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

12th Meeting of the Fachbeirat

Berlin, 9th - 11th November 2003

Reports

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

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Reports

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Report of the Executive Director

Since the last meeting of the *Fachbeirat* in November 2001, the institute has seen a number of changes and developments. Below, I will report on these developments, as well as the accomplishments of scientists in the Fritz-Haber-Institut (FHI). Our response to the recent challenges, and our actions to avert negative consequences of the recent budget cuts for our scientific work, will then be explained. Finally, the work of three service groups will be briefly summarized.

The main research projects of the FHI continue to be concerned with catalysis, as well as chemical and physical properties of surfaces, interfaces, molecules, clusters, and nanostructures. Currently, the institute has 47 positions for scientists, in addition to the 5 director positions, and 148 positions for technical staff. Of the 47 scientific positions, 4.5 are in service groups, and from the remaining 42.5 positions, 24 are tenured.

The best piece of news is that the planned appointment of Gerard Meijer as director of the new *Department of Molecular Physics* was successful. He started his full time position at the FHI in August of this year, and will give the research on “molecules/clusters”, in particular “cold molecules”, at the FHI a significant boost. Major building construction was necessary to accommodate his novel experimental setups. Building work is progressing well, and we trust that by the time of the Fachbeirat meeting in November, it will be (nearly) finished. For details please see the Chapter written by Prof. Meijer later in this booklet (page 132 ff.). In this context it is worth mentioning that our colleague Alex Bradshaw, whose influence on the present structure of the institute has indeed been significant, has decided to remain in his current position at the *Max Planck Institute for Plasma Physics* in Garching. Thus, his leave-of-absence period ended in the spring of this year.

The other great news is that the FHI was allowed to submit a proposal for a new director who will succeed Gerhard Ertl when he retires in October next year. If this proceeds as planned, a novel experimental research direction will be established at the institute, strengthening the main scientific goals of the FHI (cf. above). We are most grateful to the *Fachbeirat* for their decisive support in this matter. I will return to this topic below.

At the previous meeting of the *Fachbeirat* it was announced that the institute had applied for the establishment of an *International Max Planck Research School*. Our application was successful, and the school was inaugurated in January 2003. Under its topical name “Complex Surfaces in Material Science” the school aims at combining the expertise of several strong research groups at the Humboldt University Berlin, the Free University Berlin, and the FHI, creating a unique opportunity for foreign and German students in terms of cutting-edge research and a thorough training. At present, 14 Ph.D. students are enrolled, from many different countries including Italy, Spain, France, The Netherlands, the Czech Republic, Bulgaria, Iran. A block course on the basic principles of surface science was given in March, and regular lecture courses were given during the summer semester at the Free University; a second block course and more regular lecture courses are planned for the next semester. We receive many applications and expressions of interest, and the number of students is likely to increase with the full funding of the School expected for the beginning of 2004.

The third-party funding obtained by the FHI is gratifying. The prestigious Alexander von Humboldt (AvH) foundation recently analyzed how their AvH guest researchers are distributed among German research institutes. They called this “voting with your feet”. Among the non-university institutes, the FHI holds second place, just a minimal margin behind (with practically the same number of AvH fellows in a 4 years period as) the *Forschungszentrum Jülich,* though their scientific staff and budget is about a factor of 15 larger than ours.

Various scientists of the FHI are actively involved in *Collaborative Research Centers* (Sonderforschungsbereiche, Sfb) of the *German Research Foundation* (Deutsche Forschungsgemeinschaft, DFG), which reflects the close collaboration with the Berlin universities and other research institutes:

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)

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, G.I.F., INTAS, ESF, EU. There are also collaborations with industrial labs, e.g. BASF, Degussa, NTT, Toshiba.

Several scientists from the institute successfully obtained high-level academic appointments:

- Marcus Bäumer (Professor (C4) for Physical Chemistry at the *Universität Bremen*, October 2002)
- Tobias Hertel (Associate Professor at the Department of Physics and Astronomy, *Vanderbilt University*, Nashville, Tenn./U.S.A.; he will start there in January 2004)
- Katharina Krischer (Professor (C3) for Technical Physics at the *Technische Universität München*, April 2002)
- Jörg Neugebauer (Professor (C4) for Theoretical Physics at the *Universität Paderborn*, September 2003); he will be present at the *Fachbeirat meeting* also to discuss in retrospect the activities of his *Independent Junior Research Group*.
- Herbert Over (Professor (C3) for Physical Chemistry at the *Justus-Liebig-Universität Gießen*, January 2002)
- Catherine Stampfl (Professor at The School of Physics of *The University of Sydney*, March 2003)
- Joost Wintterlin (Professor (C3) for Physical Chemistry at the *Ludwig-Maximilians-Universität München*, April 2002)

We also proudly report the following honors bestowed on scientists of the institute:

J. Behler	- Winner of the young investigators competition, Gordon Research Conference “Dynamics at Surfaces”, 2003

Prof. Dr. G. Ertl	- Foreign Associate, National Academy of Science, U.S.A., 2002
	- Spiers Memorial Medal and Lectureship, Royal Society of Chemistry, 2002
	- Karl Ziegler Lecture, MPI Mülheim, 2002
	- FMC Lectureship, Princeton University, 2002
	- Dr. h.c., Catholic University of Leuven, 2003
	- Dr. h.c., Chalmers Univ. of Technology, Göteborg, 2003
	- Dr. h.c., University Aarhus, 2003
Prof. Dr. H.-J. Freund	- Fellow of the American Physical Society, 2001
	- Frontiers in Chemistry Lecturer, Texas A&M University, College Station, 2001
	- W. D. Harkins Lecturer, University of Chicago, 2002
	- Member of the Council, Universität Erlangen
Dr. Ch. Hess	- Otto Hahn Medal, MPG, 2002
Dr. Ch. P. Koch	- Otto Hahn Medal, MPG, 2003
Dr. J. Libuda	- Habilitation, Humboldt-Universität zu Berlin, 2003
Dr. N. Nilius	- Otto Hahn Medal, MPG, 2002
Dr. E. Penev	- Otto Hahn Medal, MPG, 2003
Dr. T. Ressler	- Liebig-Medaille der Südchemie, 2003
Prof. Dr. H.H. Rotermund	- Appointment as Adjunct Professor of Physics at Dalhousie University, Halifax (Canada), 2003
D. Rolles	- WE-Heraeus-Förderpreis, 2002
	- Glenn T. Seaborg Scholarship Award, University of California, 2002
	- Erwin-Stephan-Preis der TU Berlin, 2002

Prof. Dr. M. Scheffler	- Max-Planck-Forschungspreis, MPG+AvH, 2001 - Honorary Professor at the FU Berlin, 2001 - Medard W. Welch Award, AVS - The Science & Technology Society, 2003
Prof. Dr. P. Woodruff	- Mott Prize and Medal, Institute of Physics, U.K., 2002

The publication record of the institute continues to be very good. W. Marx (MPI Stuttgart) who performed an impact analysis wrote: “The FHI-papers published in the time window 1993-2003 obtained in average 12.97 citations per publication. The worldwide average is 6.97 in chemistry and 6.52 in physics. An impressive achievement.” Also worth mentioning is that many scientists presented invited talks at international conferences, universities, and research laboratories: On average, every day of the year a scientist from the FHI gave a talk somewhere in the world.

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. A list of these details would be quite lengthy and I trust that the *Fachbeirat* members are aware of these activities.

I will now sketch some of the unexpected problems and difficulties we had to deal with. In the first week of 2002 we were informed that the previously approved budget for building and renovations would be cut significantly. In order to secure the indispensable building constructions for G. Meijer's new department and for the successor of G. Ertl, we had to drop the planned extension building to the “Ruska-Bau” (building L, see map on the last page). Instead, it was decided that the *Department of Inorganic Chemistry* will take over the entire “building F”, and the *Mechanics Workshops* and the *Service Group for Electronics* will be placed into the “Ruska-Bau”. Consequently, the second floor of the “Ruska-Bau” was renovated, and the *Service Group for Electronics* moved there in the Fall of 2002. They are very pleased with their new “home”. The *Mechanics Workshops,* which are currently distributed over several buildings, will be consolidated in the “Ruska-Bau” in 2005. Some renovation/rebuilding of “building F”, the “new home” of the *Department of Inorganic Chemistry* was started. More is necessary and will be carried out next year. Finally, a modest reorganization of our administration was initiated, as they have to deal with some modified responsibilities and duties.

The FHI budget (personnel, investment, and running costs) was practically the same for 2002 as it was in previous years. This has been the case for 10 years, i.e., for 10 years there has been no compensation for inflation or salary increases. This year we were hit particularly hard: The budget of the FHI was cut by about 6% compared to 2002. As this cut was only announced in the spring of this year, it was very difficult to deal with it. Similar cuts also hit most other institutes of the MPG. In fact, in addition to these cuts the MPG will close down more than 20 departments of various institutes in order to balance its budget. For our institute it was discussed to delay filling Gerhard Ertl's position by 5 years (after his retirement in October 2004). Thanks to the previous reports of the *Fachbeirat*, we succeeded to pass up this threat. However, permission to continue with our original plan was only granted after accepting additional budget cuts equivalent to the costs of two “Independent Junior Research Groups” from 2005 onwards. Again, this is not a one-year cut, but a general reduction of the FHI base budget. The above mentioned 6%, as well as this additional cut, implies that we have to reduce the budget on all levels. This includes personnel, which is being reduced by 5 scientists and 8 technicians. Finally, the proposal for a new director, who should start in late fall 2004, was submitted to the President of the MPG in August. We trust that our plans for restructuring the FHI now form a stable basis for continuing with highest-quality research. From several discussions with the General Administration and the President of the MPG we trust that in the future, such unpleasant surprises will not happen again. It is worth noting that our discussions with the administration of the MPG were constructive and we are grateful to the President and the Institute-Liaison Department for their support.

I will finish this report by briefly describing the activities of what may be called “service groups”, where two timely examples will be mentioned. Finally, I will add some lines on the institute's activities to improve the public understanding of our scientific work. Other “service groups”, in particular our competent and supportive administration, the PP&B group (Personal Computers, Real-time & Image Processing), the Mechanical Workshops, the gardeners, and many more deserve to be mentioned (and praised) as well. However, this would make the report too extensive.

Service Group for Electronics (E-Lab)

This is a central institution (with 14 employees) which provides technical support at various levels to the experimental research groups. Its principal task is the development and construction of complex measuring and control equipment required for critical experiments that is not available commercially. In the last two years the *E-Lab* developed about 260 different devices. These included, for example, an ultra-short pulse generator for nanoscale electrochemistry, a position signal-buffer for a time- and position-sensitive detection system, and a burst generator and fast 15kV switch for a molecular decelerator. Furthermore, components for computer-controlled data acquisition, for example high resolution and fast AD- and DA-converters were developed. The technical consulting service supports scientists of the Institute in the configuration, modification, acquisition, and adaptation of electronic-equipment to the experiments. Periodic practical training classes and seminars on electronic measuring methods are held, particularly for the young scientists.

(The head of the Electronics Group is Georg Heyne)

Joint Network Center [Gemeinsames Netzwerkzentrum (GNZ) der Berlin-Brandenburgischen Max-Planck-Einrichtungen]

Effective June 2002, the former Computer Center at the FHI was restructured and converted into a Joint Network Center (now with 9 employees) of all Max Planck institutions in the Berlin-Brandenburg area. This includes 9 Max Planck institutes, the MPG archive, and 3 associated institutions. Its responsibilities are as follows:

- The GNZ acts as a central internet service provider for the participating Max Planck institutions. It is also responsible for the Max Planck intranet of the Berlin-Brandenburg region (BAMPI), and it is actively involved in servicing and planning for the Berlin Research Area Information Network (BRAIN), which connects all three universities and most of the research laboratories in Berlin.
- The GNZ runs a network-based backup and archive system for all participating Max Planck institutes using BAMPI as the backbone network. The central robot at the GNZ has a maximum capacity of 300 Tbytes and uses 140 Tbytes at present.
- As part of its mission, and for historic reasons, the GNZ is also engaged in certain computer-center activities at the FHI campus. It runs the local area network (LAN) of the FHI with a central firewall. The GNZ expertise was used to install firewalls in three other participating Max Planck institutes and continues to be demanded. The GNZ is also responsible (together with the PP&B group) for central printing, mail, and web services at the FHI.

(The head of the Joint Network Center is Prof. Dr. Klaus Hermann)

Public Relations Activities

The FHI is strongly committed to explaining its mission and accomplishments to the public. An important medium is press releases about exceptional research results and publications. Together with the public relations office of the MPG, 12 press releases were issued to editors and journalists over the last two years, most of which have been reported in German newspapers. One can find these releases on our homepage at *Latest News (w3.rz-berlin.mpg.de/pr/)* as well as on the Max Planck Society's website. In addition, two focused reports on our activities appeared in "Max Planck Research", the magazine of the Max Planck Society for the non-expert public. We have also contributed a webpage on our work to the *"Aktuelle Wochenschau"* of the *Deutsche Bunsen-Gesellschaft (http://www.bunsen.de),* a weekly virtual periodical of the science-to-public campaign *"Jahr der Chemie 2003"*. Images and movies were made available to science exhibitions, for instance at the *"Mainzer Wissenschaftssommer 2003"* where visitors could watch videos of reaction patterns imaged in our institute.

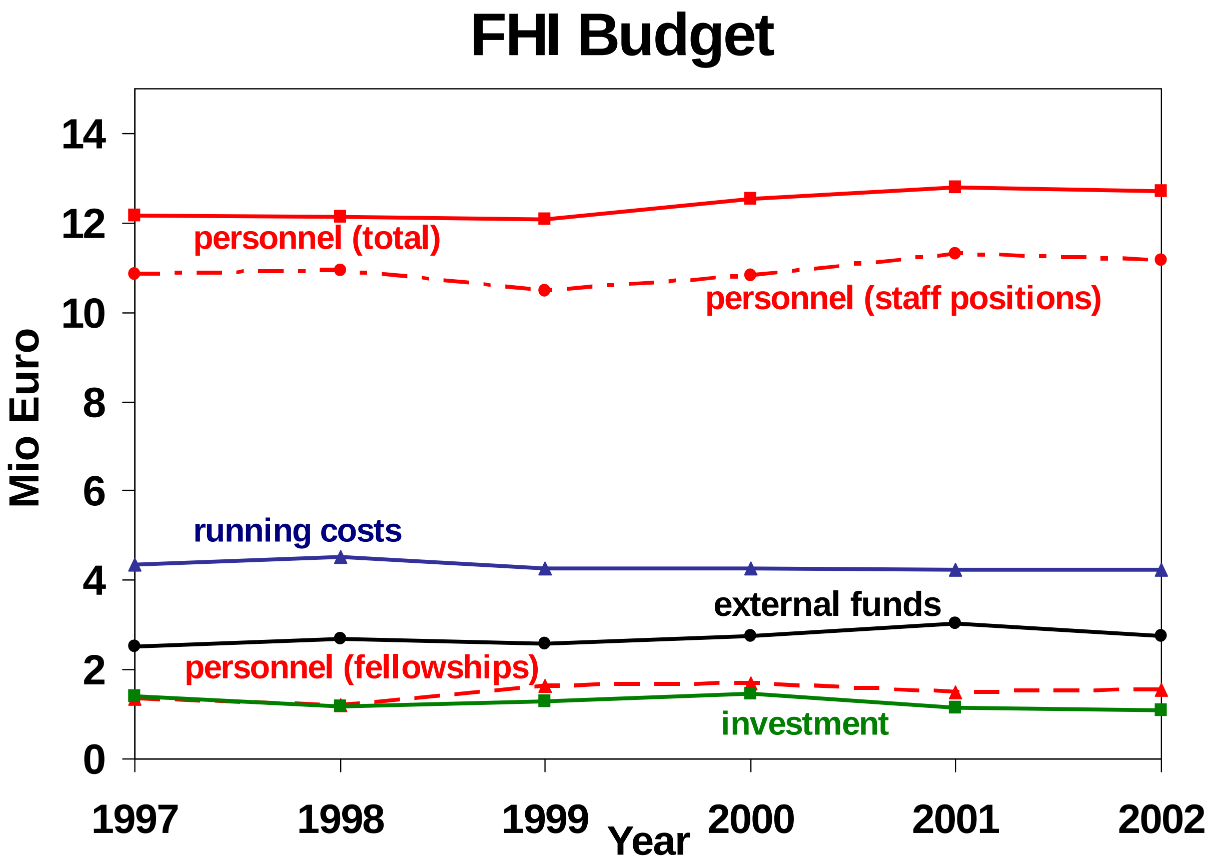
Our institute has hosted numerous visitors during the past two years. In addition to fellow scientists, we welcomed several journalists and science writers interested in the institute's current research and history. Groups of students from universities and high schools visited our laboratories. Individual high school students learned in longer hands-on training courses about work in science, during their regular curriculum or as awardees of science competitions such as *"Jugend Forscht"*.

