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

13th Meeting of the Fachbeirat

Berlin, 13th - 15th November 2005

Reports

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Max-Planck-Gesellschaft
Berlin

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Reports

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Contents

Report of the Executive Director

Since the last evaluation of the Fritz Haber Institute by the Fachbeirat in November 2003 several important developments have taken place:

• Gerard Meijer's department is now fully operational.

• Hardy Gross from the Freie Universität Berlin has been awarded one of the prestigious Max Planck Fellow positions, only recently installed by our President, at our institute.

• As proposed by the collegium, the President of the Max Planck Society had called upon Lynn Gladden from Cambridge University to become Gerhard Ertl's successor at the Institute. Unfortunately, this did not substantiate, due to personal reasons of the candidate. In spite of this negative development, the Fritz Haber Institute was encouraged to continue the search process.

The International Max Planck Research School (IMPRS) "Complex Surfaces in Materials Science" is now in full operation. Together with the Humboldt-Universität zu Berlin and the Freie Universität Berlin 27 students form 16 countries work together in the School. Every year two regular block courses of two weeks each take place and several other activities, including a visit to BASF early December 2005. We have included in this booklet a section dealing specifically with the School.

The Fritz Haber Institute has continued to actively support the career of young scientists. The institute has seen 19 habilitations over the last 10 years. Within the same period, 34 scientists (including 17 of the above) have been appointed to high academic positions at universities. The institute typically supports 80-100 PhD students. Many of them are paid through outside funding.

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

The institute also hosts about 10 apprentices in its various scientific departments and service groups.

The main research projects of the Fritz Haber Institute continue to be concerned with catalysis, as well as chemical and physical properties of surfaces, interfaces, molecules, clusters, and nanostructures. Currently, the institute has 42 positions out of which 24 are tenured for scientists, in addition to the 5 director positions and 148 positions for technical staff. In addition, 4.5 positions are in service groups.

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

SFB	290	Metallische dünne Filme: Struktur, Magnetismus und elektronische Eigenschaften (Metallic Thin Films: Structure, Magnetism, and Electronic Properties)
SFB	296	Wachstumskorrelierte Eigenschaften niederdimensionaler Halbleiterstrukturen (Growth-Correlated Properties of Low Dimensional Semiconductor Structures)
SFB	450	Analyse und Steuerung ultraschneller photoinduzierter Reaktionen (Analysis and control of ultra fast photo-induced reactions)
SFB	546	Struktur, Dynamik und Reaktivität von Übergangsmetalloxid-Aggregaten (Structure, Dynamics and Reactivity of Aggregates of Transition Metal Oxides)
SFB	555	Komplexe nichtlineare Prozesse-Analyse-Simulation-Steuerung-Optimierung (Complex Nonlinear Processes–Analysis–Simulation Control–Optimization)
SFB	658	Elementarprozesse in molekularen Schaltern auf Oberflächen (Elementary Processes in Molecular Switches at Surfaces)

Many scientists of the institute participate in DFG Priority Programs (Schwerpunktprogramme) that link institutes all over Germany. In addition, many projects are financed or co-financed by other agencies, such as the DAAD, VW foundation, BMBF, Zeitstiftung, Bayerische Stiftung, C.N.R.S., G.I.F., CAPES, INTAS, EPSRC, ESF, EU, FOM, NSF and UCSB. There are also collaborations with industrial labs, e.g. BASF, Südchemie, Degussa, Toshiba, Sumitomo, Unaxis, MAN.

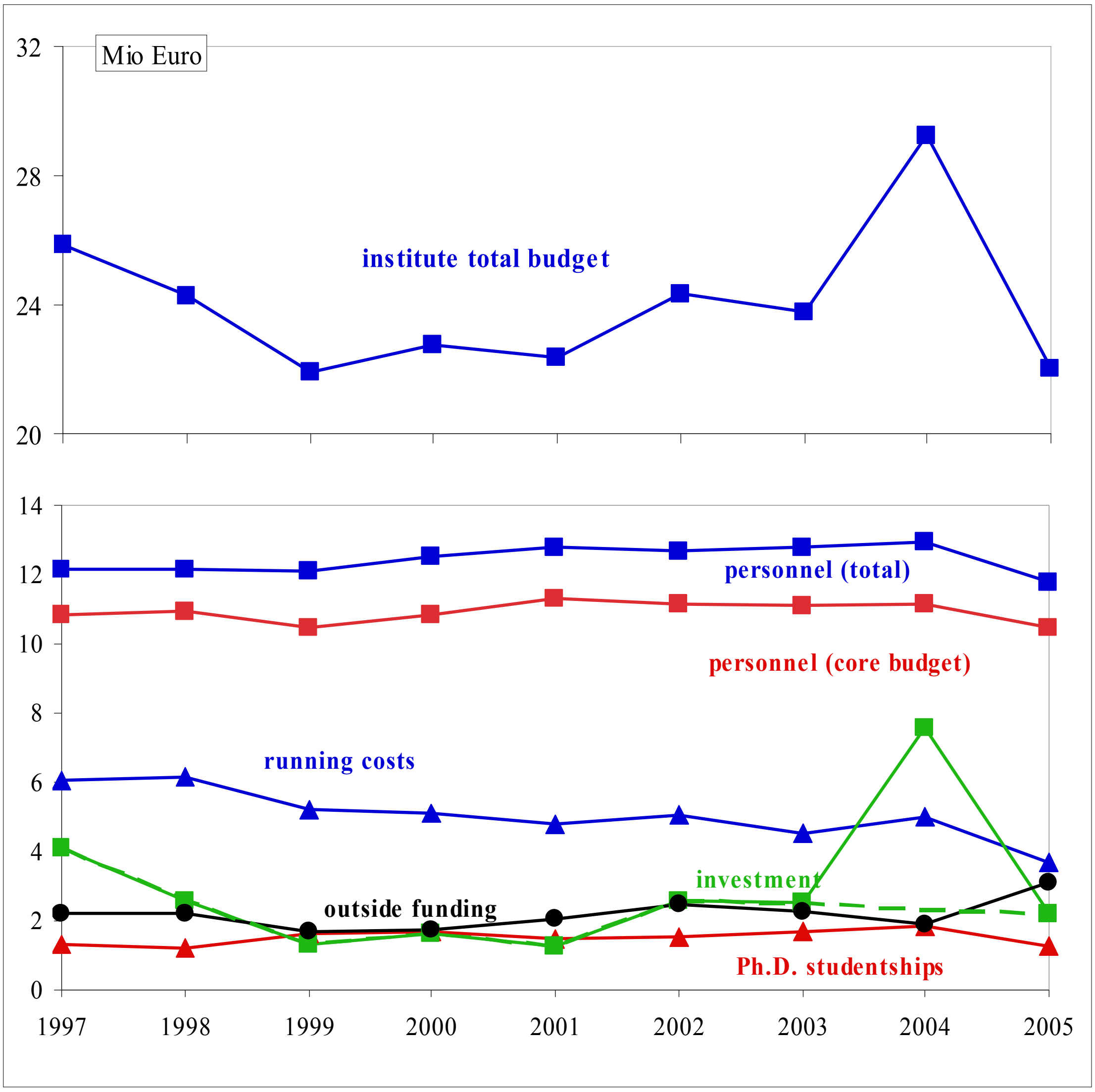
In the report for 2003 the sudden and severe budget cuts which hit the entire Max Planck Society were mentioned, with a reduction by 6 % compared to 2002. In view of the uncertainty regarding the future development for the federal science budget, the General Administration decided to adhere to a restrictive financial policy, with further severe reductions planned for the coming years 2004 through 2010. This meant, among other things, that more than 20 departments throughout the Society had to be closed down, and large budget cuts were imposed on the institutes. Fortunately, the Fritz Haber Institute managed to retain the Department of Physical Chemistry, since we were able to accommodate the budget cuts by reducing personnel. Then, in 2004, in a reversal of its previous decision, the Federal Government decided to raise the Science Budget by 3 %, thus permitting the Max Planck Society to remove some of the previously imposed constraints, although a permanent reduction of the funds for the CPT-Section of 1.7 % remains in place.

In 2004 a new method of financial planning was introduced in the Max Planck Society. The institutes now receive an annual and fixed core budget, which can be increased in step with price rises and salary increases. Any additional financial requirements such as special investments, expenditure for buildings etc. have to be separately applied for. The amount of this core budget is approximately the same as the institute's budget over the last ten years, which has remained constant throughout this period in spite of the general increase in cost of equipment and salaries.

The institute was successful in applying for scientific investments in a special program launched by the General Administration in 2004. Moreover, a new "Independent Junior Research Group" was installed, funded entirely from the institute's budget. All in all it is fair to say that, through diligent planning and savings, the institute has gone through the period of financial uncertainty without major difficulties, and looks forward to a period of funding stability.

The budget data in the figure reflect the trends described above: Overall stability! The investment shows variations due to the installment of new departments in 1996 (CP) and in 2002 (MP) as well as the special program launched by the General Administration. The external funds have increased but all other parts of the budget are near by constant. This also applies to the investment budget when taking into account by the funds due to the above-mentioned additional sources (see the dashed line from 2003 to 2005). The funds will slightly decline due to the implementation of a fixed core budget, and there is an additional effect, in particular on the running costs originating from the reduction of the PC departmental budget due to the vacancy of the directorship in 2005.

FHI Budget



Development of the Budget of the Fritz Haber Institute over the last 8 years. The total personnel is the sum of personnel financed from the core budget and the PhD studentships of the MPG. Running costs and investment refer to the budget provided by the MPG. Outside funding represents all externally awarded funds including studentships, post-doctoral positions, investment and running costs.

The renovation of the institute's buildings, some of which are more than 90 years old, as addressed in the previous report to the Fachbeirat, is going according to plan. The Department of Inorganic Chemistry will move to an outside location for about 15 months while building F is completely refurbished in line with the modern standards of a chemistry laboratory. This means that planning and preparations for the other buildings can continue. The plan, which is put into practice, calls for a renovation of building F until the end of 2006. Building L, the "Ernst-Ruska-Bau", will house all central workshop facilities, and its refurbishment will be complete in mid-2007. Once the mechanical workshop has moved out of its present location in the basement of building D, this area will be converted into laboratory space for the Department of Molecular Physics – completion is expected at the end of 2007. Finally, planning for the renovation of building A, including a new roof (to replace the makeshift one put up after World War II) will start once the new director's requirements are clear. Completion of this building is expected in mid-2008. Eventually, this will permit a modest renovation and consolidation of the offices of the institute's administration, which are currently strewn across the campus, into buildings G and H. This plan has been carefully checked for overlaps and collisions, and has been accepted by the General Administration of the Max Planck Society.

As in previous years, we proudly report on awards and honours bestowed on members of the institute:

Alexander Badinski	– Heraeus Award for outstanding study achievements, 2005
Joost Bakker	– Otto Hahn Medal for young scientists, 2005
Gerhard Ertl	– Linus Pauling Lecture, California Institute of Technology, Pasadena, 2005
	– Ångström Lecture, University of Uppsala, 2005
	– Faraday Lectureship, Royal Society of Chemistry
	– Guptil Lecture, Dalhousie University, Halifax
	– Baker Lectureship, Cornell University

Hans-Joachim Freund	– Foreign Member of the Academia Brasileira de Ciencias (since 2004) – Malcolm Dole Lecturer, Northwestern University, USA, 2005 – Langmuir Lecturer, 230th ACS Meeting, USA 2005 – Centenary Lecturer, Royal Society of Chemistry – Member of the European Research Council (ERC)
Tobias Hertel	– Habilitation, Freie Universität Berlin, 2003
Friederike Jentoft	– Habilitation, Humboldt-Universität zu Berlin, 2005
Guido Ketteler	– Otto Hahn Medal for young scientists, 2004
Thorsten Klüner	– Habilitation, Humboldt-Universität zu Berlin, 2004
Gerard Meijer	– Honorary Professor, Freie Universität Berlin, 2004 – Corresponding Member of the Royal Dutch Academy of Arts and Sciences, 2004 – Debye Lecture 2004, University of Utrecht, The Netherlands
Angelos Michaelides	– European Young Investigator (EURYI) Award, 2005
Thorsten Ressler	– Habilitation, Technische Universität Berlin, 2004
Karsten Reuter	– Habilitation, Freie Universität Berlin, 2005
Patrick Rinke	– 3rd Prize for excellent thesis, IOP Computational Physics Group, U.K., 2003
Günther Rupprechter	– Jochen Block Award 2005 (awarded by the catalysis section of DECHEMA)
Matthias Scheffler	– Max Born Medal and Prize; jointly awarded by the Institute of Physics (IOP), Great Britain, and the German Physical Society (DPG), 2004 – "Visiting Professor" at the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences, Dalian, P.R. China, 2004 – Xun Lee Lecture Award; awarded by the Institute of

	Metal Research (IMR), Chinese Academy of Sciences (CAS), Shenyang, P.R. China, 2004 – "Distinguished Visiting Professor for Computational Material Science and Engineering" at UC Santa Barbara, jointly appointed by the College of Engineering and the College of Mathematical, Life, and Physical Sciences, 2004
Robert Schlögl	– Tetelman Fellow, Yale University, USA, 2004
Melanie Schnell	– Academy Fellowship (awarded by the Berlin-Brandenburg Academy of Sciences) – Liebig-Fellowship for 3 years (starting October 2005, awarded by the „Fonds der Chemischen Industrie")
Rolf Schuster	German Founders Prize of the Startup Initiative, in the category „concept", 2nd prize, to the ECMTEC GmbH (together with Thomas Gmelin, spin-off company of two research institutions, the Fritz Haber Institute of the Max Planck Society and the chair for Micro, Miniature and Chronometric Techniques (IZFM) of the Stuttgart University)
Phil Woodruff	– Surface Structure Prize of the International Conference on the Structure of Solid Surfaces Series, 2005

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

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

Aidan Doyle	– Senior Lecturer in Physical Chemistry, Manchester Metropolitan University, Manchester, UK, 2004
Bothina Hamad	– Assistant Professor in the Department of Physics, University of Jordan, Amman, Jordan, 2005

Tobias Hertel – Associate Professor in the Department of Physics and Astronomy at the Vanderbilt University, Nashville, Tennessee, USA, 2004
Peter Kratzer – has been offered a professorship (W2) at the University of Duisburg-Essen, 2005
Jörg Libuda – offer as Professor (W2) for Physical Chemistry at University of Erlangen-Nürnberg, 2005
Randall Meyer – Assistant Professor, University of Illinois, USA 2005
Thorsten Ressler – offer as Professor (W3) at the Technische Universität Berlin, 2005
Karsten Reuter – Head of an Independent Junior Research Group, Theory Department, Fritz Haber Institute, 2005
Günther Rupprechter – offer as Professor (Chair) for Physical Chemistry at the Technische Universität Wien, 2005
Rolf Schuster – became Professor (C3) for Physical Chemistry at the Technische Universität Darmstadt, 2004

I will finish this report by briefly describing the activities of three service groups. Other service groups, in particular our competent and supportive administration, our joint network center (GNZ), the Service Group for Electronics (E-Lab), the Public Relations Group, the gardeners and many more deserved to be mentioned (and praised) as well. However, this would make the report to extensive.

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

Based on the data network infrastructure, provided by the Joint Network Center (GNZ), the PP&B group (4 employees, one trainee) is responsible for the installation and maintenance of the desktop systems (including laptops), workstations, telephone system and building facility management 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). Some remarkable examples from the last two years are the power controlling of the SMART, a high-speed/resolution camera system, calorimeter control system and a new data acquisition system. The group resides in Building S and runs an image processing lab and a newly installed video conference system. Several server systems perform services for data storage, mail, web, printing, number crunching and databases for different document archives. At the end of 2004 a new storage system for the centralized file services with a capacity of 10 TBytes has been installed. This system is based on a specialized Storage Area Network (FibreChannel) and provides a highly available service through different mechanism like RAID and Remote Volume Mirroring. The system can be easily expanded on demand. A Computer Cluster (50 Opteron CPU) was built up and is supervised by the PP&B group. A new computer server has been ordered and should be installed and running at the beginning of October 2005.

Mechanical Workshops

The mechanical workshop comprises the precision mechanical workshop (14 employees, 1 apprentice), the carpentry (2 employees) and the locksmith's shop (2 employees). As of June 1st of this year, Horst Schwäricke, who has many years of industrial experience, has been appointed as head of the mechanical workshop. In this function he is the successor of Peter Tesky, who has gone into early retirement after having served the FHI for over 40 years. In the precision mechanical workshop, highly specialized mechanical components are produced, always in close interaction with the scientists and design engineers working in one of the four experimental departments. During the last two years, a significant fraction of the overall time has been spent on constructing scientific equipment for the newly started Molecular Physics department. Production of many of the complicatedly shaped components that have recently been produced, such as, for instance, highly polished stainless steel electrodes that are used in molecule traps, would have been impossible without the newly installed (in 2003) three-and-a-half axis CNC milling machine. Also the spark erosion machine, newly purchased earlier this year, has already been efficiently used. The carpenters have been occupied by refurnishing the various offices, in particular in the renovated buildings C and D. A specialty of the locksmith's shop is the maintenance and servicing of not only rotary pumps but also of turbo molecular pumps, which are used in scientific experiments throughout the institute.

The different groups that belong to the mechanical workshop are at present still scattered over different buildings on the campus. In the coming two years, all these groups will move together into the, slightly expanded and reinforced, lower levels of building L, which will from then on serve as the main building for the mechanical workshops and electronics service group.

Library

The library collects specialist literature covering the research fields of the institute. The Library has about 15,000 monographs, 28,000 journal volumes and 100 currently subscribed print journals in stock. In addition, the Library offers about 3,000 currently subscribed electronic journals, most of them based on central MPG agreements.

The Library is constantly monitoring the publication market, especially with regard to new trends, e.g. Open Access. The MPG is practicing open access to scientific results as laid down in the "Berlin Declaration on Open Access to the Knowledge in the Sciences and Humanities" in two ways: publication in open access journals and institutional self-archiving on the eDoc Server. The Library assists the scientists by offering seminars and regular training courses on how to make best use of the eDoc Server.

The FHI Library has been testing the eDoc Server System thoroughly since its implementation and has been accompanying and promoting the further development in close cooperation with the ZIM.

There are ongoing developments of the system. Presently the Library is preparing tools to allow for downloading statistics, use of alert services and generating dynamic websites.

Furthermore, the FHI Library participates in the development and maintenance of the Max Planck Virtual Library (VLib). This system is a portal to various information resources available to members and guests of the Max Planck Society. To support that system the Library is giving feedback to VLib by intensely testing the user interface and integrating library catalogs that run with the Library system Allegro. In addition, the Library prepares manuals and offer seminars for colleagues ("train the trainer") and for

FHI scientists. Due to frequent changes of resource locations VLib requires continuous maintenance to guarantee up-to-date information for the users.

The range of electronic services of the FHI Library includes various database descriptions, access terms and conditions for e-journals as well as catalogues.

The FHI Library cooperates with external institutions such as the Friedrich Althoff consortium of scientific libraries for an optimized use of resources. Within this consortium the FHI Library is playing a very active part. The classical services as interlibrary loan service, acquisition of books and other information material, literature searches and reader service are also available. Therefore, the qualified library personnel will remain indispensable also in the new age of electronic „libraries without walls“. The acceptance of electronic media is very high within the FHI due to our constant efforts and the regular training of the users.

We would like to thank the General Administration and in particular the Presidium of the Max Planck Society for a trustful and constructive collaboration. We are all aware of the amount of work the Fachbeirat has to accomplish during its visit. The young students as well as the post doctoral visitors, the staff scientists, and clearly the directors are most grateful to all members of the Fachbeirat and we are looking forward to interesting scientific discussions. Allow me to note at the end that more information on the institute, in particular its history, can be found on its web page http://www.fhi-berlin.mpg.de

Berlin-Dahlem, September 23, 2005

Hajo Freund

Executive Director

2004-2005

International Max Planck Research School
Complex Surfaces in Materials Science

Spokesperson:

Hans-Joachim Freund

Coordinator:

Jörg Libuda until 31.07.2005

Thomas Risse

Members:

Klaus Christmann, FU
Hans-Joachim Freund, FHI
Paul Fumagalli, FU
Karsten Horn, FHI
Gerard Meijer, FHI
Horst Niehus, HU
Klaus Rademann, HU
Karl-Heinz Rieder, FU
Joachim Sauer, HU
Matthias Scheffler, FHI
Robert Schlögl, FHI
Helmut Winter, HU
Martin Wolf, FU

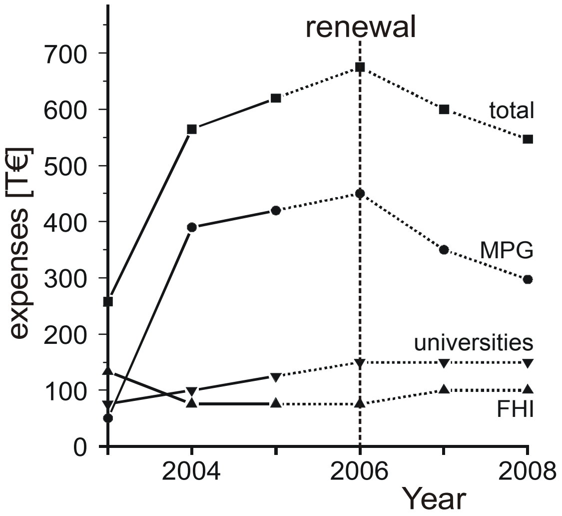
FU: Freie Universität Berlin; HU: Humboldt-Universität zu Berlin; FHI: Fritz-Haber-Institut

PhD-Student Members:

Micol Alemani, *Italy*
Hadj M. Benia,. *Algeria*
Marta Borasio, *Italy*
Veronika Brázdová, *Czech Republic*
Jan Hugo Dil, *Netherlands*
Katrin Domke, *Germany*
Christoph Freysoldt, *Germany*
Sébastien Guimond, *Canada*
Mahboubeh Hortamani, *Iran*
Sarp Kaya, *Turkey*
Ki Hyun Kim, *Korea*
Patrick Kirchmann, *Germany*
Tanya Kumanova Todorova, *Romania*
Mathias Laurin, *France*
Bo Li, *VR China*
Xinzheng Li, *VR China*
Rhys Lloyd, *UK*
Junling Lu, *VR China*
Helder Marchetto, *Italy*
Pawel Rejmak, *Poland*
Yuriy Romanyshyn, *Ukraine*
Adnan Sarfraz, *Pakistan*
Philipp Schmidt, *Germany*
Andreas Schüller, *Germany*
Julia Stähler, *Germany*
Konrad von Volkmann, *Germany*
Yongsheng Zhang, *VR China*

General Remarks:

The International Max Planck Research School (IMPRS) "Complex Surfaces in Material Sciences" (http://www.imprs-cs.mpg.de) aims at combining the expertise of several research groups, to create a unique opportunity in terms of cutting-edge research and a thorough training in the methods, concepts, and theoretical basis of the physics and chemistry of surfaces. The school started January 15th, 2003 with ten participating groups from the Freie Universität Berlin (Christmann, Fumagalli, Rieder), the Humboldt-Universität zu Berlin (Niehus, Sauer, Winter) and the Fritz Haber Institute (Freund, Horn, Scheffler, Schlögl) covering a broad range of experimental as well as theoretical expertise. By now this number has increased to 13 (Meijer, Rademann, Wolf) indicating that this program is very attractive. Even though the financial support of the Max Planck Society was strongly reduced in the first year due to the financial situation of the Max Planck Society, the school grew almost at its proposed rate. At the moment, the school has 27 students, 19 being financed by funds from the IMPRS. This is well within the range of 20-30 participants proposed at the beginning. One of the goals for all International Max Planck Research Schools is to attract foreign students to participate in these schools. In accordance with this guideline, currently 74 % of all participants and 84 % of those being financed by the IMPRS are foreign students from a broad range of 15 nationalities. The IMPRS is currently funded until the end of 2008. It may be renewed after positive evaluation which will take place by the end of 2006.



Budget of the IMPRS 2003 - 2008

The Figure presented to the left shows the total budget of the IMPRS as well as the individual contributions of the different participating organizations for the years 2003-2005. In addition, the expected evolution for the forthcoming years is drawn. The maximum of the budget in 2006 is due to the fact that the number of fellowships (nominal duration of 3 years) offered by the school, reaches its maximum after 4 of the 6 years and will decrease for the last two years. In case the IMPRS will be renewed after a positive evaluation, the budget should increase again beyond 2008.

The topics of research covered by the IMPRS encompasses a wide range of complex surfaces and interfaces. Surface science has evolved, over the last two decades, from a predominance of studies on highly idealized, single-phase, single-crystalline materials, to investigations of complex multi-phase systems such as nanoparticles, multiply layered systems, and combinations between different material classes such as metal-oxide structures. An excellent example of research in this field relates to chemical processes on surfaces. On oxide surfaces, elementary processes in heterogeneous catalysis are studied, while an understanding of reactions on semiconductors is important for a wide range of applications. Surfaces of other materials which so far have not been widely studied in surface science because of their complexity, such as nitrides and carbides, are also important from a technological point of view and will be investigated. Finally, magnetic films and multilayers are exciting topics in view of their emerging use in magnetic data storage technology.

The importance of turning towards a fundamental understanding of the properties of highly complex surfaces is highlighted, among other things, by an ever-increasing appreciation of the experimental methods and results of basic research in surface analysis by industrial scientists and engineers. Many of these techniques, such as atomic force microscopy, X-ray photoemission, and optical methods are nowadays routinely used in the industrial environment. This overlap of interest in surface processes is reflected in the high demand for well-trained scientific personnel with an excellent command of the concepts and techniques of modern surface science.

To accomplish the goals of the school, namely doing cutting-edge research and a thorough training in the methods, concepts, and theoretical basis of the physics and chemistry of surfaces, a variety of activities have been established. While the first issue is well covered by the individual PhD projects, the latter are addressed by a variety of teaching efforts. First, block courses on basic as well as advanced topics taking place every semester (for typical content see attached schedules). Since the school aims at recruiting chemists and physicists alike, the basic courses pay particular attention to the typical language barriers which exist between these fields, thus, providing a common experimental and theoretical knowledge base for more advanced topics. The block courses are expanded 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 is played by the seminar program as well as a visiting researcher's program. The students are involved in the selection of the speakers at the seminar. Postdoctoral scientists are important in guiding the students, and they are also involved in the teaching and advising efforts. It is particularly important to make sure that there is a lively exchange of ideas, and an open atmosphere of discussion across the various groups involved. To establish a suitable forum for this to happen, regular small workshops are organized, where 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. Since most of the students will later be working in industry, excursions to industry (e.g. BASF) offer the possibility to get acquainted with the industrial perspective of surface problems and the possibility to make contacts which may help in their future career.

Nowadays, so-called soft skills play an increasing role for industry when recruiting scientists. Among others this includes communication skills, proper time management, or the ability to efficiently manage a project. The school offers a variety of courses to improve these skills. These include e.g. courses on scientific presentation or scientific writing. Since a large fraction of the participants are foreign students with usually little knowledge of the German language, the school offers language courses to improve their knowledge of the German language which is important not only for their scientific work at their groups but also for the every day live in Germany.

PhD-Projects within the IMPRS:

Benia, Hadj M.: Investigation of optical and electronic properties of pure and chemically modified metal clusters.
IMPRS, Algeria, FHI/HU: Prof. Freund/Prof. Winter

Borasio, Marta: Infrared spectroscopy of model catalyst systems under ambient conditions.
IMPRS, Italy, FHI/FU: Prof. Freund/Prof. Christmann

Dil, Jan Hugo: Quantum Site Effects in thin metal films on semiconductors.
IMPRS, Netherlands, FHI/FU: Prof. Horn/Prof. Fumagalli

Guimond, Sébastien: Adsorption properties of thin vanadium oxide films.
IMPRS, Canada, FHI/HU: Prof. Freund/Prof. Rademann

Kaya, Sarp: STM, IR and XPS Investigations on deposited particles.
IMPRS, Turkey, FHI/HU: Prof. Freund/Prof. Rademann

Kim, Ki Hyun: Photo-induced processes of molecules on metal nanoparticles.
IMPRS, Korea, FHI/FU: Prof. Freund/Prof. Wolf

Kumanova Todorova, Tanya: Structure, stability and reactivity of vanadia supported catalysts.
IMPRS, Romania, HU: Prof. Sauer

Laurin, Mathias: Molecular beam experiments on model catalysts.
IMPRS, France, FHI/FU: Prof. Freund/Prof. Christmann

Li, Bo: Density functional theory studies of water adsorption at surfaces.
IMPRS, VR China, TU/FHI: Prof. Schöll/Prof. Scheffler

Li, Xinzheng: All-electron GW approximation based on FLAPW with the application to Transition Metal Oxides.
IMPRS, VR China,FHI/FU: Prof. Scheffler/Prof. Gross

Lloyd, Rhys: Investigations into Sulfated Zirconia Catalysis Using Model Thin Films.
IMPRS, United Kingdom, FHI/FU:Schlögl/Christmann

Lu, Junling: Morphologic and spectroscopic characterization of model catalysts.
IMPRS, VR China, FHI: Freund

Rejmak, Pawel: Transition Metal Ions Inside Zeolithes And Their Interactions With Small Molecules Using QM/MM Methods.
IMPRS, Poland/HU: Broclawik/Sauer

Romanyshyn, Yuriy: Reactivity studies of ordered vanadium oxide surfaces.
IMPRS, Ukraine, FHI/HU: Freund/Manzke

Sarfraz, Adnan: Deposition of Amino Acids and Derivates on surfaces.
IMPRS, Pakistan, HU: Rademann

Schmidt, Philipp: Electronic and geometric structure of molecular aggregates on vicinal single crystal surfaces.
IMPRS, Germany, FHI/FU: Horn

Schüller, Andreas: Investigation of interaction processes during grazing incidence ion scattering.
IMPRS, Germany, HU/FHI: Winter/Freund

von Volkmann, Konrad: Steering of photoinduced surface reactions using optimized femto second laser pulses.
IMPRS, Germany, FU/Frischkorn/Wolf

Zhang, Yongsheng: Oxide formation and oxidation catalysis at transition metal surface.
IMPRS, VR China, FHI/FU: Scheffler/Gross

Alemani, Micol: Manipulation of single organic molecules induced with a low temperature STM.
FU, Italy, FU: AG:Rieder (Moresco)/Horn

Brázdová, Veronika: Plane-Wave Density Functional Calculations on Transition Metal Oxides.
HU, Czech Republic, HU: Nolting/Sauer

Domke, Katrin: Near field enhanced Raman microscopy at well-defined surfaces.
FHI, Germany, FHI/FU: Ertl/Christmann

Freysoldt, Christoph: Theoretical characterization of Metal-oxides using GW-calculations.
FHI, Germany, FHI/FU: Scheffler/Gross

Hortamani, Mahboubeh: Adsorption, Diffusion, Growth and Spin Polarisation on Manganes on Si (001) and GaAs(001).
FHI, Iran, FHI/FU: Scheffler/Fumagalli

Kirchmann, Patrick: Investigation of two-dimensional metal films and one-dimensional nano-wires on semiconductor surfaces.
FU, Germany, FU: Wolf/Horn

Marchetto, Helder: Investigations on deposited metal clusters on oxide surfaces with high resolution photoelectron spectromicroscopy.
FHI, Italy, FU/FHI: Rieder/Freund

Stähler, Julia: Electron transfer and solvation dynamics of polar adsorbates using time resolved photoemission.
FU, Germany, FU: Wolf/Schwendtner

Schedule of a block course focussing on an advanced topic: Semiconductor surfaces.

	9:30 – 11:00	11:30 – 13:00
Tuesday, 29/03/05	K. Horn: Semiconductor Surfaces and Interfaces	P. Kratzer: Theory of Semiconductor Surfaces
Wednesday, 30/03/05	P. Kratzer: Theory of Semiconductor Surfaces	K. Horn: Semiconductor Surfaces and Interfaces
Thursday, 31/03/05	K. Horn: Semiconductor Surfaces and Interfaces	H. Kuhlenbeck: Oxide Surfaces
Friday, 01/04/05	H. Kuhlenbeck: Oxide Surfaces	T. Kampen: Organic Semiconductors and Electronic Transport
Monday, 04/04/05	P. Fumagalli: Optical Properties of Semiconductors	T. Kampen: Organic Semiconductors and Electronic Transport
Tuesday, 05/04/05	M. Wolf: Laser Spectroscopy at Surfaces / Ultrafast Dynamics	P. Fumagalli: Optical Properties of Semiconductors
Wednesday, 06/04/05	J. Libuda: Kinetics and Dynamics at Surfaces	M. Wolf: Laser Spectroscopy at Surfaces / Ultrafast Dynamics
Thursday, 07/04/05	J. Sauer: Zeolites	J. Libuda: Kinetics and Dynamics at Surfaces

Typical schedules of basic block courses:

	9:30 – 11:00	11:30 – 13:00
Tuesday, 02/03/04	H. Winter: Studies of Properties of Surfaces with Ion Beams, Part I	K. Christmann: Adsorption at Surfaces I - Thermodynamics
Wednesday, 03/03/04	H. Winter: Studies of Properties of Surfaces with Ion Beams, Part II	K. Christmann: Adsorption at Surfaces II - Kinetics
Thursday, 04/03/04	R. Schlögl: Reactions at Surfaces, Part I	R. Schlögl: Reactions at Surfaces, Part II
Friday, 05/03/04	P. Fumagalli: Introduction to Magnetism	P. Fumagalli: Magnetism of Thin Films
Monday, 15/03/04	G. Rupprechter: Optical Spectroscopy at Surfaces, Part I	J. Carlsson: Theoretical Methods for Surface Science, Part I
Tuesday, 16/03/04	G. Rupprechter: Optical Spectroscopy at Surfaces, Part II	J. Carlsson: Theoretical Methods for Surface Science, Part II
Wednesday, 17/03/04	W. Theis: Diffraction Methods in Surface Science	K. Horn: Electronic Structure of Surfaces - Experimental Studies I
Thursday, 18/03/04	F. Moresco: Introduction to Scanning Probe Microscopy	K. Horn: Electronic Structure of Surfaces - Experimental Studies II

	9:30 – 11:00	11:30 – 13:00
Tuesday, 05/10/04	J. Sauer: A Chemist's View of Electronic Structure	K. Hermann: Surface Crystallography
Wednesday, 06/10/04	J. Sauer: A Chemist's View of Electronic Structure	K. Hermann: Surface Crystallography
Thursday, 07/10/04	K. Hermann: Surface Crystallography	K.-H. Rieder: Surface Structure - Experimental Methods
Friday, 08/10/04	K.-H. Rieder: Surface Structure - Experimental Methods	K. Hermann: Surface Crystallography
Tuesday, 12/10/04	H.-J. Freund: Introduction to Surface Spectroscopies	K. Rademann: Electronic Properties of Nanoparticles
Wednesday, 13/10/04	K. Rademann: Electronic Properties of Nanoparticles	H.-J. Freund: Introduction to Surface Spectroscopies
Thursday, 14/10/04	J. Libuda: Kinetics and Dynamics at Surfaces	T. Risse: Magnetic Properties of Adsorbates
Friday, 15/10/04	T. Risse: Magnetic Properties of Adsorbates	J. Libuda: Kinetics and Dynamics at Surfaces

Lectures courses 2003 - 2005:

SS 03:

„Selected problems of magneto optics and scanning probe microscopy“
(Prof. Dr. P. Fumagalli)
„Experimental and theoretical aspects of surface physics and chemistry“
(Prof. Dr. K. Christmann)
„Solids and Surfaces Tutorial“
(Prof. Dr. K. Christmann)

WS 03/04:

„Selected problems of magneto optics and scanning probe microscopy“
(Prof. Dr. P. Fumagalli)
„Structural and Electronic Properties of Metal Oxides and their Surfaces: Theoretical Aspects“
(Prof. Dr. K. Hermann)
„Special Problems on Surface Physics“
(Prof. Dr. K.-H. Rieder)
„Experimental techniques of Surface Science – and how a theorist understands them …“
(Dr. K. Reuter)
„Modern Methods in Heterogeneous Catalysis Research“
(Prof. Dr. R. Schlögl and Dr. F. Jentoft)
„Structural and Electronic Properties of Metal Oxides and their Surfaces: Theoretical Aspects“
(Prof. Dr. K. Hermann)

SS 04:

„Selected experimental and theoretical aspects surface physics and chemistry“
(Prof. Dr. K. Christmann)
„Symmetry in Chemistry, Physics, and Materials Science“
(Priv.-Doz. Dr. J. Libuda)
„Selected problems of magneto optics and scanning probe microscopy“
(Prof. Dr. P. Fumagalli)
„Metal Thin Films: Structure, Magnetism, and Electronic Properties“
(Prof. Dr. K.-H. Rieder)
„Special Problems on Surface Physics“
(Prof. Dr. K.-H. Rieder)
Theoretical Materials Science
(Prof. Dr. M. Scheffler and Dr. K. Reuter)

WS 04/05:

„Experimental and theoretical aspects of surface physics“
(Prof. Dr. K. Christmann)
„Selected problems of magneto optics and scanning probe microscopy“
(Prof, Dr. P. Fumagalli)
„Group Theory of Surfaces and Clusters“

(Prof. Dr. K. Hermann)
„Experimental Methods in Surface Physics“
(Prof. Dr. H. Niehus)
„Modern Methods in Heterogeneous Catalysis Research“
(Prof. Dr. R. Schlögl and Dr. F. Jentoft)
„Ultrafast Dynamics at Interfaces“
(Prof. Dr. M. Wolf)
Theoretical Materials Science (Part II)
(Prof. Dr. M. Scheffler and Dr. K. Reuter)

SS 05:

„Structure and chemical properties of solid state surfaces“
(Prof. Dr. K. Christmann)
„Selected problems of magneto optics and scanning probe microscopy“
(Prof. Dr. P. Fumagalli)
“Introduction to Group Theory with Applications in Molecular and Solid State Physics”
(Prof. Dr. K. Horn)
„Molecular Beam Methods in Surface Physics“
(Prof. Dr. K.-H. Rieder)
„Computational Methods in Theoretical Chemistry“
(Prof. Dr. J. Sauer)
"Theoretical Solid State Physics"
(Prof. Dr. M. Scheffler)
„Ultrafast Dynamics at Interfaces“
(Prof. Dr. M. Wolf)

Legend:

A = Departments
B = Scientific Personnel
* Group Manager
C = General Facilities

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CP Prof. Freund
MP Prof. Meijer
PC Prof. Meijer (acting director)
TH Prof. Scheffler

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Department of Inorganic Chemistry

Director: Robert Schlögl

Staff scientists:

Wilhelmina Busser
Friederike Jentoft (Habilitation)
Axel Knop-Gericke
Bernd Kubias
Wolfgang Ranke
Thorsten Ressler (Habilitation) until 2005
Olaf Timpe (FHI Safety Officer)
Sabine Wrabetz

Dangsheng Su Service-Group EM (Electron Microscopy)
Hermann Sauer Service-Group EM (Electron Microscopy)

Elmar Zeitler (Emeritus)
Joachim Urban (Habilitation) until 4/30/2005

Guest scientists, staying for at least six months:

Xiaowei Chen
Qiang Fu
Weixin Huang until 12/31/2004
Igor Kasatkin
Kirill Kovnir
Vinit Makwana
Alexey Pestryakov until 09/30/2004
Jean-Phillippe Tessonier
Genka Tzolova-Müller
Elaine Vass
Tzvetomir Valeriev Venkov
Sameer Vijay until 6/30/2005
Jakob B. Wagner until 7/31/2005
Spiros Zafeiratos
Zaoli Zhang

Scientists (temporary) paid from external funds:

Marc Armbrüster
Andreas Blume
Juan José Delgado Jaén
Michael Haevecker
Christian Hess
Rolf Jentoft
Katrin Pelzer
Detre Teschner
Annette Trunschke
Di Wang
Marc Willinger

Graduate Students: 16 (9 from external funds)
\+ 1 IMPRS Student
+10 Students from University of Malaya, Kuala Lumpur, since end of 2003 (at present 3)

Technicians: 9 (+ 3 Service Group EM)

Trainees: 3

Recent Developments in the Department of Inorganic Chemistry

Director: R. Schlögl

1. General Development

1.1. Introduction

After the last meeting of the *Beirat* the Department set out to restructure its scientific organization with the aim of introducing a substantial synthetic effort for heterogeneous catalysts on the expense of its model activities based on PVD systems prominently represented by the CP Department. The Department saw a productive period (publications: 2003:64, 2004:71, 2005:76) despite the many uncertainties about its future location and the substantial administrative burden of its director serving as chairman for the CPT section. A reduction in the number of staff position had to be compensated and the introduction of a service group "electron microscopy" was consolidated. The focussing of activities and the very committed and loyal action of the co-workers in the Department resulted in the scientific productivity described in section 2 of this report. The continuous and long-term oriented efforts in the research projects allows formulating a research hypothesis described in section 3.

1.2. Personnel

The consolidation program of MPG from 2003 resulted in a reduction of one staff position. The number of technical positions could be kept constant and is higher than the MPG average due to the operation of large scale equipment with partly service character. The re-orientation into synthetic chemistry would require further increase technical personnel to support the synthetic laboratory work.

