Ising model simulations we predict that the proton order-disorder transition, which occurs in the bulk at 72 K, will not occur at the surface at any temperature below melting. Electrostatic repulsion between protons at the surface causes them to order, effectively making the surface superchilled. A simple order parameter that uniquely defines the surface energy of ice surfaces is identified. This will be useful in predicting equilibrium crystal shapes

of ice crystals and in understanding the reactivity of ice crystallites. (Ding Pan, Li-Min Liu, Angelos Michaelides, and Enge Wang)

## **IV.4 Adsorption**

### **IV.4a The CO Adsorption Puzzle Revisited by Exact Exchange plus RPA and GW**

Ten years ago, extensive LAPW studies by F. Wagner revealed that at low coverage CO adsorbs at the hollow site of Pt(111) in DFT-LDA and GGA, in contrast to experimental evidence for top site adsorption. Corresponding disagreement exists for (111) Cu and Rh. In a joint paper with P. Feibelman and several other groups this issue was then coined “the CO adsorption puzzle”. The error can be as large as 0.5 eV (for Cu(111)): A dramatic value for the *difference* of the adsorption energies of two sites. We have performed DFT calculations for CO at Cu(111) treating exchange at the exact-exchange level and correlation in the random phase approximation (RPA) – see Section III.5 above. This approach overcomes the pathologies of LDA/GGA and the correct (on-top) adsorption site is recovered. The adsorption energies themselves are also in good agreement with available experimental data. The corresponding single-particle energies are given by the  $G_0W_0$  approach demonstrating that the LDA/GGA problem is caused by an incorrect HOMO-LUMO splitting and subsequent donation/back-donation imbalance. (Xinguo Ren and Patrick Rinke)

### **IV.4b Electronic Structure, Defect Formation Energies, and**

#### ***Ab Initio* Atomistic Thermodynamics of Li-doped MgO(100)**

The catalytic activity of Li-doped MgO(100) is typically attributed to Li point defects substituting Mg in the MgO lattice. However, under reaction conditions the concentration and geometry of these centers *at the surface* remain unknown. Calculating defect formation energies as function of coverage and layer depth we find that the interaction between Li defects is attractive, in the bulk as well as at the surface and subsurface region. As a consequence we expect clustering, and in

the bulk this finding is actually in agreement with experimental results. While the tendency towards cluster or island formation is energetically more favorable at the surface, the defect formation energy is more favorable in the bulk. The mechanism of the clustering/island formation is analyzed as well as the influence of the (appropriate) treatment of exchange and correlation. (Sergey Levchenko)

#### **IV.4c N<sub>2</sub> on Graphite**

Experimental studies of the physisorption of nitrogen molecules at the graphite surface show several interesting features as a function of coverage. One question concerns the relative stability of the so-called “in-plane”, “out-of-plane”, and “pin-wheel” monolayer structures, in which the nitrogen molecules rotate between parallel and perpendicular configurations. Our dispersion-corrected density-functional theory and Møller-Plesset second-order perturbation theory studies, supplemented by high-level coupled cluster [CCSD(T)] calculations, challenge the commonly held view of closed-shell interacting species. In particular, we find a noticeable electronic polarization for nitrogen adsorbed in a perpendicular configuration, which stabilizes the perpendicular N<sub>2</sub> configuration significantly compared with the parallel configuration frequently assumed to be the ground state. We also find noticeable differences between adsorption on graphite and on a single graphene sheet. (Alexandre Tkatchenko)

### **IV.5 Dynamics at Surfaces and Catalysis**

#### **IV.5a Structure and Dynamics of Ice Nanoclusters on Metal Surfaces:**

##### **The Role of Pentagons**

Heterogeneous nucleation of water plays a key role in fields as diverse as atmospheric chemistry, astrophysics, and biology. Ice nucleation on metal surfaces offers an opportunity to watch this process unfold, providing a molecular-scale description of the initial stages of heterogeneous ice nucleation and growth. Overall our DFT and *ab initio* molecular dynamics simulations [along with collaborations with the experimental groups of Hodgson (Liverpool) and Morgenstern (Hanno-

ver)] reveal that the structure and reactivity of water and ice at even simple close-packed metal substrates is more complex than hitherto appreciated. For example, on Cu(110) an ice structure built from water *pentagons* has been identified. This and the other systems explored reveal how the subtle interplay of bonding within the overlay and to the substrate conspires to yield a rich variety of structures, showing that previous assumptions of universally applicable models such as bi-layer ice growth need to be revised. (Javier Carrasco and Angelos Michaelides)

#### **IV.5b Adsorption, Diffusion, and Reaction of $\text{NH}_x$ and H at $\text{VO}_y$ Catalysts**

Various selective oxidation reactions are processed on vanadium based metal-oxide ( $\text{VO}_x$ ) catalysts in the presence of ammonia, and adsorption and (de)hydrogenation of  $\text{NH}_x$ ,  $x < 4$ , contribute elementary steps. Using density-functional theory and a cluster approach we studied hydrogen and  $\text{NH}_x$  adsorbates at the perfect  $\text{VO}_x$  surface as well as at different reduced surfaces by introducing oxygen vacancies [with  $\text{V}_2\text{O}_5(010)$  serving as an initial model surface]. In addition to adsorption energetics, we also determine diffusion and reaction paths with corresponding energy barriers. At the perfect  $\text{VO}_x$  surface the dehydrogenation energy of  $\text{NH}_3$  is lowered considerably compared with the corresponding gas phase reaction and at the reduced surface the reaction even becomes exothermic. The calculations of diffusion paths and corresponding barriers show that  $\text{NH}_x$  and hydrogen are rather mobile at the  $\text{VO}_x$  surface. (Mathis Gruber and Klaus Hermann)

#### **IV.5c Ethylene Epoxidation over Ag-Cu Particles**

Silver-copper alloys exhibit a selectivity for ethylene epoxidation superior to pure silver, the hitherto prime catalyst for this reaction. However, the reasons for this difference are not clear, and even the surface composition, structure, and reaction mechanisms are unknown. We studied the surface structure and morphology of Ag-Cu particles by *ab initio* atomistic thermodynamics. At variance with the common assumption, we find that at temperatures and pressures of interest for practical applications the alloy is not stable at the surface, and the material dis-

plays a variety of structures with similar energetics. Under reaction conditions the catalyst is therefore likely to dynamically evolve among various. Also the calculated reaction intermediates and energy barriers reveal that the situation is very different to that at clean silver. Comparison with photoelectron spectroscopy and transition electron microscopy work in the *Inorganic Chemistry Department* supports the theoretical findings and conclusions. (Simone Piccinin and Catherine Stampfl)

#### **IV.5d Cluster Model Studies on the Catalytic Sulfidation of MoO<sub>3</sub> Oxidation of MoS<sub>2</sub> Surfaces**

Sulfidation of molybdenum trioxide, MoO<sub>3</sub>, to yield molybdenum disulfide, MoS<sub>2</sub>, is an essential step to improve the hydrotreating activity of Mo catalysts which are widely used for hydrodesulfurization (HDS), mixed alcohol synthesis, and other reactions of technological importance. On the other hand, MoS<sub>2</sub> exposed to air can form an oxidized molybdenum species at its surface where oxidic MoS<sub>2</sub> shows higher activity for HDS and alcohol synthesis compared with the clean MoS<sub>2</sub> catalyst. Applying the cluster approach together with density-functional theory we obtained detailed information and understanding about the chemistry at the MoS<sub>2</sub> (model) catalysts. The oxidation of the MoS<sub>2</sub>(0001) surface, modeled by replacing one or two sulfur ions at the surface by oxygen combined with H<sub>2</sub>O to H<sub>2</sub>S conversion in gas phase, turns out to be endothermic in the calculations which seems to disagree with experimental results at finite temperature. (Xuerong Shi and Klaus Hermann)

### **IV.6 Bio-Molecules**

#### **IV.6a Study of the Backbone Conformational Space of an Infinitely Long Polypeptide Chain**

The conformation space of proteins, covering, for example, helices, sheets, and turns, is typically mapped using dipeptides as models for the protein backbone. However, potential-energy surfaces for dipeptides calculated with *ab initio* meth-



ods exhibit some discrepancies between calculated and experimentally observed conformations which are related to the fact that dipeptides lack *long-range* electrostatics and hydrogen bonding (hb) networks. In the present work, the influence of such long-range interactions, which are actually crucial for stabilizing the secondary structure of proteins, is investigated. Analyzing the conformational space of a residue in infinite polypeptides enables us to focus on the conformational space of a single residue fully including the hb cooperativity and long-range electrostatics. The agreement between the predicted and observed conformational space (using an extensive set of data from the protein data bank) is excellent, except for the so-called polyproline II (PPII) conformational region. (Joel Ireta)