(The Public Relations Team consists of Martin Fuchs, Beatrix Wieczorek, Sabine Wrabetz, and, until August 2002, Viola Kirchner)

Finally, on behalf of all directors and of the whole institute, I wish to thank the *Fachbeirat* for their important help and the guidance they have given over the years. Their input has contributed considerably to our current status. Their influence on the institute, and this includes the vital support given to young scientists, is invaluable.

Berlin-Dahlem, August 31, 2003

Matthias Scheffler
(Chairman of the Board of Directors)



Development of the FHI budget over the last 5 years: The line “personnel (total)” shows the full budget for personnel that was provided by the MPG. It is subdivided into “staff positions” and “fellowships”. Additionally, the FHI hosts Ph.D. students, postdocs, and visiting scientists that are paid from DFG, AvH, BMBF, EU, and other projects. Their salaries and fellowships constitute the major part of the “external funds”. The “running costs” cover items such as electricity, heating, building maintenance, etc., as well as all costs for the research (incl. equipment below 5 kEUR). For the line “investment” it should be noted that this budget does not include building constructions, startup money for new directors, and equipment paid via special applications (e.g. bigger computers, BESSY).

Fritz-Haber-Institut

Organization: Scientific Personnel

01.06.2003

Legend:

A = Departments
B = Scientific Personnel
*: Group Manager
C = General Facilities
GD = Executive Director
GF = Administrative Director

BOARD OF DIRECTORS

AC	**Prof. Schlögl**
CP	**Prof. Freund**
MP	**Prof. Meijer**
PC	**Prof. Ertl**
TH	**Prof. Scheffler (GD)**

A	**Inorganic Chemistry** **Prof. Schlögl**	**Chemical Physics** **Prof. Freund**	**Molecular Physics** **Prof. Meijer**	**Physical Chemistry** **Prof. Ertl**	**Theory** **Prof. Scheffler (GD)**	**Administration** **Dr. Hamann (GF)**
B	Dr. Jentoft* Dr. Knop-Gericke* Dr. Kubias Dr. Melsheimer Dr. Ranke Dr. Ressler* Dipl.-Phys. Sauer Dr. Su* Dr. Timpe Prof. Urban	Dr. Drachsel* Dr. Ernst* Dr. Hamann* Dr. Klüner* Dr. Kuhlenbeck* Dr. Libuda* Dr. Nilius* Dr. Risse* Dr. Rupprechter* Dr. Rust*	Prof. Becker* Dr. Conrad* Dr. Cvejanovic Prof. Horn* Dr. Küpper* Dr. Prümper N.N. N.N. N.N. N.N.	Dr. Eiswirth* Dr. Hertel* Prof. Holzwarth* Prof. Mikhailov* Dr. Paulus Dr. Pettinger* Dr. Rotermund* Dr. Schulze* Dr. Schuster* Dr. Wolff Dr. Zei N.N. N.N.	Dr. Carlsson Dr. Gomez-Abal Prof. Hermann Dr. Kratzer Dr. Rinke **Independent Junior Research Group** **Dr. Neugebauer** Dr. Ireta	Personnel Budgets Purchasing Dept. Technical Services House Management Buildings
C	Mechanical Workshops Library	Crystal Processing Personal Computers, Realtime & Image Processing		Electronics Workshop	Joint Network Centre Prof. Hermann Dipl.-Phys. Kühn Dr. Preußer	

Department of Inorganic Chemistry Director: R. Schlögl

Staff scientists:

Dr. F. Jentoft
Dr. A. Knop-Gericke
Dr. B. Kubias
Dr. W. Ranke
Dr. T. Ressler
H. Sauer
Dr. D. Su
Dr. O. Timpe
Prof. Dr. J. Urban (Habilitation)
Dr. S. Wrabetz

Prof. Dr. E. Zeitler, Emeritus

Scientists (temporary) paid from external funds:

Dr. H. Bluhm
Dr. F. Girgsdies
Dr. M. Haevecker
Dr. G. Ketteler
Dr. N. Maximova
Dr. D. Niemeyer
A.T. Tham

Guest scientists, staying for at least six months:

Dr. R. Jentoft
Dr. A. Pestryakov
Dr. D. Teschner
Dr. G. Tzolova-Müller
Dr. J. Wagner
Dr. D. Wang
Prof. Dr. Z. Zhu

Graduate Students:	18	(11 from external funds)
Technicians:	12	
Trainees:	5	

Recent Developments in the Department of Inorganic Chemistry

Director: R. Schlögl

1. General development
   - 1.1 Realisation of „Infrastructure“ from the last report
   - 1.2 Development of the Internal Structure
   - 1.3 Development of Institutional Collaborations
   - 1.4 Teaching Activities
   - 1.5 Novel forms of scientific dissemination

2. Scientific Progress
   - 2.1 Iron oxide based model catalysts
   - 2.2 Zirconia and Heteropoly Acids in Hydrocarbon Activation
   - 2.3 Vanadia in C4 selective oxidation
   - 2.4 Synthesis and characterisation of Mo(VW) Oxide catalysts
   - 2.5 Cu nanoparticles / synthesis & application in oxidation and steam reforming of methanol
   - 2.6 Palladium in Selective Hydrogenation (Athena Project)
   - 2.7 Carbon in Heterogeneous Catalysis
   - 2.8. Special Report: Report on “Forschungsinitiative” Model project

3. Future Developments
   - 3.1 Consequences from the past activities
   - 3.2 The Future Direction of Research
   - 3.3 Infrastructural Requirements

1. General development

The Department AC presents its activities in detail on its homepage that can be found under: http://w3.rz-berlin.mpg.de/ac/ac.html.

Among the staff scientists the following changes occurred:

- Dr. M. Fait left in 2001 for a position in industry.
- Dr. M. Wieske left in 2001 for a permanent position at HU Berlin (Charité).
- Dr. Y. Uchida retired in 2002. His position was replaced as planned by Dr. D. Su
- Dr. M. Schur left in 2002 for a position in industry.
- Dr. D. Niemeyer joined the Department in 2002.
- Dr. G. Mestl left in 2002 for a position in industry.
- Dr. B. Kubias joined the Department in 2003.
- Dr. J. Melsheimer retired in 2003: His position is removed from the institute.

1.1 Realisation of „Infrastructure“ from the last report

The refurbishment plan for the FHI under which the Department AC should get an extension building to its previous home in building L (Ruska-Bau) had to be changed significantly under the influence of financial problems of the Land Berlin and the MPG leading to a delay in funding, and under the necessities to accommodate the new Department MP.

As a consequence the former home of the Department AC will become the central workshop facility (partly realised) and the new home of the Department AC will be the old electron microscopy building F. Into this building about 80% of the Department had to move in a provisional fashion in 2002. It is provisional as the present building F requires also massive refurbishment and it still houses groups from the Departments MP, PC and the MPI for Molecular Genetics. As a consequence the Department AC had to be reduced significantly in size and operates now under serious constraints in its infrastructure.

The relocation of the Department AC had to be achieved with a minimum of finances coming largely from the institute’s allocated research funds. This and the infrastructure situation in building F prevented the relocation of the reactor laboratory. It thus had to be dissolved. The replacement of the essential previous in-house competence for kinetic testing is realised by a combination of collaborations and by outsourcing to a start-up company RUBOCAT. Some special equipment was transferred to a start-up company in Munich (NANOSCAPE) where it is still operated through a French-German-DFG research grant within the framework of the ELCASS activity (see section 1.3).

It is evident that the infrastructural developments indicated in the last *Beirat* report could not be realised despite partly significant preparative efforts that were made towards the universal UHV system and the realisation of a new photoemission system. All financial investment was reused in other instrumentation activities.

1.2 Development of the Internal Structure

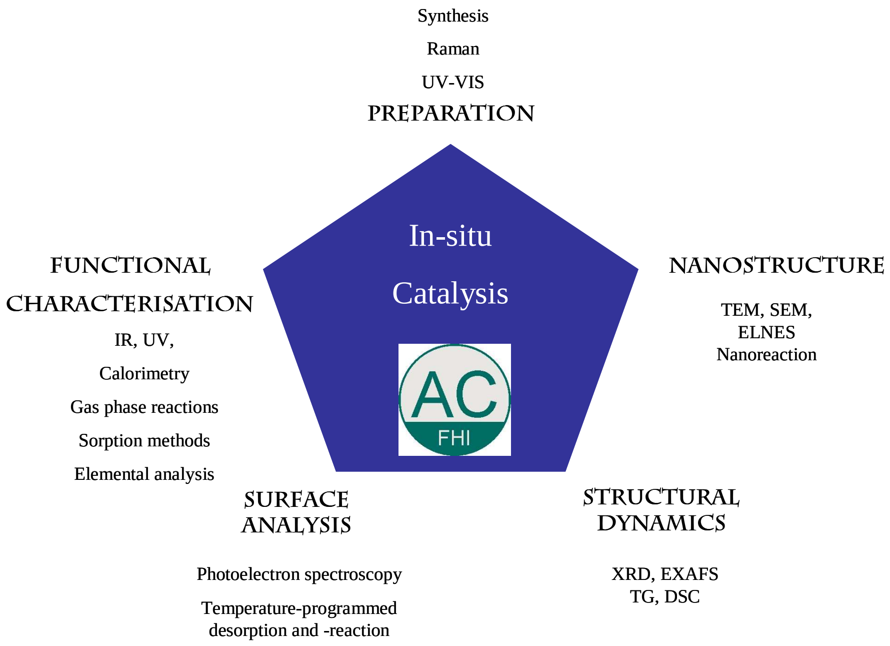
As from 2002 it became clear that the Department had to undergo another round of inflicted restructuring. It was necessary to more severely reduce the diversity of the activities than described in the last *Beirat* report. This reduction is directed towards the retention of a critical mass of methodical competence allowing performing the multi-method in-situ approach to complex systems of “real catalysts” that forms the basis of the scientific strategy of the Department. The following activities are scheduled for, or have been discontinued:

- Nanoparticles in 2005
- Model PVD films in 2002/2005
- Thermochemistry in 2002

One of the remaining 6 group activities described in the last *Beirat* report further had to go permanently. With the technical difficulties in relocating the heterogeneous reaction group and taking into account that the acquisition of kinetic reaction data is an indispensable activity that, however, may be outsourced to expert groups within and outside the country, it is now decided to permanently discontinue this activity within the Department AC as an independent activity. In addition, all the model catalyst facilities that do not support the polycrystalline film activities, will also be discontinued. This means a drastic reduction in capabilities of photoelectron spectroscopy on well-defined samples (effected 2003) and the discontinuation of the PVD synthesis and of the STM activities in 2005.

In this way, the core competence of the Department is refocused into the in-situ metrology of synthesis and function of heterogeneous catalytic systems. Scheme 1 represents the current structure indicating its main methodical activities. Some inconsistencies are caused by the multiple functions of experts in one group. These formal inconsistencies bear no functional relevance, as the core principle of intra-departmental co-operation remains unaffected.

The Department maintains competence in kinetic testing wherever it is indispensable for in-situ experimentation. Specialised methods of in-situ reactor validation, the nanocatalysis testing, temperature-programmed reaction spectroscopy and the homogeneous gas phase catalysis testing facility are examples of kinetic experiments. It is the function of Dr. B. Kubias, a renowned expert in catalytic reactor design, to support the competence and the awareness for kinetic aspects on in-situ experimentation in all methodical groups.



Scheme 1: The AC Department after its re-structuring in 2002.

The Department gains some flexibility in this way to develop its methodical activities, gets less dependent on outside resources for operating its core activities and keeps its clear profile in the international catalysis community as the “in-situ group”.

The Department has removed the 400 keV TEM instrument that was installed with significant investments over the last years as a further contribution to the resource consolidation. The instrument was vital to prove that the beam damage issue greatly affects the structural analysis of oxide catalysts such as VPO and that higher acceleration voltages at equal irradiation doses are less beam-damaging than lower voltages. The cost of maintenance of the instrument amounting to about 15% of the present annual consumables budget of the Department was prohibitive for further operation.

1.3 Development of Institutional Collaborations

In the last *Beirat* report a strong participation was announced of the Department in the German catalysis initiative CONNECAT. This did not materialize due to complex political changes in the views of the BMBF regarding fundamental studies. The realisation of the catalysis beamline at BESSY II is highly uncertain despite several very positive evaluations and preparations from the BESSY side. The Department as part of MPG has recently been excluded from all BMBF applications in the fundamental research programmes. Alternative options for realising the beamline at BESSY or at other synchrotron radiation facilities are being evaluated. Presently, the experiments are conducted at the MPG facility at BESSY II but severe application limitations are imposed due to safety concerns when using “toxic” chemicals in a flow-through apparatus at non-UHV pressures. These concerns can only be overcome in a fixed safety installation that would be highly desirable also for the reactor and conversion testing environments. From within the Department´s capabilities, the bending magnet beamline is completely designed and ray-traced, the part list is prepared and a performance test with the high-pressure XPS preliminary equipment at a similar already existing beamline was positively completed.

The activities of the Department in the EU context that were a topic at the last *Beirat* meeting were actively continued. Within the MPG initiative for material science at FP VI the Department coordinated a proposal for a hierarchical catalysis network of excellence under participation of the FHI, the MPI for Coal Research and the MPI of Colloid Science. A core structure was realised within the LEA instrument joining the FHI (Departments AC, CP and TH), the University of Strasbourg (CNRS catalysis unit, M. Ledoux) and the Department of Chemical Engineering of the University of Messina (G. Centi.) into the structure ELCASS (European Laboratory for Catalysis and Surface Science) that was officially formed as entity by a contract between the three co-operating funding bodies in 2003. The structure has held two symposia, has been awarded a DFG grant for carbon nanotube research and has started a scientist exchange programme to pursue carbon nanotube and acid-base chemistry research. The core structure further brought together a proposal for a network of excellence in catalysis

(CAMAS) that passed the first evaluation but may fail in the second stage as all other catalysis initiatives. Further active participations of the Department in EU programmes is concerned with a STREP initiative through ELCASS and two more networks of excellence proposals that are still under review.

Additional intensive scientific collaborations outside of the FHI were pursued with the following partners:

- With the Consortium “Zeitstiftung” comprising the MPI for Coal Research, the MPI for Colloid Science, the MPI for Complex Solid Systems and the Department of Chemical Engineering of TU Berlin. The evaluation of Cu-Zr based nanostructured catalysts for robust methanol steam reforming made considerable progress and yielded a joint patent application. A preliminary final report is given in section 2.
- With a large number of German universities within the DFG Schwerpunktprogramm “Brückenschläge zwischen Modell- und Realkatalyse”; the numerous co-operations are indicated in the following sections of the report.
- With the University of Cardiff / Catalysis Institute Villeurbanne on selective oxidation of butane by VPO catalysts. The research programmes were harmonized and a large number of kinetically evaluated samples were subjected to various characterisation techniques, in particular to the novel high pressure XPS. Several project leader meetings and two longer visits of one student from FHI in Cardiff ensured continuity and showed the fundamental problems with this class of catalysts being related to synthesis aspects and to the structural homogeneity on several length scales.
- With the Boreskov Institute of Catalysis in Novosibirsk two activities in application of in-situ XPS to the silver catalysed epoxidation of ethylene and in synthesis of vanadium catalysts for selective oxidation applications were continued with active bi-lateral exchanges of scientists, a joint experimental campaign at BESSY II and intensive joint experimentation/data analysis. The institute further runs an intense collaboration in the molybdenum project where several bilateral exchanges of co-workers produced much insight into the chemistry of the Mo-V-O system by utilizing the respective characterisation facilities.
- With the Combicat Consortium Malaysia (University of Malaya and Universiti Putra Malaysia), a common effort was initiated to develop synthesis protocols for nanostructured selective oxidation catalysts with minimal chemical

complexity (single phase early transition metal oxides). The research programmes of both groups were harmonised and an intensive bilateral exchange of personnel was started. The activity is the consequence of a joint initiative with the Department CP from which the Department AC has taken on responsibility for the implementation and initial production phase for selective oxidation catalysts for propane activation.