The following changes occurred amongst the scientists:

Dr. T. Ressler completed his Habilitation and obtained a W3 position at TU Berlin
Dr. F. Jentoft completed her Habilitation.
Dr. D. Niemeyer left for a management position in industry
Dr. A. Trunschke joined as group leader
Prof. Urban retired
Dr. Ch. Hess joined as Emmy Nöther fellow of the DFG

Dr. W. Busser joined as co-worker delegated to Bochum university at our partner group

The trainee programme for “Chemielaboranten” had, despite of its high quality and success (A. Trunschke and J. Kröhnert) to be reduced due to the uncertainties of the building operation. It will be resumed after consolidation of the Department according to the then available personal resources for training.

1.3 Infrastructure

At the last meeting of the *Beirat* the Department was at the onset of major changes due to the expected renovation of its buildings. The Department was further asking for support for major investments into scientific infrastructure. The positive evaluation through the last *Beirat* was very supportive to receive the necessary funding for the building and infrastructural improvements. Due to a series of complications and the necessary deeper restructuring of the building as foreseen in the initial planning the renovation was delayed by two years with the severe consequence that the Department has to move again into its third provisional housing outside the campus and that the electron microscopy activities also have to move temporarily into another building on campus (the Department has to move 5 times within 11 years of its existence). It is expected that within the next two years the Department will move into its final location in building F. The positive consequences are a well-adapted infrastructure of the refurbished building F and the opportunity to consolidate the scientific operation of the Department as outlined in section 3 of this report.

The Department received major investment grants from MPG to build the dedicated beam line at BESSY II, to purchase one of the most advanced high resolution TEM instruments and to enter into the microscopy technologies of in-situ SEM and ultra-high resolution SEM. These activities are carried out in part as service for the new ENERCHEM research initiative allowing 4 MPI to participate into these methodical innovations.

The Department is active in methodical instrument development carried out to a significant extent by our engineers M Swoboda and S. Engelschalt. The Department suffers from the loss of J. Ihmann who passed away in 2004. The in-situ XPS-UV-RAMAN instrument, the MBMS instrument, the TEM-transfer reactor, several combined in-situ cells and advanced instruments for thermal analysis and processing are the fruits of these activities that are essential for the scientific projects. The competent support from the central workshops and from the PP&B division is emphasized as without theses assets none of the development projects could have been realized.

1.4. Scientific Organization

The scientific activities of the Department rest on the internal project structure and strategic collaborations in particular for the kinetic testing of catalysts. This structure was described in the last *Beirat* report and developed as planned. The Department is active in the following projects:

No.	Designation	Title	P.I.
1	Fe	Iron oxides for the dehydrogenation of ethylbenzene (EB)	W. Ranke
2	Zr	Sulfated zirconia for the isomerization of alkanes	F. C. Jentoft
3	V	VxOy catalysts for selective oxidation reactions	Ch. Hess
4	Mo	Mixed metal molybdates for C3 partial oxidation	A. Trunschke
5	Cu	Copper as catalyst for C1 chemistry and selective hydrogenations	Th. Ressler, N.N.
6	Pd	Pd nanoparticles in selective hydrogenation reactions	A. Knop-Gericke
7	C	Nanostructured carbon for EB dehydrogenation, C4 oxidation, and selective chemisorptions	D.S. Su

Project 1 will be completed in 2006. Exploratory projects triggered by external collaborations exist for the following topics:

- Ag for epoxidation of C2 and C3 (A. Knop-Gericke)
- MBMS for the search of radical-assisted heterogeneous reactions (K. Pelzer; F. Jentoft)

The selection of projects reflects that all reactions studied involve not only either C-H activation or C-O attachment but must be treated as an entanglement of elementary steps of activation and oxidation/reduction. In the desire to arrive at a generic understanding of the multiple functionality of any catalyst in hydrocarbon conversion it is essential to study a variety of processes and catalysts exhibiting various dominating activation profiles ranging from a “reduction catalyst” to an “oxidation catalyst”. The carbon system is studied as the ideal system combining both properties without being either typically oxidic or typically metallic. Carbon hence carries the active sites in chemical isolation from the completely inert matrix phase graphite and offers the great chance to analytically and theoretically get a handle on the structure and dynamics of active sites

The collaborations with external partners were consolidated by either institutionalization and/or by exchange of co-workers. The collaboration with the group of Prof. Sharifah Bee Abd Hamid in Kula Lumpur is of particular relevance as it assists the Department not only in kinetic testing but also in synthesis efforts and in services such as high throughput BET and elemental analysis. The cooperation has produced a breakthrough result in catalyst development in the Mo project. The MoVTe system was systematically optimized by a combination of automated synthesis, improved thermal treatment and careful optimization of conditions to bring about a phase-pure matrix phase. Figure 1 shows that the project reached the highest ever reported productivity in the technologically relevant direct synthesis of acrylic acid. It is significant that the academic collaboration was able to compete favorable with industrial large laboratories working for over 15 years on this reaction.

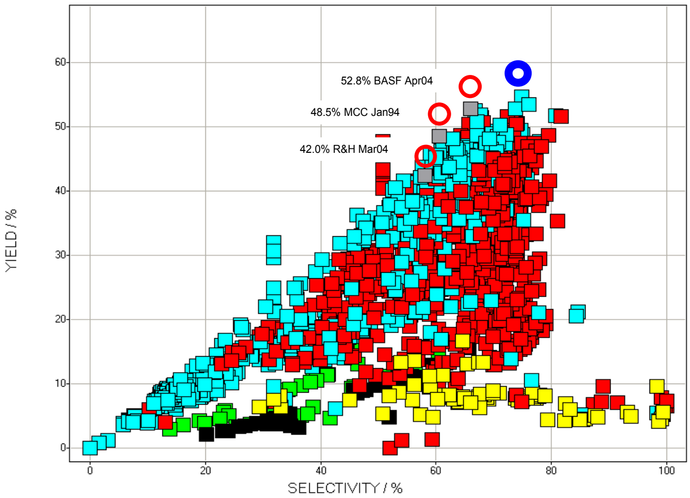

Fig. 1: Catalytic performance of FHI-NanoC MoVTe systems. The blue circle designates the best NanoC system.

The Department operates a large number of co-operations. Whereas one group of activities is of strategic relevance to the projects of the Department, it is the analytical competence of the Department rendering it attractive as partner in activities centered outside the projects. The table lists the strategic collaborations and their affiliation to the projects. The pure FHI-internal collaborations are not listed as they are well integrated in the work flows.

Collaborator	Funding	Type	Projects supported
ENERCHEM	MPG	Network	C
NanoC	Indu	Bilateral	Cu, Mo, V, C
SCAG	Indu	Network	Cu, C
ATHENA	Indu	Network	Pd, V
Nippon Kayaku	Indu	Bilateral	Mo
ELCASS	EU	Network	Zr, C
CANAPE	EU	Network	C
DFG SFB	Acad	Network	V
U Bochum	Acad/Indu	Network	Cu
TU Berlin	Acad	Bilateral	Cu, V
U New Mexico	Acad	Network	Cu
U Minnesota	Acad	Bilateral	Exploratory MBMS
CAS Dalian	Acad	Bilateral	Exploratory Ag
HAS Budapest	Acad	Bilateral	Pd

1.5. Other Activities

The Department has intensified its teaching activities. Besides participation in the IMPRS curriculum the integrated lecture course on catalysis (`http://w3.rz-berlin.mpg.de/cat`) organized by F.C. Jentoft has gained tradition and evolved into useful teaching tool for catalysis science inside the FHI and in the region a can be seen from the participation of students. The concepts of guest speakers, of a compact format (Friday mornings) and of cyclic variation of fundamental and advanced topics were successfully implemented.

The Department was very actively involved in the formulation and initial implementation of the MPG electronic dissemination strategy and its open access initiative. The MPG – BMBF project E-SCI-DOC contains many elements that were tested in the Department. A detailed account of the activities of the library acting as a key resource within the MPG for electronic media in science is given in the General Report.

In close collaboration with the CP Department it was possible to inaugurate an EU network of excellence in catalysis (IDECAT) in which the Department represents the MPG activities. It was further possible to incorporate catalysis as an independent funding topic in the coming framework 7 programme of the EU.

2. Scientific Progress

2.1 Iron oxide based model catalysts

Introduction

The production of styrene (St) from ethylbenzene (EB) is one of the ten most important industrial processes. The technical dehydrogenation of ethylbenzene to styrene is performed over potassium-promoted iron oxide catalysts in the presence of steam in excess. The reaction is endothermal (ΔH=129.4 kJ/mol) and is run between 870 and 930 K [1].In order to correlate the geometric and the electronic structure of the surfaces with their catalytic function, the study of model catalysts (preparation and characterization) and their catalytic properties (adsorption and catalysis) was continued during the last two years.

Iron oxide based model catalysts - preparation and characterization

Well-ordered iron oxide based model catalyst surfaces have been prepared in the form of thin epitaxial layers on Pt substrates and have been characterized concerning composition and structure [2,3]. In order to confirm surface structure models developed in our laboratory and elsewhere, ISS (ion scattering spectroscopy) was applied to study the surface termination (composition of the topmost layer) of very thin FeO and thick Fe_3O_4, α-Fe_2O_3 and KFe_xO_y films. It was confirmed that FeO(111) is O-terminated, Fe_3O_4(111) is Fe-terminated and α-Fe_2O_3(0001), oxidized at high pressure, is O-terminated. New is that KFe_xO_y films contain K and O but no Fe in the top layer. The only Fe containing surface is thus Fe_3O_4 which has low catalytic activity. We state that Fe is necessary but should not be in the top layer because it binds both EB and St too strongly. Since the catalytic properties had been found to be related to surface defects, it was tried to prepare model catalyst surfaces with atomic steps by growing them on a stepped Pt(9 11 11) substrate. While relatively well-defined steps form on very thin FeO(111) films, the growth of catalytically relevant thicker Fe_3O_4 films turned out to be independent of the topography of the substrate [4].

Reactivity studies - bridging the „pressure gap"

Studies of EB dehydrogenation under realistic conditions (850-900 K, p_{EB}=3.3 mbar, p_{H2O}=33 mbar) over the epitaxially grown model catalysts were continued using our single-crystal flow reactor with vacuum transfer from and to the UHV chamber [5]. The composition and surface order of the model catalysts was analysed before and after each conversion measurement. Concerning the catalytic mechanism, the results can be summarized as follows [6,7]:

- Most active is Fe^{3+} in Fe_2O_3 or KFe_xO_y.
- Fe_3O_4 is less active, probably because of a too strong bonding of EB and St.
- Deactivation of unpromoted catalysts occurs by reduction to Fe_3O_4 and by coking.
- Both can be prevented by admixture of some oxygen to the feed.
- K itself is not active but suppresses reduction and catalyses carbon removal.
- The stable phases $K_2Fe_{22}O_{34}$ and especially $KFeO_2$ are K-reservoir phases.
- Even coke has a non-negligible catalytic activity.
- "Steaming" (reaction in steam without EB) accelerates K-loss considerably.

In cooperation with A. Schüle and G. Kolios (university of Stuttgart), a microkinetic modeling of the deactivation behavior of unpromoted catalysts by reduction to Fe_3O_4 and by coking was performed. Energetic and kinetic data for adsorption and desorption of EB, St and water on the different phases were taken from earlier measurements under UHV conditions, the remaining parameters were adjusted to the initial reactivity of the pure components Fe_3O_4 and Fe_2O and the final reactivity corresponding to pure coke. Excellent agreement could be reached[8].

Interaction with atomic H

In order to close the catalytic cycle, hydrogen must be removed from the surface after dehydrogenation. One possible mechanism is that it reacts with lattice oxygen and desorbs as H_2O. The oxygen would then have to be replaced later in an oxidation step (Mars-Van-Krevelen mechanism). The observed reduction of Fe_2O_3 to Fe_3O_4 (or even to metallic Fe if no water is added to the feed) suggests that this might happen. However, the reduction rate is much slower than the rate of produced hydrogen [6,7] so that the possibility of H_2 desorption has also to be considered. Molecular H_2 does not interact with the model catalyst surfaces [9]. Therefore a high efficiency source for atomic H was constructed and applied. The interaction was studied by combining TDS, XPS and LEED. The observations[9,10] are seen as result of two sequential autocatalytically accelerated cycles of H_2O formation and desorption during exposure to atomic H with the formed oxygen vacancies being responsible for the autocatalytic mechanism. The results show that there exist (partially reduced) surface phases from which H_2 can directly be desorbed which may account for the surprising stability of the catalysts against reduction.

References
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[2] W. Weiss and W. Ranke, Progr Surf Sci **70** (2002) 1.
[3] W. Ranke and O. Shekhah, Recent Research Development in Surface Science **1** (2004) 75.
[4] G. Ketteler and W. Ranke, Journal of Vacuum Science & Technology A-Vacuum Surfaces and Films in press (2005).
[5] C. Kuhrs, M. Swoboda, and W. Weiss, Topics in Catalysis **15** (2001) 13.
[6] O. Shekhah, W. Ranke, A. Schüle, G. Kolios, and R. Schlögl, Angewandte Chemie, International Edition **42** (2003) 5760.
[7] O. Shekhah, W. Ranke, and R. Schlögl, Journal of Catalysis **225** (2004) 56.
[8] A. Schüle, O. Shekhah, W. Ranke, R. Schlögl, and G. Kolios, Journal of Catalysis **231** (2005) 172.
[9] W. Huang, W. Ranke, and R. Schlögl, Journal of Physical Chemistry B **109** (2005) 9202.
[10] W. Huang, W. Ranke, and R. Schlögl, Journal of the American Chemical Society , submitted (2005).

2.2. Zirconia in Hydrocarbon Activation

Introduction

Sulfated zirconia (SZ) materials are extraordinarily active for the skeletal isomerization of alkanes at low temperature [1]. Convincing explanations for this exceptional performance are still lacking, and the nature of the active sites—acidic, redox, or a combination—is still a matter of debate. In the past, we have overcome obstacles in the catalyst preparation[2,3] and in catalyst handling[4]. We also discovered that promoters such as iron or manganese, which increase the isomerization activity of SZ by 1–2 orders of magnitude[5,6] are incorporated into the zirconia lattice[7].

Structure and stability of sulfated zirconia catalysts

The significance of the incorporation of promoters has been investigated. Dissolved promoters stabilize the more active tetragonal phase of zirconia and lead to shrinkage of its unit cell. A model of the surrounding of the incorporated ions is being developed based on calculations (DFG-funded cooperation with Prof. S. Klokishner, Acad. Sciences of Moldova, Kishinev) and data from EPR, XAFS and optical spectroscopy. If lower valence cations such as Fe^{3+} or Mn^{3+} substitute for Zr^{4+}, oxygen vacancies must be generated for charge balance. Should lattice contraction or vacancies be responsible for the higher activity, then the action of most of the promoters reported in the literature could be explained. In order to check this hypothesis, catalysts have been prepared via co-precipitation, which yields a high degree of incorporation. Active materials were obtained. Presumably non-redox active ions, which are also incorporated and of a valence < +4, have been included, e.g. Ca and Mg are currently being tested as promoters. Two more interesting discoveries were made with respect to the zirconia bulk structure. HRTEM images (Fig. 2) reveal intra-crystalline voids in manganese promoted-sulfated zirconia. The size of these voids, typically a few nm, corresponds to the diameter as determined from N_2 adsorption isotherms. Hence, these voids seem to be part of the open mesopore system and may participate in reactions. Furthermore, a high-temperature stable sulfate species was identified. A very small fraction of the sulfate (≈2.5%) decomposes only at > 1000 K, and the decomposition goes along with a phase transition of tetragonal to monoclinic

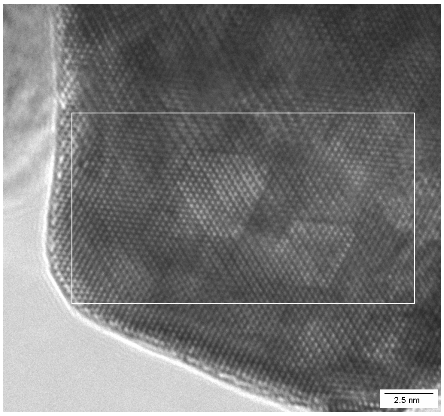

Fig. 2 HRTEM of Mn promoted SZ

zirconia. It had so far been believed that sulfate is exclusively present at the surface, but such a tightly bound species might be sub-surface (or located within the zirconia).

Characterization of sites

Results from conventional probe molecule studies have failed to explain the catalytic properties of SZ. A new criterion for the interaction between site and probe is being developed. Intensities in IR spectroscopy are related to the change in the dipole moment during vibration and will differ for a free molecule and an adsorbed state, in which the molecule is polarized through interaction with the surface. In a DFG-funded project in cooperation with Prof. V. Kazansky's group (Russian Acad. Sciences, Moscow), we are evaluating whether IR extinction coefficients can serve as a criterion for polarization and activation of bonds in a molecule. A volumetric system with IR cell was constructed such that spectra and adsorption isotherm could be recorded simultaneously. As a probe representative of small alkanes but un-reactive on SZ catalysts at 308 K, 2,2-dimethyl propane was selected. The integral molar extinction coefficients for the CH stretching vibrations were (units: km /mol): gas phase 165 ± 2, H-Mordenite 316 ± 81, FeSZ 900 ± 51. As expected, the extinction coefficient increases upon adsorption. For the first time a probe molecule experiment reveals a more pronounced effect for an SZ material than for a strongly acidic zeolite. Probe molecule studies were further successfully conducted on our model SZ system [8] which is being investigated within a DFG-funded priority program. Ammonia and butane were adsorbed on these nanocrystalline sulfated zirconia thin films supported on Si wafers. Ammonia TPD profiles closely resemble those published for active SZ catalysts[9]. Interaction of small alkanes with SZ catalyst powders is weak according to microcalorimetry data (45–60 kJ/mol) [10] and butane TPD data obtained with the films are consistent with these observations.

In situ studies on sulfated zirconia catalysts

To investigate the potential role of oxygen vacancies, we attempted to tune their concentration by variation of the oxygen partial pressure during activation (at 723 K) prior to reaction (at 323–378 K). Catalysts have been monitored by in situ UV-vis, IR, and XAS spectroscopies. There is little effect on surface sulfate and hydroxyl-groups but the oxidation state of manganese can be tuned (average valence between 2 and 3)[11-13]. The catalytic activity is clearly affected, and the maximum isomerization rate increased with the average valence of manganese after activation. The reaction profile, however, is not correlated to the manganese valence during reaction[11], ruling out that this promoter serves as redox initiator in an oxidative dehydrogenation (ODH) reaction as has been suggested for iron[14]. DRIFTS studies were performed to search for products of ODH, i.e. water and unsaturated compounds; which, however, may be immediately protonated to carbenium ions. Several bands at 1600–1650 cm^{-1} grow rapidly during the initial period of increasing conversion. These bands could represent water molecules, whose number should correspond to that of active surface intermediates. This hypothesis is confirmed by the linear correlation between isomerization rate and band area for different catalysts [15]. At 573 K, olefinic surface species and sulfide are formed on SZ, indicating that sulfate may be the oxidizing agent for ODH also at lower reaction temperatures. Manganese appears to increase the oxidizing power of sulfate. In-situ post-reaction UV-vis spectroscopic investigation of the nature of unsaturated surface species formed on SZ shows them to be almost inert towards molecular oxygen, indicating they may not be radicals (as had been proposed earlier by other authors [16]).

Conclusions

The description of the zirconia bulk structure, its morphology and stability is nearly complete. Understanding of the interaction between promoters and zirconia is advanced, but the exact interplay of these components with—possibly various species of—sulfate remains to be resolved. Although ODH via reduction of sulfate emerges as one possibility for initiation of alkane isomerization during the beginning of the reaction, future work will have to explain why SZ catalysts are active over many days without the need for re-oxidation.

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2.3 Vanadium Compounds in Selective Oxidation Reactions

Introduction

The element vanadium is a key active component in many selective oxidation catalysts. Despite extensive studies about their active state and its mode of operation which are also carried out in the CP and TH Departments of the FHI, there is still a great deal of uncertainty which of the numerous mechanistic suggestions applies to practical operations. This uncertainty hampers the development of practical oxidation catalysts to a great extent due to the key role of vanadium. The aim of this project is to get insight into the correlation between model and realistic vanadium catalysts considering structural changes of reversible and irreversible nature and to couple back this information with the model studies carried out in the FHI. The combination of electronic structure calculations with measurement and simulation of ELNES spectra is a key methodology.

n-Butane selective oxidation over vanadia nanocrystals

A micro-reactor for catalyst testing in the micrometer regime was successfully implemented within the framework of the SFB 546 of the Deutsche Forschungsgemeinschaft. V_xO_y nanoparticles were studied in the selective oxidation of n-butane towards maleic anhydride (MA). Changes in the electronic and geometric structure of the material were monitored by transmission electron microscopy (TEM), electron diffraction, electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) before and after the reaction at different temperatures within 200-400°C [1]. In the course of the temperature treatment the particles of an initially hydrated vanadium pentoxide form did undergo a radical modification of the geometric and electronic structure that finally resulted in V_2O_5 crystals. These structural changes which were resolved well by TEM, electron diffraction (phase identification) and ex-situ by micro-TG.MS were well reflected in a change in reactivity from acid catalyzed reactions to oxidative dehydrogenation of uncleaved C4. The best and stable performance as catalyst was obtained in a transient state of the phase evolution showing a mixture of phases and unknown diffraction signals. This state proved in thermal cycling experiments to be metastable towards crystallization into V_2O_5 with poor performance. The single pentavalent form is thus not the catalyst but merely its deactivation product. It became evident from XPS and from the relative intensity changes in the V and O edge of the EEL spectra that in the course of the temperature treatment the electronic structure of the nanoparticles changes from a variety of vanadium species with different oxidation states in the range of V^{3+} to V^{5+} to a material that contains only V^{5+} species. The starting V_xO_y nanocrystals were synthesized by an alkoxide/benzyl alcohol route in a steel autoclave at 200°C using vanadium (V) tri-isopropoxide as precursor [2]. The experiments serve as model study for the functional analysis of VPP catalysts where in a collaboration with G. Hutchings several strong hints for a metastable system as being the most active catalyst system have been identified by in-situ XPS that is currently being analyzed in detail.

Comparison of the geometrical and electronic structure of α- and γ-V_2O_5

Besides the more commonly known α-V_2O_5, the γ-polymorph was successfully synthesized in form of nanorods [3]. As opposed to α-V_2O_5, in γ-V_2O_5 there exist two structurally different VO_5 pyramids. Theoretical calculations of the band structure and density of states (DOS) attest a close agreement between the two structures [4]. The comparison of similar features in the DOS of V1 and the vanadyl oxygen of the adjacent layer reveal that only weak interlayer coupling is present. Thus, the picture of a distorted pyramid is more accurate than that of a distorted octahedron. In contrast to tilting of polyhedron in the unit cell, distortions within the VO_5 pyramids have a much more profound effect on the dispersion and position of the bands as they strongly affect the crystal-field splitting. In γ-V_2O_5, the superposition of contributions from two differently distorted VO_5 pyramids leads to a broadening of the bands. This is supported by the close agreement between simulated and measured electron loss near edge structure (ELNES) of the oxygen K ionization edge.

Electronic structure of VPO phases

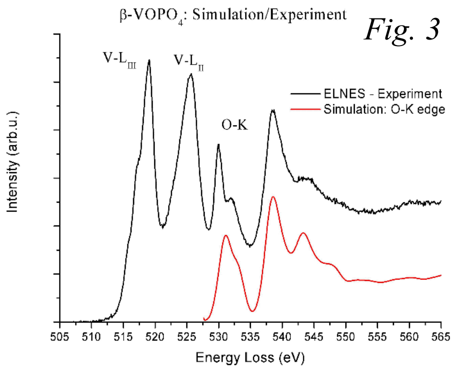

Fig. 3

Vanadium phosphorous oxides (VPO) catalysts are employed commercially for the selective oxidation of n-butane to MA. Using ab-initio simulations, various VPO phases (α_I-, α_{II}- und β-$VOPO_4$) were investigated in detail regarding their electronic structure to gain insight into their role in catalysis. The results of the calculations show that all three polymorphs have a very similar electronic structure. The arrangement of the corner sharing VO_6- und PO_4-subunit seems to play a minor role. Differences in stability are much more a result of their different three-dimensional structure. A detailed investigation of the electronic structure of β-$VOPO_4$ reveals a close agreement between the simulated oxygen K ionization edge and the results from EELS experiments [5]. The shape of the O K edge in the EELS spectrum resembles the electronic structure at the distorted VO_5 pyramid. A closer insight was gained by splitting the structure of the O K edge into the contributions from the differently coordinated oxygen atoms.

Model systems based upon SBA15-supported isolated V_xO_y sites

The synthesis, characterization and catalytic behavior of nanostructured V_xO_y embedded in mesoporous silica SBA-15 was investigated [6,7]. The individual steps of our novel synthesis approach to highly dispersed vanadia were elucidated using XPS and vibrational spectroscopy (DRIFTS, Raman): (1) The inner pores of the mesoporous matrix are functionalized via hydroxy groups leading to the formation of an organic framework consisting of ammonium propyl chains. Because of its structure it allows for a controlled introduction of vanadia into the nanopores. (2) The metal oxide precursor (decavanadate) is introduced intact into the nanopores via ion exchange without any changes in the organic framework. (3) During the calcination the V_xO_y cluster are anchored to the surface and the organic residues are completely removed from the pores. Catalytic experiments demonstrate that highly dispersed vanadia supported by SBA-15 is very selective in methanol oxidation to formaldehyde. Using 7.2 wt % V/SBA-15 we obtained the highest formaldehyde yield (72%) reported for silica supported vanadium oxide catalysts. High selectivities were observed also in the propane partial oxidation to acrylic acid. These results clearly demonstrate the important role of vanadia in commercially interesting mixed metal oxide catalysts such as Mo-V-Te-Nb oxides.

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2.4. Molybdenum oxide based catalysts in C3 selective oxidation

Introduction

Molybdenum oxide is an essential constituent of high performing catalysts applied industrially in a wide range of reactions. Examples of commercial processes are selective oxidation of propene to acrolein or acrolein to acrylic acid. The latter process requires vanadium as another basic catalyst component. This “synergy” between Mo and V in selective oxidation is a key motivation for the two projects centred around these two elements in the Department. The origin of the synergy is highly debated and a rational explanation is a long-term target of our efforts. Direct conversion of propane to acrylic acid has been succeeded over multi-component catalysts mainly consisting of molybdenum oxide modified with oxides of vanadium, tellurium and niobium. It has been shown, however, that chemical complexity is not necessarily required if molybdenum oxide exhibited adequate structural complexity. At least propene activation has been accomplished for the first time and against many predictions in the literature over pure binary molybdenum oxide if it was structurally different from orthorhombic MoO_3 [1]. Following studies were devoted to more complex systems with the structural motif of Mo_5O_{14}. In mixed transition metal oxide catalysts little is known about the cooperation of the different metal centers and their role for the stabilization of the active phase. Our research is directed to self-assembling processes of oxoanions involved in catalyst preparation in solution, rearrangement of molecular building blocks during crystallization, nanostructure and surface properties of Mo based mixed oxides. Special attention was given to $(Mo,V,W)_5O_{14}$ model systems and Mo-V-Te-Nb-O_x catalysts.

Investigation of $(Mo,V,W)_5O_{14}$ *as a model system*

In situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD) were employed to study the structural evolution of a precursor for bulk $(MoVW)_5O_{14}$ during calcination and under propene oxidation conditions. The precursor of a $Mo_{0.68}V_{0.23}W_{0.09}$ oxide catalyst was prepared by spray-drying. Subsequently, the material was activated by thermal treatment at 623 K in air and 713 K in helium. In situ XAS experiments at the Mo K edge, V K edge and W L_{III} edge revealed characteristic structural changes during the process of thermal treatment. The building blocks of the Mo_5O_{14} structure start to assemble in the precursor during the first treatment step in oxygen while the formation of long range ordered crystalline $(MoVW)_5O_{14}$ is only completed during the subsequent treatment in helium. Activation of the precursor in propene and oxygen revealed an onset of catalytic activity at ca. 570 K which coincides with the formation of crystalline $(MoVW)_5O_{14}$. In situ XAS showed that the $(MoVW)_5O_{14}$ catalyst undergoes a reversible reduction in 10 % propene. While the Mo_5O_{14} structure is stable in oxygen, it is completely reduced to a MoO_2 type material under reducing conditions at 773 K and may be re-oxidized to $(MoVW)_5O_{14}$ in the presence of oxygen. This redox behavior of the bulk material is indicative of sufficient oxygen mobility in the crystalline $(MoVW)_5O_{14}$ prepared, which is an important prerequisite for an active partial oxidation catalyst. In-situ photoelectron spectroscopy (XPS) at 0.5 mbar total pressure has been applied to investigate the electronic structure of the $(MoVW)_5O_{14}$ surface in presence of propene and oxygen. Moreover, depth profiles of the active catalysts have been measured by varying the photon energy. Compared to the bulk, a depletion of tungsten was observed on the surface of $(MoVW)_5O_{14}$ pretreated in helium at 713 K. While heating the catalyst in presence of propene and oxygen, the first oxidation products (mainly CO_2 and propanal) were detected at 613 K. At this temperature a significant loss of molybdenum oxide was registered. The molybdenum core level displays a complex structure indicating the presence of different Mo coordination spheres. The catalytic activity diminishes during prolonged reaction at 673 K as molybdenum oxide evaporate and the surface concentration of tungsten increases.

Preparation and characterization of mixed Mo-V-Te-Nb oxides

Mo-V-Te-Nb oxide mixtures appear to be the most active catalysts in the selective oxidation of propane to acrylic acid (see section 1). We have prepared $MoV_{0.3}Te_{0.23}Nb_{0.125}O_x$ catalyst precursors either by hydrothermal synthesis using ammonium heptamolybdate, telluric acid, vanadyl sulfate and niobium oxalate as starting materials or by spray-drying a slurry obtained by mixing the aqueous polyoxometalate solutions, but, applying ammonium metavanadate instead of vanadyl sulfate. Self-assembling processes of oxoanions involved in the latter preparation procedure have been studied by Raman spectroscopy [2]. Heteropolyanions of the Anderson-type, $[TeM_6O_{24}]^{6-}$, M=Mo,V, coexist with protonated decavanadate species $[H_xV_{10}O_{28}]^{(6-x)-}$ in the initially prepared ternary Mo-V-Te solution. The molybdotellurate is preserved after addition of Nb oxalate and the subsequent spray-drying process. The dried precursor was calcined in air at 548 K, which causes significant structural rearrangements. Thermal treatment at 873 K in inert atmosphere generates the active catalyst essentially consisting of two phases referred to as M1 and M2. The crystallization was studied using in situ X-ray diffraction (XRD). The local structure of the catalyst is playing an important role in the catalytic performance. We have studied the nanostructure of Mo-V-Te-Nb oxides with high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). In contrast to recent reports from DeSanto et al. [3], who claim no structural rearrangement to exist at the surface of the M1 and M2 phases, we clearly observe such structural rearrangements in both the M1 and M2 phases. In general, the crystals are encapsulated by a 1-2 nm thick structural ill-defined (non-crystalline) layer (Fig. 4). Area-confined EELS measurements reveal Mo, V, and O at the surface as well as in the bulk material. It has

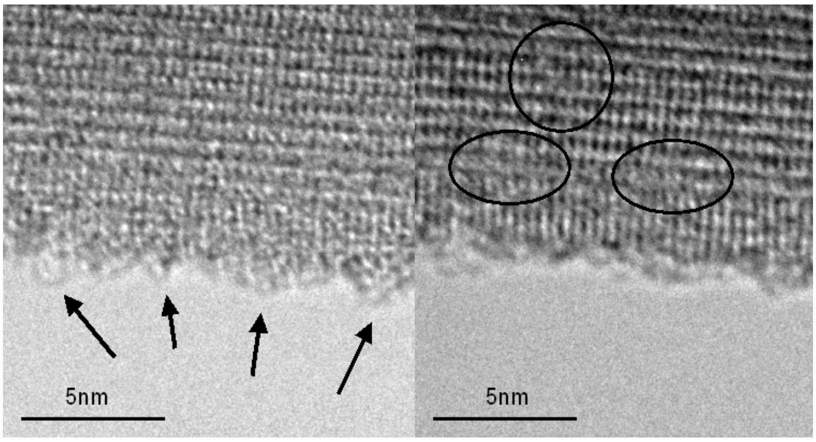

Fig. 4 Surface texturing of M1 phase viewed along the [411] zone-axis. Left: The surface texturing is shown in profile view (arrows). Right: Adjusting the defocus value reveals the surface texturing as blurring of the lattice fringe in top view (encircled).

to be stressed that the structural differences in the outermost region of the crystals are not due to contamination or to electron beam damage as the electron dose is kept at a minimum and no development of the layer is observed during longer exposure times in the electron microscope.

Recently, the addition of small amounts of further transition metals as promoters to Mo-V-Te-Nb-O_x catalysts has attracted much attention. The thermal decomposition of ruthenium salts of hetero-poly acids in the solid state gives access to highly dispersed Ru oxide species in a MoO_x matrix [4]. The concept of metastable Ru-exchanged HPA precursor species has been driven forward and combined with the preparation of promoted Mo-V-Te-Nb-O_x catalysts. The first results indicate catalytic properties in alkane oxidation differing from bulk Ru oxide containing materials.

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2.5. Application of Cu nanoparticles in the steam reforming of methanol

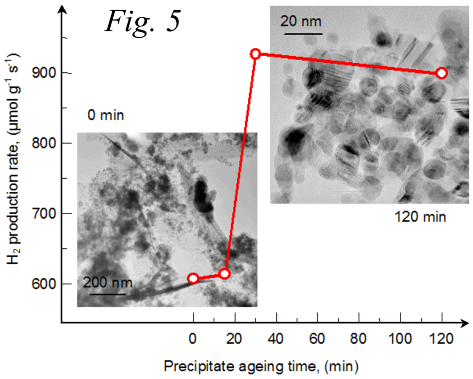
Introduction

Copper catalysts (e.g. $Cu/ZnO/Al_2O_3$) are industrially employed for methanol synthesis and the water gas shift reaction, and are also known to be active for the steam reforming of methanol. Methanol is an alternative hydrogen source for fuel cell application. In order to elucidate pathways to design highly active catalysts for methanol steam reforming, a fundamental understanding of the relation between surface structure, bulk structure, and catalytic activity is required. Moreover, because defects in the “real” bulk structure such as microstrain, impurities, and structural disorder significantly influence the performance of the corresponding copper catalyst, preparation pathways that permit tailoring the active “real structure” of the resulting catalyst are prerequisites for a knowledge-based catalyst design.

The microstructure of “real” Cu/ZnO catalysts for methanol chemistry

Microstructural characteristics of copper zinc oxide catalysts for methanol steam reforming were investigated as a function of ageing of the precipitated hydroxycarbonates during catalyst preparation. Bulk structural changes of the active catalysts under MSR reaction conditions were determined by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with on-line mass spectrometry. Reduction kinetics and phase compositions obtained from XAS data analysis were compared to conventional TPR and TG/MS results. With increasing ageing time of the precipitate the onset of reduction of the CuO/ZnO precursor is shifted from 462 K to 444 K, while a decrease in crystallite size from 110 Å (0 min) to 70 Å (120 min) is detected. The resulting higher Cu surface area of the Cu/ZnO catalysts alone, as determined by N_2O decomposition, cannot explain the strong increase in catalytic activity observed for Cu/ZnO catalysts obtained from precipitates aged for more than 15 min. The microstrain in the copper particles as detected by XRD, NMR, and XAS was determined as an additional bulk structural parameter that correlates with the increase in catalytic activity. The structural characteristics of Cu/ZnO catalysts as a function of precipitate ageing emphasize the defect-rich state of the homogeneous microstructure of highly active Cu/ZnO catalysts (Fig. 5) and its implication for the catalytic activity in the steam reforming of methanol.

Fig. 5



Structure-activity correlations of Cu/ZrO_2 catalysts for methanol steam reforming

Structure-activity relationships of a nanostructured Cu/ZrO_2 catalyst for the steam reforming of methanol were investigated under reaction conditions by in situ XAS and XRD combined with on-line mass spectrometry. Small and disordered CuO particles were identified as the main copper phase present in the precursors. After extended time on stream and treatment at 673 K in hydrogen, no significant sintering of the copper particles or deactivation of the reduced Cu/ZrO_2 catalysts was detected indicating a superior stability of the material. The initially low steam reforming activity of the Cu/ZrO_2 catalyst after reduction in hydrogen could be significantly increased by a temporary addition of oxygen to the feed. This increased activity after oxidative treatment is correlated to an increasing amount of oxygen in the copper particles. ^{63}Cu NMR studies (collaboration with MPI CPFS Dresden) detected only a minor degree of microstrain in the active copper phase of the Cu/ZrO_2 catalyst. The decreased reducibility of CuO/ZrO_2, the low degree of microstrain, and the correlation between the amount of oxygen remaining in the copper particles and the catalytic activity indicate a different metal support interaction compared to Cu/ZnO catalysts.

Kinetic studies on $Cu/ZrO_2/CeO_2$ catalysts for methanol steam reforming

Steam reforming of methanol was investigated over $Cu/ZrO_2/CeO_2$ (CZC) catalysts prepared via a novel synthetic method based on co-precipitation and polymer templating (collaboration with MPI Colloid Science Golm). The variation of the Cu loading resulted in an increased Cu crystallite size and a decreased specific surface area of the active particles. Catalytic investigations were carried out in a fixed bed reactor at 105 Pa, by applying a $CH_3OH:H_2O = 1:1$ ratio. The samples with Cu contents higher than 5 % exhibited good long-term stabilities and low CO levels during continuous operation. The kinetic model suggested for the transformation involved the reverse water-gas shift (RWGS) and methanol decomposition (MD), in addition to the SRM reaction. The apparent activation energies for the individual reactions were found to depend on the Cu content of the catalyst. Since the influence of mass transport limitations on the kinetic data could be excluded, it was established that the variation of the Cu concentration in the precursor material altered the microstructure of the Cu particles and, accordingly, the active Cu surface, which resulted in the formation of significantly different catalysts.

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2.6. Pd in Selective Hydrogenation

Pentyne hydrogenation

The initial in-situ XPS study on the hydrogenation of trans-2-pentene was completed and published [1,2] while the focus is now on the understanding of governing factors for the selectivity in triple C≡C hydrogenation. Four different palladium samples were applied in this study, two supported catalysts (5% Pd/carbon-nanotubes, 3% Pd/Al_2O_3) and two bulk palladium materials (Pd(111), Pd foil). All showed catalytic activity in the hydrogenation of 1-pentyne (~1 mbar). Both, single and total hydrogenation products were formed. Pentane is produced more in the early stage of the experiment at lower temperatures, whereas selective hydrogenation (to 1-pentene) occurred at steadily at 358 K. This latter is related with carbon retention as a special “Pd-C” phase building up in the reaction. A direct correlation between the “Pd-C” component and the 1-pentene yield was established allowing concluding that the active surface in selective triple bond hydrogenation is a non-metallic Pd phase. Valence band spectra point also to a massive charge redistribution. This spectroscopic evidence correlates perfectly with earlier catalytic works showing that propene formation from propyne occurs just after the catalyst retains a significant amount of carbon on its surface [3]. (For propane formation carbon retention was not a prerequisite!) HRTEM images of used catalysts indicate lattice expansion which is more pronounced in the surface-near area. The reason is carbon incorporation during the catalytic experiment. Depth-profiling XPS during a catalytic run on both palladium and carbon core levels reveal a maximum carbon content at intermediate information depth. The complex multi-layer structure arises from a significant amount of carbon being situated in the near-surface region i.e. in subsurface positions. The remarkable increase of palladium at the most surface-sensitive energy suggests that the gas-solid interface is not fully covered by adsorbates and that the atomically dissolved subsurface carbon is located below a 2-3 palladium-atom-thick "Pd-C" layer.

Ethene decomposition

A further goal of our work (collaboration with University of Innsbruck and University of Limerick) is to identify and characterize active phases on palladium surfaces involved in the oxidation of CO and small hydrocarbons [4,5]. Ethene decomposition on Pd(111) between 400 and 600 K leads to diffusion of carbon through the close-packed Pd(111) surface. Below 440 K only the surface is covered with CH_x deposits and carbon atoms. Beyond 440 K a "carbon covered Pd_xC_y" surface was identified. The migration rate of carbon into the Pd bulk was measured (activation energy 50.3 kJ/mole). The influence of subsurface carbon on the electronic properties of the surface at higher pressures was characterized by in-situ XPS during the oxidation reaction. The active phase is non metallic and carbon containing. A new surface oxide phase different from Pd_5O_4 is identified by in-situ XPS as active in methane oxidation on Pd at lower temperature (700 K) and 0.4 mbar total pressure. Its formation is inhibited during cooling, providing a strong rate hysteresis in methane oxidation, which is thus controlled by the chemical state of oxygen.