#### **IV.6b Secondary Structure of Polyalanine Peptides in Vacuo**

Analyzing the secondary structure of polypeptides in vacuo provides a means to verify and sharpen our understanding of the intramolecular interactions that govern the structure, folding, and misfolding of proteins. Using van der Waals corrected DFT (FHI-aims code) we analyzed the structure of alanine-based peptides Ac-Ala<sub>n</sub>-LysH<sup>+</sup> ( $n = 5, 10, 15$ ), for which a helical secondary structure was indicated by earlier gas-phase experiments. Our results are corroborated by detailed comparison with vibrational spectroscopy work at the *Molecular Physics Department*. In our calculations for the longer molecules ( $n = 10, 15$ ),  $\alpha$ -helical structure models provide good qualitative descriptions already in the harmonic approximation. Beyond this level, we can fully account for finite temperature effects and anharmonicity through Born-Oppenheimer molecular dynamics and the dipole-dipole autocorrelation function. In fact, Ac-Ala<sub>5</sub>-LysH<sup>+</sup> requires this more extensive analysis. The predicted lowest energy structure, “g-1”, is not a simple helix but instead shows an “inverted” hydrogen bond (oriented against a possible helix dipole). (Mariana Rossi and Volker Blum)



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#### *Doctoral Thesis*

*Kaghazchi, P.:* Adsorbate-induced faceting of transition metal surfaces. Freie Universität Berlin 2009.



## Invited Talks of the Members of the Theory Department

### Volker Blum

- Oct. 2007    International Max Planck Workshop on Multiscale Materials Modeling of Condensed Matter, Sant Feliu de Guíxols, Spain  
*Practical Considerations: Writing a DFT Code*
- Nov. 2007    Seminar, Universität Rostock, Germany  
*Towards the Frontiers of Electronic Structure Theory Using Local Orbitals: FHI-aims*
- Feb. 2008    TheoChem Colloquium, Universität Bochum, Germany  
*DFT and Beyond with Local Orbitals: FHI-aims, a New All-Electron / Full-Potential Code*
- Aug. 2008    FPLO Workshop, Dresden, Germany  
*Tackling Biomolecular (Secondary) Structure with Numeric Atom – Centered Orbitals*
- Oct. 2008    International Conference on Materials Discovery and Databases: Materials Informatics and DFT, Oran, Algeria  
*Untangling the Factors that Stabilize Peptide Secondary Structure*
- March 2009    IWOM<sup>3</sup> – International Workshop on Multiscale Materials Modeling, Berlin, Germany  
*Density-Functional Theory and Beyond with FHI-aims: Concepts and Applications*
- June 2009    Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Practical Electronic Structure Theory: Overview*
- July 2009    Hot topic talk, Gordon Conference on Biological Molecules in the Gas Phase and in Solution, Tilton, USA  
*Structure and Vibrations of Polyalanine Peptides in Vacuo Ac-Ala<sub>n</sub>-LysH<sup>+</sup> (n=5, 10, 15), DFT and Experiments*

### Arianna Borrelli

- July 2008    2008 Three Societies Meeting, Oxford, UK  
*Air, Fire and Glass: Meteorology as a Connecting Discipline*
- July 2008    HQ2 International Conference on the History of Quantum Physics, Utrecht, The Netherlands  
*Eugene Wigner and the Bliss of the “Gruppenpest”*
- Sept. 2008    3rd International Conference of the European Society for the History of Science, Vienna, Austria  
*Dirac’s Bra-ket Notation and the Notion of Quantum State*

- Oct. 2008 Kolloquium, Sächsische Akademie der Wissenschaften, Leipzig, Germany  
*Eugene Wigner, Gruppentheorie und die Erhaltungssätze der neuen Quantenmechanik*
- Nov. 2008 5th Variantology Workshop on Deep Time Relations of Arts, Sciences and Technologies, Naples, Italy  
*Giovan Battista Della Porta's "De Aeris Transmutationibus"*
- Aug. 2009 23rd International Congress of History of Science and Technology, Budapest, Hungary  
*A Triple Point of Mathematics: Born and Wiener's new "New Formulation of the Laws of Quantization"*

### Roberto Car

- Feb. 2009 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Quantum Protons in Hydrogen Bonded Systems*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Challenges for First-Principles Molecular Simulations*

### Johan Carlsson

- Jan. 2008 Accelrys, Cambridge, UK  
*Ab-Initio Modeling of Carbon Materials for Catalytic Applications*
- Jan. 2008 Dept. of Chemical Engineering, University of Cambridge, UK  
*Ab-Initio Modeling of the Oxidation of Vacancies in Graphene-Based Carbon Materials*
- April 2008 10th IMPRS Block Course on Synergism between Theory and Experiment: Case Studies, TU Berlin, Germany  
*Electronic Structure of Carbon Materials*
- June 2008 Bayer Technology Services, Leverkusen, Germany  
*Nanochemie und Elektronik erklärt durch Computer-Simulationen*
- Sept. 2008 NaPhoD Summer School, Alghero, Sardinia, Italy  
*Theoretical Methods for Carbon Materials*
- Sept. 2008 NaPhoD Summer School, Alghero, Sardinia, Italy  
*Oxidation as a Tool to Fine-Tune the Properties of Carbon Materials*
- Oct. 2008 Department of Colloid Chemistry, Max Planck Institute for Colloids and Interfaces, Potsdam, Germany  
*Nanochemistry in the Computer: Morphology of Carbon-Based Materials and its Application in Catalysis*



Nov. 2008 Dept. of Chemical Engineering, University of Cambridge, UK  
*Low Temperature Oxidation as a Tool for Nano-Patterning of Carbon Materials*

### **Martin Fuchs**

July 2008 XI-th Symposium on Surface Physics, Prague, Czech Republic  
*Towards an Exact Treatment of Exchange and Correlation in Materials*

May 2009 Workshop on Catalysis from First Principles, Vienna, Austria  
*Towards an Exact Treatment of Exchange-Correlation in Materials*

July 2009 Seminar, Quantum Chemistry Research Group, Humboldt University, Berlin, Germany  
*Pseudopotentials in Plane-Wave Electronic Structure Calculations*

### **Ricardo Gómez Abal**

March 2008 15th Wien2k Workshop on L/APW+lo calculations with the Wien2k code, Vienna University of Technology, Austria  
*The All-Electron  $G_0W_0$  Method Based on WIEN2k*

Nov. 2008 Meeting on Optical Response in Extended Systems (MORE 2008), Erwin-Schrödinger Institute, Vienna, Austria  
*All-Electron  $G_0W_0$  Method Based on LAPW: Implementation and Applications*

June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*The All-Electron “Gold Standard”: Augmented Plane Wave Methods*

### **Felix Hanke**

May 2008 Summer School on Modern Concepts for Creating and Analyzing Surfaces and Nanoscale Materials, Sant Feliu de Guíxols, Spain  
*Ab Initio Thermodynamic Description of Nanoporous Carbon*

July 2008 Workshop on Concepts and Strategies in Interphase Science, Liscombe Lodge, Liscomb, Nova Scotia, Canada  
*A Two-Step Mechanism for Vacancy Oxidation in Graphene*

Sept. 2008 6th Brazilian/German Workshop on Applied Surface Science, Titisee-Neustadt, Germany  
*Ab Initio Atomistic Thermodynamics of Oxygen Adsorption in Graphene Vacancies*