- With the Athena Consortium the investigation of Pd-based supported systems was started as announced in the last *Beirat* meeting. The target is the identification of common and different functional properties of Pd particles used in the Department CP for model studies as compared to technical hydrogenation catalysts studied by other partners in the consortium. A second branch of activities is closely related to the vanadium oxide project and to the carbon project of the Department AC.

1.4 Teaching Activities

Staff scientists (Prof. Urban, Drs Jentoft, Ressler) are regularly involved in the course programme of the TU and HU universities in Berlin. The AC Department covers teaching aspects within the IMPRS of the FHI on the chemistry of heterogeneous catalysts and on aspects of preparation of inorganic solids.

The Department of Inorganic Chemistry has started an educational program specifically designed for the doctoral student level. The demand for such a program definitely exists because it is neither mandatory for doctoral students to enrol in classes at the universities where they will defend their theses nor are they involved in the tutoring of undergraduate students. The aim was to fill this educational gap and at the same time provide a broader insight into the field of catalysis. The class, entitled “Modern Methods in Heterogeneous Catalysis Research: Theory and Experiment”, was offered for the first time in the winter semester 2002/03 and, following the positive resonance, will be continued in the winter semester 2003/04. The program consisted of a series of independent lectures (2 units of 90 min per week) covering subjects on catalyst preparation, testing, and characterization by a large variety of methods. The content will be varied from year to year to give the 3 year students the broadest possible experience. As the class was conducted in cooperation with Technische Universität Berlin and Humboldt Universität zu Berlin, the speakers were affiliated either with FHI (66%) or the two universities. Guest speakers came from ACA Berlin and IFOK Rostock. The lectures were given in English, and were in many cases followed by a laboratory tour with the demonstration of a certain technique. A questionnaire filled out by the students in the end demonstrated that the class was well received and that the teaching level was appropriate.

Class homepage:

http://w3.rz-berlin.mpg.de/~jentoft/lehre/catalysisclass.html and

http://w3.rz-berlin.mpg.de/~jentoft/lehre/catalysis_class_details.html

for the program WS 02/03

1.5. Novel forms of scientific dissemination

The MPG undergoes currently a transformation in its provision and production of scientific dissemination. The "journal crisis" and the challenges of the Internet for multimedial and distributed co-operation call for a transition from print information media stored in decentralised libraries to a central "library without walls" hosting databases, access systems to electronic full text and to a repository of all scientific works of the co-workers of the MPG as well as dedicated community-specific co-operation projects. The AC Department plays a very active role in supporting developments and field testing software and workflows for this new system that is being introduced to the general MPG user between 2003 to 2005. The Department further operates several databases for the documentation of original scientific results and the documentation of test samples. All members of the Department are actively involved in testing, using and improving the services of these new electronic tools. Strong support is given by the library and by the PPB service group.

2. Scientific Progress

2.1. Iron oxide based model catalysts

The production of styrene (St) from ethylbenzene (EB) is catalyzed by potassium promoted iron oxides in an endothermic dehydrogenation process at temperatures between 870 and 930 K in the presence of steam. In order to correlate the catalytic function with the geometric and the electronic structure of the surfaces we prepared model catalyst surfaces and characterize them concerning their composition and structure using the methods of surface science. After this, the energetics and kinetics of adsorption and their catalytic properties were determined. Our novel single-crystal flow reactor was now applied for extensive studies of EB dehydrogenation over unpromoted and K-promoted α-$Fe_2O_3(0001)$ hematite films and for comparison with unpromoted $Fe_3O_4(111)$ magnetite films. It occurred that initial rates were up to 10 times higher than those reported for technical catalysts. A characteristic deactivation behaviour was observed that was traced back by interrupted surface analysis with LEED and Auger to a reduction of the roughened and defected highly active Fe^{3+} oxides to Fe^{2+} (much less active) and finally to a stable and slightly active carbon-covered surface exposing no more iron oxide at all to the reactants. This state agrees in its activity well with rate data from technical and previous model studies revealing that the actual catalyst is most likely not iron oxide but modified carbon. Conversion measurements over a K-promoted model catalyst film yield a similar conversion rate as the initial rate over unpromoted films. The initial highly active steady state rate could be stabilized with admixture of oxygen in amounts much smaller than required for an oxi-dehydrogenation reaction. A technical process with O_2 in the feed could thus be advantageous. Therefore, the influence of O_2 admixture was checked in cooperation with G. Kolios and A. Schüle (DFG priority program “BRÜCKENSCHLÄGE”) in a conventional fixed bed reactor over pressed hematite powder pellets under technical reaction conditions. First experiments confirm an increase of the steady-state conversion by about a factor of 3 upon O_2 admixture.

The key results are that perfect single crystalline films of all iron oxides are fully inactive in EB dehydrogenation. Only after massive roughening high activities were observed. It is clear now that the stabilization of the defected Fe^{3+} iron oxide surface would allow for an EB dehydrogenation process far more productive than today´s technical reactions. The benefit of the reactor geometry (a 40 nm layer gave up to 5% conversion, in technical reactors 4 m bed length are required for 50% conversion) is difficult to estimate and will be addressed in further work. The active role of special “catalytic carbon” derived from the polymer styrene was clearly confirmed and gives now a direct correlation to the carbon research area. Chemisorption data of relevant species over defined carbon surfaces will also be derived in future work to allow for a comparative kinetic model of the tow reaction systems.

It is of significance that the efforts to produce and characterize the single crystalline iron oxide systems were not required to achieve a deep insight into the reaction at atmospheric pressure conditions. The availability of a thin film sample with excellent thermal conductivity and sufficient electrical conductivity was, in contrast, vital for the success of the project.

2.2 Zirconia and Heteropoly Acids in Hydrocarbon Activation

Sulfated zirconia (SZ) derived materials and heteropoly compounds are both suspected to operate by interplay between a redox and an acid function. Our research aims at revealing surface functionalities and how they are related to the bulk properties. SZ and heteropoly compounds are not active in their as-synthesized form; the active phase is formed in the feed stream. In situ studies and knowledge of the flexibility of the bulk and surface structures are thus compulsory.

SZ-based catalysts are used for alkane isomerization; they can be operated at a lower reaction temperature than zeolite catalysts. However, the nature of the active sites and the mechanism of alkane activation are not known. The activity of SZ can be promoted by addition of Mn, Fe, or Ni cations. We have thoroughly investigated the promoters, particularly their interaction with the zirconia bulk, also in the hope that conclusions on the unpromoted catalyst can be made. As the promoters do not change the catalytic performance qualitatively – the product distribution is the same and rather depends on conversion – such deductions seem possible. Another access to the mode of operation of these catalysts is given through the reaction profile, which over a few hours typically passes through an induction period, a maximum in conversion and a decline towards a more or less stable activity. We have used in situ techniques to study the oxidation state of the promoters during reaction and the formation of surface deposits. Within the DFG priority program "BRÜCKENSCHLÄGE" a cooperative project has been established that attempts to identify number and nature of active sites and that looks into the origin of deactivation by carbon deposition.

The key emphasis was however, laid on the identification of defects in the zirconia that are essential for its function in “superacid” catalysis. The identification of promoters as structural modifiers, the extreme sensitivity of the samples to extrinsic preparation variables such as batch size in calcination and grinding method in an agate mortar together with the variability of the phase composition over time on shelf are strong indicators for the essential role of defects that are labile and can quenched by oxidative regeneration of the initially deactivated catalyst by burning the polymeric hydrocarbon residues. These were clearly related to the deactivation mechanism by in-situ UV VIS studies and the role of allylic species as reaction intermediates or active sites that was put forward by several groups was clearly dismissed. The limited information available from in-situ XAS experiments will now be augmented by in-situ EPR experiments initiated in cooperation with Prof. K. Köhler at TU Munich. First attempts to model the EPR data in cooperation with Prof. S. Klokhishner for getting information on the local geometric environment reveal indeed significant differences of the promoter sites as compared to regular zirconia polyhedra. The identification of the dynamics of the sulfate co-catalyst and of the acid-base properties using in-situ FT-IR was expanded. The preparation of polycrystalline model materials of nanostructured oxides and of thin films was continued and expanded.

Heteropolyacid-based catalysts of the type $Cs_xH_{4-x}PVMo_{11}O_{40}$ with $2<x<3$ are used in the industrial production of methacrolic acid from methacrolein. We investigated the transformations that these materials undergo under gas atmospheres and at temperatures that relate to partial oxidation conditions. A full structural cycle of processes was identified with several in-situ techniques using prominently the in-situ UV-VIS and in-situ XAS/XRD methods. The self-salification of HPA to molybdenyl salts was identified and structurally described. The active state is an inorganic oligomer of defective Keggin units that retain some geometric dynamics; if this is frozen by chemical substitution in the secondary structure (Cs substitution) all activity is lost irrespective of the unchanged redox and acid base properties. These important properties were also characterized for the first time using probe molecule techniques in FT-IR and several sites with on average medium to weak acidity functions were found on activated systems. All results were collected in a comprehensive review discussing the essential role of defects in the initial perfect Keggin structure for its function as catalyst. This view is one of two schools in the field and the opposing view about the function of the intact Keggin structure was ruled out.

2.3 Vanadia in C4 selective oxidation

The project was expanded by collaborations with G. Hutchings (Cardiff) and JC. Volta (Villeurbanne). Further collaborations with the groups of A. Khalamov (Kiev) and of P. Schattschneider (Vienna) led to published results. One new activity is the construction of a microreactor for catalyst testing in micrometer regime in the framework of SFB 546 of the DFG. In-situ spectroscopy techniques in the soft X-ray range like X-ray absorption spectroscopy and photoelectron spectroscopy have been applied to study the geometric and the electronic structure of the working catalyst *surface*.

The VPP surface structure depends strongly on the temperature when heated in the reaction mixture of n-butane and oxygen. The dynamic nature of the catalyst surface is revealed by the temperature dependence of the V L_3-edge NEXAFS that represents various surface functional groups. Variations of the integrated intensity of specific resonances and their energy position were observed that indicate compositional and structural changes of the catalyst surface. One type of functional group (vanadyl termination) predominates at room temperature, whereas other groups (defected vanadyl and bridging V-O-V) dominate at higher temperatures. It is unlikely that a stoichiometric bulk phase such as vanadyl pyrophosphate could facilitate these grave reversible structural changes. Furthermore, the V L_3-NEXAFS fine structure does not match with that of the pure $(VO)_2P_2O_7$ bulk phase. Our results suggest the interaction of different phases of binary oxide and of a phosphate on the active surface on a core of vanadyl pyrophosphate. This was postulated in some papers as opposed to the predominant static view of a structure-sensitive reaction. The active oxygen for the selective oxidation does not belong to the core phase. In-situ XPS measurements allow to estimate concentration profiles of the working catalyst perpendicular to the surface. These measurements give further hints to an active phase of VPO different from vanadyl pyrophosphate. The analysis of the spectra shows a P/V ratio above 2 and an O/V ratio of up to 10 which are not compatible with vanadyl pyrophosphate.

A working hypothesis of the mode of operation was established. The interpretation of the in-situ results was greatly enhanced by using data from model studies performed in the CP Department on relevant systems. These studies revealed as core result the variability of vanadyl termination as inhibitor of reactivity of V-oxides in several bulk oxidation states and simultaneously as vital ingredient in active sites comprising defected terminations. Excellent agreements in the spectral fingerprints as well as in the chemical reactivity were found in the studies of the reference systems and of the “real world” systems.

Catalytic tests of a set of tribochemically activated VPO samples show a treatment-dependent performance challenging again the structure sensitivity hypothesis of vanadyl pyrophosphate catalyst. The material exhibits a pronounced memory effect about their chemical pre-history illustrating the metastability of the active component in the system. The micro-morphological studies of VPO standard catalysts and of novel preparations using aqueous routes reveal enormous structural complexity in this system: besides a small fraction of amorphous materials at the surface of particles, V^{5+} phases are always present correlating with differing catalytic performances. The V^{5+} can exist either as separate single particle or grown as grain on vanadyl pyrophosphate (VPP) particles. Its characteristic morphology differs from the main VPP phases, but the structure determination suffers from the high electron beam sensitivity in TEM. ELNES and theoretical modeling has progressed so far that it can be used for nano-phase analysis by spectroscopic identification of characteristic bonding situations for oxygen. Reference samples currently synthesized in collaboration with the partners in Cardiff will allow a systematic study of the crucial role of the V^{5+} phases in n-butane selective oxidation as basis of a rational forecast for the optimization potential of the system. Vanadium oxide nanowires and nanorods in oxidation states 4+ and 5+ were reproducibly synthesized by two different chemical methods in order to study the selective oxidation on model systems with well-determined surface morphology and high crystalline order.

2.4 Synthesis and characterization of Mo(VW) Oxide catalysts

The two last years yielded detailed insight into the mechanisms that control structure formation in Mo oxides. This insight allows to synthesize nanostructured molybdenum oxide different from the standard phase orthorhombic MoO_3 and to have precise control of the phase composition, about the nature of defects as well as the crystallite size and the morphology of the active phase. As already established earlier in this Department, the key defective site is the pentagonal bipyramidal MoO_7 group in the catalytically active material $Mo(VW)_5O_{14,}$. A first breakthrough was achieved by the successful synthesis of single phase Mo_5O_{14} with the composition $(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$. The fact that this single-phase material is well-performing as catalyst for propene oxidation and for acrolein oxidation dismisses the well established hypothesis that phase cooperation or geometric site isolation phenomena are essential for any selective catalytic activity.

Despite of identical long-range order a different catalytic activity is observed with differing nanostructuring (extended defects, intergrowth of unknown phases, defect ordering). A single crystalline Mo_5O_{14} material is not active at all as such but represents rather an idealized endpoint that is formed under reduced oxygen partial pressure during the organization process of a mixture of oligo anions present in the disordered pre-catalysts. Therefore two strategies were developed to understand the function or necessity of the different cations in the complex technical catalysts that are of eminent actual interest for alkane activation (the “MOVTE” family). The Mo_5O_{14}

system containing Mo, V and W was investigated to understand the catalyst pre-formation and activation process in close cooperation with the Boreskov Institute of Catalysis. In a model study, V and W were excluded and pure molybdenum systems with high structural complexity were synthesized in cooperation with COMBICAT. A systematic ordering of structure-directing variables in liquid phase synthesis of oxides was established allowing now a broader investigation of the synthetic potential of chemically simplified but structurally well-controlled oxide catalysts. It seems that certainly W and to a large extent also V act as structure-directing agents by changing the chemistry in the precursor solution as well as by modifying the local Mo-O bonding allowing for non-octahedral connectivity in an inorganic polymer. These principles are in line with general observations in other families of the rich chemistry of Mo^{6+} with oxygen (nanoscopic polyoxometallates) but have not been established in the catalytically relevant systems.

Method development was done in performing controlled precipitation and in applying in-situ UV-VIS in concentrated and precipitation solutions. These achievements will be used in all other projects of the Department. The current laboratory situation and a lack of X-ray diffraction analytical capabilities hinders a rapid expansion of this research line that will thus be attempted to be continued with the COMBICAT partner.