Site isolation by intermetallic compounds

Active-site isolation through selecting Pd-Ga intermetallic compounds (collaboration with Max-Planck-Institute for Chemical Physics of Solid States) may increase selectivity and catalytic stability [6,7]. Active-site isolation means that the Pd atoms are structurally isolated and there is an absence of ensembles of Pd atoms on the surface. In situ EXAFS and in situ XRD measurements on PdGa and Pd_3Ga_7 in inert and reactive gas atmospheres show the thermal and structural stability of the two compounds up to 650 K. BET measurements of both ball milled samples result in surface area ~1 m^2/g. Catalysis data on the hydrogenation of acetylene were performed in 0.5% C_2H_2, 5% H_2 and 50% C_2H_4. The Pd-Ga intermetallic compounds show god activity and a higher selectivity compared to pure Pd catalyst. A palladium-silver alloy ($Pd_{20}Ag_{80}$) as a reference for industrial catalysts showed stable activity of 85% whereas the Pd/Al_2O_3 gave a decreasing activity after 20 hours time on stream. The selectivities for PdGa and Pd_3Ga_7 were stable between 70-75%. The palladium-silver alloy exhibits a selectivity of 50% and Pd/Al_2O_3 reveals a selectivity of 15%. Pd-Ga intermetallic compounds are thus potential superior catalysts if the surface area can be increased. Since it is not possible to obtain nano-sized powders by melting together the elements, a new synthesis method was developed. Acetylacetonates of the elements are reduced by $LiAlH_4$ in an inert solvent (e.g. dioctylether) at elevated temperatures and under strict exclusion of air.

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2.7. Carbon in Heterogeneous Catalysis

Introduction

The project is conducted in the following three directions: i) optimisation of the oxidative dehydrogenation (ODH) of ethylbenzene (EB) to styrene (ST) over nanocarbon; ii) synthesis of carbon tube-in-tube nanostructure; iii) nano-architecturing of activated carbon. The activities will be substantially enhanced through the collaborative MPG project ENERCHEM within which so far a substantial amount of high end service for microstructural analytics has been delivered to the partner MPI in Golm and in Mainz. The efforts for these activities prevented the initiation of our own synthesis activities in ENERCHEM that will be directed towards the kinetics of pyrolysis under thermal and catalytic conditions.

Oxidative dehydrogenation of ethylbenzene (EB) to styrene(St)

This work conducted in the collaborations with CANAPE and NanoC is initiated by the results from project 1 revealing that carbon-covered iron oxide is still an active catalysts. In the past we found that special nanostructured carbons are well capable of catalyzing the oxidative dehydrogenation of EB under conditions potentially suitable for technical operation The research activities are now concentrated on i) the search for nanocarbons which can be produced in large scales and exhibit improved styrene conversion rates and selectivity as well as prolonged life times being the core obstacle in conventional carbon-catalyzed reactions; ii) the role of oxygen partial pressure in the reaction mechanism of EB conversion. The core result was that we could achieve 50% yields of ST at above 75% selectivity in an oxidative dehydrogenation mode without the addition of any steam at 623K. The lifetime of the catalyst was tested up to 400h. Unsupported carbon nanotubes from Future Carbon, Rosseter Holdings Ltd and Thomas Swan Ltd were tested for the ODH reactions. We tested for the influence of the flow rate of EB revealing that a quick feed in of EB increases the conversion of EB, but at expense of ST selectivity. Among all the tested carbon nanotubes, the single walled-nanotube from Thomas Swan exhibit, surprisingly, the highest yield of ST. This is unexpected since single walled-nanotubes do not exhibit prismatic planes needed to anchor the oxygen groups for the oxidative dehydrogenation. Intensive TEM work revealed that these CNT contain a substantial number of defects in their wall serving as anchoring sites for oxygen groups. These observations triggered a fruitful and very intensive collaboration with the TH Department to study the exact nature of such active sites and the effect of carbon structure on stability and generation of reactive defects. The scale-up experiments from 50 mg to 3000 mg revealed severe mass transport effects. To overcome the shortage that nanostructured carbon is difficult to handle in a real fixed-bed reactor, carbon nanofiber are grown on graphite felts by catalytic chemical vapor decomposition of ethane. The obtained composite is in macroscopic scale and mechanically stable, avoiding limitation due to the fine powder form of the primary structure of nanocarbons. A stable yield of 38 % of ST in the ODH of EB to ST was obtained with a selectivity of 85 % towards ST. In addition, due to the open structure with large void volume of the supported nanocarbon no pressure drop was observed.

Synthesis of carbon tube-in-tube nanostructure

Carbon tube-in-tube (CTIT) nanostructures, built by a narrower inner tube inside an outer tube, exhibit multiple intramolecular channels and surfaces and should be beneficial for sorption applications as well for mechanical re-enforcement of potential carbon filler materials. We investigated methods for a facile synthesis as the CTIT structure is difficult to assemble. Our strategy is derived from the understanding of intercalation-deintercalation reactions in graphite and includes two steps. First, the graphitic nanoparticles are disintegrated into graphene fragments by an HNO_3-based intercalation and oxidation process at defective sites, a process previously used to purify, cut, or open nanotubes. The following hydrolytic exfoliation in the second step creates the graphene units and concomitantly functionalizes the fragment edges with carboxyl and hydroxyl groups. These graphene fragments are then reintegrated by self-organization around or inside pristine nanotubes to assemble CTITs by acid-catalyzed esterification linkages between the carboxyl and hydroxyl groups.

Nano-architecturing of activated carbon

The selective chemisorption of unwanted species from drinking water (Mn, As, Hg, Fe), the modification of the properties of polymers and the use as catalysts or catalyst supports such as for the targets of ENERCHEM or for the dehydrogenation of EB or for C4 selective oxidation require novel immobilized forms of CNT/CNFs. Loose CNT/CNFs are unsuitable as they cannot be controlled in their suprastructural properties and formulating or shaping will destroy the nanostructures. A hierarchical organization of the nanocarbon on a robust carrier structure in larger dimensions is generated in the project. We choose activated carbon from natural sources as substrate. Such bio-inorganic polymers containing typically lignites and silicates are strong, well-structured in several dimensions and are reactive for modifications. In addition, the

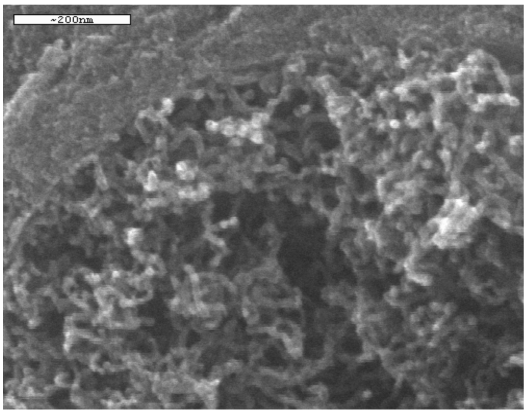

Fig. 6: Cross sectional HR SEM through a composite of activated carbon and nanotubes grown inside a macropore created by catalytic oxidation.

chemical interaction between nanocarbon and activated carbon as host is strong and inert to preserve the hierarchical structure during extended operation in corrosive media. Our method of synthesis involving a highly integrated thermal processing of carbon modified by a pre-impregnated catalyst material such as iron in several varying atmospheres is reproducible and productive. First results of adsorption experiments show a significant adsorption capacity for $[PMo_{12}O_{40}]^{3-}$ from solution which does not adsorb at all on standard activated carbon.

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3. Future Activities

3.1 Summary of the Scientific Reports

The past two years have seen a substantial confirmation of the working hypotheses formulated in the last report. The concept of catalysts being metastable with respect to its as-synthesized forms and the view that stable phases in catalysts are either precursors or decomposition products of active phases have been substantiated in all projects. The wide space of chemical diversity covered by the projects of the Department allows deriving a certain degree of generalization to this conclusion. A generic result concerns the nature of the “pressure gap” It is not so much the pressure-dependence of the coverage of a well-defined surface that accounts for the gap between observed and predicted catalytic activity but merely the propensity of catalysts to react with their gas phase environments forming unstable solid solutions or “intercalation” compounds with molecules or fragments of their reactants and products. The resulting sub-surface compounds are grossly different from adsorbate layers commonly studied in surface science. The existence of sub-surface compounds of generally non-stoichiometric composition (studied also in model systems in collaboration with the CP Department) has severe consequences on the surface free energy and thus on the microstructure of the surface-near bulk controlling to a large extent the termination of the solid. In compound solids the termination problem is of enormous complexity and can easily generate structural motifs which have no counterparts in the bulk chemistry of the compound. This is suggested by our observations and has been strongly emphasized in the work of the CP and TH Departments in FHI.

The four oxide projects have now converged in a remarkable way as they show that in all reactions there exists a metastable (with respect to standard conditions) matrix phase which is essential but insufficient to account for the catalytic performance. The missing factor is a particular ensemble of surface defects such as:

- Hydrogen-generated oxygen defects in iron oxide surfaces
- Promoter assisted oxygen deficiencies in t-ZrO_2
- Te-assisted defects of a Mo-V-mixed oxide in MoVTe systems
- Mixed-valent V_xO_y species in pseudo-binary V oxide systems

These essential defects (or “real structures” or “nanostructures”) are created by the co-operation of the following factors:

- the chemical potential of the gas phase (composition, pressure, temperature),
- the bulk reactivity of the matrix phase to equilibrate to this chemical potential given by their bulk defects (chemical memory)
- the surface reactivity given by the nanostructure of the catalyst
- the coupling of the solid state reactivity to the surface reaction kinetics fixing the mean chemical potential and its spatio-temporal fluctuation

These factors are both of intrinsic (thermodynamic) and of extrinsic (kinetic) nature. As they co-operate in controlling the dynamics of the active sites it is no surprise that neither models of thermodynamic stable character nor “standard” samples of a particular kinetic disposition can explain the evolution of catalytic function with catalyst synthesis and operation. These observations strongly underline the necessity to use in-situ methods when attempting the elucidation of structure-function correlations. These findings also underline the essential value of highest resolution real-space inspection of activated catalysts by electron microscopy with its arsenal of geometrically and chemically high resolution techniques.

The working hypothesis of the metastable dynamical catalyst further underlines the role of a controlled synthesis methodology for catalysts. In these early steps of the life of the functional material all options for restructuring in the bulk, in the sub-surface region and at the surface are pre-determined by the disposition of defects as point and ensemble defects. The relevance of the average bulk structure (phase) is less pronounced than assumed in the past and the catalyst material requires a much more careful description of its real structure than of its translational average structure which is comparatively easily accessible through diffraction techniques. It is the analysis of “dirty”-in the terminology of physicists- samples that will lead to new insight into the nature of active sites. This journey into the unknown territory of structural chemistry where standard methods of analysis are only partly helpful can now be undertaken in a meaningful manner as a guideline is provided by theory and model experiments. The enormous progress of these fields in the last decade allows now finding the relevant deviations from the stable average structure within the wide phenomenology of defects.

3.2. Consequences for the operation of the Department

The working experience of the Department has shown that only a close co-operation between highly competent groups can address the challenging task of determining the active structure of a catalyst. Besides the now well-developed in-situ analysis competence it of equal importance to use all information gained during synthesis of the catalyst and to develop methods for synthesizing model catalysts of intermediate complexity between rigorous models (as used in the CP Department) and technical catalysts with their non-essential ingredients.

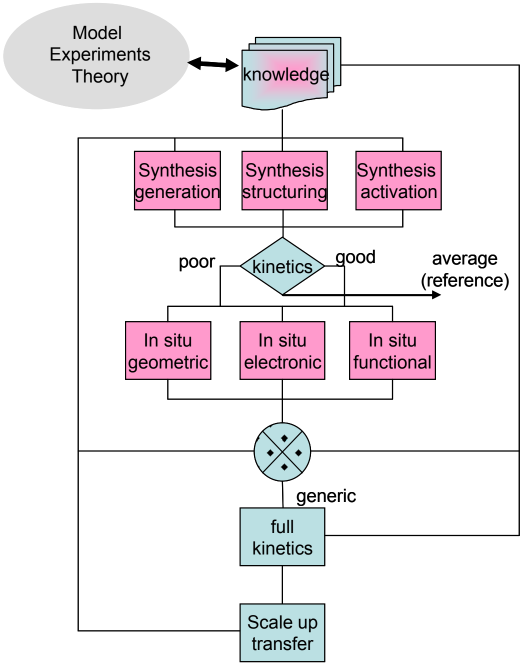

Fig. 7

This re-focusing was initiated since 2000 and can now fully be implemented with the advent of the refurbished building and the adequate infrastructure. A concentration of the resources of the Department into the essential tasks is planned as well as the implementation of a formalized work flow between the inner-departmental groups and the external collaborators. These groups are vital with their contributions of the kinetic experimental competence. It is mainly the collaboration with NanoC/COMBICAT in Kuala Lumpur from where the necessary data will be supplied for four projects. The Department will use the difficult time of the coming two years to implement and consolidate this work flow that is shown in Figure 7. In recognition of the enormous effort for the truly required sophisticated in-depth catalyst analysis it is mandatory to pre-select the systems to be studied with the complex analytical techniques according to their performance. From a comparison of system with similar chemical characteristics but widely differing performance it will be most promising to isolate the structural features and their dynamics that carry the catalytic function. It is further a characteristic of the departmental strategy to seek verification of synthetic and analytical information by scaling up the successful systems into operations typical for pilot and demonstration reactors in industry. These efforts requiring close cooperation with industrial partners deliver invaluable information about the typical performance of a system without the many disturbances from micro-reactors and laboratory feeding conditions. In order to achieve this work flow also within the Department it seems adequate to restructure the competence groups. The resources of the model system activities and in part from the geometric structure group will be pooled to augment the synthesis activities implementing in-situ analysis in synthesis and automated preparation techniques. The ability to perform high-quality X-ray diffraction experiments and to develop structural evolution scenarios by in-situ XRD will be retained. The in-situ EXAFS activity will be taken with Th. Ressler leaving the Department.

3.3 Future Scientific work

The Department will continue the projects according to the work flow indicated above. This will involve some consolidation work and in particular require the organization of data flows between the collaborating groups. Flexibility to take on new developments is always present through the exploratory projects with smaller resources and shorter time scales. The still largely phenomenological character of the projects (Mo, V, C) will be gradually evolve into a more analytical and model-building stage (Zr, Cu, Pd) as soon as the essential synthetic and kinetic base information is available for the generation of reproducible performance in a family of structurally well-defined systems. The general aim is the verification of a generic model describing the functional material "catalyst". The traditional definition of a catalyst as "material that modifies the rate of chemical reactions without being consumed in it" should be replaced by a more realistic definition stating that a catalyst is "a material that modifies the rate of a chemical reaction when it is in a dynamical metastable state which is generated by the action of the reactant with a pre-catalytic material". This change of a paradigm is depicted in Figure 8 where our present notion about a prepared

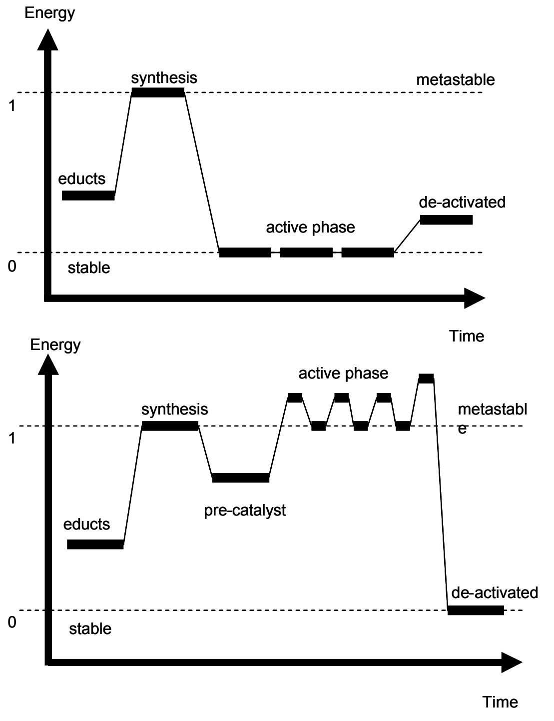

Fig. 8

and activated catalyst being a "phase" and thus an equilibrium structure is compared to the vision that catalytic action occurs on the way from the pre-catalytic form over transient and dynamical states into the equilibrated state being minority structures embedded for stabilization into matrix or support phases. This "phase state" (well detected by X-ray diffraction and characterized by large and homogeneous crystallites) of a catalyst is its de-activated form. It is obvious that the design concept of a catalyst would have to be changed completely if it were necessary to provide a good catalyst with the ability to react in its structure while it is active. Such a vision is in sharp contrast to the present practice tying to minimize structural reactivity of a catalyst to prevent it from de-activation. The design target of maximum stability for maximum lifetime is also in contrast to the intended function of catalyst namely to modify the kinetics of a chemical process by introducing a distortion into equilibrium elementary reactions. Such function seems to require a non-equilibrium state of the effecting material in order for it becoming part of the processes. The defect of a regular surface may not be a sufficient deviation from equilibrium for the many kinetically difficult-to-perform reactions.

All in-situ studies have yielded the common observation that structural dynamics is a property of active catalysts. It is not well considered in the present paradigm that catalysts adopt the small amount of active material in its structure to the gas phase environment. In our view the abundant parts of the catalyst material usually characterized are spectators or matrices and do not describe the active state. From this perspective it is clear why it is so difficult to derive physically supported structure-function correlations: the structural characterization aims at the non-relevant but abundant part of the composite material "catalyst" that we always identify even when a pure element is nominally the active catalyst. Augmenting our in-situ studies by real-space atomically resolved imaging and by reproducible and controlled defect engineering during synthesis will bring us closer to a verification of our vision and so to an enhanced understanding of the multi-dimensional challenge "heterogeneous catalysis".

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Invited Talks of the Inorganic Chemistry Department

Hendrik Bluhm

Bluhm, H.: Formation of dipole-ordered water films at platinium and mica surfaces. (Seminar talk, 2003-10-07, Institute of Chemistry, University of Leiden, The Netherlands)

Michael Hävecker

Hävecker, M., R. W. Mayer, H. Bluhm, E. Kleimenov, K. Ihmann, D. Teschner, A. Knop-Gericke and R. Schlögl: In situ characterisation of vanadium-phosphorus-oxide (VPO) catalysts for n-butane oxidation by applying X-ray absorption spectroscopy in the soft energy range. (MPG-CRG evaluation at BESSY, 2003-01-15 till 2003-01-15, Berlin)

Raimund Horn

Horn, R.: Blausäure aus Methan und Ammoniak - Untersuchungen mittels Molekularstrahl - Massenspektrometrie und Bestimmung von Ionisations- und Auftrittspotentialen. (Analytisches Seminar, 2004-05-27 till 2004-05-27, Friedrich-Schiller-Universität Jena)

Friederike C. Jentoft

Jentoft, F. C.: Isomerisierungskatalysatoren aus sulfatiertem Zirconiumdioxid: Präparation, Charakterisierung und in situ Untersuchungen. (Institutskolloquium Technische Chemie, Technische Universität Darmstadt, 2005-05-03 till 2005-05-03, Darmstadt, Germany) *Jentoft, F. C.*: Sulfated Zirconia Catalysts for Alkane Isomerization: Recent Progress. (ExxonMobil Chemical ESEP European Award Symposium, 2003-12-03 till 2003-12-04, ExxonMobil Chemical Europe, Machelen, Belgium)

Jentoft, F. C.: Characterization of Surface Sites Using IR-Spectroscopy & Microcalorimetry. (Colloquium at UMR CNRS (Ecole Européenne de Chimie, Polymères et Matériaux) - Université Louis Pasteur, 2004-02-18 till 2004-02-18, Strasbourg, France)

Jentoft, F. C.: Reaktivität von Festkörperkatalysatoren - Beteiligung der "inaktiven" Komponenten ZrO_2 und SiO_2. (Kolloquium der Fakultät für Mathematik und Naturwissenschaften II, Friedrich-Alexander-Universität Erlangen-Nürnberg, 2004-06-23 till 2004-06-23, Erlangen / Germany)

Jentoft, F. C.: Modifiziertes Zirconiumdioxid – ein interessanter Katalysator für die Alkanisomerisierung. (Kolloquium des Institutes für Chemie, Humboldt-Universität zu Berlin, 2004-10-20 till 2004-10-20, Berlin, Germany)

Jentoft, F. C.: In Situ Vibrational Spectroscopy of Reactants and Probe Molecules on Oxide Catalysts. (CECAM WORKSHOP "In situ atomic scale characterization of surfaces under high pressures: recent advances in experiment and theory", 2004-11-04 till 2004-11-06, CECAM Lyon / France)

Jentoft, F. C.: Aufklärung der Wirkungsweise von Festkörperkatalysatoren durch Infrarotspektroskopie. (Kolloquium des Instituts für Chemie, Technische Universität Berlin, 2005-04-08 till 2005-04-08, Berlin, Germany)

Jentoft, F. C.: Manganese and Iron as Promoters of Sulfated Zirconia Isomerization Catalysts. (Seminar at UOP LLC, 2005-04-22 till 2005-04-22, Des Plaines, Illinois, USA)

Jentoft, F. C.: Role of Cationic Promoters in Sulfated Zirconia Catalysts for n-Butane Isomerization. (Seminar of the Department of Chemical and Petroleum Engineering, University of Pittsburgh, 2005-04-25 till 2005-04-25, Pittsburgh, Pennsylvania, USA)

Jentoft, F. C.: Effect of Cationic Promoters on Sulfated Zirconia Catalysts. (Scientific Symposia "Science and Art in Europe“, Symposium "Catalysis: Nanotechnology with a Past", 2005-05-22 till 2005-05-24, Berlin)

Rolf E. Jentoft

Jentoft, R. E., J. Wienold, F. C. Jentoft, R. Schlögl and T. Ressler: In-Situ XAS Characterization of Catalysts. (XAS at 3rd generation Sources: Highlights and Future Prospects, 2003-06-19 till 2003-06-20, Grenoble France)

Axel Knop-Gericke

Knop-Gericke, A.: Methanol Oxidation over Cu investigated by in situ photoelectron spectroscopy. (Materials and Surface Science Institute (MSSI) Seminar, 2004-05-13, Limerick, Ireland)

Knop-Gericke, A.: Catalytically relevant Ag-systems. (AG Seminar Ludwig-Maximilian-Universität München, 2004-10-05, Munich Germany)

Knop-Gericke, A.: In situ X-ray photoelectron spectroscopy: A tool to investigate heterogeneous catalytic reactions. (Workshop: Surfaces: Out of UHV and into the Real World, 2004-11-22, Daresbury, United Kingdom)

Knop-Gericke, A.: Hochdruck Photoelektronenspektroskopie und Röntgenabsorptionsspektroskopie: In situ Methoden zur Untersuchung heteroger katalytischer Prozesse. (Institutskolloquium Technische Chemie, Technische Universität Darmstadt, 2005-05-17, Darmstadt, Germany)

Knop-Gericke, A.: High Pressure photoelectron spectroscopy: useful tool to study heterogeneous catalytic reactions. (Seminar at the synchrotron radiation facility ELETTRA, 2005-05-23, Trieste, Italy)

Wolfgang Ranke

Grillo, M. E. and W. Ranke: Combined surface science and density functional theory approach towards water ordered structures formation on magnetite. (9th Irish atomistic simulators meeting, 2004-12-16 till 2004-12-17, Cork, Ireland)

Thorsten Ressler

Ressler, T.: Application of X-ray Absorption Spectroscopy in Chemistry. (MPI für Chemische Physik fester Stoffe, 2003-10-22 till 2003-10-22, Dresden)

Ressler, T.: Rational design of heterogeneous catalysts – a new concept? (Universität Hamburg, Institut für Anorganische Chemie, 2003-10-29 till 2003-10-29, Hamburg)

Ressler, T.: Application of WinXAS for XAFS Data Analysis. (Canadian Light Source Users' meeting, 2003-11-13 till 2003-11-14, Saskatchewan, Canada)

Ressler, T.: Structure-Activity Correlations in Catalysis from Time-resolved X-ray Absorption Spectroscopy. (Canadian Light Source Users' meeting, 2003-11-15 till 2003-11-16, Saskatchewan, Canada)

Ressler, T.: Röntgenabsorptionsspektroskopie – Grundlagen und Anwendungen in der Festkörperchemie. (2. Workshop im DFG-SPP 1136, 2004-03-02 till 2004-03-02, Giessen)

Ressler, T.: Präparation und Struktur-Aktivitätsbeziehungen von Kupfernanoteilchen für die Dampfreformierung von Methanol. (SFB-Seminar Uni Bochum, 2004-03-09 till 2004-03-09, Bochum)

Ressler, T.: Von Struktur-Eigenschaftsbeziehungen zum rationalen Design von heterogenen Katalysatoren. (Symposium Anorganische Chemie – Festkörperchemie, 2004-05-24 till 2004-05-24, Ulm)

Ressler, T.: Preparation and structure-activity relationships of nanostructured copper catalysts for methanol steam reforming. (DFG SPP 1091 – Workshop „Preparation of Model Catalysts“, 2004-06-14 till 2004-06-15, Blankensee)

Ressler, T.: Struktur-Aktivitätsbeziehung von heterogenen Katalysatoren aus spektroskopischen Untersuchungen unter dynamischen Reaktionsbedingungen. (Symposium Physikalische Chemie, 2005-03-21 till 2005-03-21, Ulm)

Ressler, T.: Korrelation von Defektstruktur und Aktivität von heterogenen Katalysatoren aus in situ Untersuchungen unter dynamischen Reaktionsbedingungen, (Symposium Analytische Chemie der TU Berlin, 2005-04-11 till 2005-04-11, Berlin)

Ressler, T.: Effect of Cationic Promoters on Sulfated Zirconia Catalysts. (Scientific Symposia "Science and Art in Europe“, Symposium "Catalysis: Nanotechnology with a Past", 2005-05-22 till 2005-05-24, Berlin)

Robert Schlögl

Schmöckwitz, Germany) *Schlögl, R.*: Nanoscience and Catalysis - European Perspective. (NFS Workshop on Future Directions in Catalysis, 2003-06-18 till 2003-06-18, Arlington, VA (USA)

Schlögl, R.: Mechanochemical Preparation of Heterogeneous Catalysts: Another Way of Defect Engineering. (International Conference on Mechanochemistry and Mechanical Alloying (INCOME 2003), 2003-09-11 till 2003-09-11, Braunschweig Germany)

Schlögl, R.: Katalysatoren bei der Arbeit zugeschaut: In-Situ Spektroskopie. (Symposium zum 75.Geburtstag von Prof. Hans Bock, Inst. f. Anorganische Chemie der Johann Wolfgang Goethe-Universität, 2003-10-10 till 2003-10-10, Frankfurt a.M. Germany)

Schlögl, R.: The Concept of Model Systems in Catalysis. (Ringvorlesung WS 2003/2004, 2003-10-24, FHI, Berlin, Germany)

Schlögl, R.: In-situ Charakterisierung heterogener Katalysatoren: Etwas für Praktiker?. (DESY-Industrieforum, 2003-11-19 till 2003-11-19, Hamburg Germany)

Schlögl, R.: The impact of electron microscopy for the understanding of oxide heterogeneous catalysts. (University of New Mexico, 2003-12-01 till 2003-12-02, Albuquerque, NM USA)

Schlögl, R.: Open Acess: Die e-Science Initiative der MPG. (Fachgespräch des Bundesministeriums für Bildung und Forschung, 2004-01-14 till 2004-10-15, Berlin Germany)

Schlögl, R.: Spektroskopische Bestimmung der elektronischen Eigenschaften oxidischer Festkörper. (Ringvorlesung WS 2003/2004, 2004-02-05 TU Berlin, Germany)

Schlögl, R.: Nanostructure Oxides for Heterogeneous Catalysis. (Special Seminar, Georgia Institute of Technology, 2004-02-27 till 2004-02-27, Atlanta USA)

Schlögl, R.: High pressure in-situ XPS studies of supported vanadium oxide clusters in catalytic selective oxidation of butane. (SfB-Symposium, 2004-03-21 till 2004-03-24,

Schlögl, R.: Wie findet man einen neuen Katalysator? Strategien jenseits von Kunst und Kombinatorik. (Degussa-Workshop, 2004-05-03 till 2004-05-03, Düsseldorf, Germany)

Schlögl, R.: The Impact of In-situ Analysis of heterogeneous Catalysts for the Improvement of their Function. (DO/BES Catalysis Contractora Meeting, 2004-05-22 till 2004-05-22, Rockville, MD, USA)

Schlögl, R.: Nanostructured carbon for heterogeneous catalysis. (International Symposium on Science & Technology of nano-Catalysis, Dalian Institute of Chemical Physics, 2004-05-27 till 2004-05-27, Dalian, China)

Schlögl, R.: Heterogene Katalyseforschung auf dem Weg von der Empirie zur Wissenschaft. (GDCh-Seminar, 2004-06-11 till 2004-06-11, Frankfurt a.M., Germany)

Schlögl, R.: Nano-Catalysis. (7th International Conference on Nanostructured Materials, 2004-06-22 till 2004-06-22, Wiesbaden (Germany))

Schlögl, R.: Nanostructured Carbon as Heterogeneous Catalysts. (International Symposium on Carbon for Catalysis, CarboCat 2004, 2004-07-21 till 2004-07-21, Lausanne, Switzerland)

Schlögl, R.: The Function of V_xO_y Species in Selective Oxidation: An In-situ High Pressure XPS Study. (ACS National Meeting, 2004-08-23 till 2004-08-23, Philadelphia, PA, USA)

Schlögl, R.: Selective Dehydrogenation of Methanol to Formaldehyde. (Topsoe Catalysis Forum, 2004-08-27 till 2004-08-27, Hornbaek, Danmark)

Schlögl, R.: CO Oxidation Over Ruthenium Oxides: A View from the Material Side. (Ringberg Tagung zu Ehren Prof. Ertl, 2004-09-06 till 2004-09-10, Ringberg (Germany)

Schlögl, R.: The Application of In-situ Spectroscopy to the Functional Characterization of Heterogeneous Catalysts: Perspectives for the Synthesis. (UK Synchrotron Radiation Meeting, 2004-09-14 till 2004-09-14, Oxfordshire, Great Britain)

Schlögl, R.: Chemically Simple Nanostructured Oxide Catalysts for Alkane Activation: An Alternative to the Paradigm of Complexity?. (GdCH Wöhler-Vereinigung f. Anorganische Chemie, 12. Vortragstagung, 2004-09-15 till 2004-09-17, Marburg, Germany)

*Schlögl,R.:*The value of high-pressure x-ray photoemission and absorption spectroscopy for the in-situ study of heterogeneous catalysis. (CECAM, Lyon 2004-11-04-2004-11-06, France)

Schlögl, R.: In-situ studies of oxide catalysts: functional and synthetic implication. (Invitational lecturer at UOP LLC, 2004-11-09, Des Plaines, IL, USA)

Schlögl, R.: Bridging the material gap in heterogeneous catalysis. (Yale University, Tetelman Lecture, 2004-11-11, New Haven, Connecticut, USA)

Schlögl, R.: Open access- über die Zukunft des wissenschaftlichen Publizieren. (Hochschulrektorenkonferenz Informationsrunde für Parlamentarier „Urheberrecht für Bildung und Wissenschaft“, Wissenschaftsforum am Gendarmenmarkt, 2004-11-30, Berlin, Germany)

Schlögl, R.:High-Pressure in-situ Photoelectron Spectroscopy in Heterogeneous Catalysis: Insights into Dynamic States BESSY Nutzertreffen, 2004-12-02, Berlin, Germany)

Schlögl, R.: Oxides as Functional Materials in Heterogeneous Catalysis.(Festvortrag Eröffnung SurMat, MPI für Eisenforschung, 2004-12-17, Düsseldorf, Germany)

Schlögl, R.: N-Metall-Wechselwirkungen in der Katalyse. (Ringvorlesung, 2005-01-16, Berlin, Germany)

Schlögl, R.: Photoemission of High-Pressures Festkolloquium für. Prof. Peter Oelhafen, Universität Basel, Inst. f. Physik, 2005-01-31, Basel, Schweiz)

Schlögl, R.: The Dynamic Nature of Heterogeneous Catalysts Workshop Schloss Ringberg "Chemical Physics of Complex Adaptive Matters,.2005-02-07-2005-02-09, Ringberg, Germany)

Schlögl, R.: Styrene Synthesis. A Dual Mode of Operation of a Technical Catalyst System. (Schloss Havreholm, Symposium "Frontiers in Catalysis: A Molecular View of Industrial Catalysis", 2005-02-09, Kopenhagen, Denmark)

Schlögl, R.: Open Access and the Berlin Declaration: The MPG Strategy. (Symposium "The Future of Scientific Publishing", 2005-03-14, workshop during ACS Meeting, San Diego USA)

Schlögl, R.: Carbon Nanofibers on the Surface of Activated carbon: Potential Application in polymer and heterogeneous catalysis. (ACS National Meeting, 2005-03-17, San Diego, USA)

Schlögl, R.: Nanostructured Heterogeneous Catalysts. (CSJ National Meeting, 2005-03-28, Yokohama, Japan)

Schlögl, R.: Initiativen und Sachstand zum Thema: "Open Access". (Lecture Universität Bremen, 1005-04-20, Bremen, Germany)

Schlögl, R.: Nanostrukturierte Katalysatoren: Warum ist klein wichtig? (DECHEMA Workshop Nanomaterialien und Katalyse, 2005-04-28, DECHEMA-Haus, Frankfurt/M., Germany)

Schlögl, R.:Chemische Physik der Grenzfläche: feste Stoffe und Katalyse. (Kolloquium „Dresdner Abhandlungen zur Chemischen Physik fester Stoffe", 60th Birthday Prof. Kniep, 2005-05-06, MPI f. Chem. Phys. Fester Stoffe, Dresden, Germany)

Schlögl, R.: The Potential of MoVTe Catalysts for Propane Oxidation: The Role of Defects for the Catalytic Function. (Irsee Symposium on the Role of Vacancies, Disorder and the Relationship between Surface and Bulk Structure in Selective Oxidation Catalysis (Robert K. Grasselli Foundation), 2005-05-11, Kloster Irsee, Germany)

Schlögl, R.: Einstein und die Chemie (Opening Lecture, Einstein-Festkolloquium, 2005-05-12, Urania, Berlin, Germany)

Dangsheng Su

Su, D. S.: Nano-Carbon as High-performance Catalyst: Carbon Nanofilaments and Nanotubes in Oxidative Dehydrogenation of Ethylbenzene to Styrene: Structure-Activity Relationship. (The Symposium on Applied Chemistry of Chinese Academy of Sciences, 2003-08-15 till 2003-08-17, Changchun, China)

Su, D. S.: Nanostructured Materials in Heterogeneous Catalysis. (Autumn School 2003 on Advanced Materials Science and Electron Microscopy, 2003-09-27 till 2003-10-01, Berlin, Germany)

S, D. S.: Characterization of Diesel Particulate Matter. (Abteilungsseminar, 2004-04-28 till 2004-04-28, Institut für Festkörperphysik, TU-Wien)

Su, D. S.: Carbon Nanotubes as High Performance Catalysts. (Department Seminar, 2004-05-31 till 2004-05-31, Beijing University of Technology, Beijing, China)

Su, D. S.: Carbon Nanotubes in Heterogeneous Catalysis. (Institute Seminar, 2004-06-03 till 2004-06-03, Institute of Physics, Chinese Academy of Science, Beijing, China)

Su, D. S.: Manipulating carbon nanotubes into carbon nanobulbs and carbon Tube-in-tube Assembly. (Institute Seminar, 2004-07-01 till 2004-07-01, Ruder Boskovic Institute, Zagreb, Croatia)

Su, D. S.: EURO-IV Diesel Engine Exhaust Particulates: What Do We Know? (Department Seminar, 2005-01-01 till 2005-01-21, Institute of Isotope, Budapest)

Jacob Wagner

Wagner, J. B., H. Stig, P. L. Hansen, A. M. Molenbroek and B. S. Clausen: In situ investigations of gas-solid interactions of nanocrystals by high resolution TEM. (EMC 2004, 13th European Microscopy Congress, 2004-08-22 till 2004-08-27, Antwerpen, Belgium)

Wagner, J. B.: Transmission Electron Microscopic Characterisation of Catalysts. (2nd International School-conference on Catalysis for Young Scientists, 2005-07-25 till 2005-07-29, Novosibirsk-Altai, Russia)

Marc Willinger

Willinger, M.: Energy loss spectra of inelastically diffracted electrons as a tool for structure investigation. (International Conference on Experimental and Computing Methods in High Resolution Diffraction Applied for Structure Characterization of Modern Materials, 2004-06-13 till 2004-06-17, Zakopane, Poland)

Annette Trunschke

Trunschke, A.: Application of Solid Acid-Base Catalysts in Liquid Phase Reactions – Spectroscopic Studies and Catalysis. (Kolloquium der Fakultät für Mathematik und Naturwissenschaften II, Friedrich-Alexander-Universität Erlangen-Nürnberg, 2004-06-18, Erlangen / Germany)

Department of Chemical Physics **Director: Hans-Joachim Freund**

Group leaders:

Wolfgang Drachsel		until 31.05.2004
Norbert Ernst	(Habilitation)	
Thorsten Klüner	(Habilitation)	until 30.09.2004
Helmut Kuhlenbeck	(Habilitation)	
Jörg Libuda	(Habilitation)	until 31.08.2005
Niklas Nilius		
Thomas Risse		
Günther Rupprechter		
Hans-Peter Rust		
Shamil K. Shaikhutdinov		
Kazuo Watanabe		

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

Markus Heyde
Boonchuan Immaraporn
Dominik Kröner
Dietrich Menzel

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

Paul Bagus	*AvH Awardee*	Oscar Rodriguez de la Fuente	*AvH Fellow*
Athula W.M.T. Bandara	*AvH Fellow*	David I. Sayago	*(ARG)*
Aidan Doyle	*AvH Fellow*	Bo-Hyun Ryu	
Marcella Felicissimo	*AvH Fellow*	Martin Schmal	*AvH Awardee*
Neetha Khan	*AvH Fellow*	Joaquin Silvestre-Albero	*AvH Fellow*
Céline Lemire		Dario Stacchiola	*AvH Fellow*
Pierre Lévesque		Tomás Skála	
Fabiana Mendes		Peter Stair	*AvH Awardee*
Gianfranco Pacchioni	*AvH Awardee*	David Starr	
Randall Meyer	*AvH Fellow*	Martin Sterrer	
Martin Polcik	*(ARG)*	Jonas Weissenrieder	*AvH Fellow*
Emile Rienks		Maxim Yulikov	

Associated Research Group (ARG): Phil Woodruff

Graduate students: 24

Diploma students: 1

Technicians: 12

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.

Wolfgang Drachsel retired from his position at the Fritz Haber Institute and was replaced by Kazuo Watanabe from the University of Tokyo as group leader.

Thorsten Klüner received an offer on a professorship at the University of Oldenburg and left effective October 1st, 2004. Collaboration will continue but there will be no replacement within the department.

Jörg Libuda received an offer on a professorship at the University of Erlangen and left effective September 01, 2005. His position is planned to be taken by Swetlana Schauermann who recently received her PhD at the Humboldt-Universität zu Berlin and will spent a year as a postdoc in Cambridge.

Günther Rupprechter received an offer on a chair at the Technical University of Vienna and will leave at the end of the year 2005. His position will be taken by Martin Sterrer who joined the group a year ago on a Schrödinger Fellowship from Austria.

Shamil Shaikhutdinov was installed as group leader of a new working group “Structure and Reactivity” after working with Helmut Kuhlenbeck’s group for a year.

Phil Woodruff and his photoelectron diffraction group have been associated with the department. The staff is financed through Sfb 546 and jointly by the Inorganic Chemistry and Chemical Physics Departments.

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

1. Spectroscopy and Spectro-Microscopy
   Helmut Kuhlenbeck

2. Structure and Reactivity
   Shamil Shaikhutdinov

3. Low Temperature STM
   Hans-Peter Rust

4. Scanning Probe Spectroscopy
   Niklas Nilius, Norbert Ernst

5. Magnetic Resonance
   Thomas Risse

6. Catalysis/Laser Spectroscopy
   Günther Rupprechter, Martin Sterrer

7. Molecular Beam
   Jörg Libuda, Swetlana Schauermann

8. Photon-Induced Processes
   Kazuo Watanabe

9. Theory Group
   Thorsten Klüner

Associated Research Group: 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 studying properties of metal deposits on well-ordered oxide supports. The goal has been to prepare systems to model dispersed metal and metal oxide catalysts which capture some of the complexities of a real catalyst but can still be studied with surface science techniques, approaching rigor at the atomic level.

As far as oxide supports are concerned we mention:

- In collaboration with Joachim Sauer we have determined the structure of an ultrathin single crystalline silica film conclusively.

- In collaboration with Martin Schmal, Rio de Janeiro, and Horst Niehus at the Humboldt-Universität zu Berlin we have prepared and characterized for the first time well-ordered Nb_2O_5 films grown on $Cu_3Au(100)$.
- We have prepared MgO(100) films on the basis of known recipes and characterized the properties of surface defects, in particular the so called colour centres for the first time with scanning tunnelling spectroscopy (STS) and electron spin resonance spectroscopy (ESR).

The studies of metal deposits onto oxides substrates have come a long way. A number of highlights are mentioned:

- The imaging of individual gold atoms by STM and the first ever ESR spectroscopic study of Au on MgO(100) as a function of the nature of the defects. These studies are intimately related to the ongoing debate on the activity of small deposited Au aggregates.
- Au clusters (n=1 to 5) on a thin alumina film have been imaged at atomic resolution and their electronic states have been investigated. It has been demonstrated that the metal support of the oxide film plays a decisive role in the structure formed and it has also been shown that this is due to the specific properties of gold as opposed to other metals such as Pd for example.
- The variation of the surface potential of an ultrathin FeO(111) film on Pt(111) has been used to self-assemble Au atoms on the FeO surface.
- Individual Au, Ag and AuAg alloy nanoparticles have been characterized with respect to their plasmon resonances using a home built Photon-STM.
- Au colloid particles provided through a collaboration with Marie-Paule Pileni (Alexander von Humboldt Awardee at Fritz Haber Institute) have been investigated with the Photon-STM.