## Klaus Hermann

- Sept. 2007 IDECAT Summerschool on Computational Methods for Catalysis and Materials Science, Porquerolles, France  
*Crystallographic Tools for Surface Scientists*
- Sept. 2007 IDECAT Summerschool on Computational Methods for Catalysis and Materials Science, Porquerolles, France  
*Theoretical Aspects of Physical/Chemical Surface Properties of Oxides of Catalytic Interest*
- Oct. 2007 ACTINET Workshop on How can we Improve Coupling Theoretical Chemistry with X-Ray Absorption Spectroscopy?, Avignon, France  
*XAS at Catalytic Metal/Oxide Surfaces: Ab Initio Cluster Models Can Help to Interpret Experimental Results*
- Oct. 2007 International Symposium "From clusters to catalysts – Transition metal and transition metal oxides", Erkner, Germany  
*X-Ray Absorption at Catalytic Metal/Oxide Surfaces: Ab Initio Cluster Models Help to Interpret Experimental Results*
- Dec. 2007 Physik Department E20, TU München, Germany  
*Ab Initio Cluster Studies for X-Ray Absorption Spectroscopy: From Molecules to Surfaces and Bulk*
- April 2008 10th IMPRS Block Course on Synergism between Theory and Experiment: Case Studies, TU Berlin, Germany  
*Electron Spectroscopy on Vanadia Surfaces*
- June 2008 Kolloquium, Fachbereich Chemie, Universität Bonn, Germany  
*Reaktivität an Metall- und Metalloxydoberflächen: ab-initio-Cluster-Rechnungen unterstützen das Experiment*
- June 2008 12th International Conference on Theoretical Aspects of Catalysis (ICTAC-12), Varna, Bulgaria  
*Excitations and Reaction at Metal and Oxide Surfaces: Ab Initio Cluster Simulations Can Help to Interpret Experimental Results*
- July 2008 Colloquium, Physics Department, City University Hong Kong, P.R. China  
*Ab Initio Density Functional Theory Studies for X-ray Absorption Spectroscopy: From Molecules to Surfaces and Bulk*
- Sept. 2008 CONACYT-DFG Workshop on Free, coordinated and supported clusters: Bridging experiment and theory, Mexico City, Mexico  
*X-Ray Absorption at Catalytic Metal/Oxide Surfaces: Ab Initio Cluster Models Help to Interpret Experimental Results*
- Nov. 2008 Physik-Kolloquium, Jacobs-Universität Bremen, Germany  
*Ab Initio Density Functional Theory Studies for X-Ray Absorption Spectroscopy: From Molecules to Surfaces and Bulk*

- Jan. 2009 Fachbereich Chemie, Universität Erlangen, Germany  
*Ab Initio Cluster Studies for X-Ray Absorption Spectroscopy: From Molecules to Surfaces and Bulk*
- Feb. 2009 9th deMon Developers Workshop, Pune, India  
*New Developments in StoBe and Application to Systems of Catalytic Interest*

### **Timo Jacob**

- Aug. 2007 Seminar, University of Strasbourg, France  
*Towards a More Realistic Modeling of Electrochemical Systems*
- Nov. 2007 MMM-Workshop on Multiscale Materials Modeling of Condensed Matter, Sant Feliu de Guíxols, Spain  
*Theoretical Modeling of Electrochemical Systems*
- Dec. 2007 Seminar, Theoretische Chemie, Universität Ulm, Germany  
*First Principles Studies of Electrochemical Interfaces*
- Dec. 2007 Bunsen-Kolloquium "Electrochemistry in the Nanoregime", Rogenburg, Germany  
*First Principles Investigations on the Interface between Electrode and Electrolyte*

### **Hong Jiang**

- Aug. 2008 Condensed Matter Seminar, Duke University, Durham, USA  
*An All-Electron GW Perspective of f-Electron Systems*
- Aug. 2008 BNL Center for Functional Nanomaterials, Brookhaven, USA  
*An All-Electron GW Perspective of f-Electron Systems*
- Jan. 2009 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Tackling Localized d- and f-States: A Systematic Investigation by GW*

### **Edward Jurkowitz**

- July 2008 HQ2 International Conference on the History of Quantum Physics, Utrecht, The Netherlands  
*Planck's Unification of Physics with/in German Liberal Culture*
- March 2009 Conference on History of Materials Science Research, Göttingen, Germany  
*Computation and Calculation in Early Solid-State Physics: Abstract Theory and Real Materials*

- July 2009 History and Philosophy of Science Colloquium, University of Nancy, France  
*Understanding Vision, and Theorizing Space: Hermann von Helmholtz's and Ernst Mach's Visions of Geometry and Inner Relativity*

### **Horia Metiu**

- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Problems in Computational Catalysis*
- July 2009 Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, Lyngby, Denmark  
*Activation of Oxide Catalysts with Atomic Sized Centers*
- July 2009 Haldor Topsøe A/S, Lyngby, Denmark  
*Activation of Oxide Catalysts with Atomic Sized Centers*
- July 2009 Institute of Chemistry and Biochemistry, FU Berlin, Germany  
*Activation of Oxide Catalysts with Atomic Sized Centers*
- July 2009 UniCat-Kolloquium, TU Berlin, Germany  
*Catalyst Activation by Molecular Sized Centers*
- July 2009 Department Chemie, TU München, Garching, Germany  
*Activation of Oxide Catalysts with Atomic Sized Centers*

### **Angelos Michaelides**

- Nov. 2007 Dept. of Chemistry, The Queen's University of Belfast, UK  
*Is the Surface of Ice More Ordered than the Bulk? And Some Other Questions ...*
- Dec. 2007 Competence Center for Computational Chemistry (C4), ETH, Zurich, Switzerland  
*The Surfaces of Ice, Salt, Clay, and More: Insight from Ab Initio Electronic Structure Theories*
- Dec. 2007 The 118th Zhong-Guan-Cun Forum on Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, P.R. China  
*Water Adsorption and Ice Nucleation on Metals, Salts, and China Clay*
- Dec. 2007 International Workshop on Molecular Structure and Dynamics of Interfacial Water, Shanghai, P.R. China  
*Water Adsorption and Ice Nucleation on Metals, Salts, and China Clay*
- Jan. 2008 Physics Department Seminar, University of York, UK  
*Towards a First Principles Description of Ice Nucleation*

- March 2008 Surface Science and Catalysis Seminar, Lawrence Berkeley National Laboratory, Berkeley, USA  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- March 2008 Stanford Linear Accelerator Center (SLAC), Stanford, USA  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- April 2008 Physics Department Seminar, King's College London, UK  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- May 2008 Summer School on Modern Concepts for Creating and Analyzing Surfaces and Nanoscale Materials, Sant Feliu de Guíxols, Spain  
*Toward Very High Precision (Boredom) in the Calculation of Adsorption Energies on Ionic Surfaces*
- May 2008 Summer School on Modern Concepts for Creating and Analyzing Surfaces and Nanoscale Materials, Sant Feliu de Guíxols, Spain  
*Ice Nucleation at Interfaces*
- June 2008 Theory Sector Colloquium, Department of Chemistry, University of Cambridge, UK  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- June 2008 Mineral Physics Seminar, Department of Earth Sciences, University of Cambridge, UK  
*Towards a First Principles Description of Water Solid Interfaces*
- June 2008 International Conference on Theoretical Aspects of Catalysis XII (ICTAC-XII), Varna, Bulgaria  
*Electronic Structure Simulations of Water Solid Interfaces*
- Aug. 2008 ICSOS 9 - 9th International Conference on the Structure of Surfaces, Salvador, Brazil  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- Sept. 2008 6th Stranski-Kaishew Surface Science Workshop, Sunny Beach, Bulgaria  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- Oct. 2008 Center for Atomic-scale Materials Design (CAMD) Workshop, Stresa, Milan, Italy  
*Towards Reliable Ab Initio Modelling of Water-Solid Interfaces*
- Oct. 2008 Institute of Chemistry of Lyon Conference, École Normale Supérieure de Lyon, France  
*Probing the Structural and Dynamic Properties of Catalytic and Environmental Interfaces with First Principles*

- Nov. 2008 56th IUVESTA Workshop on Template mediated growth of nano-structures, Schlaining, Burgenland, Austria  
*Towards a First Principles Description of Salt Dissolution and Ice Nucleation*
- Nov. 2008 Ice Workshop in Prague: Ice/Vapor Interface: Molecular Modeling and Experiments, Prague, Czech Republic  
*Towards a First Principles Understanding of Water Solid Interfaces*

### **Xinguo Ren**

- July 2008 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Electron Correlation Methods in FHI-aims: Theory, Applications, and Future Prospects*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Beyond LDA and GGA – Hartree-Fock, Hybrid Functionals, MP2, and RPA in FHI-aims: A Numerical Orbital Practice*

### **Patrick Rinke**

- July 2008 International Conference on the Physics of Semiconductors, Rio de Janeiro, Brazil  
*Exciting Prospects for Solids: Exact-Exchange DFT Calculations Meet Quasiparticle Energy Calculations*
- March 2009 Frühjahrstagung der Deutschen Physikalischen Gesellschaft, Dresden, Germany  
*Quasiparticle Energy Calculations in a New Light: From Defects in Semiconductors to the f-Electron Challenge*
- June 2009 CECAM Workshop on Which Electronic Structure Method for the Study of Defects?, Lausanne, Switzerland  
*Defect Formation Energies without the Band Gap Problem: Combining DFT and GW*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*GW-Quasiparticle Calculations*