A different approach has been carried out to synthesize the MoVW oxide by a sol gel method as the low synthesis temperatures often lead to the formation of oxides with amorphous or metastable phases, which are not observed using other synthesis routes. The molybdenum alkoxide precursors are very difficult to synthesize. A preparation routine was established with the stable Mo alkylamide as precursor, which reacts with the desired alcohol to form the alkoxide. This reaction and the subsequent hydrolysis were monitored by in situ UV-Vis spectroscopy. Hydrolysis with water and acetone lead to similar supramolecular entities as the precipitation experiments described above, therefore they provide good model systems. Whilst aqueous precipitation occurred in the subsecond range, the sol gel reaction takes hours; therefore the network formation is far easier to study.

A common way of making catalyst material is the impregnation of the oxide on an amorphous support. Thin Mo- oxide films on a flat support were successfully prepared by spin coating an ammonium heptamolybdate solution onto a Si (100) wafer. Subsequent calcination leads to orthorhombic MoO_3 with a main orientation along the (020) axis. The resulting films are homogeneous with a height of about 130 nm ± 10 nm. The film thickness is dependent upon the spinning speed and the molybdenum concentration. These samples will be used in multi-in-situ experiments allowing to monitor the surface state by in-situ XPS, the average valence by in-situ UV-VIS and the ion mobility in the bulk by conductivity measurements.

Although it is assumed that the lattice oxygen of MoO_3 participates in the oxidation of propene, little is known about defects in the regular layer structure of MoO_3 that may form under reaction conditions. The question remains, how close is the “real” bulk structure of MoO_3 under reaction conditions to the “ideal” structure of orthorhombic a-MoO_3? With respect to a redox mechanism for the partial oxidation of propene on MoO_3, three stages were distinguished by an extensive combined in-situ XAS-XRD study. (i) At temperatures below ~ 600 K the participation of oxygen from the MoO_3 bulk is negligible. (ii) At temperatures between ~ 600 K and ~ 700 K oxygen vacancy diffusion in the bulk is sufficient to make a redox mechanism feasible. Because the complete re-oxidation of the “$Mo_{18}O_{52}$” type shear-structures is inhibited, a partially reduced MoO_3 with CS planes in the lattice is obtained under reaction conditions. (iii) At temperatures above ~ 700 K sufficiently fast oxygen diffusion in the lattice combined with rapid formation and annihilation of CS permits the participation of a considerable amount of the lattice oxygen of MoO_3 in the partial oxidation of propene. The work is now extended to the novel nanostructured oxides that provide much superior catalytic performance. It is assumed that the scenario described is the limiting situation for poorly selective unsubstituted oxides highlighting the essential role of either other cations or other preparation conditions to arrive at more metastable structures than shear-defected orthorhombic MoO_3. In any case the absolutely essential role of bulk structural defects for surface catalytic performance was clearly established.

2.5. Cu nanoparticles / synthesis & application in oxidation and steam reforming of methanol

Initially developed more than 20 years ago, the Cu/ZnO system, with the addition of aluminum in technical catalysts, is used for low pressure methanol synthesis and for the water gas shift reaction. More recently, with interest in fuel cell applications the steam reforming of methanol to produce hydrogen has come to be of interest. Subject of this study are the bulk properties of defect rich, and highly active Cu/ZnO catalysts with compositions of industrial interest. Following screening for methanol steam reforming activity and surface area measurement we use X-ray diffraction (XRD) line profile analysis and X-ray absorption spectroscopy (XAS) under methanol steam reforming reaction conditions to study the bulk properties of the Cu and Zn in a systematic series of Cu/ZnO catalysts.

As the conventional Cu/ZnO catalysts are not particularly stable under rapidly changing reaction conditions, new materials need to be studied, that exhibit an improved long-term stability and selectivity. Therefore, nanostructured Cu/ZrO_2 prepared by various templating techniques have been investigated to elucidate correlations between activity, stability, and structural changes under reaction conditions.

The key results are the unambiguous detection of the strain effect as vital activator of the Cu ZnO system that was achieved by changing the precipitation conditions and not by varying the composition or reaction conditions that could have obscured the origin of the change in performance. For the Cu/ZrO_2 system suitable activation parameters were found by systematic study of the solid state properties to arrive at highly active, regenerable and much more selective (towards CO_2) catalysts than offered by the Cu/ZnO system. Details can be found in the special report in section 2.8.

We have used *in situ* X-ray photoelectron spectroscopy (XPS) to investigate the catalytic oxidation of methanol over a polycrystalline copper and over Cu nanoparticles. This reaction is complementary to the steam reforming in which water is the oxidant and hydrogen the desired product. Formaldehyde is desired product for partial oxidation. In-situ near-edge X-ray absorption spectroscopy at the O *K*-edge revealed that the formaldehyde yield is correlated to the presence of a suboxide species at the sample surface that could only be detected under in-situ conditions. The goal of our experiments was to use in-situ XPS to determine the nature of the active species during the catalytic reaction, and to measure their abundance as a function of reaction conditions. By varying the incident photon energy we have also performed depth-profiling of the active species at the copper surface under reaction conditions. The objective of the two branches of research is to identify the nature of the active copper in these reactions and the method of switching selectivity between partial and total dehydrogenation. Strain and sub-oxide formation are the two tools identified by which the reactivity of metallic copper can be tuned. The experiments are connected through a project in the DFG “BRÜCKENSCHLÄGE” initiative in which theory and single crystal low-pressure experiments are performed as model studies to support the analysis of our in-situ studies.

It is now clear that Cu metal becomes activated by sub-surface oxygen that is not oxidic in nature but vital for selective oxidation. We take the view that the oxygen studied in in-situ XAS/XPS experiments is not a reagent but acts as co-catalyst: no hydrocarbon fragment can be seen on the active surface, the literature species formate and methoxy that we also find in low pressure model experiments vanish in coverage below the detection limit of 2% of a monolayer at high pressure conversion conditions.

The Cu particles need to be activated for total dehydrogenation by the action of strain induced by the substrate (Cu/ZnO) or by intercalating oxygen (Cu/ZrO_2). These particles are inactive for formaldehyde production (partial dehydrogenation) and lead to completion of the dehydrogenation chain of methanol and water. In agreement with all model experiments it is found that any form of oxide is detrimental for all kinds of reactivity. It is currently examined if a transition in reactivity can be achieved in both Cu systems by varying the oxygen partial pressure accordingly to support or prevent oxidation of hydrogen.

2.6. Palladium in Selective Hydrogenation (Athena Project)

The research project Athena (Advanced technology in catalytic chemistry and engineering for novel application) is a joint collaboration of Fritz-Haber-Institute (Departments AC and CP), University of Birmingham, University of Cambridge, University of Cardiff, University of Glasgow, Northwestern University, University of Surrey and Johnson Matthey presenting a multi-disciplinary approach to investigate heterogeneous catalytic reaction classified as selective hydrogenation, selective dehydrogenation and selective oxidation.

In the frame of this project the Department of Inorganic Chemistry studies the selective hydrogenation of C5 molecules with different functionalities on Pd based catalysts. A focal point of the activities concerns the relationship between selectivity and catalyst properties like structure, shape, carbonaceous deposits and possible support induced effects. Emphasis is placed upon the identification of common and different properties of “real world” supported Pd catalysts and the compositional analogous model systems studied in the CP Department. In addition, correlations between particulate nanostructured Pd and single crystal Pd surfaces are investigated. The methods used so far are low pressure laboratory photoemission (a dedicated instrument was built in 2003) and our in-situ XPS under working conditions that allows besides high resolution spectroscopy an in-situ non-destructive depth profiling and thus the unambiguous location of carbon on (hydrocarbon, graphitic) and under (atomic and eventually also carbidic) the metal surface.

Carbon results from decomposition of the organic substrate on clean and hydrogen pre-covered Pd that is controlled by an interplay of *sigma* and *pi* bonded molecular precursors. This interplay is controlled by particle morphology and inhibited on single crystal (111) planes under conditions of practical hydrogenation. The role of carbon on and sub-surface as vital control variable for the reactivity of Pd was established in full agreement between the model and real world system and at high and low pressures. At least 4 different carbon species were identified. Their respective role in catalysis as co-catalyst and inhibitors according to their structure and location is currently studied. It is now clear that all functions enumerated occur simultaneously. The sensitivity of these structure-function relations to the nature of the organic substrate (functionalisation) and the reaction conditions (gas phase vs. liquid phase) is currently investigated. Microstructural studies by TEM reveal a complex distribution of morphologies both of the initial Pd particles and after their intensive contact with hydrocarbons leaving behind deposits of carbon. The analysis is complicated by the low particle density on the diluted system that should not be increased for maintaining a selective system under study. In this work the intended upgrade of the SEM capabilities would be of enormous relevance as then the morphology of the particles on the practical support and its modification by carbon dissolution/coverage could be imaged directly on a real world system for the first time. The paramount importance of the morphology for reactivity was well-established by the model experiments in the CP Department using methanol decomposition and CO adsorption as probe processes.

The binary alloys PdGa and Pd_3Ga_7 were prepared in the group of Prof. Y. Grin, MPI CPFS, Dresden, and are stoichiometric compounds with ordered structures. These materials are particularly interesting as possible catalysts due to isolation of the Pd atoms in the structure. In both structures the Pd atoms are surrounded by a closed coordination sphere of Ga atoms (i.e. coordination number of 7 in PdGa and 8 in Pd_3Ga_7). Conversely, a supported Pd catalyst presents an ensemble of neighbouring Pd atoms to the reactants. We investigated the thermal stability of PdGa and Pd_3Ga_7 in the presence of various atmospheres by in situ XAS at both the Pd and the Ga K-edge, in situ XRD and by thermal analysis. We determined the structural evolution of the alloys in helium, hydrogen and oxygen from temperatures from 293 to 593 K. The result shows that the palladium-gallium alloys are stable under these conditions and that no hydrogen and oxygen inclusion as in Pd metal is detectable. Also no phase transition in this temperature range and no oxidation within the detection limit of XAS and XRD were observed. First catalytic studies show catalytic activity for propene and ethylene hydrogenation, for CO oxidation as well as high selectivity for acetylene hydrogenation to ethylene.

2.7. Carbon in Heterogeneous Catalysis

The key objective is still the optimisation of catalytic properties of nanocarbons in the oxidative dehydrogenation (ODH) of ethylbenzene to styrene and search for new ODH reactions over nanocarbons in the gas and liquid phase (in cooperation with NanoScape AG in Munich and with ELCASS, and in cooperation with the Theory

Department of FHI). Nanocarbon structures such as carbon nanofilaments and onion-like carbons have been tested to be catalytically active and selective in the ODH of ethylbenzene to styrene. In comparison to the classic dehydrogenation, the reaction enthalpy of the styrene process changes from endothermic to exothermic so that the working temperature is reduced by at least 150°C and the addition of steam is no longer necessary. The current focus is on the determination of the mode of operation by kinetic experiments (parallel oxi-dehydrogenation or consecutive oxidation of hydrogen by oxygen). Only a minor dependence between O_2 concentration and catalytic activity was observed under the chosen reaction conditions, i.e., the reaction seems to be of 0^{th} order with respect to oxygen (note: no lattice oxygen possible) within the molar ratios from 0.5 to 2.5 of oxygen to ethyl benzene. The optimisation of the surface structure of the nanocarbons by adjusting the ratio of basal to prismatic edge surface terminations is carried out using XPS and thermal analysis methods for determination of the termination mode.

The application of nanocarbons as seeds for nanostructured oxides and as supports for metal particles is investigated in collaborations with institutions in China (State Key Laboratory of Catalysis and State Key Laboratory of Coal Science). Exchange of researchers, our expertise in nanostructural characterisation of carbon and joint catalysis studies yield an intense and fruitful collaboration. Results are reported in the vanadium oxide project.

The microstructure and morphology of environmental carbon controlling its reactivity is studied in cooperation with MAN Nutzfahrzeug AG, TU-Munich and with the MPI of Polymer Research Mainz. Unlike the carbon materials studied and described above, the type of carbon investigated in this project is undesirable and to be eliminated: soot particulates in exhaust of diesel engines. The Euro IV diesel engine that will be commercialised in 2005 to fulfil the Euro IV emission standard reduces drastically the size of the soot primary particles down to 20 nm. Due to the optimised combustion conditions, the primary particles show multi-shelled fullerenoid structures that were not found, up to now, in current or earlier commercial diesel engines. In general, the Euro IV soot consists of a defined profile or regular shape in contrast to the secondary structure of carbon black or the current diesel soot. High-resolution imaging reveals that the primary particles consist of fullerene-like multiple shell structures. The primary particles then agglomerate to gain stability by a graphene-type dispersive interaction between bent strands of ribbons. In comparison, the soot emitted by a black smoking diesel engine consists of large primary particles (40 nm) made from homogeneously sized flat basic structure units that are stacked such that the interplanar interaction is maximized while the outer surface is minimized.

The fullerene-like soot results from the optimised mixing behaviour of air and diesel fuel in the combustion chamber that prevents the formation of precursor molecules necessary for the growth of conventional spherical soot particles. The temperature gravimetric analysis of the fullerene-like (F-soot) and soot produced under black smoking conditions (G-soot) in 5% O_2 reveals that the fullerene-like soot is much more reactive than the black smoke: the temperature of the combustion of F-soot is 100 K lower than that of G-soot. Also the isothermal analysis at 653 K reveals that F-soot looses weight much more rapidly than the G-soot. The reason of the high reactivity is seen in the multi-shell fullerenoid like structure of the F-soot with defective surfaces. Our experimental results on the morphology/microstructure and reactivity of new Euro IV diesel soot indicated that reducing the emission rate of soot particulate is not automatically beneficial for environment and reducing the risk for human health. This new risk potential stands opposite to the fact that the F-soot is more reactive toward oxidation and therefore much easier to eliminate.

The common objective in the carbon project is to identify and utilise the control over the surface chemistry of sp2 carbon that is given by controlling the nanostructure and defect disposition. The cooperation with the TH Department in identifying the intrinsic reactivity of bending sp2 carbon as opposed to creating local defects and their consequences on the neighbouring carbon atoms is of utmost relevance in guiding our work on synthesis and modification of real materials. This work is of fundamental interest to the core objective of the Department as no other catalytically active system for partial oxidation is chemically simpler as carbon and so the relevance of defects can be studied more clearly.

2.8. Special Report: Report on “Forschungsinitiative” Model project:

ZEIT-Stiftung
Ebelin und Gerd
Bucerius

Nano chemistry for the automobiles of the future –

Copper catalysts for the production of hydrogen by steam reforming of methanol

The research project *"Nano chemistry for the automobiles of the future"* is a joint collaboration of four Max-Planck instituts (MPI) (Fritz-Haber-Institut der MPG (Berlin), MPI für Kohlenforschung (Mülheim/Ruhr) (Prof. F. Schüth), MPI für Kolloid- und Grenzflächenforschung (Golm) (Prof. M. Antonietti), MPI für chemische Physik fester Stoffe (Dresden)) (Prof. M. Antonietti) and of the Technischen Universität Berlin (Prof. R. Schomaeker) funded by the ZEIT-Stiftung (Hamburg). Because all participating research groups possess a longstanding experience in various methods and subjects in heterogeneous catalysis and solid-state chemistry (preparation in Golm and Mülheim, structural characterization in Berlin and Dresden and reaction kinetics in Berlin), their joint efforts results in a more efficient (synergistic) and particularly tailored catalysis research and advancement. During the first three years of the project we succeeded in preparing and characterizing novel copper catalyst supported on nano-structured zirconium dioxide Cu/ZrO2 (patent pending). These catalysts seem to be promising substitutes for the conventional Cu/ZnO catalyst. With respect to the copper content the Cu/ZrO_2 catalysts exhibit an increased catalytic activity in the steam reforming of methanol compared to Cu/ZnO. Moreover, the Cu/ZrO_2 catalysts possess a considerable thermal and long-term stability during time on stream and produce significantly less carbon monoxide, which is particularly important for fuel cell applications.