The department has used the prepared model systems to study chemical reactions both under ultrahigh-vacuum as well as under ambient conditions.

- Particle size effects in hydrogenation reactions on supported Pd nanoparticles have been investigated and a strong dependence of the degree of particles size effects on the molecule to be hydrogenated under UHV conditions has been found and explained.

- Communication effects and macroscopic kinetic bistabilities on nanoparticle systems have been studied for CO oxidation.

- The oxidation of Pd nanoparticles on $Fe_3O_4(111)$ has been studied in an attempt to retrieve the involvement of oxidation of the support oxidation reactions. The formation of an oxide layer formed at the Pd-oxide interface has been shown to play a crucial role.

- Supported oxide particles (VO_x, alumina and silica) have been studied. It is shown on the basis of our model studies that a long accepted assignment of vibrational modes used when characterizing real catalytic samples had to be revised.

- Remarkable analogies between reactions under UHV and ambient pressure conditions have been found for hydrogenation reactions. For butadiene hydrogenation quantitative kinetic studies as a function of particle size have revealed that results on supported particles may indeed be extrapolated to single crystal surfaces as the size of the particle facets increase – a result that supports for the first time an *ad hoc* assumption often made.

- Remarkable differences in adsorption capabilities are revealed when co-adsorption experiments under spectroscopic control are carried out at ambient pressure. Non-linear optics (sum frequency generation (SFG)) and polarization-modulated-Fourier Transition Infrared Spectroscopy (PM IRAS) have been set up and employed.

- We have started to study photochemistry of molecules on supported Ag nanoparticles using a new apparatus combining resonant multiphoton ionization techniques with two photo-photoemission spectroscopy. Quantum dynamic calculations in collaboration with Thorsten Klüner, University of Oldenburg, are designed to find a deeper theoretical understanding of the involved elementary steps.

The department is in the process of developing a new research direction by looking at biophysical processes in protein adsorption at model membrane surfaces.

- In collaboration with Wayne Hubbell, UCLA, the adsorption of small proteins on lipid membrane models have been studied by ESR studies on spin labelled systems (both proteins and membranes).

The department continues to push the limits of experimental techniques by putting a major emphasis on instrument development.

- The first break through towards the operation of an ultrahigh resolution spectromicroscopy (SMART) have been obtained. Images including a tetrode mirror for aberration correction have been recorded for the first time.
- A high field ESR spectrometer coupled with an ultrahigh-vacuum multipurpose instrument has been designed and is being built.
- A new low-temperature STM is under construction. This instrument is planned to combine LT-STM with photon STM and a newly designed capability to record Auger spectra near atomic resolution.

Collaboration with other departments and three universities in Berlin on various problems is in place and has been reinforced by the installation of an International Max Planck Research School “Complex Surfaces in Material Science” which is now fully operative. The school is coordinated by the department.

The Department of Chemical Physics participates in two SFBs of the DFG, i.e. SFB 546 and 290, as well as in two Schwerpunktsprogrammen of the DFG (in the programme “Dynamik von Elektronentransferprozessen an Grenzflächen”: “Zeitaufgelöste Untersuchungen zur Dynamik der photoinduzierten Desorption von NO auf NiO(100): Experiment und Theorie”, and in the programme “Brückenschläge zwischen idealen und realen Systemen in der heterogenen Katalyse“: “Synthese und Partialoxidation von Methanol an wohldefinierten Modellkatalysatoren”). In addition, joint projects exist between the Department and the National Laboratory, Pune, India (funded through Volkswagenstiftung), Universiti Malaya (funded through FHI and Ministry of Research and Technology Malaysia), with the Hebrew University, Jerusalem, Israel, “Dynamics of Electronic Processes at Confined Environment” (funded through the German-Israeli-

Foundation), with Johnson Matthey PLC-Technology Centre (funded through EPSRC of the U.K.), with Claude Henry, Centre de Recherches sur les Mécanismes de la Croissance Cristalline, C.N.R.S., Marseille, “Oxide Surfaces” (funded through the European Commission), with Graham Hutchings, University of Wales, Cardiff, U.K., AURICAT (funded through the European Commission), with Gabriele Centi, University of Messina, Italy, “Integrated Design of Catalytic Nanomaterials for a Sustainable Production” (IDECAT) (funded through the European Commission), with Alessandro Fortunelli, IPCF del CNR, Pisa, Italy, “Growth and Supra-Organization of Transition and Noble Metal Nanoclusters” (GSOMEN) (funded European Commission), as well as with a variety of partners (universities) in Europe and the United States (funded through EU and other funding organisations), and also, in particular, with the Boreskov Institute in Novosibirsk, Russia.

The department has associated with it the PP&B group, which continues to make very important contributions in a variety of areas. It is headed by Heinz Junkes. The group PP&B provides computer services such as cpu resources, networks, software, mailing, purchase consulting, etc. for all members and visitors of the institute. One of the group’s tasks is the sustainable development of new process computer systems (microscope control including image processing systems for the scientists at the institute and at BESSY).

Another associated activity concerns the crystal preparation laboratory that serves the entire institute.

Progress Reports

In the following, highlights obtained in the various groups during the last two years are summarized:

Spectroscopy and Spectro-Microscopy

A major part of the studies in the past two years was devoted to the investigation of ordered, about 100Å thick $V_2O_3(0001)$ layers. These studies were performed in the framework of the Sonderforschungsbereich 546 of the Deutsche Forschungsgemeinschaft which mainly deals with the properties of vanadium oxides and aims towards a deeper understanding of catalytical processes occurring on the vanadium oxide based catalysts.

Another important activity is connected with the SMART spectromicroscope which is supervised by Th. Schmidt. It is a collaborative effort between University of Würzburg and Fritz Haber Institute.

Surface structure of the reduced $V_2O_3(0001)$ surface

$V_2O_3(0001)$ was prepared as a thin film on Au(111). Under typical UHV conditions the film is terminated by a layer of vanadyl groups which may be removed by electron irradiation. The reduced surface prepared this way was studied with STM and it appears that it is terminated by a layer of vanadium atoms, similar to the case of the reduced $Cr_2O_3(0001)$ surface which was structurally characterized a number of years ago. Contrary to the case of the vanadyl terminated surface the reduced surface is chemically highly active which may be due to the existence of easily accessible vanadium atoms at the surface.

Adsorption on $V_2O_3(0001)$

The adsorption of different gases (O_2, CO, CO_2, H_2O, and propane) on $V_2O_3(0001)$ was investigated with XPS using synchrotron radiation, vibrational spectroscopy and TDS. In all cases the vanadyl terminated surface turned out to be rather inert whereas the reduced surface is highly active. Similar to what has been observed for $Cr_2O_3(0001)$, O_2 forms a layer of chemisorbed negatively charged molecules (O_2^-) at low temperature which transform into vanadyl groups upon annealing. CO_2 appears to form a bent negatively charged precursor ($CO_2^{\delta-}$) at low temperature which at least partially dissociates upon warming up. As a result of this dissociation vanadyl groups are formed and the reduced $V_2O_3(0001)$ surface is re-oxidized. Water partially dissociates on the reduced surface leading to a layer of hydroxyl groups. These groups are stable on the surface up to temperatures of above 500 K. At this temperature H_2O desorption due to recombination of the hydroxyl groups with the hydrogen atoms of the dissociated water molecules is observed. Adsorption of CO exhibits a rather complicated temperature-dependent pattern as indicated by vibrational spectroscopy. It appears that the CO molecules desorb molecularly, but complicated structural rearrangement of the CO layers seems to occur when the film is warmed up.

The interaction of propane with the reduced surface was studied with the activity of vanadium oxides for the catalytic oxy-dehydrogenation of propane towards propene in mind. Electron spectroscopy indicates that oxygen-containing molecules form upon propane adsorption. Such species are expected to form as intermediates in the course of catalytic propene formation.

Preparation of V_2O_5 and MoO_3 thin films

In-situ preparation of ordered films simplifies the investigation of their properties since it is usually easier to prepare thin films than to handle single crystals. Preparation of ordered V_2O_5 and MoO_3 layers covering the whole surface has not been reported yet. We prepared such films on Au(111) via oxidation at elevated oxygen pressure and characterized them with STM and XPS. According to XPS the oxidation state as judged from the V2p and Mo3d chemical shift is somewhat below the value expected for the V^{5+} or Mo^{6+} which may be attributed to final state effects related to screening of the XPS core holes by substrate [Au(111)] electrons. The films are only one or two layers thick and exhibit a structure which likely does not correspond to the structures known for bulk material.

The SMART spectromicroscope

The lateral resolution in photoelectron emission microscopy (PEEM) is basically limited by aberrations, which can be overcome by suitable correction techniques. The SMART spectromicroscope uses an electrostatic tetrode mirror combined with a highly symmetric magnetic beam-splitter to compensate simultaneously for both, the chromatic and spherical aberrations. SMART aims at a lateral resolution of 2 nm with an energy resolution of 100 meV and is therefore the most ambitious project in the field of spectroscopic microscopy worldwide. In addition to the high lateral resolution a gain in transmission of up to two orders of magnitude can be obtained. The SMART competes particularly against the PEEM3 project at the Advanced Light Source which follows the identical concept of aberration correction by an electrostatic mirror, but without energy filtering. Whereas the PEEM3 project will need still 2 years for the final setup, the final setup of the SMART instrument started full operation at the UE52-PGM beam line at BESSY in November 2004.

From March to August 2004 the SMART microscope was completely reassembled, mechanically aligned and tested at the Fritz-Haber-Institute. The instrument was transferred back to the UE52-PGM beam line in September 2004. The entire installation of the final SMART version, i.e. with aberration corrector, OMEGA-filter, and electron gun, all mounted on a vibration-damped frame, was finished at the end of October.

The test measurements with this new version of the SMART are a kind of pioneering work, because the first time worldwide a PEEM with a tetrode corrector is used with soft x-rays. Though the adjustment of the correction system was very preliminary – the theoretically calculated mirror settings were used without any fine tuning – the results are very exciting. In LEEM we could already show a lateral resolution better than 14 nm. Because the interference contrast at the steps causes an additional broadening, the lateral resolution is clearly below 14 nm. This is the limit that the best LEEM/PEEM instruments without aberration correction can reach. Additionally, the increase in transmission could directly be shown by using larger apertures than those of the intermediate setup without corrector. In the limited available beam time, we could not yet demonstrate an improvement in lateral resolution in the XPEEM mode due to the fact that the alignment of the corrector in the XPEEM mode is clearly more critical compared to the LEEM mode (reflected electrons). The near future task is now to transfer this technically possible resolution to the XPEEM mode.

Beside the lateral resolution the energy resolution is the second figure of merit for a spectroscopic microscope. In the SMART the aberration corrected OMEGA filter is used as a directly imaging analyzer. The overall energy resolution is 180 meV. Deconvoluting this value with the photon resolution of the beam line, which was set to 100 meV, gives an energy resolution of 150 meV for the OMEGA filter. This means the world record for all imaging electron analyzers. Taking into account that for the high imaging quality the path energy has to be 15.000 V, the resolving power of this analyzer gives an extremely high value of 100.000! This also shows the high demands on the electron optics.

Besides the operation mode as a spectro-microscope (PEEM, XPEEM, LEEM), the SMART instrument allows further spectroscopy (NEXAFS, XPS, Auger) and diffraction methods (μ-spot-LEED, PED), even at selected areas of few nanometers size.

Structure and Reactivity

The projects continue our previous activity in studying the hydrogenation/ dehydrogenation reactions over Pd model catalysts (ATHENA) and the catalytic behaviour of supported gold nanoparticles (AURICAT). Other projects are aimed at a deeper understanding of structures of well ordered oxide films such as silica on Mo(112) (GSOMEN) and iron oxides on Pt(111). In addition, in the course of our long-term studies of structure-activity relationships for vanadia catalytic systems (SFB 546), we have initiated studies on preparation and characterization of ordered niobia films as models for Group 5 catalysts.

Hydrogenation of hydrocarbons on Pd and Pd-Ag surfaces

The reactions of ethyne, ethene and different pentenes on Pd particles deposited on a thin alumina film has been studied by temperature programmed desorption (TPD). A number of hydrocarbon transformations, such as dehydrogenation, H-D exchange reaction and hydrogenation, was observed. However, the hydrogenation to alkane is only observed on particles and not Pd(111) single crystal, which is rationalized on the basis of accessibility of subsurface hydrogen in the particles facilitating hydrogen addition to alkene.

The adsorption of trans-2-pentene on Pd particles is shown to exhibit size-specific behaviour, which results in a strong increase in hydrogenation activity (under the conditions studied) within the 1-5 nm particle size range. In contrast, ethene hydrogenation is size insensitive. The size effects are explained by the hydrogenation reactions proceeding via di-σ-bonded pentene, which is favoured on the terrace sites of large particles, and π-bonded ethene.

The effect of silver on reactivity of Pd particles in acetylene hydrogenation has been examined. The combined scanning tunnelling microscopy (STM), photoelectron spectroscopy (XPS) and infrared reflection absorption (IRAS) results show that silver segregates on the particle surface and basically blocks acetylene and hydrogen chemisorption. However, at the smallest Ag coverage, the selectivity towards ethane is found to be smaller than ethylene, which is consistent with the promoting effect of silver observed on commercial Pd-Ag catalysts of selective hydrogenation.

Surface chemistry of gold

In order to determine structure-reactivity relationships on gold catalysts, model systems involving Au metal particles deposited on well-ordered oxides (Al_2O_3, FeO, Fe_3O_4, Fe_2O_3) and carbon films were studied. Of particular interest is the role of the support in formation and stabilization of Au nanoparticles and their adsorption behaviour towards CO and oxygen.

For Au deposited at low temperatures (<100 K) on all supports studied, TPD experiments revealed a particle size effect such that smaller particles adsorb CO more strongly. The TPD and IRAS data for various supports indicate that interaction of CO with Au surfaces is essentially identical and independent on the particle size, dimensions and nature of support. It has been concluded that the CO adsorption only includes highly uncoordinated surface atoms. Annealing to 400 - 500 K causes gold sintering and particle restructuring, thus resulting in a loss of the low coordinated Au atoms, on which CO may adsorb. Gold particles are found to be inert towards molecular oxygen under the conditions studied.

In order to examine the stability of the gold particles in a reactive atmosphere, the morphology of Au particles deposited on thin FeO(111) films at elevated pressures of CO, O_2, CO + O_2, and H_2 has been examined using *in situ* STM at room temperature. The Au particles are found to be quite stable in O_2 and H_2 environments at pressures up to 2 mbar. However, in CO and CO+O_2 atmospheres, the destabilization of Au particles located at the step edges occurs leading to the formation of mobile Au species, which migrate across the oxide surface.

Iron oxide films: surface terminations of $Fe_3O_4(111)$ and α-$Fe_2O_3(0001)$

The surface structure of $Fe_3O_4(111)$ films grown on Pt(111) has been studied using CO as a probe molecule. Employing TPD, IRAS and HREELS, three adsorption states were observed, for which the adsorption energies and CO stretching frequencies were determined.

The termination of the α-$Fe_2O_3(0001)$ surface has been studied. Using IRAS and CO adsorption, the α-$Fe_2O_3(0001)$ surface has been observed for the first time to exhibit the ferryl (Fe=O) groups, coexisting with domains of the Fe-terminated surface. The close similarity of the results on hematite to the previously published results, observed in our Department on the (0001) surfaces of Cr_2O_3 and V_2O_3, strongly suggest that the M=O termination under certain oxygen pressure conditions is the most stable for the close-packed surfaces of transition metal oxides with the corundum structure.

Structure of thin silica films: revisited

During the last year, we re-investigated the structure of the silica films on Mo(112) combining STM, IRAS and XPS. The silica surface was atomically resolved by STM. DFT calculations performed by J. Sauer and co-workers at Humboldt-Universität zu Berlin revealed that the film consists of a two dimensional network of corner sharing $[SiO_4]$ tetrahedrons, with one oxygen of each tetrahedron binding to the protruding Mo atoms of the Mo(112) surface.

Group 5 model catalysts: Supported vanadia clusters and well ordered niobia films

Vanadia clusters were supported on thin alumina and silica films by V evaporation in an oxygen ambient. The vanadia particles exhibited similar morphology on both supports but differ in the extent of particle-support interactions. It is shown that these differences in the vanadia-support interface region strongly affect the CO adsorption behaviour of the particles. The measured vibrational spectra of the model systems are interpreted on the basis of theoretical calculations for model compounds and surface models for both the vanadia silica and the vanadia/alumina system performed by group of J. Sauer (HU, Berlin). The combined information is then compared with Raman spectra of real catalytic materials such as vanadia supported over δ-Al_2O_3 and mesoporous SiO_2 (MCM-41) (in collaboration with groups of P. Stair (Northwestern University, Illinois) and M. Baerns (ACA, Berlin). A consistent interpretation is developed, which shows that the accepted interpretation of vibrational spectra from vanadia catalysts must be revised.

In order to grow well ordered niobia films, we used an approach developed by H. Niehus and co-workers in HU (Berlin) using an oxygen implanted $Cu_3Au(100)$ single crystal as a substrate. Using LEED, STM and angular resolved photo-electron spectroscopy (collaboration with the group of H. Kuhlenbeck at BESSY II), the structure of niobia films grown by Nb deposition onto O/$Cu_3Au(100)$ and subsequent oxidation at elevated temperatures has been studied. The preparation leads to the formation of a flat, well-ordered thin niobia film of a hexagonal symmetry, which in turn forms a $NbO_x/Cu_3Au(100)$-(2x7) coincidence structure. The results suggest that the film consists of 2/3 ML of Nb between two oxygen layers, where Nb^{5+} cations occupy the hollow sites over the close packed O-layer.

Low Temperature STM

The activities of the group focused on the investigations of model structures used for heterogeneous catalysis, specifically on (i) Au / FeO / Pt(111), (ii) Au / Al_2O_3 / NiAl(110), and (iii) MgO / Ag(100). The experiments were performed with a low-temperature STM, suited for conductance and inelastic electron tunneling spectroscopy and a combined low-temperature STM/AFM for experiments on insulating films.

(i) The single-layer FeO film on Pt(111) forms a hexagonal Moiré cell with a lattice constant of 2.5 nm, wherein the Fe atoms alternatively occupy hcp, fcc and on top sites with respect to the Pt lattice. This modulated Pt-Fe stacking sequence induces an inhomogeneous surface potential, as concluded from the large image contrast using bias voltages above the sample work function. The contrast enhancement is the result of field-emission resonances occurring at different energies within the FeO Moiré cell, dependent on the local surface potential. Apparent-barrier height (dlnI/dz) images also reveal lateral variations in the surface potential. The inhomogeneity is attributed to small modulations in the Fe^+-O^- distance within the Moiré cell, emphasizing the polar character of the FeO film. The varying surface potential strongly affects the distribution of single Au adatoms deposited onto the FeO film at 10K. The adatoms preferentially bind to hcp domains within the Moiré cell, which is the region with the largest surface dipole. Consequently, the Au atoms arrange into a hexagonal network with 2.5 nm lattice constant at higher coverage. Inelastic electron tunneling spectroscopy was employed to characterize the adsorption of CO molecules onto the single Au adatoms.

(ii) Deposition of single Au atoms on Al_2O_3/NiAl(110) at 10 K, leads to the appearance of monomers, dimers, and short Au chains containing 2-5 atoms on the surface. Discrimination between the different species is possible by dI/dV spectroscopy, revealing a single unoccupied state around 2.2-2.6 eV for monomers, a doublet for dimers and set of unoccupied and occupied resonances for larger aggregates. While several defined orientations are found for Au dimers on the surface, the Au chains always follow a distinct direction: Independent of the orientation of the Al_2O_3 domain, they are closely aligned to the [110] direction of the NiAl substrate. This alignment gives a clear indication for a substantial role of the metal support in the Au binding process. For less electro-negative materials, such as Pd, no comparable effect is observed and Pd atoms preferentially adsorb on line defects of the oxide film.

(iii) STM and AFM studies have been performed on 4 ML thick MgO films on Ag(100), aiming for a characterization of the relationship between electronic and morphological properties of surface defects. The MgO film grows in a layer-by layer fashion and forms large rectangular islands, exhibiting {100} step edges. Topographic characterization is possible by imaging at high positive sample bias (+3.5 V). Using conductance spectroscopy, the onsets of the MgO valence and conduction band are determined to 5 eV below and 2.3 eV above E_F, respectively. Electronic defects on the edges of MgO islands become visible for tunneling at bias voltages within the band gap. One defect type is characterized by the presence of an energy level at 2 eV above the valence band, slightly depending on the local coordination of the site. A second defect type can be artificially produced by scanning at high positive voltage and shows a pair of occupied/unoccupied states at ± 1 eV with respect to E_F. Comparison with theory allows an assignment of both defect types to singly (type I) and doubly occupied (type II) oxygen vacancies. The assignment of type II defect is also inline with recent EELS experiments, showing a characteristic MgO excitation of 2.0 eV, similar to the level separation for the type II defect. The two different defects in the MgO film were also generated by electron bombardment from an external filament.

Improvements of the 4K-STM/AFM imaging sensor allows now AFM investigations with atomic resolution using a small amplitude frequency modulation atomic force microscopy technique for increasing sensitivity to short range forces. The quartz tuning fork sensor has a spring constant of about 30.000 N/m and is equipped with a Pt/Ir tip, which allows registration of AFM and STM images. This possibility was used to compare the apparent height of Al_2O_3 islands on a NiAl(110) support in STM and AFM measurements. Due to the insulating character of the oxide film, the apparent layer height strongly depends on the bias voltage in STM, whereas in the AFM mode no electronic effects have to be taken into account. The comparison of force and tunneling spectroscopy curves acquired on NiAl(110) and Al_2O_3 enables a determination of the real height of the oxide layer. Atomically resolved images on MgO / Ag(100) were acquired in the attractive and repulsive regime. A change in contrast was found when switching between both operating conditions.

Scanning Probe Spectroscopy

Two aspects related to the optical properties of single metal particles were in the focus of experiments performed in the SPS group. First, experiments on mixed Ag-Au clusters have been accomplished to study the effect of alloy formation on the photon emission properties. Second, the importance of cluster-cluster interactions on the optical behavior was explored for self-assembled arrays of Ag colloids and disordered Ag cluster ensembles with varying densities.

The optical properties of Ag and Au particles are determined by distinct extinction lines due to Mie plasmon excitations in the cluster electron gas. Since plasmon energies clearly differ in the pure materials, photon emission spectroscopy can be employed to follow the Ag-Au alloying process. We have investigated the optical properties of mixed Ag-Au clusters on Al_2O_3 / NiAl(110), stimulating photon emission from an individual cluster by electron injection from the STM tip. Alloy clusters were prepared with varying volume ratios and deposition sequences of Ag and Au. For simultaneous deposition, a single emission line is observed, which continuously shifts from the Ag to the Au plasmon energy with increasing Au amount in the deposits. The observed red-shift is reproduced by model calculations based on Mie theory and indicates complete alloying of both materials in the clusters. After successive deposition of Ag and Au, two emission peaks occur in the spectra. This observation indicates formation of shell-core particles, exhibiting two independent plasmon modes in the respective particle layer. Relative intensities and energy positions of the two modes vary with the thickness of shell and core, and reveal substantial intermixing of both materials at the interface.

The plasmon position in metal deposits is additionally influenced by electromagnetic interactions between neighboring particles on the surface. Plasmon modes oscillating perpendicular to the surface couple destructively, decreasing the particle polarizability and increasing the energy of the out-of-plane mode. In-plane plasmon oscillations experience constructive interference, which shifts the optical mode to lower energies. The influence of inter-particle interactions on the optical properties is probed for Ag nano-crystals arrays, fabricated by a reverse micelle technique in collaboration with M.P. Pileni from Paris University. Depending on their size distribution, the particles arrange into a long-range hexagonal network or form a disordered ensemble on flat HOPG substrates. Optical spectra for ordered and disordered particle layers reveal two emission peaks, which could be attributed to in-plane and out-of-plane plasmon oscillations on the basis of polarization measurements and model calculations. Plasmon energies in the particle assembly are considerably shifted from the single-particle energies, manifesting the influence of dipolar coupling in the layer. The relative intensities of in-plane and out-of-plane plasmon modes sensitively depend on the long-range order in the particle network.

For Ag particle ensembles fabricated by metal vapor deposition on a Al_2O_3 film, the mean particle density on the surface could be varied over one order of magnitude ($0.5 - 12x10^{11}$ cm^{-2}). The nucleation density on the oxide was controlled by changing Ag flux and sample temperature as well as by creating additional nucleation sites via Ar^+ sputtering of the oxide surface. With decreasing cluster-cluster distance, a pronounced blue-shift of the out-of-plane plasmon mode is detected, which is in perfect agreement to model calculations considering exclusively dipole-dipole interactions. The shift of the plasmon energy vanishes, when extremely flat Ag particles are prepared on the surface.

Another major activity of the SPS group was the design and construction of a new low-temperature STM for various spectroscopic applications on the nanometer scale. In variance to standard concepts of low-temperature STM, the specially designed He^4 cryostat allows free access to the sample, enabling experiments on the interaction of electrons and light with a confined sample area under the STM tip. Electrons and light emitted from the tunneling junction are analyzed by an HMA and a sensitive CCD detector, respectively, attached to the vacuum chamber. The new instrument has potential applications in the field of Auger-, EEL- and optical spectroscopy with a lateral resolution of some nanometer, which allows for a local topographic, electronic, optical and chemical analysis of the sample surface

Magnetic Resonance

The magnetic resonance group was engaged in three projects: the characterization of paramagnetic defects on thin epitactic MgO films, the evaluation of the structure and dynamics of adsorbed proteins, and the construction of a new high-field electron paramagnetic resonance (EPR) experiment operating at 95 GHz.

The first project is devoted to the characterization of defects in particular paramagnetic point defects on oxide surfaces using MgO as a prototype oxide surface. This project is a joint effort with the low temperature STM group which investigates the structural as well as electronic properties of these sites. The study was triggered by the important role of defects on the properties not only of the surface itself but also of adsorbates or deposited metal being in contact with these centers. EPR is well suited to investigate a certain class of defects on such surfaces namely paramagnetic point defects often called color- or F-centers. For the epitaxial MgO-film the orientation of the different sites on the surface with respect to the laboratory framework is known. With this knowledge it is possible to extract not only the g-tensor components but also the location of the sites on the surface from angular dependent EPR measurements. It was shown that the color centers produced by electron bombardment of the surface are mostly located on the edges of the MgO facets. In addition, interaction with adsorbed gas molecules or metal atoms can give further insight into the nature of these sites. It can be shown that paramagnetic defects are very reactive species which react with a large variety of gases

(CO, O_2, N_2O, NO) as well as metal atoms (e.g. Au). The reaction with some gases and metal atoms create new paramagnetic species which offers the possibility to characterize the chemistry of these centers by EPR spectroscopy.

The goal of the second project is to gain insight into the relationship between the physical and chemical properties of surfaces and their impact on the structure of adsorbed proteins. This is challenging since little is known on the details of the structural modifications which is due to a lack of experimental techniques capable to address this question. In this project we want to show that EPR spectroscopy in combination with a site-directed spin labeling approach is an appropriate tool to investigate the structure of a protein adsorbed to well-defined planar surfaces. The strategy of the site directed spin labeling is to introduce spin probes at predefined positions within the protein sequence, using molecular biology techniques (in collaboration with W. L. Hubbell, UCLA), to act as a reporter on the structure and dynamics of the protein at this residue.

As a benchmark system T4 lysozyme was adsorbed vectorally via a N-terminal 6-His-tag to a planar, zwitter-ionic lipid bilayer exposing specific binding sites for the His-tagged protein. For such a system only little interaction between the surface and the protein is expected which is in perfect accordance with the experimental results. The addition of negatively charged lipids to the lipid bilayer is expected to enhance the interaction with the positively charged T4 lysozyme. At high ionic strength of the buffer solution where electrostatic interactions are strongly shielded protein adsorption leads to a phase separation of the lipid bilayer, however, no significant structural modification of the protein is observed. Upon reduction of the ionic strength the situation changes and the protein molecules starts to form compact protein aggregates on the surface. In comparison, adsorption to a quartz surface, which has a comparable negative charge at the given conditions, leads to the unfolding of one domain of the protein at high ionic strength while the other domain containing most of the net charge is virtually unaffected by the adsorption event. This indicates that the adsorption on quartz under these conditions is strongly driven by hydrophobic interactions, in accordance with published thermodynamic measurements.

Finally, the group is engaged in the planning and construction of a new high field (95 GHz) EPR machine operating under UHV conditions. As compared to the existing EPR setup operating at 10 GHz this offers an enhanced spectral resolution combined with an improved intrinsic sensitivity. In addition, it should be possible to apply modern pulse spectroscopic techniques not feasible at X-band to be used on single crystalline surfaces, too. Since a 95 GHz EPR spectrometer is commercially available, the most important challenge for a successful implementation of the spectroscopy is the construction of an appropriate resonator structure. To accommodate the specific needs of a UHV surface science experiment it is not possible to use a monomodal resonator, instead we decided to use a semiconfocal Fabry-Perot interferometer as the resonator structure. Here, the single crystal metal surface serves as the planar mirror of the Fabry-Perot interferometer which requires a very precise adjustment of the surface in terms of distance (better than 0.5 μm) and angles (better than 0.05° in both directions) under UHV conditions inside the 60 mm wide bore of a superconducting magnet. To combine the requirements of the microwave radiation with those of the UHV technology, the UHV chamber is sealed by a 150 μm thick microwave transparent quartz window being placed between the single crystal surface and convex mirror of the Fabry-Perot interferometer. The planning of the setup is almost completed by now and the assembly of the different part has started in June this year.

Catalysis/Laser Spectroscopy

In-situ spectroscopy using sum-frequency generation (SFG) has come a long way and, after being extensively applied to fundamental questions such as atmospheric pressure adsorption of molecules, is now applied to more complex nanoparticle model catalysts (Pd-Al_2O_3/NiAl(110), Pd-Nb_2O_5/Cu_3Au(100), Co-Nb_2O_5/Cu_3Au(100)) and to various catalytic reactions (CO and ethylene hydrogenation, 1,3-butadiene hydrogenation, methanol decomposition and oxidation). The high-pressure setup for polarisation-modulation (PM)-IRAS combined with pre- and post-reaction XPS is now fully functional and was mainly employed to study oxidation reactions on Pd nanoparticles.

Nonlinear optical IR-visible sum-frequency generation (SFG) spectroscopy

SFG allows to obtain vibrational spectra of adsorbates on model catalyst surfaces from UHV up to atmospheric pressure and is, therefore, particularly suited for in-situ studies.

Model surfaces were prepared in a UHV surface analysis system (equipped with LEED, AES, TPD), and subsequently transferred under UHV into an SFG-compatible UHV-high pressure reactor, which was connected to a gas chromatograph and mass spectrometer for product analysis.

A combination of SFG and TDS was used to study the interaction of well-facetted Pd nanoparticles (mean size ~5 nm) on Al_2O_3/NiAl(110) with CO and hydrogen, which is relevant for a number of catalytic reactions, e.g. methanol synthesis or olefin/dien hydrogenation. These studies indicated that Pd-hydride formation proceeded predominantly via minority sites on Pd nanoparticles, i.e. hydrogen diffused into the particles via defects and (100) faces. Thermal decomposition of the hydride leads to an "explosive" desorption of hydrogen which may even desorb „through" a CO overlayer on the surface of the Pd particles. This effect is related to the finite size of the Pd nanoparticles and may have an impact on catalytic activity. During CO hydrogenation at 1 bar, an adsorbate structure was observed that only occurred at high pressure/high temperature. An increased fraction of weakly bonded on-top CO pointed to surface roughening or to a not-perfectly ordered CO overlayer which only occurs under reaction conditions.

SFG, TDS and AES were also applied to study the interaction of CO and H_2 with Pd-Nb_2O_5/Cu_3Au(100) and Co-Nb_2O_5/Cu_3Au(100) model catalysts (mean particle size ~ 4 nm), both under UHV and mbar pressure. For instance, for Pd-Nb_2O_5 SFG detected CO adsorption on Pd (on-top bonded CO at 2110 cm^{-1} and bridge bonded CO at 1990 cm^{-1}), but also on Nb_2O_5 (2126 cm^{-1}) at 110 K. When both the Pd and Co systems were annealed to ~300 K, irreversible (structural) changes were observed by SFG and TDS, i.e. a strong reduction in the CO adsorption capacity as well as changes of the vibrational frequencies and desorption temperatures, pointing to metal-support interaction.

Another subject of interest was methanol decomposition on Pd which proceeds either via dehydrogenation to CO and hydrogen or via methanolic C-O bond scission producing carbonaceous species (CH_x or C), the latter deactivating the catalyst. The kinetics of the evolution of these species and their preferred binding sites were analyzed, combining SFG, PM-IRAS (see below) and XPS. Post-reaction SFG spectra of CO suggested that the "CH_x" species were bound to threefold hollow sites, presumably being elemental carbon or graphite at higher temperature, and also that significant carbon dissolution in Pd occurred.

Alumina supported Pd nanoparticles (mean size 2 to 10 nm) and Pd single crystals were also used to study (selective) hydrogenation 1,3-butadiene to 1-butene, trans-2-butene, cis-2-butene and/or n-butane. Kinetic measurements by gas chromatography at 1 bar showed a very different behaviour of Pd nanoparticles as compared to single crystals. However, by correlating the catalytic activity of Pd nanoparticles for 1,3-butadiene hydrogenation with the exact particle surface structure we were able to prove that “large” Pd particles behave identical to Pd(111) single crystals, while Pd particles below 4 nm do not. As a result, although 1,3-butadiene is known to be structure-sensitive, the reaction is in fact particle size independent if the correct morphology of the Pd nanoparticle is taken into account. Hydrogen adsorption on the hydrocarbon covered Pd surface seems to be the rate-limiting step. Spectroscopic studies by SFG and XPS are currently performed.

Polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS)

Methanol dehydrogenation and partial methanol oxidation at mbar pressure were examined by PM-IRAS using a UHV-high pressure cell. Dehydrogenation proceeded via formaldehyde to CO, with both species being identified by PM-IRAS. XPS revealed substantial C-O bond scission at elevated pressure ($\geq 10^{-6}$ mbar) with the carbonaceous deposits being located both in surface and subsurface positions. During methanol oxidation at mbar pressure gas chromatography identified CO_2, H_2O, and CH_2O as products. Although the vibrational frequencies of adsorbed CO, observed on the surface during the oxidation reaction, are compatible to metallic Pd, post-reaction XPS spectra indicated a (partial) oxidation of the Pd nanoparticles under reaction conditions. This was confirmed by examining the oxidation of Pd particles and of Pd(111) under UHV and at mbar oxygen pressures (without methanol) by XPS and PM-IRAS.

Molecular Beam

The aim of the molecular beam group is to establish a connection between the geometric and electronic structure of complex surfaces, as studied by several workgroups in the department, and the reaction kinetics and dynamics at these surfaces. With respect to a fundamental understanding of particle size or support effects in heterogeneous catalysis, those kinetic phenomena are of particular interest, which lead to deviations from the kinetics and dynamics observed on simple single crystal surfaces. In combination with complex but well-defined model surfaces, the application of molecular beam techniques provides very detailed kinetic data under well-controlled conditions. These data are used to develop microscopic models describing the kinetics of surface reactions at complex and nanostructured surfaces.

The unique molecular beam spectroscopy experiment, previously developed and set up in the department, has already been successfully applied to several reaction systems, such as e.g. the CO oxidation (cooperation with C.R. Henry, CRMCN-CNRS, Marseille, France), the decomposition and oxidation of methanol (cooperation with G. Rupprechter, FHI Berlin, N. Rösch, TU Munich) and the reduction of NO (cooperation with C. S. Gopinath, Pune, India). In the last two years, the group has been mainly focussing on two new fields: (i) the development of methods and approaches which allow us to study nanoscale kinetic phenomena in catalysis and (ii) the investigation of the oxidation and reduction behaviour of supported nanoparticles:

(i) In addition to conventional structure, size and support dependent effects, there are kinetic phenomena which exclusively arise from the limited size of the reaction system. Examples are so-called communication effects, which are the result of surface diffusion of adspecies between different sites, or coverage fluctuations which arise from diffusion limitations on or between small particles. An important prerequisite in these studies is a very large range of accessible particle sizes. Towards this aim, the group has employed supported Pd model catalysts prepared by electron beam lithography (in collaboration with B. Kasemo, Chalmers Univ. of Technology, Göteborg, Sweden), which - in addition to the model systems prepared in the department via physical vapour deposition - make available particle sizes up to several hundred nanometers in diameter.

The diffusion of reactants over the particles was studied employing CO oxidation as a test reaction. Experimentally, multi-molecular beam experiments and angular-resolved detection of products were combined. Together with microkinetic simulations based on diffusion-reaction models, these experiments allow us to (a) derive information of the surface mobility of reactants under reaction conditions and (b) provide data on the distribution of local reaction reaction rates over the nanoparticle surface. As a second phenomenon, kinetic bistabilities during CO oxidation were investigated. It could be shown that macroscopic kinetic bistabilities were quenched with decreasing particle size as a result of fluctuation induced transitions between the two reactive states.

(ii) More recent work of the group focused on the oxidation behaviour of small noble metal nanoparticles. From an application point of view, this is a highly relevant topic: First, the oxidation of small supported particle is often found to be closely related to particle sintering. Secondly, the role of the oxide and surface oxide phases in catalytic reactions is not clear in many cases.

In order to experimentally approach both issues, we have performed molecular beam/IRAS studies in combination with high resolution PES (cooperation with H. Kuhlenbeck, FHI) and STM (cooperation with Sh. K. Shaikhutdinov, FHI, Berlin) work. As a first set of model systems we have chosen Pd aggregates supported on iron oxide films (FeO, Fe_3O_4) on Pt(111). It was found that at elevated temperatures the reversible oxygen uptake increases rapidly, finally leading to full surface oxidation. However, the oxidation behaviour of the Pd nanoparticles was found to be drastically different from Pd single crystals. First, it could be shown that particle growth and sintering is directly connected to the onset of surface oxidation. Secondly, PES studies employing synchrotron radiation (BESSY II) revealed that oxidation of the particles starts at the particle/support interface rather than at the particle/vacuum interface. Moreover, the formation of the interface oxide is thermodynamically preferred over oxygen chemisorption and surface oxide formation. Oxygen from this interface oxide can be reversibly transferred to the metallic part of the surface and vice versa. The result is a new storage mechanism, in which the interface oxide acts as an oxygen reservoir. Future studies will focus on the question, if the observed oxygen storage mechanism is a general effect, which is also present on other metal/oxide systems.

Photon-Induced Processes

The activities of the group are focused on the investigation of surface photochemistry, photoelectron spectroscopy, and photoelectron microscopy on supported metal nanoparticles and clean or modified metal oxides by using fs- and ns-laser pulses. The electronic structures of metal nanoparticles depend on the particle size and the morphology. By tuning the electronic structure of metal nanoparticles, it may be possible to control the photochemistry of adsorbates on their surfaces. For this purpose, we investigate the electronic structure and electron dynamics at the metal nanoparticles using two-photon photoemission spectroscopy (2PPE), and surface photochemistry by using REMPI (resonance enhanced multiphoton ionization), MS-TOF (mass selected time-of-flight), and TPD (temperature programmed desorption) measurements. We also maintain the ability to acquire two-dimensional information of the surface electronic structures and electron dynamics by a time-resolved photoelectron emission microscope (PEEM) with µm resolution.

The 2PPE measurements were conducted on silver nanoparticles supported on thin alumina films on NiAl(110). Due to the plasmon excitation, the photoelectron yield from silver nanoparticles was enhanced by a factor of hundreds compared to Ag(111). The laser power dependence clearly showed a quadratic behaviour. The 2PPE yield increased with increasing the mean particle diameter up to about 9 nm, then levelled off probably due to interactions among particles. The photon energy dependence of the 2PPE showed a pronounced peak at about 3.6 eV, which clearly demonstrates the contribution of plasmon excitation. With increasing the particle size, a spectral feature near the Fermi level grew and shifted to higher energies. From the similarity to the Ag(111) thin films on Si(111) and HOPG, this feature can be attributable to a Shockley surface state on the small (111) facets on the silver nanoparticles. Indeed, this feature was quenched by NO adsorption or shifted to lower energies by Cs adsorption as in the case of Ag(111). Using time-resolved two-colour 2PPE, we measured relaxation times of electrons of the silver nanoparticles. Compared to bulk Ag(111), relaxation times were about two times longer for the hot electrons about 1 eV above the Fermi level, which can be interpreted as a confinement effect.

Photodesorption measurements of molecules from metal nanoparticles are the next step. We have recently measured photodesorption of NO from silver nanoparticles induced by fs- and ns-lasers with a quadrupole mass spectrometer. The particle size and the photon energy dependence of the photodesorption dynamics will be further investigated.

Theory Group

The main focus of the Theory group continued to be the theoretical investigation of electronic structure and nuclear dynamics of small molecules on surfaces. In order to interpret results obtained by experimental groups of the Chemical Physics department we performed extensive ab initio calculations as well as wave packet studies.