### **Angel Rubio**

- Jan. 2009 Colloquium, Institute of Solid State and Materials, IFW Dresden, Germany  
*Excited State Dynamics of Nanostructures and Biomolecules within Time-Dependent DFT*

- March 2009 Nanoscience Foundries and Fine Analysis Meeting, Centro Nacional de Microelectronica (CSIC), Universitat Autònoma de Barcelona, Spain  
*What is the European Theoretical Spectroscopy Facility (ETSF): The Emergence of a New Infrastructure NFFA*
- March 2009 NanoCenter Seminar, University of Pittsburgh, USA  
*Boron Nitride and Graphene Nanostructures: Properties and Applications*
- March 2009 APS March Meeting, Pittsburgh, USA  
*Theoretical Description of Excited State Dynamics in (Solvated?) Nanostructures*
- March 2009 Symposium on Frontiers in Condensed Matter Physics and Nanoscale Materials, University of California, Berkeley, USA  
*Theoretical Spectroscopy of Complex Nanostructures and Biomolecules: Emergence of the ETSF*
- April 2009 Colloquium, Dipartimento di Fisica, Università 'Tor Vergata', Rome, Italy  
*Understanding Photophysical Processes in Biomolecules and Nanostructures: Recent Developments and Challenges*
- June 2009 Kolloquium, Institut für Physikalische Chemie, Universität Würzburg, Germany  
*Theoretical Spectroscopy of Nanostructures and Biomolecules*
- June 2009 E-MRS Symposium N "Carbon nanotubes and graphene low dimensional carbon structures", Strasbourg, France  
*Boron Nitride Nanotubes: Properties and Applications*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Response Functions in Low Dimensional Systems: From Optics to Transport*

## Matthias Scheffler

- Sept. 2007 3rd International Workshop on Surface Physics (IWSP) "Nanostructures on Surfaces", Polanica Zdrój, Poland  
*Formation and Properties of Silicon-Based Magnetic Semiconductor Interfaces*
- Sept. 2007 12th Nanoquanta Workshop on Electronic Excitations "Time Dependent Density Functional Theory: Advances and Prospects", Aussois, France  
*Towards an Exact Treatment of Exchange and Correlation in Materials*

- Oct. 2007 International Max-Planck Workshop on Multiscale Materials Modeling of Condensed Matter (MMM), Sant Feliu de Guíxols, Spain  
*Introduction to Electronic Structure Theory*
- Jan. 2008 Colloquium, Institut für Angewandte Physik und Zentrum für Mikrostrukturforschung, Universität Hamburg, Germany  
*Materials Science and Engineering from First Principles*
- Jan. 2008 Eröffnungskolloquium des SFB 762, Universität Halle, Germany  
*Get Real! Materials Science and Engineering from First Principles*
- Jan. 2008 Allgemeines Physikalisches Kolloquium, Fachbereich Physik, Universität Münster, Germany  
*Get Real! Describing and Understanding the Properties and Functions of Materials from First Principles*
- March 2008 The Tulane DFT Fest: Honoring the Achievements of Professor John P. Perdew, Tulane University, New Orleans, USA  
*Some Ideas on ...*
- March 2008 APS March Meeting, New Orleans, USA  
*Multi-Scale Modeling from First-Principles*
- April 2008 Workshop on Materials Science @ MPG, Reissensburg, Germany  
*Frontiers in Computational Materials*
- May 2008  $\Psi_k$  Summer School on Modern Concepts for Creating and Analyzing Surfaces and Nanoscale Materials, Sant Feliu de Guíxols, Spain  
*Introduction to Electronic Structure Theory*
- May 2008  $\Psi_k$  Summer School on Modern Concepts for Creating and Analyzing Surfaces and Nanoscale Materials, Sant Feliu de Guíxols, Spain  
*Ab Initio Modeling of Open Thermodynamic Systems - The Example of Heterogeneous Catalysis*
- May 2008 sIMMposium 2008, Radboud University Nijmegen, The Netherlands  
*Multi-Scale Modeling from First Principles*
- May 2008 Chemisches Festkolloquium, Universität Ulm, Germany  
*Get Real! Ab initio Beschreibung der Eigenschaften funktioneller Materialien*
- June 2008 8th Annual ICQS Workshop on Carbon Nanostructures, Jilin University, Changchun, P.R. China  
*Multi-Scale Modeling from First Principles*
- June 2008 Fudan University, Shanghai, P.R. China  
*The Steady State of Heterogeneous Catalysis*



- June 2008 Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP-CAS), P.R. China  
*The Steady State of Heterogeneous Catalysis*
- July 2008 Workshop on Concepts and Strategies in Interphase Science, Liscombe Lodge, Liscomb, Nova Scotia, Canada  
*Multi-Scale Modeling from First Principles*
- July 2008 ECOSS-25, Liverpool, UK  
*Get Real!*
- Aug. 2008 PIRE-ECCI Workshop on Grand Challenges in Electron Chemistry and Catalysis at Interfaces, Santa Barbara, USA  
*The Steady State of Catalysis*
- Sept. 2008 VIth “Stranski-Kaischew” Surface Science Workshop (SK-SSW 2008), Black Sea, Bulgaria  
*“Active Centers” in Catalysis – Myth or Science*
- Oct. 2008 Saint-Gobain Tech Days “Electronic Structure Calculations”, Aubervilliers, France  
*Predictive Modeling of Oxide Surfaces and Defects in Oxides*
- Nov. 2008 Ernst Mach Colloquium, Academy of Sciences of the Czech Republic, Prague, Czech Republic  
*From Atoms and Molecules at Solids Surfaces to Catalysis and Corrosion*
- Nov. 2008 GDCh-Kolloquium, Carl von Ossietzky Universität, Oldenburg, Germany  
*Get Real! The Steady State of Heterogeneous Catalysis*
- Jan. 2009 2009 MSL Workshop on Accessing Large Length and Time Scales with Accurate Quantum Methods, University College London, UK  
*Active Sites, Rate Limiting Steps, and the Systems Chemistry of Functional Materials*
- Feb. 2009 P-Kolloquium, PTB Braunschweig, Germany  
*Get Real! Ab initio Beschreibung der Eigenschaften funktioneller Materialien*
- Feb. 2009 Symposium on Supercomputing in Solid State Physics (SciSSP 2009), Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan  
*Improving the Efficiency and Accuracy of Ab Initio Statistical Mechanics by “Degree of Rate Control” Analysis*
- Feb. 2009 Physics Colloquium, Dept. of Physics, University of California, Davis, USA  
*Get Real! Ab Initio Description of Materials Properties and Function*

- March 2009 Surface Kinetics International (SKI) Conference, University of Utah, Salt Lake City, USA  
*Active Sites, Rate Limiting Steps, and the System Chemistry of Heterogeneous Catalysis*
- March 2009 Symposium on Frontiers in Condensed Matter Physics and Nanoscience, University of California, Berkeley, USA  
*Active Sites, Rate Limiting Steps, and the System Chemistry of Heterogeneous Catalysis*
- May 2009 Institut für Theoretische Physik, Department Material Physics, University Leoben, Austria  
*Multi-Scale Modeling of the Function of Materials*
- May 2009 IPP-Kolloquium, MPI für Plasmaphysik, Garching, Germany  
*Get Real! Ab Initio Description of Materials Properties and Function*
- June 2009 Annual Conference of the Canadian Association of Physicists (CAP), University of Moncton, Canada  
*Get Real! Ab Initio Description of Materials Properties and Function – the Example of Heterogeneous Catalysis*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Electronic Structure Theory & DFT: Status, Achievements, Challenges*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Sketch of the History of the Kaiser-Wilhelm / Max-Planck-Society and of the Fritz Haber Institute*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Cohesion and Structure of Transition Metals – Studied by Density Functional Theory and Beyond*
- July 2009 Summer School on Materials Modeling from First-Principles, Santa Barbara, USA  
*The Function of Materials: Multi-Scale Modeling from First Principles*
- Aug. 2009 EuropaCat IX – Catalysis for a Sustainable World, Salamanca, Spain  
*System Chemistry of Heterogeneous Catalysis - the Examples of CO and Ethylene Oxidation*

- Aug. 2009 13th International Conference on Applications of Density Functional Theory in Chemistry and Physics (DFT'09), Lyon, France  
*DFT and Beyond: A Discussion of Exact Exchange plus Local- and Nonlocal-Density Approximations to the Correlation Functional*
- Sept. 2009 Conference on Nanostructures at Surfaces, Monte Verità, Ascona, Switzerland  
*The Function of Materials: Multi-Scale Modeling from First Principles*