Activity and Selectivity of a Nanostructured CuO/ZrO_2 Catalyst in the Steam Reforming of Methanol

The catalytic properties of a novel CuO/ZrO_2 catalyst in the methanol steam reforming process were investigated at a temperature range from 250°C to 300°C at atmospheric pressure. The XRD and XAS results revealed that the CuO/ZrO_2 sample consists of small and/or disordered CuO particles and small particles of crystalline, tetragonal ZrO_2. The CuO/ZrO_2 catalyst can be activated by introducing oxygen (50 ml/min) for a short time (5 min) into the feed at reaction condition. The data obtained from contact time variation reveals that CO is produced as a consecutive product, as already has been demonstrated for CuO/ZnO/Al_2O_3. The new CuO/ZrO_2 catalyst, which was prepared by a polymer template sol-gel method, exhibits the following enhanced catalytic properties in comparison to the commercial CuO/ZnO/Al_2O_3 catalyst: (i) higher activity in terms of methanol conversion as a function of WCu/Fm, (ii) increased long term stability (i.e., less deactivation), probably because the macroporous zirconia support is more effective than ZnO/Al_2O_3 in preventing copper particle sintering, and (iii) reduced CO formation, especially significant at high methanol conversion. The work described here clearly shows that a knowledge-based preparation of heterogeneous catalysts is feasible permitting the rational design of materials exhibiting an improved catalytic performance. Elucidating structure-activity relationships is a necessary prerequisite for a rational catalyst design, however, detailed knowledge about appropriate preparation and treatment conditions resulting in the right target structure of the heterogeneous catalyst is equally important.

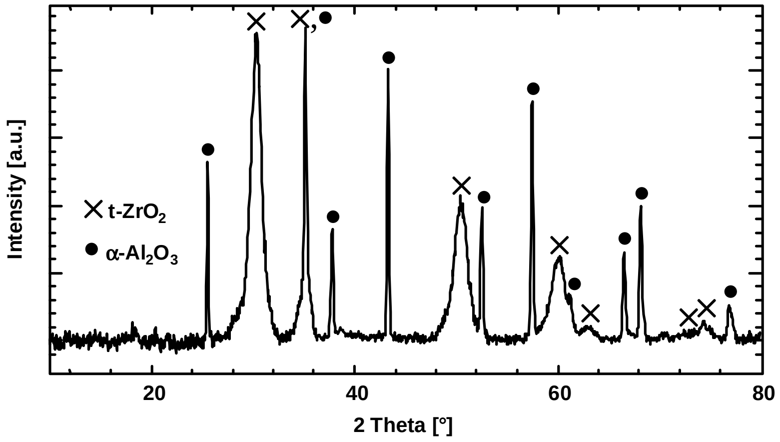


Figure 1. X-ray diffraction pattern of the CuO/ZrO_2 catalyst mixed with 50 wt. % corundum as internal standard.

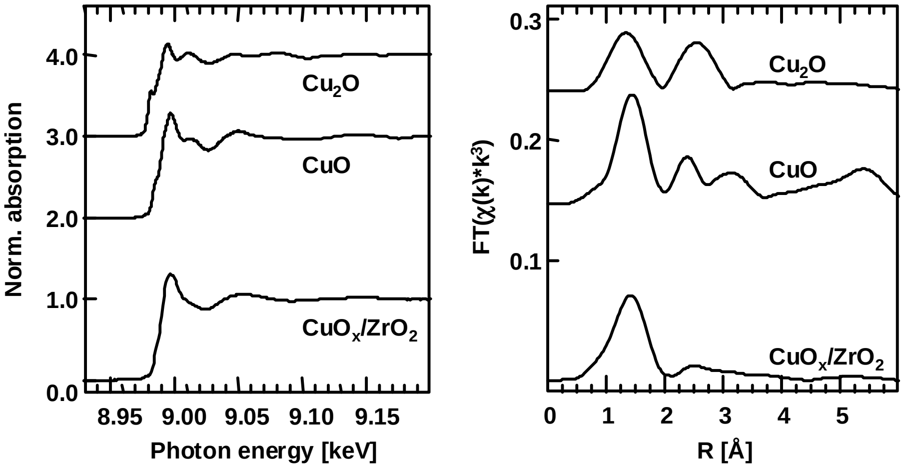


Figure 2. Cu K-edge X-ray absorption spectra and radial distribution functions of the calcined catalyst (CuO/ZrO_2) and two reference samples (Cu_2O, CuO)

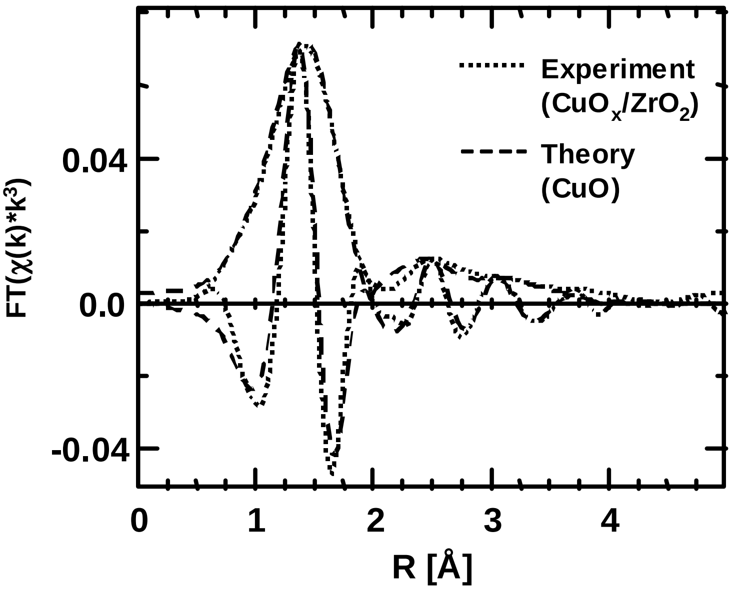


Figure 3. EXAFS fit of a CuO structure model to the experimental Fourier transformed c(k) of CuO/ZrO$_2$.

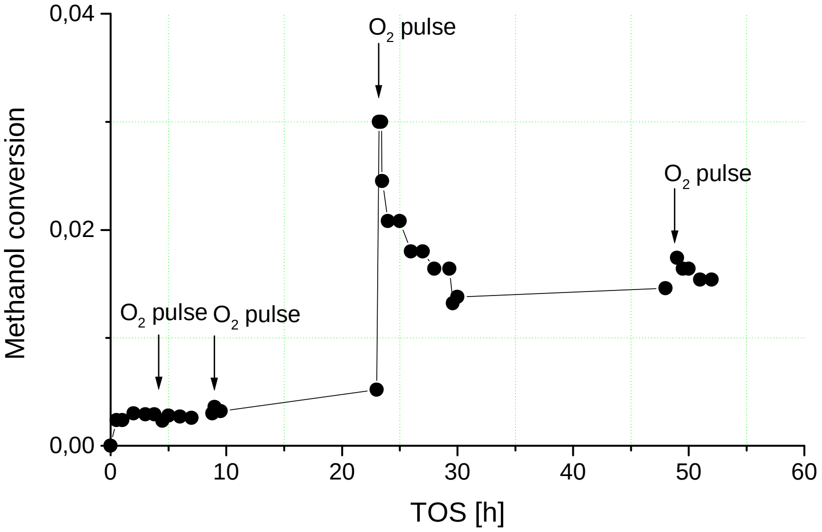


Figure 4. Activation of Cu/ZrO$_2$ catalyst by introducing O$_2$ into the feed. Reaction conditions: methanol/water molar ratio 1, T= 250°C, flow rate of methanol/water mixture = 0.07ml/min, mass of catalyst = 150 mg.

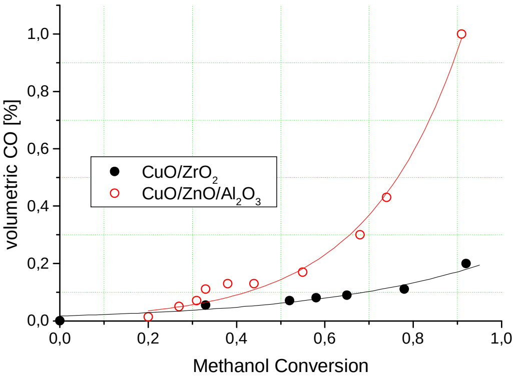


Figure 5. Comparison of activity between CuO/ZrO$_2$ catalyst and CuO/ZnO/Al$_2$O$_3$ catalyst. Methanol conversion vs. WCu/Fm ratio (WCu: mass of copper)

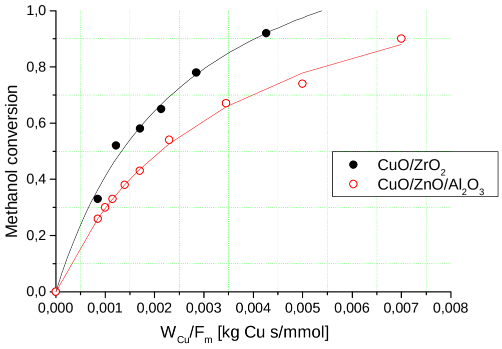


Figure 6. CO concentration in dependence on methanol conversion at 250°C.

In situ structural study on Cu/ZrO$_2$ catalysts for the steam reforming of methanol

The Cu/ZrO$_2$ catalysts investigated can be divided into three groups. First, Cu/ZrO$_2$ nanopowders were synthesized, for instance, by addition of a Cu(NO$_3$)$_2$ solution to a solution of Zr(OPr)$_4$ and tetramethylammoniumhydroxide followed by subsequent heating at 80°C for 20h The precursors were calcined at 500°C for 12h. Second, mesoporous ZrO$_2$ structures were obtained from a blockcopolymer soaked with a mixture of zirconium(IV)propylate and acetylacetonate. Subsequently, copper acetate was dissolved in the polymer solution The precursors were calcined in air at 450°C. Third, macroporous ZrO$_2$ was prepared from a polymer gel template. The template was impregnated with a solution containing Zr(OC$_3$H$_7$)$_4$, copper acetylacetonate, and propanol and left standing for several hours. Calcination in oxygen at 500°C resulted in the mesoporous ZrO$_2$. XRD (X-ray diffraction) and XAS (X-ray absorption spectroscopy) in combination with online mass spectrometry were used to characterize the structure of the Cu/ZrO$_2$ catalysts under reaction conditions. In situ XRD measurements were per-formed with a STOE STADIP P diffractometer using a Bragg–Brentano scattering geometry. In situ XAS experiments at the Cu K edge were performed at beamline E4 (HASYLAB, Hamburg).

For most of the catalysts studied, reduction of the precursor material (CuO/ZrO_2) in 2 vol% H_2/He (total 20 ml/min) or methanol and water (volume ratio 2) resulted in Cu/ZrO_2, which exhibited a rather low activity for MSR. A considerable increase in the hydrogen production rate was observed after oxygen was added (20-30 min) to the feed. The latter resulted in an oxidation of Cu to CuO followed by a partial re-reduction in the feed. Prior to the addition of oxygen, no significant changes in the long-range or short-range order structure were detected. After oxygen addition, analysis of the local structure of the copper clusters revealed characteristic mixtures of Cu and CuO with an improved catalytic activity. During reduction at 400°C for 50 min in 2 vol% H_2/He the catalysts appeared to be very stable. Figure 11 shows the radial distribution functions of spectra before and after heating to 400°C. After heating, switching back to feed at 250°C and a subsequent oxidation, a further increase in the hydrogen production rate could be observed. This suggests, that Cu clusters need to possess a minimum crystallite size in order to exhibit an increased catalytic activity.

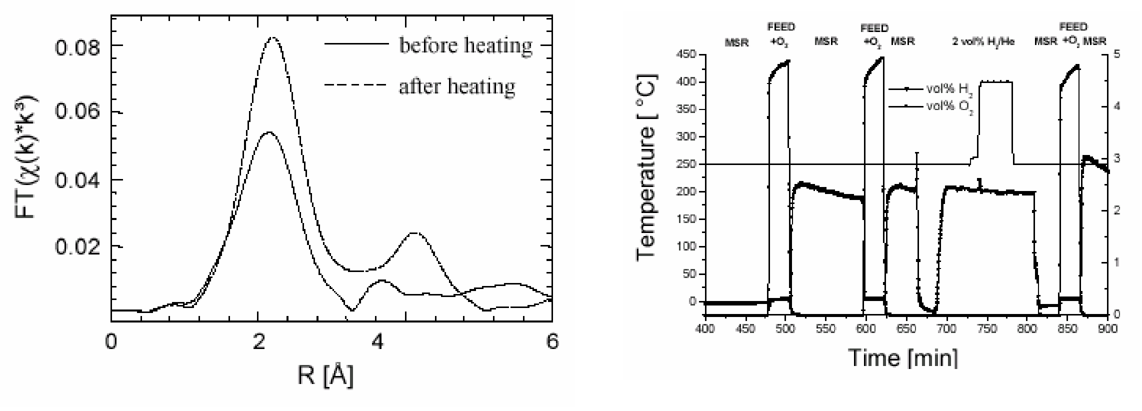


Figure 7. (left) Radial distribution functions of Cu/ZrO_2 (Cu K-edge) due to heating in 2 vol% H_2/He to 400 °C and (right) evolution of H_2 production on Cu/ZrO_2 during methanol steam reforming, oxygen pulses, and heating to 400°C in 2 vol% H_2/He

Publications

[1] H. Purnama, F. Girgsdies, T. Ressler, J. H. Schattka, R. A. Caruso, R. Schomäcker, R. Schlögl, *Activity and Selectivity of a Nanostructured CuO/ZrO_2 Catalyst in the Steam Reforming of Methanol,* Catalysis Letters, submitted.

[2] B.L. Kniep, T. Ressler, A. Rabis, F. Girgsdies, M. Baenitz, F. Steglich, R. Schlögl, *Rationales Design von nanostrukturierten Kupfer-Zinkoxid-Katalysatoren für die Dampfreformierung von Methanol,* Angewandte Chemie, submitted.

[3] H. Purnama, T. Ressler, R.E. Jentoft, R. Schlögl, R. Schomäcker, *CO Formation/Selectivity for steam reforming of methanol with a commercial CuO/ZnO/*Al_2O_3 *catalyst*, Applied Catalysis A: General, submitted.

[4] I. Kasatkin, R. Caruso, F. Girgsdies, T. Ressler, J. Schattka, J. Urban, K. Weiss, *HRTEM Observation of the Monoclinic-to-tetragonal (m-t) phase transition within a single nanoparticle of* ZrO_2, Journal of Material Sciences Letters, in press.

[5] I. Kasatkin, R. Caruso, F. Girgsdies, T. Ressler, J. Schattka, J. Urban, K. Weiss, *HRTEM study of Cu/*ZrO_2 *catalyst. An evidence of a new perovskite-like oxide* $ZrCuO_3$, Journal of Material Sciences Letters 22 (2003) 353-337.

[6] M.M. Günter, T. Ressler, R.E. Jentoft, B. Bems, *Redox Behavior of Copper Oxide /Zinc Oxide Catalysts in the Steam Reforming of Methanol studied by in situ X-ray Diffraction and Absorption Spectroscopy*, Journal of Catalysis 203 (2001) 133 - 149.

[7] M.M. Günter, B. Bems, R. Schlögl, T. Ressler, *In Situ Studies on the Structure of Copper Oxide / Zinc Oxide Catalysts*, Journal of Synchrotron Radiation 8 (2001) 619-621.

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[9] I. Böttger, T. Schedel-Niedrig, O. Timpe, R. Gottschall, M. Hävecker, T. Ressler, R. Schlögl, *Catalytic Methanol Oxidation over Copper: Observation of Reaction-Induced Nanoscale Restructuring by Means of In Situ Time-Resolved X-ray Absorption Spectroscopy*, Chemistry, A European Journal 6 (2000) 1870-1876.