In particular, the group continued to investigate laser induced desorption as the most simple surface-photochemical reaction focussing on the system NO/NiO(100). For this adsorbate-substrate system detailed quantum state resolved experiments have been performed monitoring velocity distributions for each rovibrational state of the desorbing particles. Until recently, the accurate calculation of the adsorption energy of the NO/NiO(100) system has been an unsolved problem. However, in collaboration with theory groups from Italy (G. Pacchioni), Spain (F. Illas), and the Ruhr-University Bochum (V. Staemmler), we demonstrated that high quality quantum chemical calculations (CASPT-2) are mandatory in order to obtain reliable results. Especially, all variants of density functional theory (DFT) failed to give a conclusive picture for this system. Consequently, we were able to calculate global potential energy surfaces of the electronic ground and excited states of the NO/NiO(100) system on the CASPT-2/CI level of theory for all relevant degrees of freedom. These PESs were used in subsequent multi-dimensional wave packet calculations which revealed a new mechanism concerning the origin of bimodal velocity distributions. In this mechanism a bifurcation of the wave packet in the electronically excited state can be observed, where the nuclear motion parallel to the surface plays a decisive role.

In addition to stochastic wave packet studies, the group continued the development of new methods in dissipative quantum dynamics. In collaboration with R. Kosloff (Hebrew University Jerusalem, Israel) the “Surrogate Hamiltonian” approach was significantly extended allowing for the treatment of two nuclear degrees of freedom and hundreds of bath modes in a dissipative environment.

Besides the improvement of methods in quantum dynamics, another project was devoted to the development of new methods in electronic structure theory. In collaboration with E.A. Carter (Princeton University, USA), the group continued to develop an embedding theory in which the advantages of conventional quantum chemistry and density functional theory with periodic boundary conditions are combined. Using the electron density obtained in a DFT slab calculation, an effective one-electron embedding operator can be defined which represents an embedding potential acting on a representative region of a surface, i.e. a cluster. This allows for an accurate treatment of local phenomena of substrates (adsorption of molecules, defects, adsorbate excitations) characterized by a delocalized electronic structure such as metals. This novel approach has been implemented and successfully applied to the calculation of adsorption energies of the benchmark system CO/Pd(111). Currently, the system CO/Pt(111) is investigated in detail.

Associated Research Group: Photoelectron Diffraction

This activity is headed by Phil Woodruff at the University of Warwick and Christine Lamont at the University of Huddersfield and originally involved Alex Bradshaw in the Surface Physics Department. 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 (such as the smallest chiral amino acid, alanine) on metal surfaces, the focus of the FHI-based component of the collaboration is on transition metal oxide surfaces, and particularly VO_x. During the last 2 years work has focussed on two systems, both involving ultra-thin epitaxial films of VO_x, namely VO_2 on TiO_2(110), and V_2O_3 on Pd(111). In the case of TiO_2 there have also been investigations of the structure of adsorbates on this oxide substrate; in particular, the interaction of formic acid with TiO_2(110) leads to coadsorbed formate and hydroxyl species, and the local adsorption geometry of both species have been determined. More recently, the local adsorption geometry of molecular water has also been determined on this surface; the results reveal an interesting and rather significant discrepancy in the $Ti\text{-}O_{water}$ bondlength relative to current theory which may be a key to the well-known problem in such theoretical calculations of correctly reproducing the inability of water to dissociate on un-defected

TiO_2(110). Studies of VO_2 growth on TiO_2 have proved more disappointing. Despite reports in the literature based on angle-scan X-ray photoelectron diffraction (XPD) that good epitaxy of a rutile-phase VO_2 occurs, our PhD data are indicative of very poor order, and a parallel study using normal incidence X-ray standing waves now shows that the quality of these films beyond a single atomic layer is poor.

More recently the focus of the oxide PhD work has switched to V_2O_3 grown on Pd(111), for which one obtains high-quality films as judged by sharp LEED patterns, in keeping the earlier work by the Electron Spectroscopy and Synchrotron Radiation group within CP using W(110) and Au(111) substrates. While the PhD technique is more naturally suited to studies of adsorbate structures than of clean surfaces (because it is generally not possible to distinguish between surface and sub-surface emitter atoms) significant amounts of PhD data have been collected from the clean, as-prepared, V_2O_3(0001) surface. The objective is to try to provide the first experimental determination of the surface structure of this surface which has been investigated theoretically within the TH department by Klaus Hermann and colleagues. Of particular interest is the termination of the solid structure to produce this surface and the geometry of the vanadyl, V=O, species believed to occur at this surface. Preliminary calculations indicate an encouraging sensitivity to the surface termination, but many more calculations are still required to resolve this issue. In parallel with this study of the clean surface, initial experiments on adsorbate structures have been initiated, first studying the adsorption of molecular water and the formation of surface hydroxyl species. PhD data collected from O 1s emission from surface hydroxyl species formed both by water dissociation and by exposure of the surface to atomic hydrogen show essentially identical modulations, and while a full quantitative analysis will take some time, initial data evaluation indicates that surface hydroxylation is certainly not limited to the vanadyl oxygen atoms.

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Invited Talks of the Members of the Department of Chemical Physics

Hans-Joachim Freund

2003 *Clusters, Facets and Edges: Site Dependent Selective Chemistry on Model Catalysts*
Symposium honoring Rudolf Zahradnik “Uncovering Elementary Steps in Catalysis. From the Isolated Molecule to the Bulk“, Berlin-Brandenburgische Akademie der Wissenschaften
21.11.2003, Berlin

2004 *NO Photodesorption from Oxides and Ag Nanoparticles Deposited on Oxides: REMPI and 2PPE Studies*
Symposium on Non-adiabatic Processes on Surfaces
11.01.-15.01.2004, Ein Gedi, Israel

Deposited Nanoclusters and Catalysis
Symposium honoring Klaus Heinz on the occasion of his 60th birthday
16.01.2004, Erlangen

Ecken und Kanten: Nanoteilchen als Modellsysteme für die Katalyse
Universität Magdeburg, GdCh-Vortrag
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DPG-Tagung, Symposium „Functional Nanoparticles“
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Symposium of the Collaborative Research Center 546 “Transition metal oxides - clusters, surfaces and solids - structure, dynamics and reactivity”
21.03.-24.03.2004, Berlin-Schmöckwitz

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Seminar, Nanocenter, University of Åarhus
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Oxidation Catalysts: Model Studies
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Model Catalysts: An Atomic View
27th Annual Meeting of the Sociedade Brasileira de Quimica and the XXVI Congreso Latinoamericano de Quimica
30.05.-02.06.2004, Salvador, Brazil

Clusters, Facets, Edges, and Corners: Chemistry on Nanoparticles
I-International Conference on Theoretical Aspects of Catalysis (ICTAC)
25.06.-30.06.2004, Tropea, Italy

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Seminar, TU Berlin
21.06.2004, Berlin

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228th ACS Meeting
22.08.-26.08.2004, Philadelphia, USA

X-ray Photoelectron Spectroscopy of Model Systems for Heterogeneous Catalysis
International Conference on X-Rays and Related Techniques in Research and Industry (IXCRI) 2004
15.09.-16.09.2004, Penang, Malaysia

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Nordic Conference on Surface Science 5
22.09.-25.09.2004, Tampere, Finland

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Magister Conference Series organized by the Research Center for Theoretical Chemistry (CeRQT) of the University of Barcelona
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GdCh-Vortrag in Erlangen zum 75. Geburtstag von G. Wedler
11.11.2004, Erlangen

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International Workshop on Oxide Surfaces (IWOX) 4
03.01.-08.01.2005, Aussois, France

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Rideal Conference on Chemistry and Catalysis
21.03.-23.03.2005, Glasgow, UK

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Instituto de Quimica, Univ. Nacional Autónoma de México (UNAM)
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Surfaces of Niobia and Vanadia
Group 5 Meeting
19.05.-21.05.2005, Hancock/MA, USA

Vibrational Spectra of Alumina and Silica Supported Vanadia Revisited: An Experimental and Theoretical Model Catalyst Study
Irsee III, Kloster Irsee
10.06.-11.06.2005, Irsee

Oxide Surfaces and Deposited Nanoparticles: Model catalysts at the Atomic Level
Physical Chemistry Division of the Italian Chemical Society,
34th National Congress on Chemistry
22.06.-24.06.2005, Sienna, Italy

Model Studies in Heterogeneous Catalysis
Interdisciplinary Surface Science Conference (ISSC) 15
27.06.-30.06.2005, Cardiff, UK

Malcolm Dole Summer Lectures, Northwestern University
1. *Nanoparticles as Models for Heterogeneous Catalysts: An Atomic View*
2. *Oxide Surfaces*
3. *Photochemistry at Oxide Surfaces and on Nanoparticles*
26.07.-28.07.2005, Evanston, USA

Model Studies in Heterogeneous Catalysis at the Atomic Scale
Langmuir Lecture, 230th ACS Meeting
30.08.-01.09.2005, Washington, USA

Nanoparticles and Supports as Imaged with the STM
Electron Microscopy and Analysis Group – and the Nanoscale Physics and Technology Group (EMAG-NANO) Conference 2005 "Imaging, Analysis and Fabrication on the Nanoscale"
31.08-02.09.2005, Leeds, UK

Models in Heterogeneous Catalysis at the Atomic Level
11. International Conference on the Applications of Density Functional Theory in Chemistry and Physics
11.09.-15.09.2005, Genf, Switzerland

Model Studies on Oxidation Catalysts: Characterization and Reaction
5th World Congress on Oxidation Catalysis: Plenary Talk
25.09.-30.09.2005, Sapporo, Japan

Model Studies in Heterogeneous Catalysis
National Meeting on Nano and Surface Science and Technologies
28.09.-30.09.2005, Beijing, China

Kerstin Jacobsen

2004 *Structure and Dynamics of T4 Lysozyme Adsorbed to Supported Lipid Bilayers*
Institute of Medical Physics and Biophysics, Charité/Humboldt Universität zu Berlin
26.04.2004, Berlin

Thorsten Klüner

2004 *Theoretical Investigation of Photochemical Reactions on Surfaces from First Principles*
Workshop „Non Adiabatic Processes at Surfaces“
15.01.2004, Ein Gedi, Israel

Ab initio Embedded Cluster Theory with Periodic Boundary Conditions
Seminar of the Theoretical Chemistry group of the University Potsdam
28.01.2004, Potsdam

Theoretical Investigation of Photochemical Reactions on Surfaces from First Principles Seminar of the Max-Born-Institute
04.05.2004, Berlin

Theoretische Beschreibung Photochemischer Reaktionen an Festkörperoberflächen
Seminar of the Institute of Chemistry of the University Ulm
02.06.2004, Ulm

Theoretische Beschreibung Photochemischer Reaktionen an Festkörperoberflächen
Seminar of the Institute of Chemistry of the University Jena
14.06.2004, Jena

Theorie der Photochemie auf Oberflächen: Status und Perspektiven
Seminar of the Institute of Chemistry of the University Bochum
07.12.2004, Bochum

Helmut Kuhlenbeck

2004 *Clean and Metal Modified Oxide Surfaces*
COST Chemistry D15 Working Group Meeting
29.04.2004, London, U.K.

Jörg Libuda

2004 *Model Studies in Heterogeneous Catalysis*
13. Diskussionstagung, Anorganisch-Technische Chemie (DECHEMA)
25.02.-26.02.2004, Frankfurt/Main

Reaction Kinetics on Model Catalysts: Molecular Beam Methods and Time-resolved Vibrational Spectroscopy
11th International Conference on Vibrations at Surfaces
06.06.-10.06.2004, Bar Harbor, Maine, USA

Nanokinetics: Reaction Kinetics on Model Catalysts
Universität Erlangen-Nürnberg
08.07.2004, Erlangen

2005 *Molecular Beams and Model Catalysis*
Freie Universität Berlin
18.01.2005, Berlin

Nanokinetics: Reaction Kinetics at Complex Surfaces
Leiden University
18.02.2005, Leiden, The Netherlands

Nanokinetics: Approaching Microscopic Concepts in Heterogeneous Catalysis
Universität Ulm
01.03.2005, Ulm

Nanokinetics: Reaction Kinetics at Complex Surfaces
"Science and Art in Europe" MOEL-Meeting
23.05.-24.05.2005, Berlin

Reaktionskinetik an nanostrukturierten Oberflächen
Universität Bremen
10.06.2005, Bremen

Modellstudien in der heterogenen Katalyse: Von der Struktur und chemischen Zusammensetzung zu einem mikroskopischen Verständnis der Reaktionskinetik
13. Tagung für Festkörperanalytik
26.06.-29.06.2005, Chemnitz

Niklas Nilius

2004 *Tailoring Electronic Properties of Atomic Chains Assembled by STM*
Frühjahrskonferenz der DPG
08.03.2004, Regensburg

Model Catalysts at the Atomic Scale: Metal Atoms and Clusters on Oxide Films
Dutch Scanning Probe Microscopy (SPM) Day
05.11.2004, Amsterdam, The Netherlands

2005 *Single Metal Atoms and Clusters on an Ultra-thin* Al_2O_3 *Film*
4th International Workshop on Oxide Surfaces
06.01.2005, Torino, Italy

Thomas Risse

2004 *Using ESR Spectroscopy to Investigate the interfacial Properties of Deposited Metal Particles on Oxide Surfaces*
COST Workshop
02.04.-04.04.2004, Torino, Italy

Struktur und Dynamik adsorbierter Proteine auf planaren Oberflächen mittels EPR Spektroskopie
Institute of Pure and Physical Chemistry, University Bremen
30.04.2004, Bremen

Charakterisierung nanoskopischer Strukturen auf Oberflächen mittels ESR-Spektroskopie: von deponierten Metallpartikeln zu adsorbierten Proteinen
Institute of Physical Chemistry, University Hamburg
10.05.2004, Hamburg

2005 *Elektronen Spin Resonanz an planaren Oberflächen: von deponierten Metallpartikeln zu adsorbierten Proteinen*
TU-Wien, Institut für Material Chemie
21.01.2005, Wien, Austria

ESR spektroskopische Untersuchung der Struktur von T4 Lysozym an planaren Modelloberflächen
Universität Jena, Institut für Materialwissenschaft
11.05.2005, Jena

ESR Spectroscopy on Single Crystal Surfaces: From Paramagnetic Defects to Small Ferromagnetic Deposited Particles
"Science and Art in Europe", MOEL-Workshop
23.05.-24.05.2005, Berlin

Günther Rupprechter

2003 *CO Hydrierung und Methanol Zersetzung auf Pd(111) und Pd-Al_2O_3 Modellkatalysatoren: SFG, PM-IRAS und XPS Spektroskopie*
Technische Universität Darmstadt
09.12.2003, Darmstadt

Summenfrequenz-Spektroskopie an Modellkatalysatoren
Colloquium of the Austrian Chemical Society
15.12.2003, Innsbruck, Austria

In-situ Spektroskopie an Pd(111) und Pd-Al_2O_3/NiAl(110): Oberflächenstruktur und katalytische Aktivität
Colloquium of SFB 445, Universität Duisburg-Essen
17.12.2003, Duisburg

2004 *CO-H interaction and H-dissolution probed by SFG and TDS*
Universität Ulm
06.02.2004, Ulm

Optical Spectroscopy at Surfaces
Lecture as part of the “International Max Planck Research School”
10.03.2004, Berlin

CO Hydrierung und Methanol-Zersetzung auf Modellkatalysatoren
Kolloquium des SFB 616: „Energiedissipation an Oberflächen“,
Universität Essen
25.05.2004, Essen

Reaktionen an Pd Modellkatalysatoren: Summenfrequenz-Laserspektroskopie und Polarisations-Modulations-Infrarotspektroskopie"
Max-Planck-Institut für Plasmaphysik
10.06.2004, Garching

Hydrogenation and dehydrogenation reactions under UHV and 1 bar
DFG-workshop „Preparation of model catalysts in the materials gap“,
15.06.2004, Blankensee (Potsdam)

Summenfrequenzspektroskopie an katalytischen Nanoteilchen
Universität Hannover
07.06.2004, Hannover

Catalytic reactions on Pd-Al_2O_3 and Pd(111): SFG, PM-IRAS and XPS
Universität Erlangen-Nürnberg
01.07.2004, Erlangen

Vibrational spectroscopy on model catalysts
European Union COST Chemistry Action, University of Barcelona
09.10.2004, Barcelona, Spain

Oxide supported Pd nanoparticles: structure and adsorption properties
Heinrich-Heine-Universität Düsseldorf
13.12.2004, Düsseldorf

2005 *Catalytic reactions on well-defined model catalysts*
University of Washington, Department of Chemistry
10.01.2005, Seattle/USA

Catalytic reactions on Pd nanoparticles and Pd(111)
Center for Atomic-Scale Materials Physics (CAMP) and Department of Physics, Technical University of Denmark
14.01.2005, Lyngby, Denmark

Structure and activity of Pd-alumina model catalysts
University of Glasgow
21.01.2005, Glasgow, Scotland

Adsorption and reactions on model catalysts
University of Cambridge
01.02.2005, Cambridge, England

SFG and PM-IRAS spectroscopy on supported Pd nanoparticles
University of California at Berkeley and E.O. Lawrence Berkeley National Laboratory
10.02.2005, Berkeley, California/USA

Adsorption and reactions on model catalysts
Universität Ulm
01.03.2005, Ulm

Model systems for heterogeneous catalysts
DECHEMA-Workshop "Nanomaterialien und Katalyse"
28.04.2005, Frankfurt

SFG and PM-IRAS: applications and limitations
CNRS summer school “New tools for in-situ investigations of surfaces and nano-objects”
10.05.2005, Aussois, France

Swetlana Schauermann

2004 *Model Catalysts for Kinetic Studies*
DFG-Schwerpunktprogramm Heterogene Katalyse, Workshop “Preparation of Catalysts in the Materials Gap“
14.06.-15.06.2004, Blankensee

Martin Sterrer

2005 *STM Characterization of Point Defects on MgO(001)/Ag(100) Surfaces*
COST Workshop
13.05.-14.05.2005, Torino, Italy

Phil Woodruff

2003 *Understanding Adsorbate Bonding Through Quantitative Surface Structure Determination*
7th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-7)
16.11.-20.11.2003, Nara, Japan

2004 *Surface Crystallography and its Relation to Catalysis*
British Crystallography Association Spring Meeting
05.04.-08.04.2004 Manchester, U.K.

Determining the Structure of Organic Molecule-metal Interfaces
Encuentro de Física y Química de Superficies (FyQS1)
04.11.-07.11.2004, San Carlos de Bariloche, Argentina

Understanding Adsorbate Bonding Through Quantitative Surface Structure Determination
Centro Atómica Bariloche e Instituto Balseiro
06.11.2004, San Carlos de Bariloche, Argentina

Understanding Adsorbate Bonding Through Quantitative Surface Structure Determination
Universität Dortmund
14.12.2004, Dortmund

2005 *What Can we Learn from Surface Bondlengths? – The Role of Precision in Surface Crystallography*
8th International Conference on the Structure of Surfaces
17.07.-22.07.2005 München, Germany

Department of Molecular Physics **Director: Gerard Meijer**

Group leaders:

Knut Asmis	
Uwe Becker	(Habilitation)
Hendrick Bethlem	
Horst Conrad	(Habilitation)
André Fielicke	
Bretislav Friedrich	(Habilitation)
Gert von Helden	
Karsten Horn	(Habilitation)
Jochen Küpper	
Bas van de Meerakker	
Wieland Schöllkopf	

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

Thorsten Kampen	(Habilitation)
Andreas Osterwalder	
Jens Viefhaus	

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

Joost Bakker		Irena Labazan	AvH Fellow
Markus Braune		Adela Marian	
David Carty		Achim Peters	
Marçin Frankowski		Axel Reinköster	
Steven Hoekstra		Melanie Schnell	Liebig Fellow
Jeong Won Kim	AvH Fellow	Nicolas Vanhaecke	

Guest scientists (temporary):

Boris Sartakov	RAS, Moscow, Russia

Graduate students:	15
Diploma students:	4
Technicians:	12

Recent Developments in the Department of Molecular Physics
Director: Gerard Meijer

On Monday, December 1st, 2003, shortly after the last meeting of the *Fachbeirat*, the moving trucks with a variety of molecular beam machines and laser systems, coming from the FOM Institute for Plasmaphysics in Nieuwegein, The Netherlands, arrived at the FHI. In the weekend just before this, a group of three graduate students and four post-doctoral scientists had moved with “their machines” from The Netherlands to Berlin as well, to continue their research work at the FHI. Possession was taken of the fully renovated Building C, and with the help of the technicians at the FHI and with the (temporary) help of research technicians from the University of Nijmegen and from the FOM Institute, the experiments were installed at their new home and brought back into operation in about three months time. Unfortunately, the modifications that were required to resolve a vibration-isolation problem in the air-handling units installed throughout the lab, and in particular also above the optical tables, forced us out of operation again for almost two months in the summer of 2004. Including the one month of preparation prior to the move, this meant that we effectively lost about half a year of experimentation time with this move.

The research projects that are described below in the section on “Molecular physics studies with infrared radiation”, connected to the Free Electron Laser for Infrared eXperiments (FELIX), have largely continued at the FOM Institute in The Netherlands, and have hardly been influenced by the move. In these research projects, the IR optical properties and dynamics of molecules, clusters and nano-crystals are studied in the gas-phase. Highlights have been the measurement of the IR spectrum of a gas-phase protein, the measurement of the far-infrared vibrational spectra of isolated metal clusters and the spectroscopic identification of polyhedral vanadium oxide cages in the gas phase. To be able to perform complementary studies to those at the FELIX facility, a commercially available table-top IR laser system with an associated molecular beam machine has been installed at the FHI. A detailed presentation of the progress in this research area is given on the posters MP1 through MP5.

Most of the experimental set-ups and laser systems that have now been installed in the main experimental hall and in the adjacent laboratories of Building C are devoted to research projects that are described below in the section on “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 of trapped samples of molecules are actively explored. Our research on Cold Molecules is embedded in a European network with the same theme until September 2006. Highlights of our research have been the trapping of OH radicals and the use of these trapped radicals to measure their infrared radiative lifetime. Other highlights have been the demonstration of a novel electric trap for ground-state molecules and the, very recent, demonstration of the deceleration of a “real” molecule, benzonitrile. The progress in this research area, together with a variety of planned future research projects, is presented on the posters MP6 through MP16.

Apart from these new research activities at the FHI, the research activity of two groups that originate from the former Department of Surface Physics is described in the sections on “VUV photoionization studies” and on “Electronic structure of surfaces and interfaces”. This work is presented in more detail on the posters MP17 through MP21.

It has been an eventful, exciting and busy two years in which the “FOM group”, in the meantime strengthened by an international team of young researchers, had to get used to the life at the FHI and in Berlin in general. Similarly, the scientists and the technical support staff already present in the department at the FHI had to get used to the new colleagues and to the new kind of experiments. It has all been a very positive experience, and although I realize that not everything can be measured via this, I am happy to report that in this year already three articles have appeared in *Phys. Rev. Lett.*, describing measurements that have been performed at the FHI, in machines, moved from The Netherlands, that have been completed and brought into operation over here.

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 over 2.5 - 250 μm, e.g. the full "molecular fingerprint" region, and the possibility of user-controlled wavelength scanning. The feature that really distinguishes FELIX from all other FELs 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 choose to evaporate off an electron instead (thermionic emission). 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.

In 2006 an extension of FELIX, the Free Electron Laser for IntraCavity Experiments (FELICE), will become operational. We are involved in the design, and we will be involved in the future operation, of a molecular beam machine that will be an integral part of FELICE. This experiment will allow for studying vibrational modes with low IR absorption cross section, like the M-C stretch of metal carbonyls, IR resonance enhanced multiple photon ionization of metal clusters, and finally, it will become possible to investigate coherent IR multi-photon absorption processes.

At the FHI we are setting up a Raman shifter to produce pulsed mid-IR laser radiation via stimulated backward Raman scattering in crystalline para-hydrogen at 4 K. The Raman shifter will extend the wavelength range currently accessible from our difference frequency mixing IR laser system from 5 µm to (further than) 10 µm. This light source will, for instance, be used for IR spectroscopic studies on metal cluster hydrocarbon complexes, both to investigate the structures of the adsorbates and, in a second step, to study the interaction with co-adsorbed oxidants. These studies can thus give insight into the mechanisms of (selective) hydrocarbon oxidation reactions.

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

During the last years, the laser desorption molecular beam set-up at FELIX has been extensively used to record the IR spectra of a variety of amino-acids and small peptides, using well-kown IR-UV double resonance ionization detection schemes. Molecules complexed with a known number of solvent molecules, in particular water, have been investigated as well. In all these studies, the comparison of the experimentally recorded IR spectra to theoretically calculated spectra is used to draw conclusions on the conformational structure of the molecules and the molecular complexes. An important step forward has been made in that we have shown that the IR-UV double resonance scheme can also be applied to unravel the structure of peptides that do not contain an aromatic amino-acid, by including an aromatic ring in the N-protecting group; measurements have been performed on the peptides ZProNHMe and ZAibProNHMe (Z= benzyloxycarbonyl).

The FT-ICR spectrometer at the FELIX facility has been upgraded with an electrospray ionization source, and a novel ion transport and injection scheme (patent pending) has been developed to inject ions from this source into the ICR-cell. Using IR multiple photon dissociation spectroscopy, this has enabled us to measure the first mid-IR-spectrum of a gas phase protein (cythochrome c) as a function of charge state.

At the FHI a commercially available, narrow-band pulsed IR laser system has been set up and this has been used in an IR-UV double resonance experiment to get structural information on the benzene dimer, a much studied model system that nevertheless still provides many puzzles.

Spectroscopy and chemistry of metal clusters and cluster complexes (André Fielicke)

The main focus of our research is the structural characterization of bare metal clusters and of metal cluster-ligand complexes in the gas phase. Those systems can be used as model systems for studying adsorption and reaction processes that are relevant for heterogeneous catalytic reactions. Using the intense IR light emitted from FELIX it becomes possible to observe resonant photo-dissociation by excitation of internal vibrational modes of the ligands, modes related to the metal-ligand bond, or internal modes of the metal cluster. Thus, aided by complementary theoretical calculations, structural information for isolated cluster-complexes can be obtained.

In collaboration with *David M. Rayner* and *Benoit Simard* (NRC, Canada) we are investigating the vibrational properties of adsorbates, mainly CO, on late transition metal clusters. The influence of cluster size, charge state and coverage on the metal-CO interaction has been studied. It has been observed, for example, that for small rhodium clusters the type of CO binding (atop or bridging) strongly depends on size and charge state. For charged clusters, the size dependence of the CO stretching force constant for atop bound CO can be modelled under consideration of the effective electron density available for back-donation in the CO π^* orbitals and the influence of electrostatic polarization. Since CO effectively acts as a probe for electron density, our gas phase studies deliver reference data for experiments with deposited nanoparticles and allow to quantify the charge transfer via metal support interaction.

To identify the geometrical structures of free metal clusters we developed a new method that relies on the far-infrared photo dissociation spectroscopy of metal cluster-rare gas complexes. Although similar experiments have been performed in the UV/visible spectral range before, in the far-infrared the vibrational modes, and thus the geometric structures, are probed directly. A highlight has been that we deduced, in collaboration with *Christian Ratsch, Jörg Behler* and *Matthias Scheffler* (FHI, Theory Dept.), structural motifs for vanadium and niobium clusters containing up to 15 metal atoms. These investigations will be extended towards systems that are more relevant in catalysis, like the late transition and coinage metals. Recently, first results have been obtained for small silver clusters.

At the FELIX facility we have constructed a new experimental set-up that will allow us to investigate the thermo-chemistry of (co-)adsorbed species on metal clusters by a combination of a variable temperature flow reactor with IR spectroscopic structural characterization.

Optical properties of VO clusters and strongly hydrogen-bonded systems (Knut Asmis)

During the last two years we have continued to focus on (i) the experimental characterization of the structure, stability and reactivity of mass-selected clusters and cluster ions in the gas phase and on (ii) the development of new - and on the improvement of existing - experimental techniques to perform these experiments.

At the FELIX facility we have used infrared photo-dissociation spectroscopy of mass-selected, cooled cluster ions to study the geometric and electronic structure of various compounds, including transition metal oxide cluster ions, protonated ammonia clusters and partially hydrated sulfate ions. More recently we have installed a novel laser vaporization source which enables us to produce bimetallic clusters, adding a new dimension of complexity to the photo-dissociation experiments with FELIX. We have also significantly improved our setup to characterize the reactivity of mass-selected ions at variable temperature in the ion trap.

A research highlight in the past two years was the spectroscopic identification of polyhedral vanadium oxide cages in the gas phase. In collaboration with *Joachim Sauer* (Humboldt University Berlin) we were able to reveal an unexpected correlation between the spectra of a vanadium oxide surface and the spectra of cluster ion cages of moderate size. Motivated by these findings we are currently studying the reactivity of these clusters towards SO_2 by measuring reaction rates at various temperatures, identifying reaction products using infrared spectroscopy. The ultimate goal of these experiments is to shed light on the working mechanism of vanadium oxide-based catalysts in the industrially very important synthesis of sulfuric acid.

Cold molecules

Getting full control over both the internal and external degrees of freedom of 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 molecules with an electric dipole moment, i.e. with an internal anisotropic charge distribution, can be spatially manipulated with static inhomogeneous electric fields, as these molecules experience a (small) net force in such fields. We have demonstrated that neutral molecules can be manipulated in velocity space as well when time-varying electric fields are being used. This method is based on the notion that a molecule in a quantum state in which the dipole moment is anti-parallel to an external electric field will be attracted to regions of low electric field. Therefore, molecules in such a "low-field" seeking state will be decelerated on their way from a region of low electric field into a region of high electric field. If the electric field is switched off while the molecules are still in the region of high electric field, the molecules will not regain their lost kinetic energy. This process can be repeated until the average velocity is reduced to an arbitrarily low value. A properly timed switching of the electric fields ensures that a bunch of molecules can be kept together in the forward direction ("phase stability") throughout this deceleration process. Transverse stability is achieved by using an electrode geometry that produces a minimum of the electric field on the molecular beam axis, thereby continuously focusing the beam. Although the forces that can thus be exerted on neutral particles are many orders of magnitude smaller than those exerted on charged particles, the various schemes allow one to perform all the operations on neutral polar molecules that are successfully used throughout on charged particles.

In order to obtain a maximum initial density of state-selected molecules at a minimum initial temperature, we make use of the process of adiabatic cooling in a pulsed gas expansion. In a pulsed supersonic expansion, densities of 10^{12} molecules/cm^3 per quantum-state can in principle be reached at a temperature of around 1 K. Typical velocities in a molecular beam are in the 250-2000 m/s range, however, preventing trapping of these dense low-temperature samples in the laboratory frame. The process in our Stark decelerator can be viewed as slicing a bunch of molecules with a very narrow velocity distribution (determined by the settings of the decelerator) out of the original beam, and decelerating these to arbitrarily low absolute velocities. In this process the phase-space density, defined as the number of molecules per unit volume and per unit momentum space, remains constant and one can thus efficiently transfer the high phase-space densities from the moving frame of the molecular beam to the laboratory frame. The molecular beam exiting the Stark decelerator has a continuously tuneable laboratory velocity and a narrow velocity distribution and can be used for a large variety of experiments.

Deceleration and trapping of small free radicals (Bas van de Meerakker)

In the summer of last year, a new generation molecular beam deceleration and trapping machine, designed such that a large fraction of the molecular beam pulse can be slowed down and trapped, has become operational. We have used this machine to decelerate beams of ground-state OH radicals, and we have investigated the operation characteristics of a Stark decelerator in unprecedented detail. We have experimentally 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, experimentally verified, complete description of the complex three-dimensional motion of the molecules through the decelerator, which is crucial for the design and construction of future, longer versions of a decelerator. The decelerated beam of OH radicals has subsequently been loaded into a quadrupole electrostatic trap. Depending on the details of the trap loading sequence, typically 10^5 OH ($X^2\Pi_{3/2}$, v=0, J=3/2) radicals can be trapped for times up to several seconds at a density of 10^7-10^8 mol/cm^3 and at a temperature in the 50-500 mK range. The long interaction time afforded by the trap has been exploited to measure the infrared radiative lifetime of vibrationally excited OH radicals, yielding the most accurate value to date for the Einstein *A* coefficient in the Meinel system of OH.

Development of manipulation and trapping elements (Rick Bethlem)

A few years ago, we demonstrated an electrostatic storage ring for neutral molecules. In this prototype ring, bunches of molecules were confined in circular orbits, but the molecules were not kept together tangentially; the molecules gradually spread out until they filled the entire ring. We have now designed and constructed a sectional storage ring, consisting out of two hexapole half-rings, that allows for a bunching scheme to counteract the spreading out of the packet of molecules along the ring, similar to bunching schemes used in charged particle storage rings. The injection beam line for this sectional storage ring has been brought into operation, and we have demonstrated that we can simultaneously produce two decelerated and longitudinally cooled packets of molecules with different velocities, and that both of these packets can subsequently be coupled into the storage ring.

For many applications of cold polar molecules, trapping of molecules in high-field seeking states is required. We have experimentally demonstrated a novel AC electric trap, and we have used it to trap ammonia molecules in high-field seeking states. For these ground-state ammonia molecules the depth of the AC electric trap is about 10 mK, and the trapping volume is about 20 mm^3. We have studied the stability of the AC electric trap as a function of switching frequency, and we have characterized the spatial distribution and the temperature of the trapped cloud of molecules.

Micro-structured devices to manipulate molecules (Horst Conrad)

In this project we manipulate polar molecules using electric field gradients produced by micro-structured electrodes. The ultimate goal is to produce a variety of molecular manipulation tools, including lenses, mirrors, guides, conveyer belts, decelerators, storage rings and traps, all integrated on a chip. In a first test experiment, we have demonstrated that by applying modest voltage differences to micrometer-sized gold electrodes, deposited on a sapphire substrate, electric fields up to 150 kV/cm can be produced. In particular, we have constructed a switchable micro-structured electrostatic mirror for polar molecules, which we have used for normal incidence reflection of a beam of ammonia molecules.

We have now worked out a design for a decelerator and a trap, consisting of a periodic array of micro-structured linear electrodes deposited on an approximately 4 cm long planar insulator substrate, which we will experimentally test in the near future.

Deceleration and trapping of large (bio-) molecules (Jochen Küpper)

A new, dedicated alternate gradient (AG) decelerator molecular beam machine has been constructed at the FHI, and has become operational earlier this year. With this machine one can decelerate molecules in high-field seeking states, and we aim to use this machine for the deceleration of large poly-atomic molecules like benzonitrile, as well as of different conformational structures of amino-acids like, for instance, tryptophan. For the quantum state selective detection of benzonitrile and other large molecules laser induced fluoresecence detection using a newly installed cw narrowband laser system is applied. Test experiments on the AG decelerator machine have been performed with metastable CO molecules; to investigate the transverse focusing properties in an AG decelerator, two-dimensional imaging experiments have been performed as well. Most recently, focusing and deceleration of benzonitrile in its lowest rotational state have been demonstrated.

Analytical modelling and theoretical support (Bretislav Friedrich)

A quasi-analytic model for the Stark decelerator has been developed, based on a Fourier analysis of the time-dependent electric fields inside the decelerator. This model explains the key features of the longitudinal motion of the molecules, including the presence of phase stable regions around overtones of the fundamental frequency and the appearance of additional phase stable regions due to interference of individual waves in the Fourier-series.

Possibilities to construct a more stable electrodynamic trap for polar molecules in high-field seeking states have been investigated in an analytical model. In particular, it has been demonstrated that using concave electrodes, rather than the convex electrodes that are conventionally used, a more stable trap can be produced. Experiments are currently underway to verify this conjecture.

Sympathetic cooling of molecules (Wieland Schöllkopf)

In this project we will investigate the possibility of cooling a cloud of polar molecules via elastic collisions with a magnetically trapped, and evaporatively cooled, cloud of Rb atoms. Simultaneous cooling and trapping of atoms and molecules in a single vacuum chamber seems impractical due to the large number of magnetic field coils, electrodes and laser beams required. Therefore, in our approach, atoms and molecules will first be cooled and trapped separately and then the cold atom cloud will be moved to overlay with the molecular cloud. During the last two years, the set-up to produce a dense cloud of magnetically trapped Rb atoms has been built up. The effusive beam of Rb atoms coming out of an oven is slowed down in a Zeeman slower, captured in a standard magneto-optical trap and transferred to a magnetic trap. As the coils for the magnetic trap are mounted on an accurate translation stage, the cold Rb cloud can be moved into a separate UHV chamber where the molecules will be trapped as well.

Buffer-gas cooling of molecules (Achim Peters)

In collaboration with *Achim Peters*, junior professor at the Humboldt University in Berlin, one of the proven alternative methods to produce trapped samples of cold molecules, namely buffer-gas loading in a cryogenic cell followed by trapping in an inhomogeneous magnetic field, is also pursued at the FHI. In our present set-up we have a superconducting quadrupole magnet using a ^{3}He-^{4}He dilution refrigerator. From the various methods available for introducing atoms and molecules into the buffer gas cell, we have focused for now on laser ablation of a solid precursor material. Over the last two years the dilution refrigerator set-up has been built and recently we have succeeded in loading of chromium atoms into the magnetic trap, where they have been trapped at ~1.5 K for about ~ 0.5 seconds.

VUV photoionization studies (*Uwe Becker*)

We have continued to concentrate our effort on single and multiple electron emission processes following photo-ionization, with particular emphasis on scattering and coherence phenomena. The activities have been focused on coherent and incoherent photoelectron emission processes in homo- and hetero-nuclear diatomic molecules, valence and inner-shell photoelectron emission and diffraction in fullerenes, and multiple photoelectron and Auger electron emission in closed shell atoms and small molecules.

The scattering and coherence phenomena in molecular photoelectron emission were studied on the showcase examples for K-shell photo-ionization, CO and N_2. In the course of these studies, on which we already reported in part at the last meeting of the *Fachbeirat*, the following comprehensive picture of these processes could be derived: core electron photoemission of diatomic hetero- and homo-nuclear molecules is, in almost every respect, a natural quantum marker experiment similar to double-slit experiments based on mechanical devices, which have recently been performed using photons as particles with varying quantum properties, in particular wave and particle properties. In our molecular double-slit experiment, the homo-nuclear case mimics the interference fringes and anti-fringes of the macroscopic experiments by the energy-dependent oscillations in a variety of photo-ionization parameters, the most prominent one being the parallel diffraction behaviour of the *gerade* and *ungerade* channels of the N_2:N(1s) photoelectron emission. In contrast, hetero-nuclear diatomic molecules show angle-dependent photoemission behavior that carries “which way” information in complete analogy to the “which way” information carried in macroscopic double-slit experiments in form of the “which slit” information. The only difference is that in the molecular case, this information is an “in/out” information concerning the photoelectron emission direction with respect to the molecule rather than a “left/right” information. This analogy has been corroborated by a series of extensive measurements. In addition, we have shown for the first time that the transition between the two cases is a gradual transition rather than a complementary one. It corresponds to the gradual decoherence process observed in macroscopic double-slit experiments with C_{60}, where external heating with subsequent photon emission serves as symmetry violating element. In our experiment, isotope substitution has been employed instead. These experiments will open a new field of photoelectron emission studies dedicated to reveal further details of the transition from delocalization to localization, a showcase example for decoherence processes in quantum systems.

The scope of the fullerene studies was extended to new phenomena in valence and inner-shell photo-ionization. In the well-established quantum oscillations of the valence sub-shells of C_{60} and C_{70}, a new and unexpected behavior was observed, namely a difference between gas phase and amorphous phase samples regarding the partial cross section ratio, which exhibits the oscillatory structure. The distinct differences between the two aggregate phases can be explained by electron transfer from the adsorbed fullerene to the substrate in the case of C_{70} but not for C_{60}, highlighting the role of symmetry for adsorption processes. In the case of inner-shell processes, it could be shown that plasmon excitation associated with C_{60}:C(1s) photoelectron emission is responsible for the rapidly increasing rate of triply charged C_{60} ions above the carbon 1s-threshold, levelling off at an unusually high rate of 40 %. The existence of this fullerene specific process has been proven by different measurements, e.g. angle-resolved electron-electron coincidence experiments.

The same type of experiments was used for the extensive exploration of double-electron emission, in particular double Auger emission processes. First exploratory investigations followed by more systematic studies were performed for all rare gases and a variety of small molecules. They all show that double Auger emission is very general and by no means a negligible process, which often contributes a 10-20% fraction to the total Auger yield. Besides this quantitative determination of the double Auger intensity, highly differential measurements concerning the coincident angular distribution have also been performed. They reveal a great similarity between double photoelectron and double Auger ejection. These studies may open a new field of Auger spectroscopy on highly correlated materials in the same way Auger spectroscopy served as a probe of "single particle dominated" solid matter in the past.

All these studies were based on the extensive use of synchrotron radiation at both national facilities BESSY in Berlin and HASYLAB at DESY in Hamburg. The studies will be expanded to a new level of exploration with the start of experiments at the VUV Free Electron Laser (VUV-FEL) at DESY in Hamburg just three months ago.