### **Annabella Selloni**

- Feb. 2009 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Water on TiO<sub>2</sub> Surfaces*
- March 2009 Seminar, Dept. of Chemical Sciences, University of Padova, Italy  
*Water on TiO<sub>2</sub> Surfaces*
- April 2009 2009 MRS Spring Meeting, San Francisco, USA  
*Materials-Related Aspects of TiO<sub>2</sub>-Based Photocatalysis*
- April 2009 Seminar, Department of Materials Science, University of Milano-Bicocca, Italy  
*Materials-Related Aspects of TiO<sub>2</sub>-Based Photocatalysis*
- May 2009 COST Action Training School on Environmental Applications of TiO<sub>2</sub> Photocatalysis, University of Oulu, Finland  
*First Principles Modeling of TiO<sub>2</sub> Surfaces*
- May 2009 Seminar, Bremen Center for Computational Materials Science, University of Bremen, Germany  
*Materials-Related Aspects of TiO<sub>2</sub>-Based Photocatalysis*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Overview of Plane Wave Methods*
- July 2009 2009 Gordon Research Conference on Thin Film & Crystal Growth Mechanisms, Colby-Sawyer College, New London, USA  
*Structure, Defects and Water Adsorption on Titania Surfaces*

### **Aloysius Soon**

- May 2009 Joint Seminar, Physikalisches Institut, University of Karlsruhe and the Institute for Solid State Physics, Forschungszentrum Karlsruhe, Germany  
*Understanding Surface Nanostructures on Metal Surfaces: An Ab Initio Thermodynamics Approach*

## Alexandre Tkatchenko

- March 2008 CSRI, Sandia National Labs, New Mexico, USA  
*Conformational Hierarchies of Weakly-Bonded Systems:  
Accuracy of Dispersion-Corrected DFT*
- Jan. 2009 Seminar, Fritz-Haber-Institut, Berlin, Germany  
*Towards a Tractable Non-Empirical Method for an Accurate  
Description of van der Waals Interactions*
- Feb. 2009 University of California at Berkeley, USA  
*Accurate Molecular van-der-Waals Interactions from Ground-  
State Electron Density*
- Feb. 2009 CSRI, Sandia National Labs, New Mexico, USA  
*Accurate Molecular van-der-Waals Interactions from Ground-  
State Electron Density*
- March 2009 IWOM<sup>3</sup> – International Workshop on Multiscale Materials  
Modeling, Berlin, Germany  
*Accurate Molecular van der Waals Interactions from Ground-  
State Electron Density*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward  
a First-Principles Understanding of Materials Properties and  
Functions, Berlin, Germany  
*Understanding van der Waals Interactions - Status and Current  
Solutions*

## Mina Yoon

- March 2009 APS March Meeting, Pittsburgh, USA  
*First Principles Design of Electric-Field-Assisted High Capacity  
Hydrogen Storage Media*
- May 2009 Workshop on Hydrogen Storage in Metal-Organic Frameworks,  
Jacobs University, Bremen, Germany  
*Electric Field Assisted H-Storage*





**Independent Junior Research Group**

**Head: Karsten Reuter**

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

Juan Beltrán  
Vladimir Froltsov

Ralf Gehrke  
Yongsheng Zhang

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

Jelena Jelić	NSF
Matteo Maestri	AvH Fellow
Li Sheng	AvH Fellow

Xin Tan	AvH Fellow
Wei-Bing Zhang	AvH Fellow

**Graduate students:** 10

**Diploma students:** 1





## **Recent Developments in the Independent Junior Research Group**

**Head: Karsten Reuter**

### **I. General Remarks**

The group head has accepted an offer for a chair (W3) in theoretical chemistry at the Technical University Munich starting on October 1, 2009. The Independent Junior Research Group (IJRG) “*First-Principles Statistical Mechanics*” therefore officially ends on September 30, 2009. In order to allow for a smooth transition and enable those group members who are not moving to Munich to finish their projects regularly, the head of the Theory Department, Prof. Matthias Scheffler, has kindly offered to provide the required resources (office space, computer access). The Max-Planck-Gesellschaft furthermore provides the full budget for one more year. During this transition time the group head will continue to work at the FHI on a 20% basis (“im Nebenamt”).

In the last two years of existence the IJRG continued in its general research objective to develop and apply general-purpose multiscale materials simulation methodology. Aspiring a material-specific modeling of predictive quality the necessary basis in this endeavor is electronic structure theory. A prevalent focus in our activities therefore concerns linking corresponding first-principles calculations with simulation techniques at the statistical mechanics or continuum level that then allow to address meso- or macroscopic system properties and functions. Present activities comprise both the route via different resolutions in different parts of the system (concurrent modeling, embedding) and the route via coupling of differently resolved techniques by parameter exchange (sequential modeling, hand-shaking). With increasing system complexity a central bottleneck in the latter concept is that the amount of required first-principles parameters becomes computationally intractable. An emerging theme we are pursuing to overcome this limitation is to resort to the stringent use of sensitivity analyses in the coarse-grained simulations. If these analyses indicate an insignificant dependence of the simulation outcome upon variations of a given parameter, a rough estimate provided by lower-level (and computationally less demanding) theory may be suffi-

cient. On the contrary, if the analyses reveal a sensitive dependence, a high (first-principles) accuracy is required, potentially even dictating to go beyond semi-local density-functional theory (DFT) as the present-day workhorse for large-scale electronic structure theory calculations. In this way, the resulting multiscale simulations may not only become feasible, but naturally encompass a control of the propagation of error from the quantum to the statistical/continuum description. While the latter is an obvious prerequisite for any quantitative simulation, it is also indispensable to establish a reverse-mapping capability from the larger scale to the finer resolution. Multi-scale modeling with such capability is at present in its absolute infancy, but centrally required within the on-going shift from probing what is there towards direct manipulation and the design of new materials with tailored properties.

## II. Funding, Personnel and Related Activities

Over the last two years the group size fluctuated including visitors between 10 and 15 members. Apart from the IJRG budget directly provided by the Max-Planck-Gesellschaft (MPG), funding for the positions comes predominantly from research projects within the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), the Alexander von Humboldt (AvH) foundation, or the European Union (EU), where projects preceded by the superscript <sup>(ThD)</sup> are in collaboration with the Theory Department:

- <sup>(ThD)</sup>Institut Français du Pétrole – Ph.D. Student Programme “*Kinetic Monte Carlo Simulations of Gas Solid Reactions and Applications to Hydrotreating Catalysts*”, K. Reuter and M. Scheffler, until 12/2008
- <sup>(ThD)</sup> DFG Collaborative Research Centre (Sonderforschungsbereich) SFB-“*Molecular Switches at Surfaces*“, K. Reuter and M. Scheffler, until 06/2009
- <sup>(ThD)</sup> EU Early Stage Training Network “*Molecular Networks at Phase Boundaries (MONET)*”, A. Michaelides, K. Reuter, and M. Scheffler

- DFG Project “*Ab Initio Description of Non-Adiabatic Effects in Dissociative Adsorption*”, K. Reuter and A. Groß (U Ulm, D)
- EU COST Action P-19 “*Multiscale Modeling of Materials*”, K. Reuter
- Interdisciplinary MPG Initiative on “*Multiscale Materials Modeling of Condensed Matter (MMM)*”, K. Reuter
- DFG Cluster of Excellence (Exzellenzcluster) CoE-314 “*Unifying Concepts in Catalysis (UniCat)*”, K. Reuter
- DFG Grant for German-Argentinian Cooperation “*Surface Coverage Effects on the Adsorption Dynamics of H<sub>2</sub> on Metal Surfaces*”, A. Groß (U Ulm, D), K. Reuter, and H.F. Busnengo (U Rosario, Ar)

Among these projects, it is especially the MMM initiative and the EU COST action that integrate the IJRG nicely into the multiscale modeling community within the MPG and at the European level. With respect to the Berlin universities and research institutions, strong links are ensured through the participation in the collaborative actions SFB-658 and CoE-314. This also comprises regular teaching activities within the related Berlin Graduate School of Natural Sciences and Engineering (BIG-NSE) and the International Max-Planck Research School (IMPRS) “*Complex Surfaces in Materials Science*”. The multinational and interdisciplinary character of the group is furthermore strengthened by longer-term visitors. Within the last two years visiting Ph.D. students came from the Institut Français du Pétrole in Paris (N. Dinter), the Institut für Kristallzüchtung Berlin (H. Guhl), and the University of Illinois-Chicago (J. Jelić). Postdoctoral visitors came from Pacific Northwest National Laboratory (Dr. D.H. Mei) and the University Rosario (Dr. P. Abufager), with the latter visit leading to the above listed joint German-Argentinian project that will enable frequent exchanges between the involved groups in the next years.