3. Future Developments

The Department will continue for the next two years all projects that are currently operated. The iron oxide thin film project will be discontinued in 2005 as consequence of the restructuring of the Department and due to the intensive engagement of the Department CP using the iron oxides for other purposes than as catalyst for EB dehydrogenation. Also HPA systems will be no longer studied except for reference purposes in other projects when the accumulated know-how is suitable.

3.1 Consequences from the past activities

A common conclusion can be drawn from the results of all projects in the Department concerning the “material science” of heterogeneous catalysis. The active phase as analysed by in-situ techniques is not the nominal bulk phase used as “pre-catalyst”, but a metastable material with structural and compositional properties that are in the focus of all projects and in some cases have already been identified.

- In the HPA system the active phase is a lacunary (defective) Keggin unit forming a polymer with linkers removed from the Keggin units (autopolymerisation).

- In the zirconia isomerisation catalyst the active phase is likely to be a cluster involving an oxygen defect in the zirconia and a particular arrangement of a sulphate unit.
- In the Cu project the pure copper for methanol oxidation is only active when it contains a surface-intercalated or “sub-surface” oxygen species that is not an oxide. It disappears instantaneously by disproportionation when switching off the catalytic reaction. The Cu/ZnO system requires strained Cu particles for optimum activity in methanol synthesis whereby a large fraction of this disorder evolves from post-precipitation processing of the pre-precursor Cu-Zn hydroxy-carbonate. The Cu-ZrOx system studied for the methanol steam reforming reaction requires strained Cu particles that are composed of a nucleus of Cu oxide covered by Cu metal, all supported on ZrOx.
- In the Mo project, it was found that not stoichiometric MoO_3 but shear structure defects like $Mo_{18}O_{52}$ constitute the active phase for propene oxidation when orthorhombic MoO_3 is used as pre-catalyst. Other phases of “hydrated MoO_3” yield active and selective catalysts without the hitherto considered “essential” cationic additives (V, Bi etc) nor with shear structure defects. The active material occurs in the form of Mo_5O_{14} or as supramolecular oxide with distinct defects in the long range order (nanocrystalline). Highly crystalline forms of these phases are inactive.
- In the Fe project, it was proven that defective hematite is an excellent catalyst for the ethylbenzene (EB) dehydrogenation. The technical system is, however a particular carbon form supported on the promoted iron oxide with a much lower but sustained activity. Perfect graphite is a poor catalyst for EB oxi-dehydrogenation.
- In the Pd project a similar situation occurred where only systems with a massive “contamination” of carbon prove to be active and selective in hydrogenation.
- It was found in the vanadium project that active VPP catalysts contain on a bulk of VPO a surface layer with grossly different chemical composition than that of VPP. This different material is evidently involved in the catalytic turnover as shown by correlations between spectral features of the VxOy entities with the production of MA from butane.
- In the carbon project, it was shown in collaboration with the TH Department that only defect sites of graphite can carry chemical reactivity whereas planar graphene structures are not reactive in bond-breaking reactions. This theoretical

result is in excellent agreement with the experimental results from the EB oxi-dehydrogenation studies.

The variety of systems and phenomena allow the conclusion that the existence of a metastable form of the active phase in or on a bulk phase is a general phenomenon. It is not the active catalyst but a pre-form of it that is synthesized or studied in “static” ex-situ or UHV experiments. This is considered as the origin of the material gap in heterogeneous catalysis research. Two consequences for further work arise from this view:

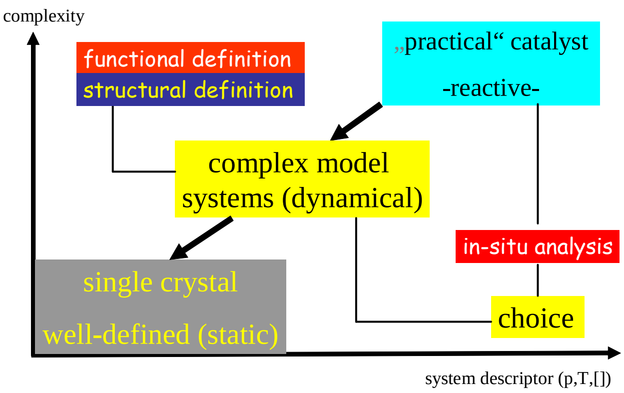
If the difference between active and pre-form is pertinent due to a change in the reaction environment (gas composition, temperature, pressure) it needs to be checked if the metastable active phase can be frozen-in. This extremely relevant problem was not addressed in a systematic way in the past as it requires extensive time-resolved in-situ studies that are not trivial to perform. Such experiments are now under way in all projects of the Department.

If active catalysts are metastable with respect to their inactive stoichiometric equilibrium precursors and can be frozen-in, then it should be possible to synthesize such metastable forms. If the active form, however, can not be obtained as material, it would be a major breakthrough if the activation process could be controlled by optimisation of the pre-catalyst. The MoO_3 project gives great hopes in this direction.

The co-operation with the Department CP has shown that for bridging the material gap it is very difficult to take samples from either the model or real world and introduce them in the respective analytical instrumentation of the other side. The boundary conditions imposed on each experiment are too diverse for the two worlds of experimentation. It is rather essential to define on each side of the gap the structure of the active material and to find suitable synthetic procedures within the boundary conditions of high and low pressure experimentation. A much more fruitful cooperation does occur in this way via transfer of knowledge rather than transfer of samples. This was evidenced in the successful interpretation of spectroscopic data from the AC Department using reference experiments on well-defined model oxides performed in the CP Department in the framework of the DFG centre of excellence and the Athena projects.

3.2. The Future Direction of Research

The Department intends to create pathways of heterogeneous catalyst *synthesis* replacing the conventional way of *preparation* based on empirical knowledge. Here, a large activity is required to investigate and to control the parameter space of each unit operation of catalyst synthesis. These operations are usually precipitation (impregnation, sol-gel synthesis), ageing, washing, drying, calcination, activation. Only if all of these steps are understood individually and in their respective interaction, a rationally founded and hence reproducible synthesis can be achieved of a catalytic material for fundamental functional studies as well as for practical testing.



Scheme 2: The target of the Department is the rational development of complex model systems. The current profile of the Department allows defining the choices of systems to be synthesized on the basis of in-situ observations of technical systems rather than on pragmatic arguments of nominal catalyst composition or availability of equilibrium phases of a compound catalyst.

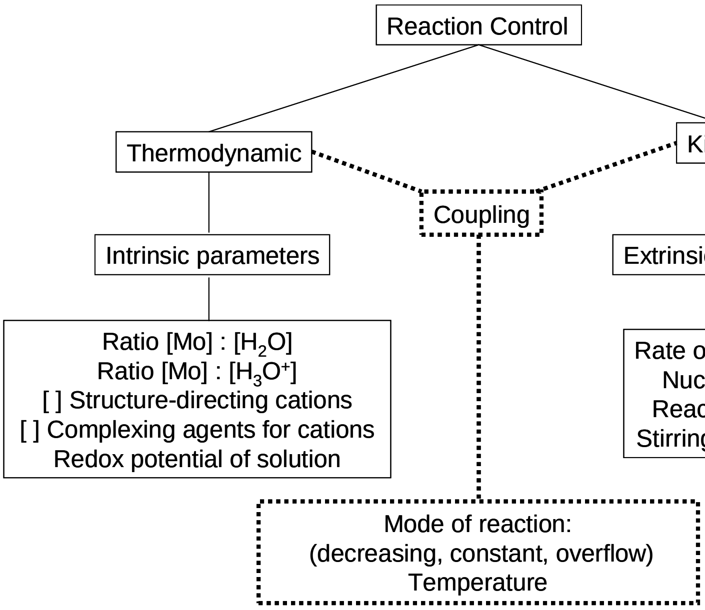
The Department AC is uniquely positioned at the crossroads of synthetic inorganic chemistry and metrology augmented by method development capabilities. Using these elements it seems possible to arrive at the development of truly rational synthesis procedures of nanostructured (defined in several dimensions of size) catalytic materials that can be used as intermediate systems to build the experimental bridge between complex technical and the present model systems. It will be necessary to develop in addition to the bare materials also suitable handling forms for in-situ experimentation such as thin films or nanocrystals. Such catalyst forms require the adaptation of testing environments to allow the novel systems to be used for static model experiments with validated functional performance. Scheme 2 indicates the target development of the Department that will be pursued in five of the research areas:

- Mo oxides for selective oxidation
- Cu for methanol reactions
- V oxides for selective oxidation
- C for dehydrogenations
- Pd for hydrogenation/dehydrogenation

The Department seeks to develop chemically simplified but structurally complex model systems that retain the full function of practical catalysts but exhibit defined structuring at atomic and at nanoscopic length scales.

The lead idea is to replace the essentially uncontrollable auto-activation of a pre-catalyst by a synthesis of the active form. This form is considered an inorganic polymer of basic structural units representing the active sites interlinked by spacers such that they can act individually in elementary steps but will retain the necessary structural dynamics. Such systems are neither surfaces of metals nor crystalline (thin film) semiconductors used today as model systems. In the world of supported systems a similar principle holds producing “rough” active particles stabilised by dissolved atoms from the reactants exhibiting a dynamical substrate interaction to minimise the kinetic barrier to structural adaptations as opposed to smooth particles with strong and rigid substrate interactions. It is part of ongoing projects (e.g. the ATHENA collaboration) to prove that this distinction is really the true discriminator between static models and dynamic “real world” systems.

The task of rational synthesis is complex and requires a shift in paradigm that presently pays little attention to the preparative aspects of “simple water chemistry”. Synthetic operations need to be feedback-controlled using in-situ probes. The kinetic aspects of controlling the atomic and nanostructure of a metastable product can only then be analysed and eventually be exploited for generating novel catalytic forms of materials. The chemistries of Mo and V provide excellent examples for the richness of metastable forms of “simple” oxides (molybdenum blue!). The boundary conditions of unit operations need to be optimised rather than “set” by chemical intuition. For the unit operation of precipitation of a single phase the complexity of the control issue is shown in scheme 3. The independent investigation of the parameters is insufficient as both kinetic and thermodynamic variables are relevant and as there is a set of coupling variables from which the reaction temperature is of outstanding weight for the resulting product.

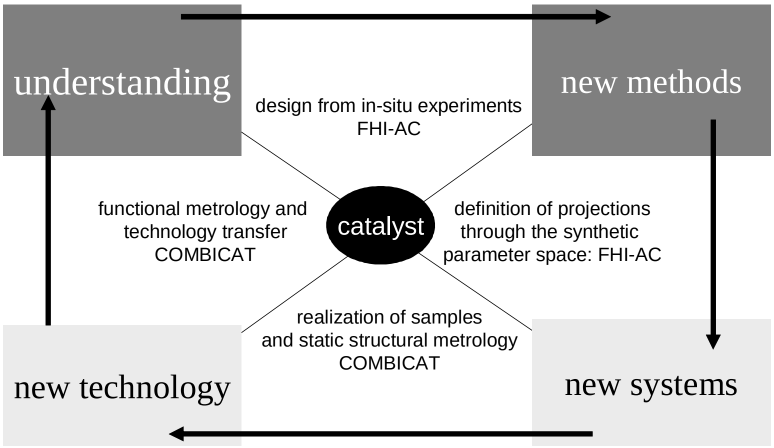


Scheme 3: Parameters of precipitation reactions for the example of MoO3 ex molybdate solutions.

In addition, novel methods of aqueous and non-aqueous solid formation processes will be explored. The endo-exotemplating techniques, hydrothermal synthesis and ultrafast precipitation techniques by solvent exchange and high pressure techniques are concepts to be implemented within the framework of resources available to the Department.

It occurs that the necessary depth of information will not be achieved in useful timescales by conventional chemical laboratory experimentation. It is rather planned to develop the required control and feedback systems for unit operations and to investigate a few sections through the parameter space with conventional preparative laboratory techniques. This information will be used to create a novel form of high throughput experimentation (*hthe*) for robotic synthesis. It is not a large compositional variation of “libraries” that is the target of present automation and high throughput strategies but it is the exploration of the interconnections of synthesis variables for one and the same chemical compound. The potential of this approach was shown in the Cu project with unravelling the chemistry of the post-precipitation processes of the Cu-ZnO synthesis. The necessary instrumentation augmented with the feedback systems (in-situ metrology) does not exist today but will be created from components of existing *hthe* systems for pharmaceutical applications and from new equipment. The *hthe* approach is further instrumental to guide the search through the synthetic parameter spaces for which the functional characterisation (kinetic testing) will be used as lead variable.

This project can only be realised in collaboration with at least one strategic partner who is prepared to work on the *hthe* approach as far as the synthetic aspect is concerned and who has expertise and test capacity for the functional analysis of materials dedicated to fundamental science. The reward for this partner is a knowledge-driven *hthe* approach that avoids the scale-up issue with minimal materials available in today´s operation and that may be as fast in finding a robust novel catalyst as the present library design strategies aiming at chemically extremely complex materials. This partner will be the COMBICAT consortium with whom ongoing activities in the general direction of the development have been started successfully. The research strategy of the two groups is much in parallel with the common goal of generating a genuine strategy to produce novel nanostructured heterogeneous catalytic systems. The COMBICAT consortium with its strong links into application-driven developments will additionally provide an efficient technology transfer. The necessary intense collaboration will be ensured by a significant mutual exchange of researchers that has already been started. Finally, the COMBICAT consortium has investigated sections of the synthetic parameter spaces for the molybdenum and for the vanadium systems and the two groups develop a common research interest in nanostructured carbon materials. These materials will play a significant role in the induced synthesis of nanostructured metal oxide systems. The distribution of responsibilities is indicated in Scheme 4.



Scheme 4: Work flow and division of tasks in the collaborative effort AC/FHI-COMBICAT

Both partners will be open to bring in other co-operations to gain a maximum efficiency while maintaining sharp group profiles. The results of the effort will be contributions to

- The understanding of the dynamical aspects of a working material “catalyst” required for the design of model systems useful for mechanistic studies.
- The generation of new methods of in-situ analysis and *hthe* synthesis.
- The reproducible and documented generation of novel catalytic systems characterised by a minimum chemical complexity and a maximal nanostructural definition.
- The identification of the potential of these novel catalysts in applications such as selective oxidation and energy storage by synthesis-reforming processes.

It is the concept of the Department to attempt a systematic and consistent approach to the general problem of material science of catalysis in order to verify the suitability of novel concepts and methods. This can only be achieved if all aspects from a functional concept through a validated synthesis up to the practical verification will be conducted in a concerted fashion with partners, as no single group alone will be strong enough to realise a work flow as indicated in scheme 4.

3.3 Infrastructural Requirements

The realisation of this medium-term research objective requires for the Department a few boundary conditions to be clarified. The necessary operating resources for this project will be provided from the institutional funding using the resources liberated by the internal restructuring described in section 1. External funding through governmental and industrial sources that have helped to arrive at the present status will be acquired as long as these programmes do not lead to unreasonable diversification in the objectives.

The Department needs safe prospects regarding its laboratory and office spacing and the necessary building operations. During the time of this report is written, the planning process has been started again with several options being studied. Each of them will strongly affect the productivity of the Department in 2005. It is pointed out that the planning process is strongly supported by the Bauabteilung of the GV.

The Department needs further access to investment resources to renew its analytical instrumentation. Most of the workhorse equipment is now 10 years and older (taken from previous activities from within the FHI or brought to the FHI in the appointment process) and needs systematic renewal. The large scale instrumentation needed is listed in descending priority. The renovation programme should be conducted throughout the next 5 years.

- In-situ SEM
- Powder X-ray diffraction
- High-resolution SEM
- TEM-ELNES at 300 keV
- In-situ FT-IR
- In-situ UV-VIS
- In-situ Raman
- Laboratory surface analysis

The Department needs further constant investment for the creation of the new synthetic equipment. The stand-alone systems and in-situ probes can be realised with the investment resources that were given to the Department on average over the last 5 years. These resources cannot cover the robotic instrumentation. If no solution within the framework of collaborations can be realised, an attempt will be made to acquire an external research grant for this dedicated instrument development project.