Electronic structure of surfaces and interfaces (*Karsten Horn*)

The research related to the properties of low-dimensional systems, and surface/interface problems in particular, has centered on several topics. Using the capabilities of the beamlines funded by the MPG at BESSY to provide circularly polarized X-rays, the possibility to detect molecular chirality in the adsorbed state was investigated. Ever since Pasteur discovered the handedness in the optical activity of molecules, chirality has been recognized as a most important aspect of molecular structure. In heterogenous catalytic processes, the conversion of pro-chiral reagents into one particular isomer is usually induced by adsorbing chiral molecules ("modifiers") onto catalytically active surfaces. Hence the characterization of chiral centers in adsorbed molecules is desirable; however, conventional optical absorption methods fail, because of the low concentrations involved. Using circular dichroism in core level photoemission, a clear dichroism is in fact observed in photoemission from the carbon 1s level of (R,R)- and (S,S)-butanediol on Si(100), and from tartaric acid on Cu(110), and is equal but opposite for the two enantiomers; the achiral (R,S) form does not exhibit a dichroism, a proof that the dichroic signal is caused by the chiral nature of the molecular environment. These data are certainly promising for an application of circular dichroism for the study of chiral adsorbates. However, a competing process arising from the handedness of the geometry of the photoemission experiment, which occurs also in achiral (e.g. linear) molecules needs to be taken into account as well. Current work focuses on a clarification of the different aspects of the method, and its possible wider application to chiral adsorbates.

The study of electronic states in low-dimensional systems has meanwhile continued with experiments concerning thin lead and indium layers on Si(111) and Si(100), as part of our collaboration within a European program "Self-organized Nanostructures". In contrast to practically all other metallic quantum well systems which are "well-behaved", the quantum well states in Pb layers on Si(111) exhibit a dispersion $E(k_{\parallel})$ that can be described by an effective mass parameter which is up to a factor 10 higher than expected from bulk Pb. This unusual phenomenon is a challenge to our understanding of metallic quantum well states, and no clear-cut explanation is so far available. We find that Pb films on other substrates, notably single crystalline graphite, do not exhibit a similar effect. Finally, work on complex metallic alloys, and quasi-crystals among them, continues, within the recently formed Network of Excellence "Complex Metallic Alloys" funded by the European Union and comprising about 20 European laboratories. As part of this effort we are examining the complex alloy b-Mg_2Al_3 with 1168 atoms in the unit cell.

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Chin, W., I. Compagnon, J.-P. Dognon, C. Canuel, F. Piuzzi, I. Dimicoli, G. von Helden, G. Meijer and M. Mons: Spectroscopic evidence for gas-phase formation of successive β turns in a three-residue peptide chain. Journal of the American Chemical Society **127**, 1388-1389 (2005).

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Crompvoets, F. M. H., H. L. Bethlem and G. Meijer: A storage ring for neutral molecules. In: Adv. in At., Mol. & Opt. Phys., Vol. **52,** in press (2005).

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Fielicke, A., G. von Helden and G. Meijer: Far-infrared spectroscopy of isolated transition metal clusters. European Physical Journal D **34**, 83-88 (2005).

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Meerakker, S. Y. T., N. Vanhaecke, G. Meijer: Stark deceleration and trapping of OH radicals. Annual Review of Physical Chemistry, in press (2005).

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Merritt, J. M., J. Küpper and R. E. Miller: Entrance channel X-HF (X=Cl, Br and I) complexes studied by high-resolution infrared laser spectroscopy in helium nanodroplets. Physical Chemistry Chemical Physics **7**, 67-78 (2005).

Moore, D.T., J. Oomens, J. R. Eyler, G. von Helden, G. Meijer and R. C. Dunbar: Infrared spectroscopy of gas phase Cr^+ coordination complexes: determination of binding sites and electronic states. Journal of the American Chemical Society **127**, 7243-7254 (2005).

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Parschau, M., T. Kampen and K.-H. Ernst: Homochirality in monolayers of achiral meso tartaric acid. Chemical Physics Letters **407**, 433-437 (2005).

Polfer, N. C., B. Paizs, L. C. Snoek, I. Compagnon, S. Suhai, G. Meijer, G. von Helden and J. Oomens: Infrared fingerprint spectroscopy and theoretical studies of potassium ion tagged amino acids and peptides in the gas phase. Journal of the American Chemical Society **127**, 8571-8579 (2005).

Ratsch, C., A. Fielicke, A. Kirilyuk, J. Behler, G. von Helden, G. Meijer and M. Scheffler: Structure determination of small vanadium clusters by density-functional theory in comparison with experimental far-infrared spectra. Journal of Chemical Physics **122**, 124302-1-124302-15 (2005).

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Rolles, D., M. Braune, S. Cvejanovic, O. Geßner, R. Hentges, S. Korica, B. Langer, T. Lischke, G. Prümper, A. Reinköster, J. Viefhaus, B. Zimmermann, V. McKoy and U. Becker: Isotope-induced partial localization of core electrons in the homonuclear molecule N_2. Nature, in press, 2005

Valle, J. J., J. R. Eyler, J. Oomens, D. T. Moore, A. F. G. van der Meer, G. von Helden, G. Meijer, Ch.L. Hendrickson, A. G. Marshall and G. T. Blakney: Free electron laser-Fourier transform ion cyclotron resonance mass spectrometry facility for obtaining infrared multiphoton dissociation spectra of gaseous ions. Review of Scientific Instruments **76**, 023103-1-023103-7 (2005).

Veldhoven, J. van, H. L. Bethlem and G. Meijer: ac Electric trap for ground-state molecules. Physical Review Letters **94**, 093001-1-093001-4 (2005).

Dissertationen (Doctoral Theses)

Crompvoets, F. M. H.: A storage ring for neutral molecules. Radboud University Nijmegen, The Netherlands, 2005.

Rolles, D.: Scattering and coherence phenomena in the photoionization of small molecules. Technische Universität Berlin, Germany, 2005**.**

Tallarida, M: Electronic properties of semiconductor surfaces and metal/semiconductor interfaces. Freie Universität Berlin, Germany, 2005.

Diplomarbeit (Master Thesis)

Bardizza, G.: Setup of a narrow bandwidth UV/VIS laser system for high-resolution spectroscopy of cold large molecules. University Milano, Italy, 2005.

Invited Talks of members of the Department of Molecular Physics

Knut Asmis

Jan 2004	Seminar Physikalische Chemie, Technische Universität München, Germany: *Probing strong hydrogen bonds and cold metal oxide clusters with infrared photodissociation spectroscopy*
Jan 2004	Chemistry Seminar, University of British Columbia, Vancouver, Canada: *Probing strong hydrogen bonds and cold metal oxide clusters with infrared photodissociation spectroscopy*
Feb 2004	Chemistry Seminar, University of California, Santa Barbara, USA: *Probing strong hydrogen bonds and cold metal oxide clusters with infrared photodissociation spectroscopy*
Mar 2004	Symposium of the DFG Colloborative Research Center 546, Berlin, Germany: *Gas phase infrared spectroscopy of strong hydrogen bonds: The protonated water dimer and related systems*
May 2004	Department Seminar, TU Chemnitz, Germany: *Probing strong hydrogen bonds and cold metal oxide clusters with infrared photodissociation spectroscopy*
June 2005	53rd American Society for Mass Spectrometry (ASMS) Conference on Mass Spectrometry, San Antonio, TX, USA: *Infrared photodissociation spectroscopy: About strong hydrogen bonds and metal oxide clusters*
Aug 2004	Gordon Conference on Water and Aqueous Solutions, Plymouth, NH, USA: *Probing strong hydrogen bonds and cold metal oxide clusters with infrared photodissociation spectroscopy*
Sep 2005	CFN-Symposium: Cluster als molekulare Nanostrukturen, Bad Herrenalb, Germany: *Schwingungsspektroskopische Untersuchungen an teilweise solvatisierten Ionen in der Gasphase*

Joost Bakker

Dec 2004	FOM Institute for Plasma Physics, Nieuwegein, The Netherlands: *Structural identification of gas-phase biomolecules using infrared spectroscopy*
Dec 2004	Workshop "Biomolecules in the gas phase", Soeterbeeck, The Netherlands: *Structural identification of gas-phase biomolecules using infrared spectroscopy*

Uwe Becker

Dec 2003	Conference on Atomic and Molecular Physics, Muzaffarpur, India: *Atomic and molecular photoionization*
Jan 2004	Seminar, Nat. Synchrotron Radiation Res. Center (NSSRC), Hsinchu Science Park, Taiwan: *Localization of core electrons in homonuclear diatomic molecules*
Sep 2004	MAX-Lab, Workshop on "Our future light source", Lund, Sweden: *Time-resolved photoelectron spectroscopy using free electron lasers*
Dec 2004	International Workshop "Atom2004", MPI für Physik Komplexer Systeme, Dresden, Germany: *Towards-time-resolved photoelectron spectroscopy of molecules*
Mar 2005	Symp. "New trends in gas phase VUV/soft x-ray high resolution spectroscopies at SOLEIL", Orsay, France: *Symmetry breakdown in* N_2*:N(1s) core electrons by isotope substitution*
July 2005	20th International Conference on x-ray and inner-shell processes X05, Melbourne, Australia: *Probing the transition from non-localization to localization by K-shell photoemission from isotope-substituted* N_2
July 2005	XXIV. International Conference on Photonic, Electronic and Atomic Colisions, Rosario, Argentina: *Coherence and intramolecular scattering in molecular photoionization*
Aug 2005	Symposium on New Science in the VUV/Soft X Ray Range, Campinas, Brazil: *Time-resolved molecular spectroscopy: A future field of FEL-based applications*

Hendrick Bethlem

Mar 2004	Meeting of the American Physical Society, Montreal, Canada: *Deceleration and trapping of polar molecules using time-varying electric fields*
Feb 2005	Physics Colloquium, Radboud Univ., Nijmegen, The Netherlands: *Testing the standard model using cold molecules*
Feb 2005	Midterm Meeting "Europ. Research and Training Network on Cold Molecules", Hannover, Gemany: *Deceleration and trapping of polar molecules in high-field seeking states*
July 2005	WEH-Seminar "Control of quantum correlations in tailored matter", Freudenstadt, Germany: *Trapping polar molecules*
July 2005	13th General Conference of the European Physical Society "Beyond Einstein – Physics for the 21st Century", Bern, Switzerland: *Deceleration and trapping of polar molecules in high-field seeking states*

Hugo Dil

April 2004	Seminar, FB Physik, Free University Berlin, Germany: *Quantum size effects in ultrathin films*
May 2004	Seminar, Sfb450 "Analyse und Steuerung ultraschneller photoin duzierter Reaktionen (Analysis and control of ultra fast photo-induced reactions)", Berlin, Germany: *Self organisation and localisation in thin metal overlayers*
June 2004	Seminar, FB Physik, Free University Berlin, Germany: *Self organisation and localisation in thin metal overlayers*

André Fielicke

Feb 2004	Seminar, Sfb450 "Analyse und Steuerung ultraschneller photo-induzierter Reaktionen (Analysis and control of ultra fast photo-induced reactions)", Berlin, Germany: *Probing the structures of pure metal clusters and metal cluster complexes*

Feb 2004	Seminar, University Utrecht, The Netherlands: *IR spectroscopy of metal cluster complexes with FELIX*
May 2005	Seminar, Steacie Inst., NRC Canada, Ottawa, Canada: *IR multiple photon absorption spectroscopy for structure determination of clusters and cluster complexes*
Sep 2005	CFN-Symposium: Cluster als molekulare Nanostrukturen, Bad Herrenalb, Germany: *Strukturbestimmung von Metallclustern und Cluster-Komplexen mittels IR-Mehrphotonen-Dissoziations-Spektroskopie*

Bretislav Friedrich

Dec 2003	Seminar "Moleküle im Rechner", Free Univ. Berlin, Germany: *Bringing molecules to attention: an old story with new twists*
Jan 2004	Workshop on Ultra-Cold Polar Molecules, Inst. for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA: *Cool molecular micro-beams, frigid clusters, and gelid molecular diffraction images*
Apr 2004	Colloquium, Dept. of Chemistry, Univ. of Warsaw, Poland: *From the new world of ultra-cold molecules*
Apr 2004	Seminar, Dept. of Chemical Physics, Heyrovsky Inst., Czech Academy of Sciences, Prague, Czech Republic: *Slowing and trapping of molecules*
Aug 2004	9th Brijuni Conf. on Matter under extreme conditions, Brijuni, Croatia: *The Stark accelerator/decelerator viewed as a biased pendulum*
Oct 2004	Colloquium, Dept. of Physics, Syddansk Univ., Odense, Denmark: *From the new world of cold molecules*
Nov 2004	Colloquium, Dept. of Chemistry, Seoul Nat. Univ., Seoul, Korea: *From the new world of cold molecules*
Dec 2004	International Conference "Stereodynamics 2004", Osaka, Japan: *Orientation, deceleration and trapping of molecules in nonresonant fields*
Jan 2005	Colloquium, Techn. Univ. Berlin, Inst. für Atomare Physik, Berlin,

	Germany: *Slowing, cooling and trapping of molecules*
June 2005	Seminar Sfb 450 "Analysis and control of ultrafast photoinduceed reactions", Fritz-Haber-Institut, Berlin, Germany: *Directional states of molecules: Retrospects and prospects*
July 2005	International Conference "Theory of ultra-cold molecules", Telluride, Colorado, USA: *Traps for ground-state molecules*

Gert von Helden

Nov 2003	Colloquium, Free Univ. Berlin, Germany: *Exciting gas-phase biomolecules using a free-electron laser*
Dec 2003	Colloquium, Technical Univ. München, Germany: *Exciting molecules and clusters using the free-electron laser FELIX*
Mar 2004	Annual spring meeting of the German Physical Society (DPG), München, Germany: *Free-electron laser based IR spectroscopy of gas-phase cluster ions*
June 2004	ECCN Meeting, Rothesay, Isle of Bute, Scotland, UK: *Free-electron laser-based IR spectroscopy of gas-phase clusters and biomolecules*
Sep 2004	XIIth International Symposium on small particles and inorganic clusters, Nanjing, China: *IR spectroscopy of gas-phase clusters*
June 2005	International Workshop on IR microscopy and spectroscopy with accelerator-based sources, Rathen, Germany: *Infrared spectroscopy of gas-phase molecules and clusters using an IR-FEL*
July 2005	Gordon Research Conference on "Biological molecules in the gas phase", Maine, USA: *Charge-state resolved mid-infrared spectroscopy of a gas-phase protein*

Rainer Hentges

July 2004	8th European Conf. on Atomic and Molecular Physics (ECAMPVIII),

Rennes, France:
Interference effects in the photoionization of ultrafast dissociating molecules

Karsten Horn

Oct 2003	Workshop on "Elementary Excitations in Quasicrystals", Chemnitz, Germany: *Electronic bands in quasicrystals investigated by photoemission*
Dec 2003	Colloquium, Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden, Germany: *Elektronische Struktur-Photoemission an dünnen Schichten und komplexen Legierungen*
Jan 2004	Colloquium, FB Physik, Univ. Dortmund, Germany: *Elektronische Struktur in ein bis fünf Dimensionen? Photoemission an dünnen Schichten und Quasikristalle*
May 2004	Seminar, FB Physik, Humboldt-Universität zu Berlin, Germany: *Elektronische Strukturuntersuchungen mittels Photoemission: von niederdimensionalen Systemen zu komplexen Legierungen*
May 2004	Colloquium, Sonderforschungsbereich 616, University Essen, Germany: *Elektronische Strukturuntersuchungen mittels Photoemission: von niederdimensionalen Systemen zu komplexen Legierungen*
June 2004	Joint Colloquium, MPI für Chemische Physik fester Stoffe and Institut für Anorganische Chemie, Technical Univ. Dresden, Germany: *Elektronische Strukturuntersuchungen mittels Photoemission: von niederdimensionalen Systemen zu komplexen Legierungen*
Mar 2005	Physics Section, Academy of Sciences of the Czech Republic, Prague, Czech Republic: *What photoelectron spectroscopy teaches us about the electronic structure of solids*
June 2005	Colloquium, Naturwissenschaftliche Fakultät, Karl-Franzens-Universität Graz, Austria: *Seltsame Festkörper: die Quasikristalle und ihre elektronischen Eigenschaften*
Sep 2005	Plenary lecture, XIIth Internat. Summer School "Nicolas Cabrera", Miraflores de la Sierra, Spain: *Frontiers in Science and Technology: synchrotron light as a powerful*

tool for materials analysis

Thorsten Kampen

May 2004	Sonderforschungsbereich (Sfb616) "Energy dissipation at surfaces", Univ. Duisburg-Essen, Germany: *Organisch-anorganische Halbleiter-Heterostrukturen*
June 2004	Institut für Physik, Humboldt-Universität zu Berlin, Germany: *Organic (molecular) semiconductor interfaces: structural, chemical and electronic properties*
Mar 2005	Plenary lecture, 69th Annual Meeting of the German Physical Society (DPG), Berlin, Germany: *Electronic structure of organic interfaces*
May 2005	Inst. für Festkörperphysik, Techn. University, Berlin, Germany: *Organische Moleküle zur Oberflächenfunktionalisierung und Herstellung von Halbleiterbauelementen*
May 2005	Inst. für experimentelle und angewandte Physik, Univ. Kiel, Germany: *Organische Moleküle zur Oberflächenfunktionalisierung und Herstellung von Halbleiterbauelementen*
June 2005	Symposium zur Physik von Oberflächen und Grenzflächen, Physik-Dept., Technical University München, Germany: *Organische Moleküle zur Oberflächenfunktionalisierung und Herstellung von Halbleiterbauelementen*
July 2005	FB Physik, Martin-Luther-University, Halle-Wittenberg, Germany: *Organische Moleküle zur Herstellung von Halbleiterbauelementen und Oberflächenfunktionalisierung*

Sanja Korica

Sep 2005	Nano Europe, Nano Conference, St. Gallen, Switzerland: *Phase-dependent differences in the partial cross section oscillations of* C_{70}

Jochen Küpper

May 2004	103rd Gen. Assembly Deutsche Bunsen-Ges., Dresden, Germany: *Stark-Abbremsung und Kühlung von großen Molekülen*

Aug 2004	Special Symposium, 228th ACS Nat. Meeting, Philadelphia, Pennsylvania, USA: *Manipulating molecules with electric fields*
June 2005	Quantenseminar, Institut für Quantenoptik, University Vienna, Austria: *Towards ultracold chemistry: Manipulating molecules with electric fields*
July 2005	Special symposium "Ultracold molecules", International Quantum Electronics Conference, Tokyo, Japan: *Towards ultracold chemistry: manipulation of polar molecules with electric fields*

Bas van de Meerakker

Mar 2004	Workshop on Chemistry of Cold Molecules, Kyoto, Japan: *Manipulation of molecules with electric fields*
May 2005	International Symposium on Molecular Beams, Hersonissos, Crete, Greece: *Hot topic: Deceleration and electrostatic trapping of CH radicals*

Gerard Meijer

Oct 2003	Colloquium, Phys. & Chem. Dept., Heriot Watt Univ., Edinburgh, UK: *Cold molecules*
Nov 2003	General Colloquium, FOM Inst for Plasmaphysics, Nieuwegein, The Netherlands: *Cold molecules; on stage ....*
Jan 2004	ITAMP/CUA2004, Workshop on Ultracold Molecules: Formation and Collisions, Cambridge, MA, USA *Manipulation of molecules with electric fields*
Jan 2004	Colloquium, Karlsruher Chemische Gesellschaft, Univ. Karlsruhe, Germany: *Molecular physics studies with an infrared free electron laser*
Jan 2004	Chemistry Colloquium Free Univ. Berlin, Germany: *Cold molecules*

Mar 2004	Physics Colloquium, Harvard Univ., Cambridge, MA, USA: *Cold molecules*
Mar/Apr 2004	International Symp. on "BEC, from atoms to molecules", Durham, UK: *Manipulation of molecules with electric fields*
Apr 2004	Gen. Physics Colloquium, Univ. Aarhus, Denmark: *Manipulating polar molecules with electric fields*
May 2004	NSRIM Symposium, Evening lecture, Radboud Univ. Nijmegen, The Netherlands: *Cold molecules, back home*
May 2004	Phys. Colloquium, Univ. Greifswald and IPP Greifswald, Germany: *Manipulation of molecules with electric fields*
May 2004	35th Meeting of the Div. of Atomic and Molecular and Optical Physics (DAMOP), Tucson, Arizona, USA: *Manipulation of molecules with electric fields*
July 2004	Plenary lecture, 8th Eur. Conf. on Atomic and Molecular Physics (ECAMP VIII), Rennes, France: *Manipulation of molecules with electric fields*
July 2004	27th International Symposium on Free Radicals, Taipei, Taiwan: *Manipulation of molecules with electric fields*
Aug/Sep 2004	9th Brijuni Conf. on Matter under extreme conditions, Brijuni, Croatia: *Manipulation of molecules with electric fields*
Sep 2004	Ertl Symposium "Surface Science Quo Vadis?", Ringberg Castle, Tegernsee, Germany: *Manipulation of molecules with electric fields*
Sep 2004	International Conf. on Dynamics of Molecular Systems (MOLEC XV), Nunspeet, The Netherlands: *Manipulation of molecules with electric fields*
Sep 2004	5th International Conf. on Low Temperature Chemistry (LTC5), Berlin, Germany: *Cold molecules*
Oct 2004	Debye lecture 2004, Univ. of Utrecht, The Netherlands: *Manipulation of molecules with electric fields*
Oct 2004	Colloquium, Max-Born-Institut, Berlin, Germany:

	Manipulation of molecules with electric fields
Oct 2004	Inaugural Lecture, Physics Colloquium, Free Univ. Berlin, Germany: *Molecular physics at the Fritz Haber Institute*
Nov 2004	Optics and Condensed Matter Colloquium, Inst. for Applied Physics, Univ. Bonn, Germany: *Manipulation of molecules with electric fields*
Nov 2004	Physical Chemistry Colloquium, Christian-Albrechts-Univ. Kiel, Germany: *Molecular physics studies with an infrared free electron laser*
Nov 2004	Colloquium, Chemistry Dept., Univ. Oslo, Norway*:* *Manipulation of molecules with electric fields*
Nov 2004	Physics Colloquium, ETH Zurich, Switzerland: *Cold molecules*
Nov/Dec 2004	Colloquium, International Workshop "Atom2004", MPI für Physik Komplexer Systeme, Dresden, Germany: *Manipulation of molecules with electric fields*
Dec 2004	The James Franck Programme Meeting on "Dynamics of Cold Molecules", The Weizmann Inst., Rehovot, Israel: *Manipulation of molecules with electric fields*
Jan 2005	Gordon Res. Conf. on Molecular Energy Transfer, Buellton, CA, USA: *Manipulation of molecules with electric fields*
Jan 2005	Chemical Physics Seminar, California Institute of Technology, Pasadena, CA, USA: *Manipulation of molecules with electric fields*
Jan 2005	Nanoscience Workshop on "Computational Tools for Molecules, Clusters and Nanostructures", Karlsruhe, Germany: *Cold molecules*
Feb 2005	ESF Exploratory Workshop on "Ultracold Chemistry", Mulhouse, France: *Manipulation of molecules with electric fields*
Mar 2005	69th Annual Meeting of the German Physical Society (DPG); "Physik seit Einstein", Berlin, Germany: *Manipulation of molecules with electric fields*

Mar 2005	Workshop on "New trends in nuclear, atomic and molecular physics", Heidelberg, Germany: *Manipulation of molecules with electric fields*
Apr 2005	Festkolloquium XIV. Heidelberger Graduiertenkurse Physik, and Conf. on Atoms and Molecules near Surfaces, Heidelberg, Gemany: *Cool molecules*
Apr 2005	Physics Colloquium, Humboldt Univ. zu Berlin, Germany: *Manipulation of molecules with electric fields*
May 2005	Atomphysik-Seminar, Gesellschaft für Schwerionenforschung, Darmstadt, Germany: *Manipulation of molecules with electric fields*
May 2005	Physics Colloquium, Technical University, Graz, Austria: *Manipulation of molecules with electric fields*
June 2005	International Symposium on "Interstellar reactions from gas phase to solids", Pillnitz, Germany: *Manipulation of interstellar molecules with electric fields: the OH radical*
June 2005	Festkolloquium der Max-Planck-Gesellschaft im Einstein-Jahr "Einsteins unvollendete Revolution: Grenzprobleme der Wissenschaft 1905 und 2005", Berlin, Germany: *Mit Molekülen spielen*
June 2005	Plenary lecture, 60th International Symposium on Molecular Spectroscopy, Columbus, Ohio, USA: *Deceleration and trapping of neutral polar molecules*
Aug 2005	40th IUPAC Congress, Beijing, China: *Manipulation of polar molecules with electric fields*
Sep 2005	International Workshop on "Quantum Computing with Polar Molecules", Arlington, Virginia, USA: *Deceleration and trapping of polar molecules*
Sep 2005	Physics Colloquium, Yale Univ., New Haven, Connecticut, USA: *Deceleration and trapping of neutral polar molecules*

Daniel Rolles

July 2004	XIVth International Conf. on Vacuum Ultraviolet Radiation Physics (VUV 14), Cairns, Australia:

Probing the degree of core hole localization in isotope substituted N_2 *via photoelectron spectroscopy*

July 2005	International Workshop on Photoionization, Campinas, Brazil: *Partial* $1\sigma_g/1\sigma_u$ *Core hole localization in nitrogen by isotope substitution*

Jens Viefhaus

Jan 2004	HASYLAB Users' Meeting, Hamburg, Germany: *Double Auger decay studied by time-of-flight electron coincidence spectroscopy*
Feb 2004	Seminar, LURE, Orsay, France: *Double Auger decay*
Mar 2004	Seminar, Technical Univ. Vienna, Austria: *Untersuchung von Doppel-Auger-Zerfällen mittels Elektron-Elektron-Koinzidenz-Spektroskopie*

Other activities of members of the Department of Molecular Physics

Bretislav Friedrich

Co-Editor: "Topical Issue on ultra-cold polar molecules", European Physical Journal D, Vol. 31, No. 2, pp. 149-445.
Teaching: A course at the Technical Univ. Berlin (Institut für Atomare Physik): "From the new world of cold molecules" (SS 2005, VL 0234 L180).
Session Chair: Gordon Research Conference on "Molecular Interactions", New London, NH, USA, July 2004.

Gerard Meijer

Symposium organizer (with Roger Miller), "Chemistry at ultra-low temperatures", 228th National ACS Meeting, Division of Physical Chemistry, Philadelphia, USA, 24th to 26th August 2004.
Chair of topical session on "Cold atoms and molecules", Meeting CLEO/Europe-EQEQ, Munich, Germany, 13th to 16th June 2005.

Department of Physical Chemistry

Director until Nov. 2004: Gerhard Ertl
Acting Director: Gerard Meijer

Group leaders:

Markus Eiswirth		
Tobias Hertel	(Habilitation)	until 31.12.2003
Josef F. Holzwarth	(Habilitation)	until 30.11.2005
Karl Jacobi	(Habilitation)	until 31.10.2004
Alexander S. Mikhailov		
Bruno Pettinger		
Harm H. Rotermund	(Habilitation)	
Wilfried Schulze		until 28.02.2005
Rolf Schuster	(Habilitation)	until 31.07.2004
Mau-Scheng Zei		until 31.12.2004

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

Tae-Geun Noh
Gennaro Picardi
Alexei L.N. Pinheiro
Bin Ren
Takayuki Suzuki
Yevgenyi Temko
Ming Chun Xu
Dai Zhang

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

Sergio Alonso	EU Marie Curie Fellowship
Sabine Azouani-Couderc	DFG Fellowship
Sarah L. Horswell	EU Marie Curie Fellowship
Raymond E. Kapral	AvH Awardee
Hiroshi Kori	AvH Fellowship
Alan C. Luntz	AvH Awardee
Ursula A. Paulus	DFG Fellowship
Oliver Rudzick	DFG Fellowship
Pablo Sánchez Bodega	AvH Fellowship
Yuichi Togashi	JSPS Fellowship

Graduate students:	6
Diploma students:	1
Technicians:	6

Recent Developments in the Department of Physical Chemistry

Director until 11/ 2004: Gerhard Ertl, Acting Director: Gerard Meijer

Since the last meeting of the Fachbeirat the following changes occurred among the staff scientists:

- Gerhard Ertl retired from his position as Director in October 2004.
- Tobias Hertel became Associated Professor of Physics at the Vanderbilt University, Nashville, TN, USA, in January 2004.
- Josef F. Holzwarth will retire in November 2005.
- Karl Jacobi retired from a part-time position in October 2004.
- Wilfried Schulze retired in February 2005.
- Rolf Schuster became Professor of Physical Chemistry (C3) at the Technische Universität Darmstadt in August 2004.
- Mau-Scheng Zei retired at the end of 2004.

As the Fachbeirat is well aware, the offer by the President of the MPG, Peter Gruss, to Lynn Gladden from Cambridge University, of a Directorship at the Fritz Haber Institute as Head of the Department of Physical Chemistry was not accepted, so that this position has not yet been filled. At present, Gerard Meijer is the Acting Director while Harm H. Rotermund takes care of current affairs.

The work of the remaining groups concentrates on theoretical and experimental studies on aspects of nonlinear dynamics in various interface reactions, in part within the framework of DFG Sfb 555: “Komplexe nichtlineare Prozesse” as well as on the development of Raman spectroscopy of nanoscale objects.

1. Complex systems

Engineering of self-organizing chemical systems cannot be based on the same principles as traditional chemical technology. Application of rigid controls may destructively interfere with the fine interactions between the elements of a system responsible for its self-organization. Instead, spontaneous activity of a system could be steered in a desired direction by applying weak control impulses and imposing various feedbacks. In this manner, transitions between different organization states can be initiated and new forms of collective behavior can be achieved. The aim of this project is to explore, theoretically and experimentally, new directions in chemical engineering. In continuation of the previous research, pattern formation in the CO oxidation reaction on platinum, under global delayed feedback and periodic forcing through the gas phase, have been studied. These investigations have been extended to composite materials created by microlithography. The second research direction involves local manipulation and control of reaction patterns by focused laser beams on microlithographically modified catalytic surfaces.

The activities in the area of nonlinear dynamics and complex surface reactions have been broadened and moved towards important practical applications by starting experimental and theoretical research on critical nonequilibrium phenomena during the onset of pitting corrosion. In a way, this has been a move back to the roots of the institute, when during the nineteen twenties optical investigations of the passivity of iron and steel had been performed by L. Tronstad (Nature *124*, 373, 1929) under the guidance of Fritz Haber and Herbert Freundlich. Recently front propagation in the regime of metastable pitting on stainless steel has been visualized, for the first time, by utilizing simultaneously contrast-enhanced optical microscopy and elliptical microscopy for surface imaging (EMSI). While the contrast-enhanced optical microscopy allows real time *in situ* observations of the creation of single pits at the diffraction limit (about 2 µm), EMSI images at the same time show the depletion of the oxide layer, although, due to experimental restrictions, only at a spatial resolution of about 20 µm.

Parallel theoretical investigations have led to a new view on the development of corrosion, in which diffusion-mediated interactions between metastable corrosion pits play a key role. The sudden onset of corrosion is rationalized as a critical phenomenon involving an autocatalytic explosion of corrosion pits. Theoretical analysis and numerical simulations of the proposed mathematical models reproduce the experimental observations well.

Further experimental studies with electrochemical systems concerned the propagation of potential excitations in the course of an electrochemical reaction (formic acid oxidation on platinum). On a thin Pt ring electrode small sections were insulated, which caused various novel effects such as period-doubled pulses, trapped oscillatory states and, in particular, pronounced velocity changes, which may serve as models for ‘saltatory’ conduction across the Ranvier nodes in nervous systems.

On the theoretical level, nanoscale pattern formation was studied for surface chemical reactions with promoters, and for Langmuir monolayers formed by organic lipid or amphiphilic molecules disposed on a water–air interface. The patterns representing stationary periodic structures or traveling waves are maintained and controlled in such systems by chemical reactions, illumination or transmembrane flows.

In another activity, research was focused on enzymes acting as cyclic protein machines. Statistical methods for the analysis of experimental data of single-molecules fluorescence correlation spectroscopy have been developed and applied to determine the operation mechanism of the enzyme cholesterol oxidase. Similarly, stochastic simulations of pattern formation and molecular cycle synchronization phenomena in enzymic arrays have served to shed light on these complex phenomena.

In an even more abstract sense, progress has been made in predicting dynamic instabilities from a chemical reaction mechanism by using concepts from algebraic topology as analytic tools. One can define certain algebraic structures (polynomial rings) as the kinetic terms of a reaction mechanism (rewritten in binomial form). After a change of basis these can be solved for their roots in the form of a deformed toric variety, allowing solutions for the multiplicity of the states and the location of bifurcations. In this way, a complete mechanistic classification of chemical oscillators including competitive autocatalyses and nonautocatalytic systems could be achieved. The methods were successfully applied to a number of real systems, such as oscillating Langmuir-Hinshelwood mechanisms (e.g. CO oxidation), the electrocatalytic oxidation of formic acid, the peroxidase oscillator and the calcium oscillations in cilia during olfactory response. The latter system is interesting because it includes refractoriness with respect to a stimulus without exhibiting excitability (Eiswirth, Mikhailov, Rotermund).

2. Raman spectroscopy

The sensitivity of Raman spectroscopy can be immensely enhanced by the excitation of surface plasmons by primary (visible) light, but this surface-enhanced Raman spectroscopy (SERS) is restricted to rough surfaces of silver or gold. Another approach, that of tip-enhanced Raman spectroscopy (TERS), is based on the optical excitation of localized surface plasmons between the Au (or Ag) tip of a scanning tunneling microscope and any (smooth) arbitrary surface, whereby a very strong local field enhancement is achieved in the cavity. Spectra from various adsorbed organic and inorganic molecules were recorded in this way. With the dye malachite green isothiocynate, as few as 200 molecules underneath the tip can be ‘seen’ by this technique. Using the ClO_4^- stretch vibration, the dependence of the TER band intensity on the distance to the substrate was recorded. For a tip radius of 20 nm the TERS signal was found to decrease by one order of magnitude for 10 nm vertical displacement of the tip. Thus, a powerful tool for vibrational spectroscopy with spatial resolution in the nanometer regime is being developed (Pettinger).

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Late 2003

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Suzuki, T., Y. Temko, M.C. Xu and K. Jacobi: Atomic structure of InAs quantum dots on GaAs(112)A. Surf. Sci., accepted.

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Dissertationen

Hagen, Axel: Ladungsträgerdynamik in Kohlenstoff-Nanoröhren – Optische Experimente zur Charakterisierung und Untersuchung der Lebensdauern elektronisch angeregter Zustände in Kohlenstoff-Nanoröhren. FU 2005.

Noh, Tae-Geun: Spatiotemporal pattern formation in the electro-oxidation of formic acid on Pt. Effect of electrode geometry and lowered symmetry. FU Berlin 2005.

Sensse, Anke: Convex and toric geometry to analyze complex dynamics in chemical reaction systems. Otto-von-Guericke-Universität Magdeburg 2005.

Department of Physical Chemistry

Invited Lectures at Conferences

Markus Eiswirth

“Nonautocatalytic oscillators and olfactory response”.
Engineering of Chemical Complexity, Berlin, 5-7 May, 2004.

Gerhard Ertl

“Controlling surface reactions”, 50th AVS Meeting, Baltimore, USA, Nov. 2003.

“Elementary steps in the surface chemistry of hydrogen”, Zahradnik Symposium, Berlin, Nov. 2003.

“Controlling surface reactions”, 20th Anniversary SAOG Meeting, Fribourg, Switzerland, Jan. 2004.

“Reactions at surfaces: From atoms to complexity”, EMPA-Symposium, Zurich, Switzerland, May 2004.

“Limits of surface reactions”, Symposium on nanocatalysis, Dalian, China, May 2004.

“Surface science and intermediates in the activation of CO and N_2”, Royal Society of Chemistry Meeting on Catalysis, London, June 2004.

“Controlling interface reactions”, Gordon Research Conference on Chemistry of Interfaces, Kimball, NH, USA, Aug. 2004.

“Elementary processes in catalysis at surfaces”, ETH workshop: Future concepts in energy related catalysis”, Ascona, Switzerland, March 2005.

“Molecules at surfaces and mechanism of catalysis”, Alfred Nobel Symposium, Stockholm, June 2005.

“Strukturbildung an Festkörper-Oberflächen”, GDCh-Jahrestagung, Düsseldorf, Sep. 2005.

Josef F. Holzwarth

“Interaction between the bio-surfactant Surfactin and lipid membranes”. 227th ACS Meeting, Symposium in Memory of Arthur Adamson. Anaheim, CA, March 2004.

“Star and linear homopolymer of the (2-dimethylamino)ethyl methacrylate and their interaction with surfactants”. Fast Reactions in Solution FRIS 2004, Discussion Group Meeting of the Royal Society of Chemistry, Burgos, Spain, September 2004.

“Aggregation of block-copolymers in aqueous solutions: Thermodynamics, structure and dynamics”. Australian Colloid & Interface Symposium, Sydney, February 2005.

Alexander S. Mikhailov

“Networks of protein machines”. Symposium on Networks of Interacting Machines, Berlin, December 2003.

“Traveling waves in two-component Langmuir monolayers”. Symposium Engineering of Chemical Complexity, Berlin, June 2004.

“Evolutionary design of functional networks”. Conference on Science of Complex Networks, Aveiro, Portugal, August 2004.

“Reaction-induced microstructures in surface systems with phase transitions”. Workshop on Surface Science Quo Vadis?, Schloss Ringberg, September 2004.

“Reaction-induced microstructures in liquid monolayers with phase transitions”. Symposium, Dresden, October 2004.

“What is a society?” Symposium on Oscillations, Chaos, and Network Dynamics, Kyoto, Japan, November 2004.

“Corrosion onset as a nonequilibrium critical phenomenon”. Symposium on Linearity, Fluctuations, and Complexity, Brussels, Belgium, March 2005.

“Corrosion onset as a nonequilibrium critical phenomenon”. ICTP Summer School Design and Control of Self-Organization in Physical, Chemical and Biological Systems, Trieste, Italy, July 2005.

“Networks of interacting machines”. EU Thematic Institute ‘Information and Material Flows in Complex Networks’, Schloss Goldrain, Italy, July 2005.

“Nonequilibrium structures in reactive soft matter”. JSPS Symposium on Perspectives of Nonlinear Science in Materials Research, Kyoto, Japan, September 2005.

“Are enzymes molecular machines?” DFG-JSPS Symposium on Nonequilibrium Pattern Formation, Kyoto, Japan, September 2005.

“Evolutionary design of robust signal transduction networks”. Symposium on Noise and Robustness in Genetic Networks, France, September 2005.

“Corrosion onset as a nonequilibrium critical phenomenon”. 20th Memorial Yukawa Symposium on Self-Organized Structures and Dynamics far from Equilibrium, Nishinomiya, Japan, October 2005.

“Nonequilibrium structures in reactive soft matter”. Workshop Developments of Nonequilibrium Physics in Material and Biological Sciences, Kyoto, October 2005.

Bruno Pettinger

“Tip-Enhanced Raman Spectroscopy at Single Crystalline Metal Surfaces. Recent
Developments and Perspectives for Electrochemical Applications”,
Keynote Lecture at the Symposium of Interfacial Electrochemistry, ISE 2004,
Thessaloniki, Greece, 19-24 September 2004.

“Hydroxide Adsorption of Ag(hkl) Electrodes Studied by in-situ SHG and ex-situ
LEED”.
10th International Conference on Electrified Interfaces, Spa, Belgium, 11-16 July 2004.

“Tip-enhanced Raman spectroscopy at single crystalline metal surfaces.
Hints for surface restructuring and surface chemistry”.
2nd ISE Spring Meeting, Xiamen, China, 7-10 March 2004.

Harm H. Rotermund

“Real time imaging and control of pattern formation during catalytic surface reactions”. International Symposium on Advanced Physical Fields, Tsukuba, Japan, March 2004.

“Spatiotemporal pattern formation in catalysis”. Surface Canada Conference, University of British Columbia, Vancouver, Canada, May 2004.

“Control of pattern formation during catalytic surface reactions by local laser heating”. Gordon Conference for Oscillations and Dynamic Instabilities in Chemical Systems”, Bates College, Lewiston, Maine, USA, July 2004.

“Shedding light on surface reactions: Real time imaging and control of pattern formation during catalysis”. Ringberg Meeting, Tegernsee, Germany, September 2004.

“Chaos und Ordnung auf Oberflächen“. 123. Versammlung der Gesellschaft Deutscher Naturforscher und Ärzte (GDCh), Passau, Germany, September 2004.

“Echtzeitbeobachtung von Oberflächenphänomenen: Das Photoemissions-Elektronenmikroskop und optische Abbildungsverfahren“. WE-Heraeus-Ferienkurs “Dynamik in dünnen Schichten und Grenzflächen“, Magdeburg, Germany, September 2004.

“Die CO-Oxidation unter die Lupe genommen: Raum-zeitliche Strukturbildungen bei nichtlinearen Oberflächenreaktionen und der Einfluss äußerer Randbedingungen”. WE-Heraeus-Ferienkurs “Dynamik in dünnen Schichten und Grenzflächen”, Magdeburg, Germany, September 2004.

“Reaction diffusion systems”. Surface Science Summer School, University of Nottingham, UK, August 2005.

“Patterns in surface reactions: the oscillatory case – experiments”. Int. Workshop on Nonlinear Pattern Dynamics in Complex and Reactive Fluids far from Equilibrium”, Kyoto, Japan, September 2005.