Apart from the involvement in public events like the Berlin Long Night of the Sciences or the Girls Day, the group was again active in the organization or co-organization of international workshops or symposia:

- Symposium on “*Chemical Reactions at Nanomaterials: Progress from in-situ Experimental Studies and Theoretical Investigations*” at the Spring Meeting of the German Physical Society, Dresden (D), March 26, 2009 (R. Denecke, K. Reuter, and A. Stierle)
- Hands-On Tutorial on ab initio Molecular Simulations “*Toward a First-Principles Understanding of Materials Properties and Functions*”, Berlin (D), June 22 – July 1, 2009 (V. Blum, K. Reuter, and M. Scheffler)

Further incidences noteworthy to report are:

- Having already received the Otto Hahn Medal of the MPG in 2007, Dr. Jutta Rogal (now Ruhr-Universität Bochum, D) has also been awarded with the Ernst Reuter Prize of the Free University Berlin for her outstanding Ph.D. thesis. Since then, two further Ph.D. theses have been completed within the IJRG (R. Gehrke, Y. Zhang).
- The IJRG has been very successful in attracting Alexander von Humboldt fellows, presently hosting Dr. Tan, Dr. Zhang and Dr. Maestri. With Dr. Maestri the second member with a chemical engineering background adds to the interdisciplinary character of the group, otherwise roughly equally composed of physicists and chemists.
- The group head has been reelected as the spokesperson of all IJRGs within the Chemical Physical Technical Section of the MPG. Within this function, he also has guest status within the strategic Perspektivenkommission of the MPG since January 2009. He has also become a member of the steering committee of the COST Action P19 “*Multiscale Modeling of Materials*”, and has been invited to the scientific advisory board of the Psi-k Network connected with the function as spokesperson for the working group “*Multiscale Modeling*”.

### III. New Concepts, Methods and Techniques

#### III.1. Electronic structure level

The overall first-principles input typically required in multiscale materials simulations is formidable. This holds even if this input is suitably reduced through the use of sensitivity analyses as sketched in Section I, and is aggravated if the analyses indicate the necessity for accuracy beyond the one provided by standard DFT with local or semi-local exchange and correlation (xc) functionals. Improving the efficiency of large-scale calculations at the electronic structure base is therefore an everlasting concern, as are methodological advances that enable more accurate large-scale calculations at a tractable computational cost. An alternative to such higher level theory is benchmarking against experiment, which then requires the formulation and implementation of approaches to compute the measured signatures.

- Semi-empirical dispersion correction approaches (DFT-D) are a computationally appealing route to overcome the well-known limitation of local or semi-local DFT xc functionals with respect to long-range van der Waals interactions. We have implemented several prevalent DFT-D schemes into a self-contained module which can be easily coupled to existing DFT codes. Interfaced to the CASTEP code, this module provides dispersion-corrected total energies, forces and stress, and therewith enables dispersion corrected geometry optimizations, phonon calculations or molecular dynamics simulations. In addition, the interface supplies the necessary routines for the Hirshfeld charge partitioning scheme, as this is employed in the recent DFT-D scheme due to Tkatchenko and Scheffler to allow for a variation of the  $C_6$  coefficients of differently bonded atoms (E. McNellis, J. Meyer).
- In order to assess the electronic non-adiabaticity of the adsorption dynamics at metal surfaces we have implemented a time dependent perturbative approach recently suggested by Timmer and Kratzer into the CASTEP code. This approach enables the calculation of (approximate) electron hole pair spectra of impinging atoms and molecules using (adiabatic) ground

state DFT calculations only. An efficient reformulation and parallel implementation allows the application to much larger systems as those considered by the original authors (J. Meyer).

- The IJRG also continues its support for the new in-house DFT code FHI-aims. On-going activities center on the implementation of a perturbative treatment of spin-orbit coupling, as well as of computational core-level spectroscopy within the transition-potential ansatz for both clusters and extended solids (M. Gramzow, together with V. Blum (ThD)).

### III.2 Matching of electronic and mesoscopic regime

As stated in Section I the group currently pursues both embedding and hand-shaking linkage concepts between electronic and atomistic/statistical level. A central concern for an error-controlled multiscale modeling in either concept is how the linkage enables uncertainty contained at one level of description to propagate through to the other level. Within embedding approaches possible inaccuracies of the employed atomistic potential should not affect the target quantities in the quantum mechanically described region. Within hand-shaking approaches uncertainty in the first-principles parameters should not affect the mesoscopic simulation results. Embedding formulations suitably exploiting a higher accuracy of differential corrections are one way of minimizing error propagation into the quantum region. Sensitivity analyses allow pinpointing those hand-shaking parameters for which high accuracy is required. Other parameters on the other hand may be provided with significant uncertainty e.g. through lower-level theory at a much reduced computational cost.

- The application of quantum mechanics/molecular mechanics (QM/MM) embedding approaches to metallic systems is limited by the large cluster sizes required to properly describe the metallic band structure. In a QM/metal approach to adsorption we therefore employ periodic boundary conditions in DFT calculations of the surface with and without adsorbate. Subtracting the two yields a well localized interaction, which is then considered in an extended substrate region modeled at the semi-empirical

potential level. Providing a conserved energy, the resulting Hamiltonian is well suited for *NVE* molecular dynamics and allows us to study the energy dissipation into substrate phonons during the adsorption process

(J. Meyer).

- Kinetic Monte Carlo (kMC) simulations require a rate constant for every elementary process considered. With increasing system complexity, and therewith number of elementary processes, computing all rate constants from first-principles can quickly become computationally intractable. An intriguing alternative could be to start the simulations with less accurate rate constants available at lower computational cost, and only refine those rate constants through first-principles calculations for which a sensitivity analysis indicates that a high accuracy is needed. Issues in such an approach concern the source for the initial estimates, how inaccurate the latter may be, and the reliability of the employed sensitivity analysis. We are currently exploring this route for kMC simulations of different heterogeneous catalytic systems with features that quickly lead to an exuberant number of inequivalent elementary processes. This comprises reaction schemes with increased number of reaction intermediates or significant lateral interactions, or a complex and temporally or spatially varying lattice structure of the surface active sites. On-going case studies address the Ostwald process at  $\text{RuO}_2(110)$ , the methane activation to syngas on  $\text{Rh}(111)$ , and the CO oxidation at oxidizing  $\text{Pd}(100)$  (M. Hoffmann, M. Maestri, C. Mangold, in collaboration with M. Scheffler (ThD)).

### III.3 Simulations at the meso- and macroscopic scale

Compared to the underlying first-principles calculations, the computational cost of the coarse-grained mesoscopic simulations is usually not an issue in the approaches pursued by the group. This changes, if the mesoscopic statistical simulations themselves are coupled to further coarse-grained techniques to capture aspects that require going to macroscopic scales. In this situation,

improved efficiency of the lower scale technique and efficient coupling concepts become as important as in the linkage of quantum to statistical description.

- The success of first-principles kMC simulations in the modeling of heterogeneous catalytic processes relies on the accurate treatment of the reactive surface chemistry. However, in particular, for technologically relevant environments, i.e., at near-ambient pressures and elevated temperatures with concomitant higher product formation rates, heat and mass transport in the gas-surface system becomes increasingly important. This concerns for instance the transport of formed products away from the active surface and how efficiently the large amount of heat generated by the exothermic surface reactions can dissipate into the system. In order to study corresponding effects we integrate the first-principles kMC simulations for the surface kinetics into a computational fluid dynamics modeling of the macro-scale flow structures. While its efficient formulation readily allows addressing more complex reactor geometries, the novel approach has first been used to assess heat and mass transfer limitations in in-situ studies of single-crystal model catalysts (S. Matera).

## **IV. Applications**

### **IV.1. Structure of gas-phase clusters through spectroscopic fingerprinting**

Obtaining information on the atomic arrangement of gas-phase clusters in the sub-nm size range remains a challenge to experiment. While the measurement of vibrational frequencies is particularly sensitive to the internal cluster structure, the geometry itself can only be ascertained through comparison with corresponding data for structural models computed from first-principles. This holds equally for core level spectroscopies as a sensitive probe of the electronic structure. We therefore identify low-energy isomers through an extended first-principles sampling approach and compute their corresponding spectroscopic signatures. Comparison to vibrational data for small cationic Co clusters from resonance enhanced multiple photon dissociation spectroscopy reveals an unexpected



influence of the rare gas probe atoms employed in this technique. Comparison to X-ray absorption spectroscopy data of metal-doped Si clusters confirms endohedral polyhedra as lowest-energy isomers

(R. Gehrke, M. Gramzow, in collaboration with A. Fielicke and G. Meijer (MP Department) and T. Lau and T. Möller (TU Berlin)).