It is of decisive importance that the Department retains and improves its access to synchrotron radiation facilities. The key in-situ experiment providing insight into the nature of the active sites and thus into the structural entities that are targets for synthesis all depend on synchrotron radiation. Of unclear status is here the development at BESSY II for the high pressure XPS system that requires a stable operation environment allowing to meet the safety standards for operation of flow-through experiments with relevant chemicals (See also section 1.3).

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Ahmad, R.: n-Butane and n-Pentane isomerization over sulfated zirconia catalysts investigated by In Situ UV-vis-near-IR diffuse refelctance spectroscopy, Freie Universität Berlin, Fachbereich Biologie, Chemie, Pharmazie, Berlin (2003-03-25).

Bems, B.: Untersuchungen zur Präparation von Kupfer-Zink-Hydroxykarbonaten als Vorläufersubstanzen von Kupferkatalysatoren, Technische Universität Berlin, Berlin (2003-06-11).

Wienold, J.: In situ Charakterisierung der thermischen Behandlung von Polymolybdaten mit EXAFS und XRD, Technische Universität Berlin, Berlin (2003-01-24).

Diplomarbeiten

Braun, S.: Preparation and analysis of thin films of MoO_3 on Si(100), Freie Universität Berlin, Berlin (2003).

Invited Talks of the Inorganic Chemistry Department

Hendrik Bluhm

Bluhm, H.: In situ photoemission spectroscopy for environmental science and catalysis. (Seminar des Instituts für Physikalische Chemie, 2001-11-21 to 2001-11-21, Erlangen, Germany).

Bluhm, H.: In situ photoemission spectroscopy for environmental science and catalysis. (Seminar talk, 2001-11-27, University of Erlangen, Department of Physical Chemistry (Prof. Steinrück), Erlangen, Germany).

Bluhm, H., M. Hävecker, A. Knop-Gericke, V.I. Bukhtiyarov, D.F. Ogeltree, M. Salmeron, R. Schlöhl: In situ photoemission spectroscopy investigation of the methanol oxidation over copper. (Workshop “Catalysis from first principles“, 2002-02-21 to 2002-02-23, Vienna, Austria).

Bluhm, H.: The surface of ice. (Seminar talk, 2002-05-14, Abteilung Biophysik, University of Ulm, Germany).

Bluhm, H., M. Hävecker, A. Knop-Gericke, E. Kleimenov, D. Teschner, R. Schlögl: In situ XPS fort he investigation of catalysts under reaction conditions, “Science on the fly”, 2002-09-12, BESSY, Berlin, Germany).

Bluhm, H.: XPS and NEXAFS investigation of the liquid-like layer on ice. (Colloquim talk, FOM Institute voor Atoom- en Molecuulfysica, 2002-10-07, Amsterdam, The Netherlands).

Bluhm, H., M. Hävecker, A. Knop-Gericke, R. Schlögl, D.F. Ogeltree, M. Salmeron, V.I. Bukhtiyarov: In situ XPS for catalysis research. (Seminar talk, Schuit Institute of Catalysis, Technical University Eindhoven, 2003-01-15, Eindhoven, The Netherlands).

Bluhm, H.: In situ XPS for investigation of catalysts under working conditions. (Talk on the MPG-CRG evaluation at BESSY, 2003-01-16).

Bluhm, H., M. Hävecker, A. Knop-Gericke, R. Schlögl, D.F. Ogeltree, M. Salmeron, V.I. Bukhtiyarov: High pressure XPS for catalysis research and environmental science. (Max Planck Institute for Metal Research, 2003-05-06, Stuttgart, Germany).

Bluhm, H., M. Hävecker, A. Knop-Gericke, R. Schlögl, D.F. Ogeltree, M. Salmeron, V.I. Bukhtiyarov: High pressure XPS for catalysis research and environmental science. (Seminar talk, Hahn-Meitner-Institut Berlin, 2003-06-17, Berlin, Germany).

Bluhm, H., M. Hävecker, A. Knop-Gericke, R. Schlögl, D.F. Ogeltree, M. Salmeron, V.I. Bukhtiyarov: High pressure XPS for catalysis research and environmental science. (ICESS-9 International Conference on Electronic Spectroscopy and Structure, 2003-07-30, Uppsala, Sweden).

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

Michael Hävecker

Hävecker, M., A. Knop-Gericke, R.W. Mayer , H. Bluhm, M. Fait and R. Schlögl: In situ characterization of vanadium-phosphorous-oxide (VPO) catalysts for n-butane oxidation by applying X-ray absorption spectroscopy. (DFG-Schwerpunktprogramm Workshop, 2002-04-25 to 2002-04-26, Blankensee).

Friederike C. Jentoft

Jentoft, F.C.: Zirconiumdioxidkatalysatoren für die Alkanisomerisierung. (Physikalische Chemie, Universität Bremen, 2002-04-18, Bremen, Germany).

Jentoft, F.C.: Sulfatiertes Zirconiumdioxid als Katalysator für die Skelettisomerisierung von Alkanen. (Kolloquium des Instituts für Technische Chemie, Universität Leipzig, 2003-04-15, Leipzig, Germany).

Rolf Erik Jentoft

Jentoft, R.E., J. Wienold, T. Ressler: In Situ XAS for Characterization of Solid Catalysts. (Hasylab Users Meeting 2003, 2003-01-30, Hamburg, Germany).

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

Yvonne Joseph

Joseph, Y.: Spectroscopic investigations on the surface chemistry of iron oxide model catalyst films. (Seminar, Physik, Freie Universität Berlin (Prof. Kaindl), 2001-04).

Joseph, Y.: Spectroscopic investigations on the surface chemistry of iron oxide model catalyst films. (Seminar, Physikalische Chemie, Freie Universität Berlin (Prof. K. Christmann), 2001-07).

Joseph, Y.: Spektroskopische Untersuchungen zur Oberflächenchemie von Eisenoxid-Modellkatalysatoren. (Seminar, FB Chemie, Univ. Oldenburg (Prof. K. Al-Shamery), 2001-07).

Guido Ketteler

Ketteler, G.: Preparation and Characterization of epitaxial metal oxide films. (Seminar in the group meeting of Dr. Miquel Salmeron, Lawrence Berkeley Laboratory, University of California, 2003-04-21, Berkeley).

Ketteler, G.: Preparation and Characterization of epitaxial metal oxide films. (Seminar in the group meeting of Prof. Cynthia Friend, Harvard University, Department of Chemistry and Chemical Biology, 2003-04-28, Boston, USA).

Axel Knop-Gericke

Knop-Gericke, A.: In situ X-ray spectroscopy methods in the soft energy range for the investigation of heterogeneous catalytic reactions. (ELCASS Meeting, 2002-11, Arc et Senans).

Knop-Gericke, A.: Photons: In situ X-ray absorption spectroscopy in the soft energy range. (Ringvorlesung WS 2002/03, FHI Berlin, Germany).

Knop-Gericke, A.: In situ X-ray absorption spectroscopy in the soft energy range for the investigation of heterogeneous catalytic reactions. (Technical University Eindhoven, 2003-01-15, Eindhoven, The Netherlands).

Knop-Gericke, A.: In situ Characterisation of vanadium-phosphorus-oxide (VPO) catalysts for n-butane oxidation by applying X-ray absorption spectroscopy in the soft energy range. (Talk on the MPGCRG evaluation at BESSY, 2003-01-16).

Jörg Melsheimer

Melsheimer, J.: A contribution of in situ UV/Vis spectroscopy to the identification of species formed during the isomerization of n-butane and n-pentane on sulfated zirconia. (Seminar of the Department of Chemistry at Yarmouk University, 2002-05, Irbid, Jordan).

Melsheimer, J.: Improved Experimental Setup for In Situ DR UV/Vis/near-IR Spectroscopy of n-Alkane Isomerization on Sulfated Zirconia. (7th International Conference on Chemistry and its Role in Development ICCRD´7, 2003-04-14 to 2003-04-17, Mansoura & Sharm El-Sheikh, Egypt).

Dirk Niemeyer

Niemeyer, D.: Preparation of well defined model catalysts and their characterisation with sensor technology. (Glassgas sensors meeting, 2002-05-10 to 2002-05-10, Freiburg, Germany).

Niemeyer, D.: Methods for preparation and characterisation of heterogeneous catalysts (1st International School-Conference on Catalysis for Young Scientists, 2002-12-02 to 2002-12-06, Novosibirsk, Russia).

Thorsten Ressler

Ressler, T., R. Schomäcker, M. Antonietti and R. Schlögl: Towards direct production of CO-free hydrogen from methanol. (10th Roermond Conference on Catalysis: Hydrogen in Catalysis, 2002-07-01).

Ressler, T.: In situ bulk structural investigations of Cu/ZnO catalysts. (Chemistry Kolloquium, 2002-09-21, MPI für Kolloide und Grenzflächen, Golm, Germany).

Ressler, T.: Struktur-Funktionsbeziehungen von Festkörpern in der heterogenen Katalyse. (Anorganisch und Analytisches Kolloquium, 2003-06-17, Bergische Universität Wuppertal, Germany).

Ressler, T.: Principal Component Analysis of X-ray Absorption Spectra. (BioXAS Workshop, EMBL Hasylab, 2003-06-18 to 2003-06-21, Hamburg, Germany).

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Robert Schlögl

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Schlögl, R.: Heterogene Katalysatoren bei der Arbeit zugesehen: In-situ Spektroskopie an Oxidationsprozessen (GdCH-Vortrag, TU Chemnitz, 2003-06-12, Chemnitz, Germany).

Schlögl, R.: Katalyse – Ein Duett fürs Leben. (Lange Nacht der Wissenschaften an der TU Berlin, 2003-06-14, Berlin, Germany).

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Dangsheng Su

Su, D.S.: Influence of the Dynamic Diffraction on Si L ELNES. (Challenges in ELNES - Third Meeting, 2001-12-13 to 2001-12-14, Lyon, France).

Su, D.S.: Transmission Electron Microscopy of VPO-catalysts. (Department Seminar at Haldor Topsoe A/S, 2002-01-29 to 2002-01-29, Lyngby, Denmark).

Su, D.S.: ELNES and NEXAFS of Vanadium Oxides and Vanadium Phosphorus Oxides. (Seminar at the Technical University of Graz, 2002-02-14 to 2002-02-14, Graz, Austria).

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Su, D.S.: Tribochemical Modification of Bi-promoted VPP Catalysts. (Department Seminar, 2002-09-17 to 2002-09-18, Jagellonia University, Cracow, Poland).

Su, D.S.: Morphologische Untersuchungen an Diesel-Ruß. (Abteilungsseminar, Continental AG, 2002-10-25 to 2002-10-26, Hannover, Germany).

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Su, D.S.: TEM and EELS of VPO-Catalysts. (Institute Seminar, University of Malaysia, 2002-12-23 to 2002-12-30, Kuala Lumpur, Malaysia).

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Su, D.S.: ELNES and NEXAFS of Vanadium Oxides. (Institute Seminar, Institute for Metal Research of the Chines Academy of Science, 2003-02-24 to 2003-02-25, Shengyang, China).

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Su, D.S.:HRTEM of Diesel Soot Particles. (Department Seminar, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 2003-04-01 to 2003-04-02, Shanghai, China).

Su, D.S.: Fullerene-like Soot in the New Generation EURO-IV Diesel Engines. (Department Seminar of the R. Boskovic Institute, 2003-05-28 to 2003-05-28, Zagreb, Croatia).

Su, D.S.: Understanding the Structure and Property of Diesel Soot Particles: Contributions of HREM and EELS. (6th Multinational Congress on Microscopy, 2003-06-01 to 2003-06-05, Pula, Croatia).

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 Aplied Chemistry of Chinese Academy of Sciences, 2003-08-15 to 2003-08-17, Changchun, China).

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

Detre Teschner

Teschner, D.: Trans-2-pentene on Pd(111) and Pd foil (UPS and XPS study). (Athena meeting, 2002-12, Sedgefield).

Teschner, D.: Hydrogenation of trans-2-pentene on palladium foil: an in situ XPS study. (Athena meeting, 2003-05, Sunderland).

Joachim Urban

Urban, J.: Structure and Properties of Metal Clusters. (University of the Witwatersrand, Physics Separtment, 2002-08-29, Johannnesburg, South Africa).

Urban, J.: Growth of Nanoparticles (1-10 nm) by Inert Gas Aggregation: Structual Characterisation by High Resolution Electron Microscopy. (2nd French German Crystal Growth Meeting, 2003-03-10 to 2003-03-13, Nancy France)

Marc Willinger

Willinger, M.: EELS near edge structures. (MULTIMETOX TEM 2002, 2002-09-26 to 2002-09-27, Warsaw, Poland).

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

Staff Scientists:

Dr. M. Bäumer	(Habilitation)	until 01.10.2002
Dr. W. Drachsel		
Dr. N. Ernst	(Habilitation)	
Dr. H. Hamann		
Dr. T. Klüner		
Dr. H. Kuhlenbeck	(Habilitation)	
Dr. J. Libuda	(Habilitation)	
Dr. N. Nilius		
Dr. T. Risse		
Dr. G. Rupprechter		

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

Dr. Boonchuan Immaraporn
Dr. Konstantin Neyman
Dr. Shandong Yuan

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

Dr. Anders Carlsson
Prof. Ulrike Diebold
Dr. Aidan Doyle
Dr. Paolo Galletto
Dr. Javier Giorgi
Prof. Claude Henry
Dr. Markus Heyde
Dr. Viktor Johánek
Dr. Vassiliy Kaichev
Dr. Celine Lemire
Dr. Randall Meyer
Dr. Marek Nowicki
Dr. Oscar Rodrigues de la Fuente
Dr. Shamil Shaikhutdinov
Prof. Peter Stair

Scientists (temporary) paid by FHI:

Dr. Dominik Kröner

Graduate Students: 22 (3 International Max Planck Research School)
(9 paid from external funds)

Technicians: 11

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 of Chemical Physics:

- Dr. Marcus Bäumer received an offer on a chair in Physical Chemistry (C4) at the University at Bremen and left the Department effective October 1st, 2002.
- Dr. Heiko Hamann took over the position as Administrative Director effective January 1st, 2002.
- Dr. Jörg Libuda finished his habilitation at the Humboldt Universität zu Berlin.
- Dr. Niklas Nilius upon returning from his stay at the University of California at Irvine became group leader of the Scanning Probe Spectroscopy Group.
- Dr. Hans-Peter Rust and his low temperature STM facilities have been fully integrated into the department and he remained in his capacity as group leader.

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

1. *Structure and Spectroscopy*
   Dr. Helmut Kuhlenbeck
2. *Low Temperature Scanning Tunneling Microscopy*
   Dr. Hans-Peter Rust
3. *Scanning Probe Spectroscopies*
   Dr. Norbert Ernst, Dr. Niklas Nilius
4. *Magnetic Resonance*
   Dr. Thomas Risse, Dr. Heiko Hamann
5. *Laser Spectroscopy and Catalysis*
   Dr. Günther Rupprechter
6. *Molecular Beams*
   Dr. Jörg Libuda
7. *Photon-Induced Processes*
   Dr. Wolfgang Drachsel
8. *Theory*
   Dr. Thorsten Klüner

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.

In our attempts to prepare model systems for heterogeneous catalysts one important step forward has been the first time ever preparation of a single crystalline $SiO_2(111)$ film on Mo(112). We have compared growth of Pd particles on SiO_2 and Al_2O_3. Also, a considerable effort has been taken up to prepare iron oxide thin films as supports for metal particles. Here we could benefit from extensive experience Dr. Shaikhutdinov gained earlier in collaboration with Dr. Weiss in the Inorganic Chemistry Department. Pd deposits have been imaged of FeO(111) with atomic resolution including the oxide particle interface allowing for a determination of adsorption sites. We have identified a case where the metal wets the oxide surface due to its polar nature. Au nanoparticles on such supports have been imaged and their adsorption properties have been monitored in relation to their low temperature CO oxidation abilities.