Invited Seminars and Colloquia (selection)

Markus Eiswirth

Topological methods for chemical reactions.
Institute for Applied Mathematics, University of Heidelberg, December 2003.

Stoichiometric network analysis.
MPI f. Physics of Complex Systems, Dresden, April 2004.

Gerhard Ertl

ETH Zurich, Feb. 2004

Katholieke Universiteit Leuven, March 2004

University of Wales, Cardiff, April 2004

Technische Universität Darmstadt, April 2004

Rheinisch-Westfälische Technische Hochschule Aachen, December 2004

California Institute of Technology, Pasadena, Jan. 2005

Université de Paris, April 2005

University of Uppsala, June 2005

Universität Karlsruhe, December 2005.

Alexander S. Mikhailov

Taming Winfree turbulence of scroll waves in excitable media.
University of Hiroshima, Japan, November 2004.

Sudden onset of corrosion as a nonequilibrium critical phenomenon.
DFG SFB 555 Colloquium, Berlin, December 2004.

Nonequilibrium pattern formation in reactive soft matter.
MPI f. Metallforschung, Stuttgart, February 2005.

Sudden onset of corrosion as a nonequilibrium critical phenomenon.
University of Sapporo, Japan, February 2005.

Are enzymes molecular machines?
FOM Inst. for Atomic and Molecular Physics (AMOLF), Amsterdam, September 2005.

Bruno Pettinger

Tip-Enhanced Raman Spektroskopie an Einkristallinen Gold- und Platin-Elektroden.
Seminar at the Institute of Physical and Theoretical Chemistry, (Prof. Baltruschat), University Bonn, 12 November 2004.

In situ Raman Spectroscopy: Fundamentals and Applications.
IMPRS-Colloquium "Modern Methods in Heterogeneous Catalysis"
3 December 2004.

Tip-Enhanced Raman Spectroscopy. Molecules under Giant EM Fields.
Lecture at Dept. of Chemistry and Applied Biosciences (Prof. Zenobi), ETH Zürich, Switzerland, 28 April 2005.

A Fine Needle Boosts Raman Scattering (Tip-enhanced Raman spectroscopy (TERS)).
ICSOS 8, Munich, Germany, 18-22 July 2005.

Tip-Enhanced Raman Spectroscopy (Apertureless Near-Field Raman Spectroscopy).
Lecture at UK Summer School 2005, The University of Nottingham, UK,
21-26 Aug. 2005.

Harm H. Rotermund

Some twists and turns in the path of improving surface activity.
University of Delaware, Newark, August 2003.

Control of catalytic surface reactions by local laser heating.
Dalhousie University, Halifax, Canada, August 2003.

Putting surface reactions under a magnifying glass:
Real time imaging of catalytic reactions.
University of Cambridge, UK, January 2004.

Spatio-temporal addressing of surface activity.
University of Hokkaido, Sapporo, Japan, March 2004.

Photoemission Electron Microscopy:
PEEM and other tools to image catalytic surface reactions.
Photon Factory, Tsukuba, Japan, March 2004.

Phenomena in nonlinear dynamics: From pattern formation during catalytic surface reactions to pitting corrosion of stainless steels.
Colloquium, Dalhousie University, Halifax, Canada, September 2004.

From metastable pitting corrosion to propagating fronts on stainless steel.
Dalhousie University, Halifax, Canada, May 2005.

Chaos und Ordnung auf Oberflächen.
Europaschule Reutershagen, Rostock, June 2005.

Rost an Edelstahl.
Christophorusschule, Rostock, June 2005.

Oberflächenreaktionen unter die Lupe genommen.
Visit of the winners ‘Jugend forscht’ at the FHI, August 2005.

Real time imaging methods in heterogeneous catalysis.
Lecture series at the FHI, December 2005.

Other activities

Members of the department served widely in editorial boards of journals and in advisory and organizing committees of conferences, as well as referees for numerous research proposals and journals.

In particular:

– Josef F. Holzwarth is the European Editor of Langmuir.

– Alexander S. Mikhailov is the Mentor of the Minerva Junior Research Group on Biological Computation, Weizmann Institute, Rehovot, Israel. He is also Editor-in-Chief of the series “Lecture Notes on Complex Systems”, World Scientific Publ. Co., since 2003, Member of the Advisory Board, Zeitschrift für Naturforschung, since 2004, Member of the Advisory Board, Chaos: an Interdisciplinary Journal of Nonlinear Science (American Institute of Physics), since 2003, Editor of Physica D: Nonlinear Phenomena, since 2005.

– Alexander S. Mikhailov and Harm H. Rotermund organized the 3rd International Symposium “Engineering of Chemical Complexity”, Berlin, 5–7 May 2004, and they are preparing the 4th International Symposium “Engineering of Chemical Complexity”, Berlin, 7–9 June 2006.

– Bruno Pettinger and Katrin F. Domke organized the SERS – Round Table Discussion at the FHI, Berlin, 25–27 October 2004.

Theory Department

Director: Matthias Scheffler

Group leaders:

Johan Carlsson	
Klaus Hermann (50% head of the Joint Network Center, GNZ)	(Habilitation)
Joel Ireta	
Peter Kratzer	(Habilitation)
Angelos Michaelides	
Karsten Reuter (since Jan. 2005 head of an Independent Junior Research Group)	(Habilitation)

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

Marvin A. Albao
Sami Amira
Jörg Behler(*IG*)
Volker Blum
Mikael Borg
Abir De Sarkar(*IG*)
Beate Flemmig(*IG*)
Martin Fuchs
Ricardo I. Gómez Abal
Marcus John
Suljo Linic
Patrick Rinke
Mira Todorova
Hua Wu
Hongsuk Yi
Dengke Yu

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

Martin Friák	
Bothina Hamad(*IG*)	AvH Fellow
Qing Miao Hu(*IG*)	AvH Fellow
Timo Jacob	
Adam Kiejna	
John Kitchin(*IG*)	AvH Fellow
Christine Kolczewski	
Aleksey Kuznetsov	AvH Fellow
Bernhard Lehner(*IG*)	AvH Fellow
Hakim Meskine(*IG*)	

Horia Metiu(*IG*) (jointly with E.K.U. Groß)	AvH Awardee
Angelos Michaelides(*IG*) (until Jan. 2005)	AvH Fellow
Radu Alexandru Miron	AvH Fellow
Kazuhito Nishitani	
Gianfranco Pacchioni (jointly with H.-J. Freund)	AvH Awardee
Mats Persson	AvH Awardee
Angel Rubio (jointly with E.K.U. Groß)	AvH Bessel Awardee
Chris Van deWalle	AvH Awardee

Graduate students: 33 (7 of them together with the *IG*)

Diploma students: 3

(IG) Jointly with the *Independent Junior Research Group*

Recent Developments in the Theory Department

Director: M. Scheffler

I. General Remarks

The main research directions of the *Theory Department* continue to be focused on understanding fundamental aspects of the chemical and physical properties of surfaces, interfaces, clusters, and nanostructures. Much of this work is related to (heterogeneous) catalysis, and some work is done in the field of biophysics. Most calculations begin with density-functional theory (DFT) and are then complemented with methods from thermodynamics or statistical mechanics.

A particular gratifying recognition of the work done in the *Theory Department* during the last years was the 2004 Born Medal and Prize, jointly awarded by the German and British Physical Societies. The citation reads: "For *his excellent contributions to theoretical surface physics, in particular the combination of density functional theory and statistical mechanics to model adsorbates and catalytic processes*". This prize thus honors the work that started in the mid eighties on "*ab initio* thermodynamics" and in particular our "*ab initio* statistical mechanics" studies. In fact the techniques embodied in the concept of "*ab initio* thermodynamics" are now widely employed also by others to study the structure and composition of surfaces of compound materials and of adsorbate phases under realistic temperature and pressure conditions. And with "*ab initio* statistical mechanics", which we started developing about nine years ago, we have been aiming at "*Bridging the length and time scales: from ab initio electronic structure calculations to macroscopic proportions*" (Ψ_k Newsletter 1997). With this approach all possibly relevant microscopic processes and parameters are evaluated by DFT and their statistical interplay is then determined with the kinetic Monte Carlo (kMC) method. These studies were performed mainly with ***Paolo Ruggerone*** (since 1996), ***Kristen Fichthorn*** (since 1999), ***Peter Kratzer*** (since 2000), ***Rossitza Pentcheva*** (since 2001), and ***Karsten Reuter*** (since 2003). While previous, *empirical* kMC studies got along with just 4-5 adjustable parameters, the predictive, atomistic treatment requires one to consider on the order of 30 processes, even for simple systems. The success of the method, initially applied to growth at Al(111) and then to growth of Ag(111), GaAs(001), and Co/Cu(100) was tremendous. Being able to look at mesoscopic length scales and investigating the time evolution from picoseconds to seconds, as well as performing reliable statistical averages, brought novel and unexpected insight. The newest breakthrough and the next higher level is the description of catalysis at $RuO_2(110)$, where also chemical reactions in a thermodynamic open system were considered. This work by Karsten Reuter will be the oral contribution at the visit by the *Beirat.*

Aside from aiming at the most realistic *ab initio* simulations of matter by striving to bridge the length and timescales, we also always critically assess the accuracy of our most important tools (DFT-LDA or DFT-GGA) and endeavor to go beyond present day functionals (methods) for ground and excited states. Keywords along this line are *optimized effective potentials* (exact-exchange method), the *GW* approach, *quantum Monte Carlo* calculations, and a new approach that concentrates on localized corrections to the exchange-correlation functional. Furthermore, considerable effort is being invested in the development of new all-electron DFT and all-electron *GW* codes.

With these sophisticated theoretical methods we investigate a wide variety of physical phenomena. Much of this research is curiosity driven, with the task of solving specific scientific puzzles often posed by experimental observation or with the desire (and need) to achieve deeper insight into as yet not- or even miss-understood phenomena. Traditionally we have focused on gaining deeper understanding of the physics and chemistry of interfaces that are of specific relevance to catalysis and semiconductors. This remains to be true, although in recent years we have been also examining interesting systems of relevance to spintronics, electrochemistry, atmospheric chemistry, and biophysics.

Central to all our research is the desire and responsibility to educate and train top-quality students and postdocs. The lively atmosphere paired with high-quality science of the *Department* forms the basis for productive and fruitful research. The large number of applications we get from highly motivated young scientists is testament to our success in this regard. This is, e.g. reflected in the number of Alexander von Humboldt (AvH) fellows (scientists younger than 40 years) and AvH senior scientists who “vote with their feet” by visiting us each year.

Members of the *Department* are also involved in organizing workshops and summer schools (see Section II below) and we are active in tightening links to institutes in China such as *The International Center for Quantum Structures* (ICQS) at the *Institute of Physics* (IoP) of the *Chinese Academy of Sciences* (CAS) in Beijing and the *Dalian Institute of Chemical Physics* (DICP-CAS). At the Beijing institute Matthias Scheffler serves on the advisory board, and Enge Wang (director at the IoP) will spend several months at the FHI in the coming years. At the Dalian institute, the premier catalysis-science institute in China, a *Max Planck Partner Group* “First-Principles Theory of High-Pressure Oxidation Catalysis” is being established. This close tie will facilitate joint projects and will officially start in January 2006 with a “Group-Inauguration Workshop” soon thereafter. We are also part of another program involving the Dalian institute: “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 *University of California, Santa Barbara* (UCSB), should help to intensify collaborations through the exchange of graduate students. Indeed in the future we will strengthen our interactions with the UCSB. In a joint action of the *College of Engineering and the College of Mathematical, Life & Physical Sciences* Matthias Scheffler was appointed “Distinguished Visiting Professor for Computational Material Science and Engineering” and from December 2005 he plans to spend about three months per year in Santa Barbara. Moreover, the connections to UCSB will be further supported by the “UCSB-MPG program” which was recently established to support joint activities and exchange of students and postdocs between scientists working in *Materials Science* in the MPG and UCSB. The inauguration ceremony for this program took place in September, and the coordinators are Matthias Scheffler for the MPG and Anthony Cheetham for the UCSB. Both of these recent developments will give motivated students from the *Department* the opportunity to go to UCSB to work with our colleagues from materials, chemical engineering, chemistry, biochemistry, and biophysics.

Finally it is a pleasure to mention that earlier this year the MPG introduced a new scheme for improving ties with outstanding senior university lecturers by appointing them as *Max Planck Fellows*. Such appointments are connected with some financial support provided by the MPG to build a small working group. As also described in the report of the *Executive Director*, the FHI had suggested that Hardy Gross from the *Free University Berlin* be appointed *Max Planck Fellow*. The proposal was strongly supported by the theoreticians of the former and present *Fachbeirat*, and Hardy Gross became one of only five *Max Planck Fellows*. The fellowship is a well deserved distinction for Hardy Gross’ scientific achievements. It concerns the FHI as a whole, and the *Theory Department* in particular. Needless to say that his appointment strengthens our links with him and his group.

The following Section mentions aspects concerning the personnel and related activities. Then, in Sections III and IV some recent highlights of work performed in the *Theory Department* are briefly outlined: Section III describes conceptual, methodological, and technical developments which enable us to study new types of problems and/or improve the accuracy of calculations. Then, in Section IV, the main fields that are studied in the *Theory Department* are listed, and some recent results mentioned.

Most of the work performed in collaboration with Karsten Reuter is not discussed here, as it is covered in his Chapter.

II. Personnel and Related Activities

Since the last visit of the *Fachbeirat* in November 2003 several noteworthy developments have taken place with the following scientists receiving impressive awards and/or offers of prestigious positions:

- Jörg Neugebauer became a director at the Max Planck Institute for Iron Research in Düsseldorf in November 2004.
- Karsten Reuter successfully competed in an open competition for the position of head (W2) of an *Independent Junior Research Group* in the *Theory Department*. This post was widely announced and evaluated by a committee of most prominent scientists: Kurt Binder (Johannes Gutenberg-Universität Mainz); Patrick Bruno (Max Planck Institute for Microstructure Physics Halle); Eberhard K.U. Gross (Free University Berlin); Klaus Kern (Max Planck Institute for Solid-State Research Stuttgart); Johannes Pollmann (Westfälische Wilhelms-Universität Münster). Further details of this appointment are described in K. Reuter's chapter below.
- Peter Kratzer has been offered a W2 professorship at the University Duisburg-Essen. He is likely to assume this position in spring 2006.
- Angelos Michaelides received one of only two European Young Investigator (EURYI) awards in 2005 for projects within Germany. This will enable the development of an independent "EURYI group" in the *Theory Department* lead by A. Michaelides from October 2005.

Members of the *Theory Department* were and are actively taking part in several *Collaborative Research Centers* (Sonderforschungsbereiche (SFB)) of the *German Research Foundation* (Deutsche Forschungsgemeinschaft (DFG)) which reflects the close contacts and collaboration with the Berlin universities and other research institutes. In addition they take part in DFG *Priority Programs* (Schwerpunktprogramme (SPP)) and various *Networks of Excellence* and other European (EU and ESF) and international programs:

- SFB 290: M. Scheffler, P. Fumagalli, J. Paggel (Metallic Thin Films: Structure, Magnetism, and Electronic Properties, project B10; spokesperson: K.-H. Rieder), until 12/2004
- SFB 296: P. Kratzer, M. Scheffler (Growth-Correlated Properties of Low-Dimensional Semiconductor Structures, project A5; spokesperson: D. Bimberg)
- SFB 546: K. Hermann (Structure, Dynamics, and Reactivity of Aggregates of Transition Metal Oxides, project C6; spokesperson: J. Sauer)
- SFB 658*(IG)*: K. Reuter, M. Scheffler (Elementary Processes in Molecular Switches at Surfaces, project C4; spokesperson: M. Wolf)
- SPP 1091*(IG)*: K. Reuter, M. Scheffler (Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis; spokesperson: R. Imbihl)
- DFG – Bilateral Cooperation (POL): M. Scheffler, A. Kiejna (First Principles Studies of Adsorbate Structures at Metal and Oxide Surfaces)
- DFG – Bilateral Cooperation (POL): K. Hermann, M. Witko (Catalysis/Transition Metal Compounds), until 06/2004
- VolkswagenStiftung – Partnership Program: P. Kratzer, A. Chakrabarti (Thin Ternary Films and Quantum Dot Formation in III-V Compound Semiconductor Materials)
- EU – Research Training Network (RTN): M. Scheffler (Nano-Scale Photon Absorption and Spectroscopy with Electrons, NANOPHASE; coordinator: R. Godby), until 05/2004
- EU – Integrated Infrastructure Initiative (I3): M. Scheffler, H. Lederer (Distributed European Infrastructure for Supercomputing Applications, DEISA; chairman: V. Alessandrini)
- EU – Network of Excellence (NoE): M. Scheffler, A. Schindlmayr, P. Rinke (Nanoscale Quantum Simulations for Nanostructures and Advanced Materials, NANOQUANTA; coordinator: R. Godby)
- EU – Network of Excellence (NoE): P. Kratzer, M. Scheffler (Self-Assembled Semiconductor Nanostructures for New Devices in Photonics and Electronics, SANDiE; coordinator: M. Grundmann)

- EU – Network of Excellence (NoE): R. Schlögl, H.-J. Freund, M. Scheffler (Integrated Design of Catalytic Nanomaterials for a Sustainable Production, IDECAT; coordinator: G. Centi)
- EU – Specific Targeted Research Project (STREP)$^{(IG)}$: K. Reuter, M. Scheffler (Oxidation of Nanomaterials, NanO_2; coordinator: A. Stierle)
- EU – Marie Curie Host Fellowship for Early Stage Research Training (EST)$^{(IG)}$: A. Michaelides, K. Reuter, and M. Scheffler (Molecular Networks at Phase Boundaries, MONET; coordinator: J.N. Andersen)
- ESF – Physical and Engineering Sciences Committee (PESC): M. Scheffler (Towards Atomistic Materials Design, Psi-k; chair: P. Dederichs and V. Heine)
- ESF – Physical and Engineering Sciences Committee (PESC): M. Scheffler (Molecular Simulations in Biosystems and Material Science (SimBioMa); chair: B. Smit)
- ESF – Marie Curie Actions, Human Resources and Mobility: M. Scheffler (Psi-k Training in Computational Nanoscience; chair: P. Dederichs)
- ARC – Australian Research Council, Discovery Project: C. Stampfl, M. Scheffler, A. Freeman (*Ab initio* Theory in Complex Materials and Surfaces: Prediction and Design of Functional Structures)
- NIST Database # 42 Project: K. Hermann, M. Van Hove, P. Watson (Surface Structure Database)
- UCSB – University of California, Santa Barbara; College of Engineering and College of Mathematical, Life & Physical Sciences: M. Scheffler
- Toshiba corporation (Japan): P. Kratzer, M. Scheffler, K. Nishitani (High-k Dielectrics), until 03/2005

The superscript$^{(IG)}$ indicates a collaboration with the *Independent Junior Research Group* of Karsten Reuter.

Scientists of the *Theory Department* were also 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 in the *International Max Planck Research School*. They organized or co-organized conferences on topics in surface science and biophysics, and ran several international workshops on methods for electronic structure calculations, impacting upon the careers of numerous students of theoretical surface science.

- 23rd European Conference on Surface Science (ECOSS 23), 4–9 September 2005, Berlin, Germany
- Future Trends in Material Science (a UCSB-MPG Workshop), 11–14 September 2005, Berlin, Germany
- The Big $\Psi_{\mathbf{k}}$ Conference: Towards Atomistic Materials Design, 17–21 September 2005, Schwäbisch Gmünd, Germany
- IPAM *Long Program* on "Bridging Time and Length Scales in Materials Science and Bio-Physics", 12 September – 16 December 2005, Los Angeles, U.S.A.. The leading organizers of the general program are Russel Caflisch (UCLA, Mathematics and Materials Science), Christian Ratsch (UCLA, Mathematics), Karsten Reuter, and Matthias Scheffler (FHI). Part of this *Long Program* are several workshops. The FHI is particularly active in the following:
    - *Workshop I*: Multiscale Modeling in Soft Matter and Bio-Physics, 26–30 September 2005; organizers: Cecilia Clementi (Rice University) and Joel Ireta (FHI)
    - *Workshop II*: Multiscale Modeling in Condensed Matter and Materials Sciences, 17–20 October 2005; organizers: Peter Kratzer (FHI), Christian Ratsch (UCLA), Dimitri Vvedensky (Imperial College, London, U.K.)
    - *Workshop III*: Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions - A Hands-On Computer Course, 30 October – 5 November 2005; organizers: Peter Blaha and Karlheinz Schwarz (Vienna University of Technology), Karsten Reuter and Matthias Scheffler (FHI)
- Workshop on "Growth, Electronic and Optical Properties of Low-Dimensional Semiconductor Quantum Structures", 9–12 June 2005, Kühlungsborn, Baltic Sea, Germany; organizer: Peter Kratzer (FHI)
- 2nd Nanoquanta Young Researchers' Meeting, 2–4 May 2005, Berlin, Germany; organizers: Martin Friák and Patrick Rinke (FHI)
- Workshop on "Probing Potential Energy Surfaces (PPES-III)", 3–8 April 2005, Zermatt, Switzerland; organizers: Karsten Reuter and Matthias Scheffler (FHI)
- CECAM–$\Psi_{\mathbf{k}}$ Network Workshop on "The Nature of Hydrogen Bonding and Density Functional Theory", 2–5 June 2004, Lyon, France; organizers: Joel Ireta, Martin Fuchs, and Matthias Scheffler (FHI)
- deMon Developers Workshop on "Local Orbital Methods for Solids, Clusters, and Molecules" 30 March – 3 April 2004, Dresden, Germany; organizers: H. Eschrig and M. Richter (IFW Dresden), T. Heine and G. Seifert (TU Dresden), K. Hermann (FHI)

The computational facilities at the *Department* are good. In Berlin we are operating two Linux clusters, one with Xeon and one with Opteron processors, and at the RZG (Rechenzentrum Garching) of the MPG we have access to the IBM p690 and p575 Power5 systems. Our participation in the above mentioned DEISA *Integrated Infrastructure Initiative* as well as computer time from other collaborations was and is, however, crucial in order to be able to compete with other groups in particular those in the U.S.A., Japan, Switzerland, and the U.K.

III. New Concepts, Methods, and Techniques

III.1 Beyond Today's Density-Functional Theory

At present, DFT is the best method for describing the electronic, magnetic, structural, and vibrational properties of poly-atomic systems. If combined with the supercell approach, one can ensure that the treatment of the exchange-correlation (xc) functional remains the only relevant approximation. Although recent years have seen the development of improved xc functionals, it is still our view that actual DFT calculations give a somewhat blurred or even distorted picture of reality. Obviously, it is necessary (or at least advisable) to check the reliability of the results. Typically the route followed in the *Department* has been to use the LDA as well as GGA, and if the results differ significantly, we tend to trust neither of them.

Several co-workers in the *Department* are developing a more rigorous approach for dealing with the problem. The following routes are being considered:

- The "exact-exchange" (EXX) approach is a variant of the more general optimized effective potential method and improves on certain shortcomings of the commonly used jellium based xc functionals (such as e.g. LDA or GGA). We have implemented EXX in our plane-wave DFT code and complemented it with the *GW* method for a thorough assessment of its benefits for electronic structure calculations. (A. Qteish, P. Rinke, in collaboration with J. Neugebauer, now MPI Düsseldorf)
- In order to describe anisotropic systems, several improvements have been added to our *GW* plane-wave pseudopotential code, retaining the computational efficiency of the space-time method the code is based on. The improvements enable us to calculate the excitation spectrum of thin films and surfaces.

Furthermore, we have identified finite size effects that go beyond DFT and are now in a position to describe the transition from a film to a surface system all within the same suite of computational tools. (P. Eggert and C. Freysoldt)

- About two years ago we started developing an all-electron *GW* scheme, based on the APW+lo formulation of the WIEN2k package. Obviously this is a challenging goal. A first version of the code is already running, and we will soon start to improve its efficiency. Our experience with the pseudopotential plane-wave code underlines the importance of an all-electron code, in particular when transition metals are to be studied. (R. Gómez Abal and X. Li)
- We also continued an earlier idea that the inaccuracies in DFT-LDA or DFT-GGA calculations stem from a rather localized contribution and largely from self-interaction. Our improved xc-treatment starts by calculating geometries and energies using the DFT supercell approach. After self-consistency is achieved, clusters of various sizes are cut out, and for these clusters more accurate electronic-structure calculations are performed, e.g. by using the B3LYP functional, the Møller-Plesset perturbation theory (MP2) or the coupled cluster approach. The difference (e.g. $\Delta E = E_{MP2}^{cluster} - E_{LDA}^{cluster}$) is then added to the supercell results. (Q.M. Hu and K. Reuter)

III.2 Developing a New Atom-Centered Basis-Set Code

Over the last years scientists in the *Theory Department* where involved in developments of several quite different electronic-structure codes: In particular we mention here Green-function codes, the FHI plane wave pseudopotential (PWPP) code, and several important contributions to the FP-LAPW (WIEN2k) code and the atom-centered basis-set code DMol^3. While the PWPP code is very efficient, the frozen-core approximation, but also the pseudoization of the potential, imply some uncertainty, and the two all-electron codes FP-LAPW and DMol^3 were always important for benchmarking new studies. Using atom-centered basis functions has several advantages, in particular CPU time, memory requirements, scaling with the number of atoms, and treatment of non-periodic and periodic systems on an equal footing. Systematic tests demonstrated that high accuracy can routinely be achieved with numerical atomic-like orbitals. This then initiated the development of a completely new code. Though all-electron, its efficiency promises to be on par with or better than the best PWPP codes, while having a noticeably higher accuracy. (V. Blum, R. Gehrke, J. Behler, and K. Reuter)

III.3 A Monte Carlo Approach on the Energy Axis

About six years ago we developed a hybrid statistical mechanics method that encompasses the use of a lattice-gas Hamiltonian (LGH) and subsequent Monte Carlo (MC) calculations. Obtaining the LGH from DFT calculations of the electronic structure presents a far from trivial part in this procedure. Once available, such a Hamiltonian allows for a great flexibility, since it can be evaluated for any lattice occupation be it dense or sparse, periodic or disordered. In addition to standard MC, we have now implemented the new MC algorithm of Wang and Landau (PRL (2001)), in which the density of configurational states is obtained explicitly. This enables us to calculate very efficiently thermodynamic quantities such as the free energy, entropy, specific heat, and the temperature of order-disorder phase transitions. (M. Borg, M. Todorova, and C. Stampfl)

III.4 Bond-Order Potentials for Semiconductor Nanostructures

In order to investigate semiconductor nanostructures in atomistic detail, new bond-order based potentials have been developed which enable us to treat systems with a few hundred thousands of atoms. For example, the "hybrid approach" that was previously developed in the *Theory Department* was generalized to a method capable to describe also "small" quantum dots ($N < 5,000$ atoms), where facets are too small to develop a surface reconstruction. Also the energies associated with edges between such facets are treated properly. (T. Hammerschmidt and P. Kratzer)

III.5 Improvements in the Stockholm-Berlin (StoBe) cluster code

The StoBe (<u>Sto</u>ckholm-<u>Be</u>rlin) program package, developed in collaboration with L.G.M. Pettersson (University of Stockholm) for the calculation of chemical/physical properties (including excitations) of large molecules and clusters 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 user community. They include

- the incorporation of (relativistic) Dolg pseudopotentials which are available for the whole table of elements,
- improved evaluation of electronic core excitations for the interpretation of experimental NEXAFS spectra,

- improved treatment of vibrational excitations (eigenmode analysis) which is presently ported to run in a parallel CPU environment.

(K. Hermann)

IV. Applications – Some Highlights

IV.1 Structure

Solving atomic structures is a common activity for the natural scientist. A structure whether of relevance to molecular biology, chemical physics, catalysis, or another area is considered “solved” when an atom-by-atom structural understanding of the molecular or solid state systems involved has been obtained. Solving atomic structures is a necessary prerequisite for analyzing and understanding the properties and function of surfaces, and of materials in general. Of particular interest, also in view of interactions and collaborations with the experimental departments of the FHI, are surfaces of transition metals and their oxides, as well as III-V semiconductor surfaces and quantum dots. Special focus was therefore put on oxides and surface oxides of V, Ru, Rh, Pd, Ag, and Pt, of GaAs and InAs surfaces, of InAs quantum dots, and of nanoporous carbon.

- Different vanadium oxides, in particular V_2O_5 and V_2O_3, are studied employing large cluster models. These studies aim at identifying catalytically active surface oxygen where hydrogen adsorption at coordinatively unsaturated V_2O_5 surfaces as well as electronic oxygen core excitations at V_2O_3 are considered. The latter make an evaluation of theoretical O 1s NEXAFS spectra possible and yield very good agreement with measured spectra. (P. Hejduk, C. Kolczewski, and K. Hermann)
- In a combined structural and NEXAFS study the equilibrium geometry of three phenylpropenes on Cu(111) have been calculated using large cluster models. The theoretical NEXAFS spectra obtained for these geometries show excellent agreement with recent NEXAFS measurements and help to identify possible catalytic epoxidation routes of propene. (C. Kolczewski and K. Hermann)
- For the late *4d* transition metals and for Pt emphasis was put on understanding the effect of realistic environmental situations (realistic (*T, p*)): *Out of the vacuum, into real life!* Here experimentally known adlayer structures were

confirmed, and some novel “surface oxides” identified. This highlights the transition from the “old surface science” that was (and is) important to study well prepared but often academic situations to the “new surface science” where more realistic environmental conditions are taken into account. (J. Rogal, A. Michaelides, J. Kitchin, T. Jacob, and K. Reuter)

- We also started generalizing the *ab initio* thermodynamics approach by including the situation encountered in electrolytes and fuel cells. (T. Jacob)
- The investigations into the electronic structure of self-assembled semiconductor quantum dots, pursued in collaboration with B. Koiller and co-workers from Universidade Federal do Rio de Janeiro, were continued and extended. Employing a tight-binding scheme with second-nearest neighbor interactions, we calculated *selected* electronic states of a nanostructured system consisting of several hundred thousands of atoms. Specifically, the effect of intermixing during post-growth annealing on the electronic and optical properties was investigated for InAs quantum dots embedded in a GaAs matrix. We could explain the observed blueshift of the quantum dot's photoluminescence after annealing and why intermixing enhances the oscillator strength for electron-hole recombination, while reducing its anisotropy for in-plane polarized light. (R. Santoprete, B. Koiller, R. Capaz, A. Kleinsorge, and P. Kratzer)
- Experiments performed in the *Department of Inorganic Chemistry* have shown that a variety of carbon materials, are able to catalyze chemical reactions. Particularly interesting is here nanoporous carbon (NPC), which is a class of sp^2-bonded carbon materials with a high defect concentration, although still not amorphous. We analyzed the microscopic structure of NPC in terms of its structural motifs, and the results show that combinations of non-hexagonal rings in the structure have a strong influence on the chemical properties of the material. Aiming to describe the oxidative dehydrogenation of ethylbenzene on NPC materials we are currently working on developing a microscopic model for this reaction. (J. Carlsson, S. Linic, and S. Durdagi)

IV.2 Dynamics

The dynamics of atoms is studied using “on the fly” *ab initio* molecular dynamics (AIMD), e.g. for the scattering and dissociative adsorption of molecules, for looking at diffusion at surfaces and surface vibrations, and to study properties of liquids, e.g. water, and the water/NaCl interface. (A. Michaelides, J. Behler, and B. Li)

With such calculations we are able to simulate time spans of several picoseconds. For some situations this provides useful information. However, in many cases this is far from sufficient and possibly grossly misleading. For example, for obtaining a good statistical average for describing molecular scattering and sticking our neural-network approach, to represent the potential-energy surface, was developed further. This enables us to extend the time span into the nanosecond regime and provides a good statistical average in order to evaluate the sticking coefficient. (J. Behler, S. Lorenz, and K. Reuter)

However, when one is concerned with *the function* of materials the nanosecond time span is still not sufficient. For example, under realistic conditions a chemical reaction at a catalyst surface may only occur once every millisecond per surface unit cell, and corrosion typically proceeds with a speed of one atomic layer per minute. The method of choice for understanding systems such as these is the "first-principles kinetic Monte Carlo approach". It only introduces one assumption, namely that transition-state theory is applicable, which has been in fact tested to hold. Then the "first-principles kinetic Monte Carlo approach" is indeed a coarse-grained MD without loss of any relevant information. In this way investigations of time spans of several seconds or even minutes become possible. (K. Reuter and J. Rogal)

IV.3 Spin-Electronics Materials

Motivated by magnetic metal-semiconductor heterostructures to be applied for injection of spin-polarized current, there is a demand for magnetic thin films compatible with silicon substrates. We have investigated various intermetallic compounds of manganese and silicon for their suitability for this purpose. One class of materials are Mn-silicides that could possibly be grown by reactive epitaxy on Si. With the help of DFT calculations, we could identify MnSi in a hitherto unknown, epitaxially stabilized form (the CsCl crystal structure) as a novel candidate material. These MnSi thin films are predicted to display sizeable magnetic moments at the surface and interface Mn atoms, but their ferromagnetic order gets lost for thicker films (after depositing several monolayers of MnSi).

Alternatively, the ferromagnetic half-metal Co_2MnSi is a promising candidate material, due to its robust ferromagnetism even well above room temperature. For this materials system, we investigated both the $Co_2MnSi(001)$ surface, as well as the

$Co_2MnSi(001)/Si(001)$ interface to learn under which conditions the half-metallic properties of bulk Co_2MnSi are retained at surfaces or heterostructures. Analyzing the surface energies of $Co_2MnSi(001)$ obtained from DFT calculations, we find that surface terminations comprised of a layer of only Mn atoms, only Si atoms, or a mixture of both are thermodynamically stable, depending on the chemical environment. Only in the first case of pure Mn termination, however, is half-metallicity retained. For $Co_2MnSi(001)/Si(001)$ heterostructures, our calculations predict the presence of undesirable interface states, whereas the half-metallic gap of bulk Co_2MnSi is recovered only a few layers away from the interface. Future work is planned to address the effect of the interface electronic structure on the spin injection efficiency. (S.J. Hashemifar, H. Wu, M. Hortamani, and P. Kratzer)

IV.4 Biophysics

The properties of biomolecules result from a subtle interplay between covalent bonds and non-covalent interactions (hydrogen bonding and van der Waals forces). We aim to get insight into the underlying physics that govern the biological processes by properly accounting for the non-covalent interactions in atomistic and coarse-grained modeling of biomolecules. In particular, we investigate the role of hydrogen bonding and its cooperative effect on the thermodynamic and kinetic stability of alanine and glycine polypeptides in helical conformations.

Diffusion (quantum) Monte Carlo (DMC) can provide accurate total energies for molecules and solids. Our calculations of hydrogen bonding and stacking energies in different complexes show that DMC results agree well with those of certain post-Hartree-Fock calculations. In certain cases a high-level treatment of correlations, beyond MP2, is found to be necessary. Furthermore, the DMC results confirm that DFT-GGA successfully describes the cooperative strengthening of hydrogen bonds. (M. Fuchs, C. Filippi, and J. Ireta)

We use DFT-GGA to investigate the potential-energy surface (PES) of infinitely long alanine and glycine polypeptides. The PES reveals minima associated with π-helix, α-helix, and 3_{10}-helix conformations, which differ in the hydrogen bonding pattern they form. Thermodynamic corrections to the enthalpic stabilities are hereby found to play an important role for the relative stability of these helical confirmations. An analysis of the vibrational free energy shows e.g., that the π-helix is destabilized at room temperature with respect to the other helices. (L. Ismer, J. Ireta, and J. Neugebauer)

Molecular dynamics simulations of helices up to 20 residues long using the AMBER force field, which adequately reproduces the DFT-GGA data, reveal that the associated free energy exhibits minima representing mostly α- and mostly 3_{10}-configurations at room temperature. This confirms the necessity to include both states in coarse-grained models for helices. (R.A. Miron, M. John, and J. Ireta)

Recent Developments in the Independent Junior Research Group

Head: Karsten Reuter

I. General Remarks

The new *Independent Junior Research Group* (IJRG) "First-Principles Statistical Mechanics" at the *Theory Department* officially began operation on January 1, 2005. Our research aims at a quantitative modeling of materials properties and functions, primarily in the fields of surface science and heterogeneous catalysis. Corresponding functions typically arise out of the complex interplay of a larger number of molecular processes. While the individual process properties are determined at the electronic structure level, their statistical interplay develops only over mesoscopic lengths and times. The work within the IJRG concentrates therefore on achieving an accurate, first-principles description of all individual processes, and on combining them appropriately within a thermodynamic or statistical mechanic treatment.

In this context, our present and planned methodological developments may be grouped into three different areas: i) Improved description at the electronic structure level, e.g. with respect to accuracy or computational efficiency; ii) Improved matching to the statistical mechanics techniques, e.g. which processes need to be considered with which accuracy; and iii) Improved solutions of the statistical mechanics problem, e.g. efficient sampling of the vast configuration spaces. Particularly with respect to the latter category, we are also initiating projects comparing statistical atomistic with coarse-grained continuum descriptions, thereby extending our multiscale modeling efforts over the full range from electronic up to macroscopic regimes. Some of these methodological aspects will be further outlined in Section III.

With respect to the investigated systems several projects are concerned with catalytic oxidation reactions at late transition metal (TM) or TM alloy surfaces. Under technological conditions, this involves oxygen partial pressures of the order of atmospheres, which is why also the O_2 dissociation dynamics, oxide formation and oxide surfaces are issues within this category. We are thereby continuing and adding to the efforts of the former "*Catalytic Reactions at Surfaces*" work group at the *Theory Department*, out of which the IJRG originated. In addition, we are now also opening up new research directions, where the first-principles statistical mechanics methodology may be suitably applied. Most prominently this concerns the catalytic and materials properties of small metal clusters, as well as the function and ordering behavior of switchable or chiral molecules at surfaces. Most of this work is embedded in larger national and international collaborative efforts as detailed in Section II, in addition to the existing strong links to the *Theory Department*. Section IV highlights some recent results in the on-going projects.

II. Funding, Personnel and Related Activities

A key goal in the months preceding and following the official starting date of the IJRG was to secure funding for the targeted group size of around 10 people. Apart from the IJRG budget directly provided by the Fritz-Haber-Institute or through personalized scholarships, e.g. from the *Alexander von Humboldt Foundation*, this concerns at present primarily external funding from the *German Research Foundation* (Deutsche Forschungsgemeinschaft (DFG)) and from the European Union (EU) within the 6th framework program. As a result of these efforts, the IJRG is now participating in several national and international, smaller and larger collaborative research projects. All projects preceded by the superscript$^{\text{(ThD)}}$ are in collaboration with the *Theory Department*, while particularly the activities within the newly founded DFG *Collaborative Research Center* (Sonderforschungsbereich) SFB 658 establish also close contacts and collaboration with the Berlin universities and research institutions.

Concerted actions:

- SFB 658$^{\text{(ThD)}}$: K. Reuter and M. Scheffler (Elementary Processes in Molecular Switches at Surfaces, project C4; spokesperson: M. Wolf)
- SPP 1091$^{\text{(ThD)}}$: K. Reuter, M. Scheffler (Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis; spokesperson: R. Imbihl)
- EU – COST Action COST P19: K. Reuter (Multiscale Modelling of Materials; COST national coordinator: E. Auranen)
- EU – Marie Curie Host Fellowship for Early Stage Research Training (EST)$^{\text{(ThD)}}$: A. Michaelides, K. Reuter, and M. Scheffler (Molecular Networks at Phase Boundaries, MONET; coordinator: J.N. Andersen)
- EU Specific Targeted Research Project (STREP)$^{\text{(ThD)}}$: K. Reuter, M. Scheffler (Oxidation of Nanomaterials, NanO$_2$; coordinator: A. Stierle)

Individual projects:

- DFG Project: K. Reuter, and A. Groß (Ab Initio Description of Non-Adiabatic Effects in Dissociative Adsorption)
- EPSRC Project: W. Hofer, and K. Reuter (Dynamic Processes in the Adsorption and Formation of Organic Molecules on Surfaces)

At the moment of writing this report, the IJRG consists of 8 members, i.e. apart from the group head 4 PhD students and 3 postdoctoral fellows. Since several of these will leave the group until the end of the year, the group has engaged in an active job announcement and recruiting process to maintain and extend to the targeted group size. Up to now we were fortunate to contract three new PhD students and one postdoctoral fellow to start within the next six months. With nationalities from Sweden, Morocco, Nigeria and Iran, these newcomers allow to maintain the group's highly international character. Further recruiting possibilities, also at the national level, may arise from regular teaching, which the group head will take up at the Free University next year, having completed the German Habilitation procedure in May 2005. Further visibility of the group and its activities is expected through conference and workshop organization. In 2005 this includes:

- Workshop on "Probing Potential Energy Surfaces (PPES-III)", Zermatt, Switzerland, 3–8 April 2005; organizers: K. Reuter and M. Scheffler
- Symposium on "Atomic-Scale Understanding of High-Pressure Catalysis" during the 23rd European Conference on Surface Science (ECOSS 23), Berlin, Germany (D), 4–9 September 2005, K. Reuter and J.W.M. Frenken (Leiden University, The Netherlands)
- IPAM Long Program on "Bridging Time and Length Scales in Materials Science and Bio-Physics", 12 September–16 December 2005, Los Angeles, (U.S.A.). The leading organizers of the general program are Russel Caflisch (UCLA, Mathematics and Materials Science), Christian Ratsch (UCLA, Mathematics), Karsten Reuter and Matthias Scheffler (FHI), and therein in particular the Workshop on "Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-on Computer Course", 30 October–5 November 2005, organizers: Peter Blaha and Karlheinz Schwarz (TU Vienna, Austria), K. Reuter and M. Scheffler (FHI)

As part of the organization of the latter program, the group head will spend 11 weeks at UCLA this fall. Four present and two future members of the IJRG will also attend extended periods of this program, most of them being actively involved in the hands-on workshop. This attendance will not only ensure appropriate supervision during the group head's absence from Berlin, but will also expose a significant fraction of the IJRG to the multiscale modeling community present at the long program.