#### IV.2. O<sub>2</sub> dissociation dynamics at metal surfaces reloaded

Despite its ostensible simplicity a fundamental elementary process like the dissociative adsorption of O<sub>2</sub> at metal surfaces is still far from being understood. Open questions concern the change of spin state from gas-phase triplet to adsorbed singlet atoms, as well as the dissipation of the energy freed in the highly exothermic process. We had previously rationalized the enigmatic low sticking coefficient of O<sub>2</sub> at Al(111) in terms of a hindered spin transition and had shown that when constraining the dissociation dynamics completely to the spin-triplet state good agreement with the experimentally measured sticking coefficient can be achieved. We now extend this approach by allowing non-adiabatic spin transitions within mixed quantum-classical molecular dynamics simulations based on the fewest switches algorithm. With these simulations we demonstrate that scattering of a beam of singlet O<sub>2</sub> molecules would enable an independent assessment of the role of spin-selection rules for the adsorption dynamics, as the repelled molecules exhibit characteristic kinetic, vibrational and rotational signatures arising from the non-adiabatic spin transition. In contrast, we find only negligible electronically non-adiabatic effects during the O<sub>2</sub> dissociation at Pd(100). However, here the energy dissipation into phononic degrees of freedom is so slow that we observe a transient mobility of the adsorbed, but not yet equilibrated oxygen atoms (J. Meyer, in collaboration with C. Carbogno and A. Groß (U Ulm, D) and J. Behler (RU Bochum, D)).

#### IV.3. First-principles statistical mechanics approach to step decoration at surfaces

When it comes to the interaction with a reactive environment, atomic steps at solid surfaces are often perceived as nucleation centers for adsorbate-induced morphological transitions like oxide formation or corrosion in our oxygen-rich atmosphere. When aiming to qualify this role at the atomic scale an important first task is to identify the structure and composition at the step edge under realistic gas-phase conditions. Unfortunately, the large computational cost connected with first-principles calculations of stepped surfaces presently prevents a proper exploration of the huge configurational space of possible step structures and allows at best for approximate treatments of entropic effects at elevated temperatures. We address these limitations by suitably combining thermodynamic considerations for the contact with a surrounding  $O_2$  gas-phase and a first-principles parameterized lattice-gas Hamiltonian to explore the oxygen adsorption at a close-packed (111) step at Pd(100). We identify a wide range of gas-phase conditions comprising near atmospheric pressures and elevated temperatures around 900 K, in which the step is decorated by a characteristic O zigzag arrangement. For catalytic processes like the high-temperature combustion of methane that operate under these conditions our approach thus provides first insight into the structure and composition at a prominent defect on the working surface (Y. Zhang).

#### IV.4. Structure and energetics of azobenzene at coinage metal surfaces

Treating the adsorption of complex organic molecules at metal surfaces with high-level theories that include non-local van der Waals interactions by construction is still barely tractable. We therefore explore the use of computationally inexpensive semi-empirical dispersion correction schemes to semi-local DFT (DFT-D). For the molecular switch azobenzene at Ag(111) we compare to detailed structural and energetic data from X-ray standing wave and temperature programmed desorption measurements. Particularly the most recent DFT-D scheme due to Tkatchenko and Scheffler provides quite accurate structural properties, albeit at a rather sizable overbinding. We analyze the features of present DFT-D implemen-

tations that would question the applicability of this approach to metal surfaces and trace this geometry-unspecific overbinding predominantly to the neglected screening of dispersive interactions to more distant substrate atoms (E. McNellis, J. Meyer, in collaboration with P. Tegeder and M. Wolf (PC Department and FU Berlin, D) and G. Mercurio and F.S. Tautz (FZ Jülich, D)).



## Publications of the Independent Junior Research Group

2008

*Behler, J., K. Reuter, and M. Scheffler:* Nonadiabatic effects in the dissociation of oxygen molecules at the Al(111) surface (16 pages). Phys. Rev. B **77**, 115421 (2008).

*Bredow, T., C. Tegenkamp, H. Pfnür, J. Meyer, V.V. Maslyuk, and I. Mertig:* Ferrocene-1,1'-dithiol as molecular wire between Ag electrodes: The role of surface defects (7 pages). J. Chem. Phys. **128**, 064704 (2008).

*Carbogno, C., J. Behler, A. Groß, and K. Reuter:* Fingerprints for spin-selection rules in the interaction dynamics of O<sub>2</sub> at Al(111). Phys. Rev. Lett. **101**, 096104 (2008).

*Kitchin, J.R., K. Reuter, and M. Scheffler:* Alloy surface segregation in reactive environments: First-principles atomistic thermodynamics study of Ag<sub>3</sub>Pd(111) in oxygen atmospheres (12 pages). Phys. Rev. B **77**, 075437 (2008).

*Rieger, M., J. Rogal, and K. Reuter:* Effect of surface nanostructure on temperature programmed reaction spectroscopy: First-principles kinetic Monte Carlo simulations of CO oxidation at RuO<sub>2</sub>(110). Phys. Rev. Lett. **100**, 016105 (2008).

*Rogal, J.:* Catalytic oxidation at surfaces: insight from first-principles statistical mechanics. J. Phys.: Condens. Matter **20**, 064240 (2008).

*Rogal, J., K. Reuter, and M. Scheffler:* CO oxidation on Pd(100) at technologically relevant pressure conditions: First-principles kinetic Monte Carlo study (12 pages). Phys. Rev. B **77**, 155410 (2008).

*Schmidt, R., E. McNellis, W. Freyer, D. Brete, T. Gießel, C. Gahl, K. Reuter, and M. Weinelt:* Azobenzene-functionalized alkanethiols in self-assembled monolayers on gold. Appl. Phys. A **93**, 267-275 (2008).

*Zhang, Y. and K. Reuter:* First-principles statistical mechanics approach to step decoration at surfaces. Chem. Phys. Lett. **465**, 303-306 (2008).

### *Doctoral Thesis*

*Zhang, Y.:* First-principles statistical mechanics approach to step decoration at solid surfaces. Freie Universität Berlin 2008.

*Blum, V., R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler:* Ab initio molecular simulations with numeric atom-centered orbitals. *Comp. Phys. Comm.* **180**, 2175-2196 (2009).

*Carbogno, C., J. Behler, K. Reuter, and A. Groß:* Signatures of nonadiabatic O<sub>2</sub> dissociation at Al(111): First-principles fewest-switches study. *Phys. Rev. B*, submitted.

*Froltsov, V.A. and K. Reuter:* Robustness of ‘cut and splice’ genetic algorithms in the structural optimization of atomic clusters. *Chem. Phys. Lett.* **473**, 363-366 (2009).

*Gahl, C., R. Schmidt, D. Brete, E. McNellis, W. Freyer, R. Carley, K. Reuter, and M. Weinelt:* Structure and excitonic coupling in self-assembled monolayers of azobenzene-functionalized alkanethiols. *J. Am. Chem. Soc.*, submitted.

*Gehrke, R., P. Gruene, A. Fielicke, G. Meijer, and K. Reuter:* Nature of Ar bonding to small Co<sub>n</sub><sup>+</sup> clusters and its effect on the structure determination by far-infrared absorption spectroscopy (11 pages). *J. Chem. Phys.* **130**, 034306 (2009).

*Gehrke, R. and K. Reuter:* Assessing the efficiency of first-principles basin-hopping sampling (10 pages). *Phys. Rev. B* **79**, 085412 (2009).

*Guhl, H., W. Miller, and K. Reuter:* Oxygen adatoms at SrTiO<sub>3</sub>(001): A density functional theory study. *Surf. Sci.*, submitted.

*Lizzit, S., Y. Zhang, K.L. Kostov, L. Petaccia, A. Baraldi, D. Menzel, and K. Reuter:* O- and H-induced surface core level shifts on Ru(0001): prevalence of the additivity rule (9 pages). *J. Phys.: Condens. Matter* **21**, 134009 (2009).

*Matera, S. and K. Reuter:* First-principles approach to heat and mass transfer effects in model catalyst studies. *Catal. Lett.*, in print.

*McNellis, E., J. Meyer, A.D. Baghi, and K. Reuter:* Stabilizing a molecular switch at solid surfaces: A density functional theory study of azobenzene at Cu(111), Ag(111), and Au(111) [10 pages]. *Phys. Rev. B* **80**, 035414 (2009).

*McNellis, E., J. Meyer, and K. Reuter:* Azobenzene at coinage metal surfaces: The role of dispersive van der Waals interactions. *Phys. Rev. B*, submitted.

*Mercurio, G., E. McNellis, I. Martin, S. Hagen, F. Leyssner, S. Soubatch, J. Meyer, M. Wolf, P. Tegeder, F.S. Tautz, and K. Reuter:* Structure and energetics of azobenzene at Ag(111): Benchmarking semi-empirical dispersion

correction schemes. Phys. Rev. Lett., submitted.

*Meskine, H., S. Matera, M. Scheffler, K. Reuter, and H. Metiu:* Examination of the concept of degree of rate control by first-principles kinetic Monte Carlo simulations. Surf. Sci. **603**, 1724-1730 (2009).

*Reuter, K.:* First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Concepts, status and frontiers. To appear in: Modeling Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System. (Ed.) O. Deutschmann, Wiley-VCH, Weinheim.

*Schnadt, J., J. Knudsen, X.L. Hu, A. Michaelides, R.T. Vang, K. Reuter, Z. Li, E. Lægsgaard, M. Scheffler, and F. Besenbacher:* Experimental and theoretical study of oxygen adsorption structures on Ag(111) [10 pages]. Phys. Rev. B **80**, 075424 (2009).

*Doctoral Thesis*

*Gehrke, R.:* First-principles basin-hopping for the structure determination of atomic clusters. Freie Universität Berlin 2009.





## Invited Talks of the Members of the Independent Junior Research Group

### Ralf Gehrke

- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Making Electronic Structure Theory Work: Self-Consistency, Total Energy Derivatives (Forces), Structure Optimization*

### Erik McNellis

- May 2009 Seminar, Institut für Experimentalphysik, FU Berlin, Germany  
*Molecular Switches at Surfaces: The Role of Dispersive van der Waals Interactions*
- May 2009 SFB-Tagung "Molecular Switches: Elementary Processes and Applications", Salzgitter, Germany  
*Molecular Switches at Surfaces: The Role of Dispersive van der Waals Interactions*

### Karsten Reuter

- Sept. 2007 Accelrys Nanotechnology Consortium Meeting, Dublin, Ireland  
*First-Principles Statistical Mechanics for Heterogeneous Catalysis*
- Sept. 2007 European Congress and Exhibition on Advanced Materials and Processes (Euromat 2007), Nürnberg, Germany  
*Error-Controlled Multiscale Modelling Approaches to Surface Chemistry and Catalysis*
- Oct. 2007 International Max-Planck Workshop on Multiscale Materials Modeling of Condensed Matter (MMM), Sant Feliu de Guíxols, Spain  
*Introduction to Monte Carlo and Kinetic Monte Carlo Methods*
- Feb. 2008 Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany  
*Materials Properties and Functions of Nanoscale Clusters from First-Principles Statistical Mechanics*
- Feb. 2008 ESI Visitors Program on Metastability and Rare Events in Complex Systems, Vienna, Austria  
*Error-Controlled Multiscale Modeling Approaches to Surface Chemistry and Catalysis*

- Feb. 2008 Frühjahrstagung der Deutschen Physikalischen Gesellschaft, Berlin, Germany  
*Error-Controlled Multiscale Modeling Approaches to Surface Chemistry and Catalysis*
- April 2008 10th IMPRS Block Course on Synergism between Theory and Experiment: Case Studies, TU Berlin, Germany  
*Oxygen on Transition Metal Surfaces*
- April 2008 Inaugural Workshop of the Materials Simulation Laboratory, London, UK  
*Error-Controlled Multiscale Modeling Approaches to Surface Chemistry and Catalysis*
- April 2008 ISTA Symposium on Frontiers of Materials Science, Vienna, Austria  
*Frontiers in Multiscale Materials Modeling*
- April 2008 DEISA Symposium, Edinburgh, UK  
*Molecular Switches at Metal Surfaces*
- May 2008 Physikalisches Kolloquium, Universität Kiel, Germany  
*First-Principles Statistical Mechanics Approaches to Surface Physics and Catalysis*
- May 2008 Kolloquium für Physikalische und Theoretische Chemie, Technische Universität München, Germany  
*Error-Controlled Multiscale Modeling Approaches to Surface Chemistry and Catalysis*
- May 2008 CECAM Workshop on Accurate Energetics of Condensed Matter with Quantum Chemistry Methods, Lausanne, Switzerland  
*Towards an Exact Treatment of Exchange and Correlation in Materials*
- June 2008 COST Conference on Multiscale Modeling of Materials, Brno, Czech Republic  
*Frontiers in Multiscale Catalysis Modeling*
- July 2008 Winter School at the 53rd Annual Conference of the South African Institute of Physics, Limpopo, South Africa  
*First-Principles Statistical Mechanics Approaches to Surface Physics and Catalysis*
- Aug. 2008 XVII International Materials Research Conference, Cancun, Mexico  
*Towards an Error-Controlled Multiscale Materials Modelling*
- Sept. 2008 Freie Universität Berlin, AG Dr. F. Noe, Germany  
*The Rare-Event Problem in Heterogeneous Catalysis Modelling*

- Oct. 2008 Materials Science and Technology Conference and Exhibition 2008, Pittsburgh, USA  
*Frontiers in Multiscale Catalysis Modeling*
- Nov. 2008 Seminar, Center for Atomic-Scale Materials Design, Technical University of Denmark, Lyngby, Denmark  
*Towards an Error-Controlled Multiscale Catalysis Modelling*
- Nov. 2008 Seminar der Kondensierten Materie, Universität Basel, Switzerland  
*First-Principles Statistical Mechanics Approaches to Surface Physics and Catalysis*
- Jan. 2009 International Workshop on Computation in Catalysis, München, Germany  
*Frontiers in Multiscale Catalysis Modelling*
- Jan. 2009 14th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods, Trieste, Italy  
*Towards an Error-Controlled Multiscale Catalysis Modelling*
- March 2009 10th Netherlands Catalysis and Chemistry Conference, Noordwijkerhout, Netherlands  
*Frontiers in Multiscale Catalysis Modelling*
- March 2009 NIC Winter School on Multiscale Simulation Methods in Molecular Sciences, Jülich, Germany  
*First-Principles Statistical Mechanics Approaches to Surface Physics and Catalysis*
- March 2009 IWOM<sup>3</sup> – International Workshop on Multiscale Materials Modeling, Berlin, Germany  
*Frontiers in Multiscale Catalysis Modelling*
- March 2009 237th National Meeting of the American Chemical Society, Salt Lake City, USA  
*What Can we Learn from Empirically Determined Kinetic Parameters?*
- March 2009 41st Polish Annual Conference on Catalysis, Kraków, Poland  
*Frontiers in Multiscale Catalysis Modelling*
- April 2009 Kolloquium, Physikalische Chemie, Ludwig-Maximilians-Universität München, Germany  
*Frontiers in Multiscale Catalysis Modelling*
- May 2009 International Workshop on Catalysis from First-Principles, Vienna, Austria  
*From UHV to In-Situ: Multiscale Modeling Across the Pressure Gap*

- June 2009 2nd US-China Partnership Conference on Surface Science and Heterogeneous Catalysis, Dalian, P.R. China  
*From UHV to In-Situ: Multiscale Modeling Across the Pressure Gap*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Microscopy and Spectroscopy: DFT-Based Analysis of Surface Science Techniques*
- June 2009 Hands-on Tutorial on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions, Berlin, Germany  
*Ab Initio Thermodynamics & Kinetic Monte Carlo*
- July 2009 Summer School on Modelling in Energy Science, München, Germany  
*Multi-Scale Modeling: The Molecular Approach*
- July 2009 Physik Department, Technische Universität München, Germany  
*First-Principles Statistical Mechanics Approaches to Surface Physics and Catalysis*
- Sept. 2009 European Conference on the Structure of Surfaces (ECOSS-26), Parma, Italy  
*Quantitative Modeling of Surface Reactivity at Atmospheric Pressures*
- Sept. 2009 10th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures, Granada, Spain  
*Quantitative Modeling of Surface Reactivity at Atmospheric Pressures*
- Oct. 2009 COST Training School on Electrocatalysis at the Nanoscale, Reims, Germany  
*First-Principles Based Modeling of Surface Physics and Catalysis*
- Oct. 2009 4th Meeting on the Physics and Chemistry of Surfaces (FYQS), La Plata, Argentina  
*Quantitative Modeling of Surface Reactivity at Atmospheric Pressures*





## Notes