The group runs their calculations on Linux clusters (3 IBM Blade Centers with 14 double 2.8 GHz Xeon processors each) and 23 Compaq ES-45 servers (4 shared-memory processors each). In addition, we have access to shared-memory IBM SP4/SP5 computers (Regatta) at the MPG computing center in Garching. At present, this provides adequate computing time for the group's various projects. However, the Compaq ES-45 servers (installation: 01/2002) have reached some age, and in particular when the full targeted group size will be reached in Spring 2006, additional computing resources will be needed.

III. New Concepts, Methods and Techniques

III.1. Electronic structure level

For the required electronic-structure calculations, almost all projects in the IJRG rely at present on density-functional theory (DFT) using local-density or gradient-corrected exchange correlation (XC) functionals. Combined with the supercell approach, this provides in most cases a sufficiently accurate surface energetics at an intense, but still affordable computational cost. Still, particular processes need an improved description, while the large number of energy evaluations required for the sampling of vast configuration spaces demands further reduction of the computational cost. For a coarse pre-screening of the configuration spaces, routes trading accuracy for computational demand are then also of interest. Activities in the IJRG aim therefore at developments beyond today's DFT, aim to improve the efficiency of current DFT, or aim at alternative methods for a crude, low-cost energetics:

- Having hitherto primarily relied on full-potential DFT implementations, we have systematically benchmarked the reliability of the computationally much less demanding ultra-soft pseudopotential or the projector augmented wave method. Our results show that seemingly irrelevant imprecisions appearing in the scattering properties of the pseudopotential can have a large influence on the surface energetics. If these scattering properties are carefully addressed, excellent agreement can, however, be obtained. (A. de Sarkar, J. Rogal, J. Kitchin; in collaboration with A. Kiejna (University of Wroclaw, Poland) and G. Kresse (University Vienna, Austria))

- In preparation for the envisaged studies of small metal clusters we participate in the medium-term efforts of the Theory Department developing a new local-basis DFT code. (R. Gehrke, J. Behler; in collaboration with V. Blum$^{\text{(ThD)}}$)
- If the major error in local-density or gradient-corrected DFT stems from rather localized contributions like e.g. self-interaction, a local correction can be obtained through more accurate electronic structure calculations of small clusters. Previous work in the Theory Department realized such an "exploiting the nearsightedness" approach through combined DFT and electronic quantum Monte Carlo (QMC) calculations. We now used the combination DFT + hybrid functional (B3LYP) or many-body perturbation theory (MP2) to obtain the correct adsorption site of CO at close-packed transition metal surfaces. (Q.M. Hu)
- In orbital-free DFT one aims at expressing the kinetic-energy functional (KEF) directly in terms of the electron density, superseding the necessity of introducing Kohn-Sham orbitals. While this would significantly reduce the calculational costs, all hitherto developed approximate KEF expressions are too crude for a quantitative energetics. We are presently exploring whether they would nevertheless still be helpful for a first rough estimate, e.g. when sampling energetically rather unfavorable parts of configuration space, before "zooming in" with more quantitative methods. (R. Gehrke)

III.2 Matching of electronic and mesoscopic regime

In the multi-scale modeling terminology, most algorithms employed in the IJRG would be denoted as "hand-shaking": the electronic structure information is transferred to the statistical mechanics techniques in form of computed first-principles parameters. Crucial questions then concern which parameters are needed and at which accuracy. In addition, there is often a need to suitably coarse-grain the system, in order to keep the total amount of parameters tractable and to bring out the essential physics. The IJRG is currently addressing a number of such issues:

- For systems with site-specific adsorption, lattice-gas Hamiltonians (LGH) provide a fast enough energetics to properly sample, via Monte Carlo (MC) simulations, the huge configuration spaces determining the mesoscopic ordering behavior. To make the simulations quantitative, the lateral interactions in the LGH have to be suitably parameterized with first-principles data. In several projects, our efforts aim at identifying which interactions are best included, which DFT calculations are best used for the parameterization and how the reliability of a given parameterization can be assessed. (C. Lazo, Y. Zhang, J. Kitchin)

- Kinetic Monte Carlo (kMC) simulations of surface systems allow to explicitly follow the time evolution over time scales of the order of seconds or longer. The crucial input parameters are the rates of individual processes, which can be obtained from DFT and transition state theory. Since in the latter the energetic barriers enter exponentially, it is traditionally believed that a high ("chemical") accuracy is required for the process energetics. In contrast, we find in simulations of the CO oxidation at RuO2(110) that under conditions leading to high catalytic activity, the overall product formation rate is quite insensitive to modest variations in the individual process rates. In the interplay of a large number of processes, such variations are largely compensated, suggesting that an appropriate treatment of the process statistics is at least of equal importance as the accurate description of individual processes.
- In view of these last results, aiming first at an accurate DFT computation of all relevant process rates before initiating the kMC simulations is not the best strategy. In more complex systems, this may anyway become unfeasible due to the sheer number of processes itself, or the difficulties in identifying them at first hand. Instead, we are now pursuing more adaptive routes, in which we first assess in kMC simulations whether additional processes are important for the mesoscopic observables of interest. Only if the latter are appreciably affected by small variations in the process rates, is an accurate computation of the energetics of this process via DFT required. (J. Rogal)

III.3 Simulations at the mesoscopic scale

Once the first-principles parameters are available, thermodynamic or statistical mechanics techniques can be employed to quantitatively analyze meso- or macroscopic system properties and functions. Due to the high computational cost of obtaining the parameters, achieving an optimum sampling with a minimum number of first-principles input is a crucial aspect. In view of a multi-scale modeling, possibilities to further coarse-grain the system, e.g. by mean-field approaches, are then another area of interest:

- As part of our DFT-LGH based Monte Carlo simulations addressing the mesoscopic ordering behavior of adsorbates, and following earlier work by M. Borg *et al.*(ThD), we are comparing the efficiency of standard Metropolis sampling with that suggested by Wang and Landau. In the latter the density of configurational states is explicitly obtained, which in turn allows to directly compute thermodynamic quantities such as the free energy, entropy or specific heat. We find this sampling scheme to be superior in determining the order-disorder transition, at a reduced overall number of MC steps. (C. Lazo)
- KMC simulations of heterogeneous catalytic systems fully account for the microscopic correlations, fluctuations and spatial distributions at the surface. In contrast, this is neglected in the prevailing microkinetic rate equation approach based on the mean-field approximation. Since our kMC simulations reveal particularly large fluctuations and a non-stochastic adsorbate arrangement in the active state of the RuO2(110) surface, this suggests that a rate equation approach would fail in describing this system. We are currently assessing this quantitatively with rate equation calculations based on the same first-principles data. (in collaboration with H. Metiu (UCSB, U.S.A.))

IV. Applications

IV.1. Oxygen-metal interactions and oxide formation

Studying the effect of realistic environments (multi-component gas phases at realistic pressure and temperature) on metal surfaces is one of the core activities within the IJRG. Of particular interest are oxygen-containing environments, which may eventually lead to the formation of oxides at the surface. Present projects deal primarily with the series of late TMs from Ru to Ag, aiming to achieve a trend understanding. Concerning the on-surface O chemisorption, this involves not only work on the low-index TM surfaces, but recently also on vicinals and on alloys of these TMs. Addressed are the mesoscopic ordering behavior, the prominent role played by steps, as well as a possible segregation reversal induced by high oxygen pressures. (Y. Zhang, J. Kitchin)

Higher oxygen loads at the surface lead to the formation of sub-nanometer thin oxidic films. While at Ru such “surface oxides” are only precursors, they become thermodynamically stable phases under certain gas phase conditions at Pd and Ag. The computed (T, p) stability range of the surface oxide at Pd(100) has been confirmed by surface X-ray diffraction experiments, which also provided first insight into the kinetics of the oxide formation process. The detailed knowledge of the atomic structure and stability provides now the firm basis for ensuing work addressing the role played by this surface oxide in the context of CO oxidation catalysis at technologically relevant pressures. This basis is still lacking in the case of the well-known *p*(4x4) surface oxide at Ag(111). Our detailed investigations have shown that the prevailing structural model is significantly incomplete and needs revision, which at present prevents further studies elucidating the role played in partial oxidation reactions. (J. Rogal; in collaboration with A. Michaelides(ThD), A. Stierle (MPI for Metals Research, Germany), and E. Lundgren (Lund University, Sweden))

IV.2 The steady-state of heterogeneous catalysis

Considering the surface to be in a "constrained equilibrium" with the reactant gas phase yields first insight into the catalyst surface structure and composition during steady-state operation. Application of this approach to the CO oxidation reaction at Ru(0001) and Pd(100) shows that in both cases the catalyst surface is at ambient pressures covered by oxides. In the case of Ru this is a thick, bulk-like film, while at Pd this is a sub-nanometer thin surface oxide. KMC simulations allow furthermore to assess how the kinetics of the on-going reactions affects the surface populations, as well as to quantify the overall catalytic activity. At the Ru oxide surface, such effects lead to the formation of a disordered and dynamic adsorbate composition, which deviates from any structure hitherto characterized in ultra-high vacuum (UHV) experiments. Obtaining unprecedented quantitative agreement with measured conversion rates for environmental conditions ranging from UHV up to technologically relevant pressures, we find the reaction mechanism with the most favorable energy barrier to contribute only little to the overall CO_2 production. (J. Rogal)

IV.3 Non-adiabatic effects in the dissociative adsorption at surfaces

The widely employed adiabatic, or Born-Oppenheimer approximation relies on the ability of the electrons to adjust at any time instantaneously to the slower motions of the atoms. Due to low transition matrix elements, this must not necessarily be valid e.g. during the molecular impingement on a surface. For this, we developed and implemented a locally-constrained DFT method, which allows to compute diabatic potential energy surfaces (PESs) corresponding to different charge and spin states of the impinging molecule. Particularly, for the dissociative adsorption of oxygen we can thus analyze trajectories, where the molecule continues to travel in the initial spin-triplet configuration up to distances close to the surface. Barriers on this triplet PES account for the enigmatic low sticking probability of thermal O_2 at Al(111), and such spin selection provides also first insight into the controversially discussed adsorption mechanism at this surface. (J. Behler)

Publications of the Theory Department

(Including the Independent Junior Research Group - since January 1, 2005)

Late 2003

Chen, Z., H. Jiao, G. Seifert, A.H.C. Horn, D.K. Yu, T. Clark, W. Thiel, P. von Ragué Schleyer: The structure and stability of Si_{60} and Ge_{60} cages: A computational study. J. Computational Chemistry **24**, 948-953 (2003).

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Friedrich, C.: Geometrische, elektronische und vibronische Eigenschaften der reinen und defektbehafteten V_2O_5(010)-Oberfläche und deren Wechselwirkung mit Adsorbaten: Theoretische Untersuchungen. FU Berlin 2004.

Mandreoli, L.: Density Based Kinetic Monte Carlo Methods. TU Berlin 2004.

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Diplomarbeit (Master Thesis)

Badinski, A.: Electronic correlation calculations of small molecules with quantum Monte Carlo methods. TU Berlin 2004.

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Habilitation (Habilitation)

Reuter, K.: First-principles statistical mechanics for oxidation catalysis. FU Berlin 2005.

Invited Talks of the Members of the Theory Department

Jörg Behler

Jun 2004	Workshop on Catalysis from First Principles, Høsterkøb, Denmark *Non-Adiabatic Spin Effects in the* O_2*-Dissociation on Al(111)*
Jan 2005	Department of Mathematics, UCLA, Los Angeles, U.S.A. *Dissociation of Oxygen Molecules on the Al(111) Surface*
Jul 2005	Seminar at Department of Chemistry and Applied Biosciences, ETH Zürich, Lugano, Switzerland *Dissociation of Oxygen at Al(111): The Role of Spin Selection Rules*
Jul 2005	Seminar at Institute of Theoretical Physics, TU Clausthal, Germany *Dissociation of Oxygen at Al(111): The Role of Spin Selection Rules*
Nov 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Comparison of Different Methods and Codes: (L)APW, LMTO, PAW, Pseudo Potentials, Gaussian, etc.*

Johan Carlsson

May 2005	Seminar at Institut für Festkörperphysik, Technische Universität Berlin, Germany *Theoretical Study of Curvature Effects in Defective Nanotubes*

Alexey Dick

Oct 2004	German-Korean Seminar on Applied Physics and Mathematics, Heidelberg, Germany *Scanning Tunneling Microscopy and Spectroscopy Simulations of Magnetic and Nonmagnetic Surfaces*

Martin Fuchs

Jun 2004	CECAM - Ψ_k Network Workshop on The Nature of Hydrogen Bonding and Density Functional Theory, Lyon, France *Diffusion Monte Carlo Study of Hydrogen Bonded Model Systems*
Sep 2004	International Workshop on Time Dependent Density-Functional Theory: Prospects and Applications, Benasque, Spain *Use of the Adiabatic-Connection Fluctuation-Dissipation Approach to Exchange-Correlation in the Ground State*

Jan 2005	XII International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods, Trieste, Italy *Diffusion Monte Carlo Study of Hydrogen Bonded Systems*
Jun 2005	CECAM Workshop on Van der Waals Forces and Density Functional Theory, Lyon, France *Quantum Monte Carlo Calculations of Noncovalently Bonded Systems*
Sep 2005	CECAM Workshop on Ab initio Simulation Methods Beyond Density Functional Theory, Lyon, France *Diffusion Monte Carlo Applied to Hydrogen and Van der Waals Bonds*
Nov 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Comparison of Different xc Functionals: From LDA to GGA and Beyond*

Klaus Hermann

Jan 2004	Colloquium at the Universität Erlangen, Germany *Relaxation of Differently Terminated Vanadium Sesquioxide Surfaces: Ab Initio DFT Cluster Studies*
Mar 2004	San Luis III Symposium on Surfaces, Interfaces, and Catalysis, Merida, Venezuela *Electronic Behavior and Reactive Adsorption of Small Molecules at Vanadium Oxide Surfaces: Ab Initio DFT Cluster Studies*
Mar 2004	International Symposium of the Collaborative Research Center 546 on Transition Metal Oxides - Clusters, Surfaces, and Solids - Structure, Dynamics, and Reactivity, Berlin, Germany *Properties and Reactive Adsorption of Small Molecules at Vanadium Oxide Surfaces: Ab Initio DFT Cluster Studies*
May 2004	deMon Developers Workshop, Tropea, Italy *Latest Developments of the StoBe-deMon Cluster Code: Methods and Applications*
Jun 2004	X International Conference on Theoretical Aspects of Catalysis, Tropea, Italy *Reactive Oxygen Sites and Adsorption at Vanadium Oxide Surfaces: Ab Initio DFT Cluster Studies*
Jul 2004	Department of Chemistry, Ruhr-Universität Bochum, Germany *Electronic and Vibrational Excitations at Oxide Surfaces: Cluster Models for Vanadium Oxide*

Jul 2004 Institute for Nuclear Waste Disposal, Forschungszentrum Karlsruhe, Germany
Physical / Chemical Properties of Vanadium Oxide Surfaces and Reactive Adsorption of Small Molecules: Ab Initio DFT Cluster Studies

Sep 2004 3rd EFCATS School on Catalysis, Ustroń, Poland
Quantum Chemical Methods and their Application to Systems of Relevance in Heterogeneous Catalysis

Dec 2004 Seminar Series at Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland
Basics of Surface Crystallography

Feb 2005 Seminar at Advanced Synchrotron Light Source, Lawrence Berkeley National Laboratory, Berkeley, U.S.A.
Quantum Chemical Approach to X-Ray Spectroscopy: Application to Small Molecules and Surfaces

Apr 2005 Department of Physics, Universität Augsburg, Germany
Electronic Behavior and Reactive Adsorption of Small Molecules at Vanadium Oxide Surfaces: Ab Initio DFT Cluster Studies

May 2005 International Symposium on Science and Art in Europe, Berlin, Germany
Electronic / Vibrational Excitations and Reaction at Oxide Surfaces: Cluster Models for Vanadium Oxide

Nov 2005 5th International Nano-Science Symposium on Theories and Simulation Methods for Soft X-Ray Solid State Spectroscopy, Tsukuba, Japan
Quantum Chemical Approach to X-Ray Spectroscopy: Application to Small Molecules and Surfaces

Joel Ireta

Jan 2004 Statistics Seminar at University of San Luis Potosi, Mexico
DFT Study of the Stability of the Secondary Structure of Proteins

Jul 2005 CINSaT Colloquium, Center for Interdisciplinary Nanostructure Science and Technology, Kassel University, Germany
Density Functional Theory Study of the Secondary Structure of Proteins: Stability and Structural Transitions in Polyalanine

Timo Jacob

Feb 2005 Workshop of the Oxygen Reduction Network, ZSW Ulm, Germany
The Reaction Mechanism at the Fuel Cell Cathode

May 2005 Final Colloquium, Priority Program (SPP 1060) of the German Research Foundation (DFG), Bamberg, Germany
Theoretical Description of Electrocatalytic Processes in Fuel Cells

May 2005 First German/New Zealand Workshop on Heavy and Superheavy Elements, Auckland, New Zealand
Reactions on Pt and Pt-Based Surfaces

Jun 2005 Solid State Colloquium, Technische Universität München, Germany
Towards a Realistic Description of Electrochemical Systems

Sep 2005 Seminar at Interdisciplinary Research Center for Catalysis (ICAT), Technical University of Denmark, Lyngby, Denmark
Towards a Realistic Description of Electrochemical Systems

Peter Kratzer

Nov 2003 Physikalisches Kolloquium, Christian-Albrechts-Universität zu Kiel, Germany
Einblicke in die chemischen Elementarprozesse bei der Halbleiter-Epitaxie – Ergebnisse von ab initio-Methoden

Dec 2003 Wissenschaftliches Zentrum für Materialwissenschaften, Phillips-Universität Marburg, Germany
Theorie der Oberflächendiffusion und des Wachstums von III-V-Halbleiter-Nanostrukturen

Jun 2004 Conference on Electronic Structure Simulations of Nanostructures, University of Jyväskylä, Finland
Growth-Related Structural and Electronic Properties of InAs Quantum Dots on GaAs

Jun 2004 Workshop on Modelling of Self-Assembled Semiconductor Nanostructures, CECAM, Lyon, France
Growth-Related Structural and Electronic Properties of InAs Quantum Dots on GaAs

Sep 2004 Workshop on Ab initio Methods for Correlated Spintronics Materials, Mont Sainte Odile, France
Theoretical Investigations of MnSi and Co_2MnSi *Thin Films as Candidates for Spin Injectors: Structural, Electronic, and Magnetic Properties*

Oct 2004 Seminar at Universität Duisburg-Essen, Essen, Germany
Neue Einblicke in die Materialphysik mit Hilfe von Monte-Carlo Methoden

Nov 2004	Seminar at Universität Osnabrück, Germany *Einblicke in die chemischen Elementarprozesse bei der Halbleiter-Epitaxie – Ergebnisse von ab initio-Methoden*
Nov 2004	Seminar at Universität Regensburg, Germany *First-Principles Investigation of Surface Diffusion and Growth of III-V Semiconductor Nanostructures*
Dec 2004	49th Symposium on Solid State Physics, Department of Atomic Energy, Guru Nanak Dev University, Amritsar, India *Calculation of Structural, Electronic and Magnetic Properties of MnSi and* Co_2MnSi *Thin Films*
Jan 2005	Colloquium at the Centre for Advanced Technology, Indore, India *First-Principles Investigation of Surface Diffusion and Growth of III-V Semiconductor Nanostructures*
Jan 2005	Japanese-German Symposium on Frontiers in Science, Mainz, Germany *Atomistic Simulations of Processes at Surfaces*
Feb 2005	Colloquium at the College of Nanoscale Science & Engineering, University of Albany-SUNY, Albany, U.S.A. *Theoretical Investigations of MnSi and* Co_2MnSi *Thin Films as Candidates for Spin Injectors: Structural, Electronic, and Magnetic Properties*
May 2005	International Conference on Crystallization and Electrocrystallization: Fundamentals and Applications, Varna, Bulgaria *Beyond Standard Nucleation Theory: Insights from Atomistic Simulations of Two-Dimensional Island Nucleation Based on First Principles Results*
Sep 2005	Workshop on Si Surface – Electronic Structure and Dynamics, Max-Born-Institute, Berlin, Germany *Theory of the Electronic Structure of the Si(001) Surface Revisited*
Sep 2005	SFB 616 Workshop "Energiedissipation an Oberflächen" Remagen, Germany *Moderne theoretische Methoden zur Beschreibung der elektronischen Struktur von Oberflächen – veranschaulicht am Beispiel der Si(001)-Oberfläche*
Oct 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Multi-Scale Modeling of Semiconductor Surfaces and Nanostructures*

Nov 2005 IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A.
Algorithms for Total-Energy Minimization and Forces

Bernhard Lehner

Jan 2004 Seminar on Experimental and Theoretical Aspects of Surface Chemistry, Freie Universität Berlin, Germany
Kinetische Monte-Carlo Simulationen von Desorptionsprozessen

May 2004 Seminar at Philipps-Universität Marburg, Germany
Kinetische Monte-Carlo Simulation der Desorption

Angelos Michaelides

Mar 2004 APS March Meeting, Montreal, Canada
Exploring the Catalytic Activity of a Noble Metal: The Ag Catalyzed Ethene Epoxidation Reaction

Jul 2004 Seminar at Lawrence Berkeley National Laboratory, Berkeley, U.S.A.
Probing Catalytic Activity with the DFT Microscope

Jul 2004 Seminar at Max-Planck-Institut für Metallforschung, Stuttgart, Germany
Watching Ice Nucleation, One Molecule at a Time, with the DFT Microscope

Nov 2004 CECAM Workshop on In Situ Atomic Scale Characterization of Surfaces under High Pressures: Recent Advances in Experiment and Theory, Lyon, France
Probing the Catalytic Activity of a Noble Metal: Ethylene Epoxidation on Ag(111)

Dec 2004 Physic Colloquium, Freie Universität Berlin, Germany
Simulating Ice Growth, One Molecule at a Time, with the DFT "Microscope"

Apr 2005 Ice Surfaces and Interfaces Meeting, Wolfson College, Cambridge, U.K.
What Can DFT Tell Us About Ice Nucleation on Metal Surfaces?

Sep 2005 UCSB-MPG Workshop on Future Trends in Materials Sciences, Berlin, Germany
Solid Water Interfaces

Sep 2005 Ψ_k 2005 Conference, Schwäbisch-Gmünd, Germany
First-Principles Simulations of Water-Solid Interfaces

Oct 2005	EU Nanotechnology Science Forum, Berlin, Germany *Quantum Mechanics: From Ice Nucleation to Cloud Formation*

Karsten Reuter

Dec 2003	École Normale Supérieure, Lyon, France *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modelling in Heterogeneous Catalysis*
Dec 2003	Seminar at Surface Science Research Center, University of Liverpool, U.K. *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modelling in Heterogeneous Catalysis*
Dec 2003	Oberflächen-Seminar, Universität Erlangen-Nürnberg, Erlangen, Germany *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modelling in Heterogeneous Catalysis*
Mar 2004	APS March Meeting, Montreal, Canada *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Apr 2004	Condensed Matter and Materials Physics Conference (CMMP 04), Warwick, U.K. *With Ab Initio to the Mesoscale? Challenges and Prospects for the Modeling in Heterogeneous Catalysis*
May 2004	Workshop of RTN on Surface Active Sites and Emission Control Analysis, Magdeburg, Germany *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
May 2004	Spring Meeting of the European Materials Research Society (E-MRS 2004), Strasbourg, France *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Jun 2004	ESF Workshop on Catalysis from First-Principles, Magleås, Denmark *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Jun 2004	Conference on Electronic Structure Simulations of Nanostructures (ESSN2004), Jyväskylä, Finland *Towards a Predictive Modeling of the Mesoscale: Matching Density-Functional Theory with Statistics*

Sep 2004	DAAD Summer School on Modelling of Strongly Correlated Many-Particle Systems, Ekaterinburg, Russia *A Short Introduction to Surface Physics*
Sep 2004	DAAD Summer School on Modelling of Strongly Correlated Many-Particle Systems, Ekaterinburg, Russia *Multiscale Modeling in Materials Sciences, Particularly First-Principles Statistical Mechanics*
Sep 2004	Institute of Metal Research (IMR), Chinese Academy of Sciences, Shenyang, P.R. China *Nanometer and Sub-Nanometer Thin Films at Surfaces of Late Transition Metals*
Nov 2004	CECAM Workshop on In-situ Atomic Scale Characterization of Surfaces under High Pressures: Recent Advances in Experiment and Theory, Lyon, France *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Nov 2004	CCLRC Workshop on Surfaces: Out of UHV and into the Real World, Daresbury, U.K. *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Dec 2004	Kolloquium des SFB 513, Universität Konstanz, Germany *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Jan 2005	Seminar at Department of Surface Science, Waseda University, Tokyo, Japan *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Jan 2005	Symposium on Surface Physics 2005 (SSP'05), Shizukuishi, Japan *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Feb 2005	5th Stranski-Kaischew Surface Science Workshop (SK-SSW05), Pamporovo, Bulgaria *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
May 2005	Workshop on Catalysis: Nanotechnology with a Past, Berlin, Germany *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*

May 2005	Theory Group Seminar at Max-Planck-Institut für Polymerphysik, Mainz, Germany *Electron Densities, Elementary Processes and Rates: What Multi-Scale Modeling Can Tell Us About Catalysis …*
Jun 2005	Physikalisches Kolloquium, Universität Hannover, Germany *Über Elektronendichten, Elementarprozesse und Raten: Was uns eine Multiskalenmodellierung über Katalyse verraten kann*
Jun 2005	Seminar at Institut für Festkörperphysik, Forschungszentrum Karlsruhe, Germany *Electron Densities, Elementary Processes and Rates: What Multi-Scale Modeling Can Tell Us About Catalysis …*
Jun 2005	89th International Bunsen Discussion Meeting on Chemical Processes at Oxide Surfaces: From Experiment to Theory, Meschede, Germany *Relevance of Oxide Formation in Oxidation Catalysis: An Emerging Trend Understanding from First-Principles Statistical Mechanics?*
Jun 2005	Seminar at RWTH Aachen, Germany *Electron Densities, Elementary Processes and Rates: What Multi-Scale Modeling Can Tell Us About Catalysis …*
Jun 2005	Universität Potsdam, Germany O_2 *Dissociation at Al(111): The Role of Spin Selection Rules*
Jul 2005	10th Symposium on Surface Physics (SSP-10), Prague, Czech Republic *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Jul 2005	American Conference on Theoretical Chemistry, Los Angeles, U.S.A. *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Sep 2005	Ψ_k 2005 Conference, Schwäbisch-Gmünd, Germany *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Oct 2005	Workshop on Multiscale Modeling in Condensed Matter and Materials Sciences, Los Angeles, U.S.A. *The Steady-State of Heterogeneous Catalysis, Studied with First-Principles Statistical Mechanics*
Nov 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Bridging Scales: Ab Initio Thermodynamics*

Nov 2005 IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A.
Bridging Scales: Ab Initio Molecular Dynamics and Kinetic Monte Carlo

Patrick Rinke

Sep 2004 International Conference on Theory and Modeling of Electronic Excitations in Nanoscience, AcquaFredda di Maratea, Italy
Exact-Exchange-Based Quasiparticle Calculations of II-VI Compounds and Group III Nitrides

Mar 2005 DFG NANOQUANTA Workshop on Orbital Functionals for Exchange and Correlation: The Optimized Effective Potential and Related Methods, Berlin, Germany
Combining Quasiparticle Energy Calculations with Exact-Exchange Density-Functional Theory

Mar 2005 Seminar at University of California, Santa Barbara, U.S.A.
Excited States in Semiconductors and Insulators: Ab inito Quasiparticle Bandstructures of II-VI Compounds, Group-III-Nitrides and High-k Dielectrics

May 2005 Seminar at Universiät Wien, Austria
Combining Quasiparticle Energy Calculations with Exact-Exchange Density-Functional Theory: Valence Band Spectra for Semiconductors

Sep 2005 356. WE-Heraeus-Seminar on 40 Years of the GW Approximation for the Electronic Self-Energy: Achievements and Challenges, Bad Honnef, Germany
Combining Quasiparticle Energy Calculations with Exact-Exchange Density-Functional Theory

Sep 2005 Ψ_k 2005 Conference, Schwäbisch Gmünd, Germany
Combining Quasiparticle Energy Calculations with Exact-Exchange Density-Functional Theory

Nov 2005 IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A.
Exact Exchange

Jutta Rogal

Nov 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Charge Densities, Energy Bands, Density of States, and Fermi Surfaces*

Matthias Scheffler

Nov 2003	International Symposium on Structure and Dynamics of Heterogeneous Systems – SDHS'03, University of Duisburg-Essen, Duisburg, Germany *Ab Initio (from the Electronic Structure) Statistical Mechanics – New Insights into Heterogeneous Catalysis*
Dec 2003	2nd International Conference on Materials for Advanced Technologies (ICMAT 2003) and 7th IUMRS International Conference in Asia (IUMRS-ICA 2003), Singapore, Indonesia *Atomistic Thermodynamics and Statistical Mechanics from First Principles – Applications to Crystal Growth and Heterogeneous Catalysis*
Jan 2004	School of Physics, The University of Sydney, Sydney, Australia *New Insights into Heterogeneous Catalysis by Ab Initio Statistical Mechanics*
Jan 2004	Symposium on Surface Physics 2004 (SSP'04), Shizukuishi, Japan *New Insights into Heterogeneous Catalysis by Ab Initio Statistical Mechanics*
Feb 2004	Computational Science & Engineering Department, CCLRC Daresbury Laboratory, Daresbury, U.K. *New Insights into Heterogeneous Catalysis by Ab Initio Statistical Mechanics*
Feb 2004	2nd Annual University of California Surface Science and Applications Symposium, San Diego, U.S.A. *Ab Initio (from the Electronic Structure) Statistical Mechanics Conditions*
Feb 2004	MPG/UCSB Workshop on Future Trends in Materials, UCSB, Santa Barbara, U.S.A. *Get Real! The Importance of Complexity for Understanding the Function of Surfaces*

Mar 2004	The XXXVIII Annual Conference of the Finnish Physical Society, Oulu, Finland *Computational Nanoscale Research that will Catalyze Industrial Processes*
Mar 2004	APS March Meeting, Montreal, Canada *Reflections on “Chemical Accuracy” and “Nearsightedness”*
May 2004	Inaugural Colloquium of the Institute for Theoretical Solid State Physics at the Leibniz Institute for Solid State and Materials Research Dresden (IFW), Germany *Computational Nanoscale Research that will Catalyze Industrial Processes*
May 2004	Spring College on Science at the Nanoscale, ICTP, Trieste, Italy *Nanometer-Scale Physics – the Examples of Semiconductor Quantum Dots and Heterogeneous Catalysis (3 lectures)*
Jun 2004	Colloquium on the Occasion of Prof. I. Broser’s 80th Birthday, Technische Universität Berlin, Germany *Nanophysics: Quantum Dots and Heterogeneous Catalysis*
Jun 2004	4th Annual Workshop of the International Center for Quantum Structures (ICQS) on Spintronics: From Fundamentals to Future Information Technology, Beijing, P.R. China *Present Status of Ab Initio Electronic Structure Calculations: From the Earth Core to Quantum Dots to Mad Cow Disease*
Jun 2004	Colloquium at the Wuhan University, Wuhan, P.R. China *Nanometer-Scale Physics – the Examples of Semiconductor Quantum Dots and Heterogeneous Catalysis*
Jul 2004	Colloquium at the Philipps-Universität Marburg, Germany *Nanophysics Applied to Quantum Dots and Heterogeneous Catalysis*
Aug 2004	Colloquium at the Institute for the Theory of Advanced Materials in Information Technology (ITAMIT), Minneapolis, U.S.A. *Statistical Mechanics from First Principles*
Sep 2004	Conference on Computational Physics 2004 (CCP2004), Genova, Italy *The Steady-State of Heterogeneous Catalysis, Studied by First-Principles Statistical Mechanics*
Sep 2004	Workshop on Surface Science Quo Vadis?, Schloss Ringberg, Germany *Interaction of Oxygen with Metal Surfaces*
Sep 2004	Colloquium at the Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian, P.R. China *Interaction of Oxygen with Metal Surfaces*

Sep 2004	Colloquium at the Institute of Metal Research (IMR), Chinese Academy of Sciences, Shenyang, P.R. China *Interaction of Oxygen with Metal Surfaces*
Sep 2004	Computational Electrochemistry Workshop on the Application of Atomistic Computer Simulation Methods to Interfacial Electrochemistry, Akrotiri, Santorini Island, Greece *Statistical Mechanics from First Principles*
Oct 2004	Department of Materials Science and Engineering, Massachusetts Institute of Technology (MIT), Cambridge, U.S.A. *Statistical Mechanics from First Principles: Application to Surface Chemical Reactions and Heterogeneous Catalysis*
Nov 2004	GDCh-Kolloquium, TU Dresden, Germany *Nanophysik - am Beispiel von Quantenpunkten und heterogener Katalyse*
Nov 2004	CCP9 Conference, Max Born Prize Lecture, Daresbury, U.K. *Statistical Mechanics from First Principles*
May 2005	207th Meeting of the Electrochemical Society, Quebec, Canada *Modeling of "Real Life" Catalysis from First Principles*
May 2005	Workshop on the Theory-Experiment Interface in Fuel Cell Electrochemistry, US Army Research Office, Quebec, Canada *Predictions for Heterogeneous Catalysis*
May 2005	19th North American Catalysis Society Meeting, Philadelphia, U.S.A. *Heterogeneous Catalysis Studied by Ab Initio Statistical Mechanics*
May 2005	Inaugural User Meeting, Center for Nanophase Materials Sciences (CNMS), Oak Ridge, U.S.A. *Get Real! The Importance of Complexity for Understanding the Function of Nano-Scale Structures at Surfaces*
May 2005	Symposium on Molecular Simulations and Computer Experiments: Do they Change the Future? – Dedicated to the memory of Carl Moser, CECAM, Lyon, France *Statistical Mechanics from First Principles*
Jun 2005	5th Annual ICQS Workshop on Macroscopic Quantum Phenomena, Beijing and Nanjing, P.R. China *Modeling Materials' & Bio-Molecular Properties & Functions from First Principles*
Jun 2005	Workshop on Defects and More, Institute of Physics, London, U.K. *Get Real! The Importance of Complexity for Understanding the Function of Nano-Scale Structures at Surfaces*

Jun 2005	Interdisciplinary Surface Science Conference (ISSC 15), Cardiff, U.K. *New Insights into Chemical Reactions at Surfaces and Heterogeneous Catalysis Obtained by Statistical Mechanics from First Principles*
Aug 2005	2005 Gordon Research Conference on Dynamics at Surfaces, Andover, New Hampshire, U.S.A. *Adsorption and Reaction Dynamics of Oxygen at Metal Surfaces, Studied by First-Principles Statistical Mechanics*
Oct 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Basics of Density-Functional Theory and Fast Guide to Actual Calculations*

Arno Schindlmayr

Sep 2004	Workshop on Ab initio Methods for Correlated Spintronics Materials, Mont Sainte Odile, France *Quasiparticle Electronic Structure and Energetics of Point Defects on Semiconductor Surfaces*
Oct 2004	NAREGI Workshop on Electronic Transport, Excitation and Correlation in Nanoscience, Sapporo, Japan *Quasiparticle Electronic Structure and Energetics of Point Defects on Semiconductor Surfaces*

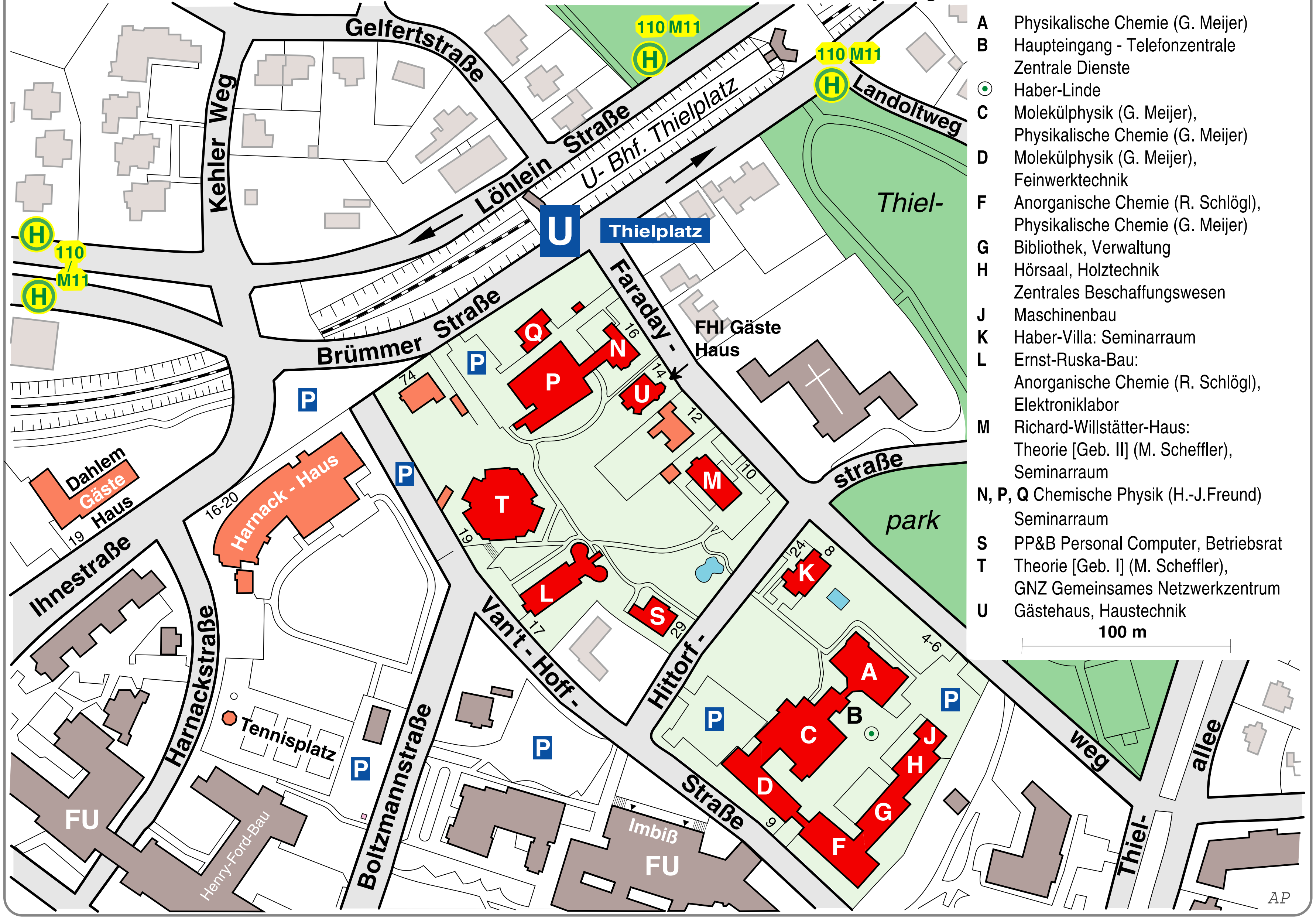
Mira Todorova

Nov 2005	IPAM Workshop on Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions – A Hands-On Computer Course, UCLA, Los Angeles, U.S.A. *Calculating Core-Level Shifts, Surface Core-Level Shifts, STM Images*

Hua Wu

Oct 2003	NATO Workshop on Physics of Spin in Solids, Baku, Azerbaijan *First-Principles Study of Ferromagnetic Si-Mn Sandwich Films on Si(001)*

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



A	Physikalische Chemie (G. Meijer)
B	Haupteingang - Telefonzentrale Zentrale Dienste
⊙	Haber-Linde
C	Molekülphysik (G. Meijer), Physikalische Chemie (G. Meijer)
D	Molekülphysik (G. Meijer), Feinwerktechnik
F	Anorganische Chemie (R. Schlögl), Physikalische Chemie (G. Meijer)
G	Bibliothek, Verwaltung
H	Hörsaal, Holztechnik Zentrales Beschaffungswesen
J	Maschinenbau
K	Haber-Villa: Seminarraum
L	Ernst-Ruska-Bau: Anorganische Chemie (R. Schlögl), Elektroniklabor
M	Richard-Willstätter-Haus: Theorie [Geb. II] (M. Scheffler), Seminarraum
N, P, Q	Chemische Physik (H.-J.Freund) Seminarraum
S	PP&B Personal Computer, Betriebsrat
T	Theorie [Geb. I] (M. Scheffler), GNZ Gemeinsames Netzwerkzentrum
U	Gästehaus, Haustechnik

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