The molecular beam activities are in full operation and a variety of remarkable results have been obtained, including the identification of site specific reactivities throwing light on how to control selectivity in chemical reactions at nanoparticles. Also, kinetic bistabilities and facet specific reactions as a function of particles size have been investigated. Hydrogenation of hydrocarbons has been studied as a function of particle size clearly showing how important the investigation of nanoparticles is, as the corresponding single crystals do not show this reactivity.

Non-metal modified oxide surfaces are naturally always at the focus of the department’s activities. Vanadium sesquioxide has been shown to exhibit an unexpected, so-called vanadyl termination which controls chemical reactivity towards a variety of molecules in a distinct manner. The information can be transferred to studies of vanadium oxide nanoparticles deposited on an alumina film, whose atomic structure including that of the line defects has been now finally been possible to be imaged using the low temperature STM facilities. Inelastic tunneling spectroscopy of adsorbed molecules is under way.

Bimetallic Pd-Co particles with respect to their supporting magnetic properties have been probed based on the experience the group had gained on studies of pure metal nanoparticles, whose properties have finally been analysed and the results are published. IR investigations of the bimetallics allowed us to reveal metal segregation within the particles.

In-situ spectroscopy using sum-frequency generation (SFG) has come a long way to systematically study the influence of higher pressures on adsorption properties. We have set up a new apparatus to compare SFG with results from a linear spectroscopy (i.e. Polarisation modulation (PM)-IRAS) also capable of probing adsorption at ambient conditions.

The activities in the laser desorption group have been shifted to the study of clusters also, i.e. to the study of Ag nanoparticles, aimed at studying the influence of plasmon resonance excitation on the nanoparticle surface chemistry. Here synergies with the photon-STM investigations are important.

The theory group continues to support the experimental studies on dynamics and pushes forward conceptual aspects as well as computational possibilities. New model calculations including damping dynamics explicitly via a surrogate Hamiltonian approach have been successfully completed. Also, with respect to materials modelling the group has made key contributions.

On the development of new scientific instrumentation the department continues to collaborate with the Department of Inorganic Chemistry in building a photoelectron microscope with ultimate resolution (SMART) at BESSY II. First results have been obtained at a building stage where the corrector is not yet included. The last step is in progress. The low temperature group actively develops a low temperature AFM based on the tuning fork concept. As mentioned above a PM-IRAS apparatus including additional diagnostic tools, in particular XPS, has been set up.

The FIM activities in the group have been terminated effective July 2002 to make space for the low temperature STM/AFM activities.

Collaboration with other departments and two 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”. We appreciate help of the Fachbeirat in receiving funding for this activity.

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 programs “Dynamik von Elektronentransferprozessen an Grenzflächen”: “Zeitaufgelöste Untersuchungen zur Dynamik der photoinduzierten Desorption von NO auf NiO(100): Experiment und Theorie” and in the program “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 (funded through the German-Israeli-Foundation), with Johnson Matthey PLC-Technology Centre, (funded through EPSRC of the U.K.), with Claude Henry, C.N.R.S., Centre de Recherche sur les

Mécanismes de la Croissance Cristalline, Marseille, “Oxide Surfaces” (funded through the European Commission), with Graham Hutchings, University of Wales Cardiff, U.K., AURICAT (funded through 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.

The department has associated with it the PP&B group. It 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).

Progress Reports

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

Structure and Spectroscopy

The structure and spectroscopy group consists of the former electron spectroscopy group led by Dr. Kuhlenbeck and the structure group of Dr. Bäumer who accepted a professorship position at the University of Bremen and thus left the Fritz Haber Institute. Group leader is Dr. Helmut Kuhlenbeck. Dr. Shamil Shaikhutdinov leads a subset of this group.

The group follows a number of projects. Part of the projects is dedicated to the study of clean and adsorbate covered oxide surfaces. Here the focus is put onto different vanadium oxide surfaces (V_2O_3(0001), VO_2(110), and V_2O_5(001)) and ordered silica films on Mo(112).

Another part of the projects deals with the study of structure-activity relationships of model catalyst systems consisting of metallic or oxidic clusters deposited on ordered oxide surfaces. One of these projects basically continues the previous activity of studying hydrogenation/dehydrogenation reactions over Pd model catalysts. Another project is aimed at understanding the chemistry of deposited gold clusters. In addition, more generally, we have extended studies of different metal/oxide systems to iron oxide films as supports for metal particles. This allows us to study support effects on the reactivity of metal deposits and mechanisms of catalytic reactions including reducible oxide supports. The case of oxidic active model catalyst component is represented by vanadia clusters deposited onto alumina films on NiAl(110).

Finally, the setup of the spectro-microscope SMART in co-operation with different external research groups (project leader: Prof. E. Umbach, University of Würzburg) is one of the projects of the group. Here the major topic is machine development but also scientific investigations have been performed.

Alkene chemistry on Pd surfaces: nanoparticles vs single crystal

We have studied the reactions of ethene, cis- and trans-2-pentene on Pd(111) surfaces and Pd particles deposited on a thin alumina film by temperature programmed desorption (TPD). A number of hydrocarbon transformations, such as dehydrogenation and H-D exchange reactions, occur on both Pd systems. However, alkene hydrogenation reactions under low pressure conditions do not occur on Pd(111) single crystals whereas they proceed efficiently on Pd nanoparticles.

We have shown that surface roughness alone or the presence of low-coordinated Pd atoms, which are definitely found on the particles, are not sufficient to enable the hydrogenation reaction. Since molecular alkene desorption is quite similar for both Pd systems we have examined the interaction of hydrogen with the Pd systems in order to understand why particles are active for hydrogenation whereas Pd(111) single crystals are not. The comparative study clearly shows that the particles contain a significant fraction of hydrogen which is more weakly bound than on Pd(111). Therefore, it is near at hand to assume that it is the difference in the hydrogen adsorption behaviors that leads to different hydrogenation activities of Pd(111) and Pd particles. From this we have concluded that weakly bonded hydrogen is a key species for the alkene hydrogenation reaction.

The weakly bonded state directly relates to the presence of “sub-surface” hydrogen, which exists in both Pd systems. However, due to the limited size of the particles the hydrogen atoms can not escape deeply into the bulk which means that they are available for hydrogenation of adsorbed ethene molecules, whereas for Pd(111) the H atoms diffuse so deeply into the bulk that they are not accessible to the alkene molecules and therefore hydrogenation does not occur. In other words, the accessibility of the hydrogen atoms is enhanced on the particles due to the nanoscale dimensions. This explains why nanoparticles are more active than crystals for alkene hydrogenation under vacuum conditions.

One may expect that under real reaction conditions hydrogenation also occurs on Pd crystals due to the enhanced accessibility of sub-surface hydrogen formed at high pressure. Indeed, this is the case for ethene hydrogenation observed at 5 mbar over

Pd(111) (Laser Spectroscopy and Catalysis Group). However, experiments performed in the Inorganic Chemistry Department revealed no activity of Pd(111) for trans-2-pentene hydrogenation at 0.2 mbar in the temperature range from 300 to 550 K. These results probably reflect differences in the kinetics of the hydrogen migration into the bulk and the rate limiting reaction step (hydrogen addition to alkene).

Based on the correlation between TPD spectra of alkene and hydrogen gases and the hydrogenation activity in co-adsorption experiments, we have proposed a model of overlapping desorption states, which may predict the hydrogenation activity and the active species involved in the reaction.

Reactivity of gold: size and supports effects

We have studied CO adsorption on gold particles deposited on well-ordered alumina and iron oxide films with TPD and infrared reflection absorption spectroscopy (IRAS). Scanning tunneling microscopy (STM) was used to provide the structural characterization. The data show that the adsorption of CO on gold exhibits a size effect in that small particles adsorb CO more strongly. The desorption temperature extends up to ~ 300 K which has been never observed for Au single crystal surfaces. However, the size effect strongly vanishes after annealing to 500 K.

Theoretical calculations of Norskov’s group suggest that the presence of highly uncoordinated gold atoms has a remarkable effect on the strength of CO adsorption. It seems likely that it is this type of atoms that is responsible for the presence of the high temperature desorption state (at ~ 300 K) which is lost upon annealing due to sintering and restructuring effects.

Interestingly, gold deposits may form monolayer islands ~ 3 nm in diameter when deposited at low coverage on a FeO(111) film as observed by STM. It has turned out that these islands and large gold particles, formed at higher Au coverage, exhibit identical CO adsorption behavior as observed by TPD and IRAS. Only a single IRAS peak with a CO stretching frequency of 2108 cm^{-1} has been observed for all Au deposits annealed to 500 K independent on Au coverage. Therefore, we assert that size effects observed for the low temperature oxidation of CO are not a function of particle thickness (so called “quantum size effects” as suggested for Au/TiO_2) but rather most likely associated with the presence of highly uncoordinated gold atoms.

For a given particle size (~ 3 nm), the CO desorption temperature (~ 170 K) is essentially independent of the supports studied. Therefore, support effects seen for CO oxidation on real catalytic systems must arise from the interaction of oxygen rather than CO with these catalysts. In addition, the nature of the support and its defect structure may be important for the formation and stabilization of very small Au particles.

Formation of metal monolayer islands on FeO(111)/Pt(111)

We have studied Pd deposited on a thin FeO(111) film grown on a Pt(111) substrate. Palladium deposition at ~ 130 K results in a random nucleation of the Pd particles, which are basically 1-3 layers thick depending on Pd coverage (measured at 300 K). Annealing to 600 K results in Pd spreading on the oxide surface such that extended Pd monolayer islands are formed. At increasing coverage, the first layer gets nearly completed and the second layer starts to grow. Therefore, the results clearly indicate wetting of Pd on FeO at elevated temperatures in contrast to other oxide supports previously studied.

We have atomically resolved the metal-oxide interface structure with STM and performed *ab initio* calculations of the Pd/FeO system corroborating the experimental results. The most stable geometry found by the calculations was Pd occupying on-top sites on the oxygen layer with a calculated adsorption energy of 2.7 eV/atom. The calculations fully agree with high-resolution STM images.

Similar to Pd, annealed gold deposits also form monolayer islands at low coverages, but the growth becomes three-dimensional with increasing Au coverage. It seems likely that other transition metals also form such monolayer islands on FeO(111).

The reactivity of metal monolayer islands was tested using CO as a probe molecule. As mentioned in the previous section, we have found that CO adsorption on gold is essentially similar to that of the large gold particles and the bulk gold. In contrast, we have observed that CO adsorption on Pd islands is remarkably weaker than on Pd particles and Pd(111) (desorption temperatures are 400 to 460 K, respectively). This finding has been fully supported by DFT calculations showing the lowering of the d-band of Pd layer, thus resulting in a weaker interaction with CO orbitals.

Therefore, the results show that a thin FeO(111) film can be used as a suitable oxide support for the study of the chemical properties of metal deposits with reduced dimensions.

We are currently studying the morphology of metal (Pd, Au) deposited on Fe_3O_4(111) and Fe_2O_3(0001) films as well as CO and O_2 adsorption on these surfaces. Preliminary results show that CO may react with lattice oxygen at the Pd/oxide periphery. The reactivity is enhanced for the oxygen pre-treated surfaces.

Thin silica films

Ultra-thin crystalline silica layers grown on a Mo(112) substrate were prepared and shown to be useful oxide supports in surface science model catalyst studies. As the oxide support material plays an important role in the catalytic process, a multi-technique surface science study was employed to characterize the morphological and electronic properties of the hetero-epitaxial system SiO_2/Mo(112). We studied the long-range order of the silica epilayer which grows commensurate with a *c*(2x2) surface unit mesh on the Mo(112) substrate by low-energy electron diffraction (LEED). The defect structure of the silica epilayer as characterized in a spot profile analysis (SPA)-LEED study, revealed antiphase domain boundaries splitting the silica epilayer into an array of silica crystal grains (~ 30 Å x 50 Å). Aiming to prepare flat silica surfaces, the change in the surface roughness with progress in the film preparation was monitored in a combined SPA-LEED and scanning tunneling microscopy (STM) study and seen to influence also the Si-O stretching frequency in the infrared-reflection-absorption spectra. In STM images of the final silica film an average surface roughness of about 1 Å is detected. We succeeded to image the silica film unit cell periodicity. A combined Auger electron spectroscopy and ultraviolet photoelectron spectroscopy valence band study confirmed the silica film stoichiometry and the growth of a 4:2 coordinated silica polymorph on the Mo(112) surface. These various surface science studies allow us to propose two models for the growth and structure of the silica epilayer on the Mo (112) surface, namely a tridymite/cristoballite and a **α**/**β**-quarz model, both exhibiting only a small lattice mismatch with respect to the Mo(112) support.

Surface termination of V_2O_3(0001)

Ordered vanadia surfaces and deposited vanadia clusters were investigated in the framework of the Sonderforschungsbereich 546 which deals mainly with vanadium oxides. Vanadium oxides exhibit catalytic activity for several reactions, most of them involving the transfer of oxygen atoms. Thin films of V_2O_3(0001) were prepared on Au(111) and W(110) by evaporation of vanadium in an oxygen atmosphere with the final film thickness typically being between 60 and 120 Å. The films exhibit a LEED pattern with sharp spots and low background intensity. One of the research topics was the surface termination of the films. Using different methods (IRAS, HREELS, photoelectron spectroscopy) it could be shown that the surface has a high tendency to form vanadyl groups if oxygen is available. These vanadyl groups are not part of the bulk structure of V_2O_3. They are strongly bound; even annealing at temperatures of more than 1000 K does not remove them. Removal is possible by electron bombardment and oxygen adsorption restores them. In XPS spectra of the V2p range the vanadyl groups lead to a surface core level at higher binding energy which points towards a higher oxidation state of the surface vanadium atoms. Simple counting of the vanadium-oxygen bonds at the vanadyl-terminated surface leads to an oxidation state of 4+. Correspondingly the V3d state near to the Fermi energy is more intense for the surface reduced by electron irradiation than for the vanadyl surface since the V3d occupation is directly correlated with the vanadium oxidation state. The vanadyl groups are strongly bound and block the surface vanadium atoms which may be the main reason why the vanadyl-terminated surface is chemically much less active than the reduced one.

Adsorption on V_2O_3(0001)

As pointed out above, vanadium oxides are catalytically active for several reactions. It is often claimed that vanadium oxidation states of 3+ or 4+ are the ones which are important for the catalytic activity. The probably most important reaction is the catalytic oxy-dehydrogenation of propane to propylene: $C_3H_8 + ½ O_2 \rightarrow C_3H_6 + H_2O$. In this context different adsorbates (CO, CO_2, O_2, H_2O, propane, propane+O_2 propylene, propylene+O_2, ethylene, and ethane) on V_2O_3(0001) have been studied, mainly using photoelectron spectroscopy. The vanadyl terminated surface is chemically not very active as already noted above. All studied adsorbates desorbed at comparably low temperatures and reactions were not observed. The opposite is true for the reduced surface where vanadium atoms are freely accessible. For the case of CO molecular adsorption as well as CO_2 formation was observed. CO_2 decomposes, H_2O dissociates and forms OH groups (stable up to about 500 K), and O_2 re-establishes the surface vanadyl layer. In the case of the propane, propylene, propane+O_2, and propylene+O_2 adsorbates the formation of oxidized hydrocarbons could be observed with corelevel spectroscopy. However, a detailed assignment of this species is still missing. TDS measurements (already started) and IRAS studies (to be started) will hopefully help to clarify details of the reaction and to identify reaction products and intermediates.

Vanadia particles

The interaction of CO molecules with a model catalyst system formed by alumina-supported vanadia particles was studied utilizing infrared (IR) spectroscopy. A thin, well-ordered alumina film grown on the NiAl(110) alloy surface was used as a support oxide. The structural characterization of this model system has been performed previously by applying scanning tunneling microscopy, X-ray photoelectron spectroscopy, and IR spectroscopy. Exposure to CO at 90 K results in a complex adsorption behavior as a function of vanadia particle size. At high vanadia coverages, only one CO species can be detected that interacts with vanadyl groups (VdO) present at the surface of the particles. At lower coverages, however, three further species were observed. Their existence seems to be correlated with either defect sites or with special sites provided at the vanadia-alumina interface. Furthermore, particles in this coverage regime are capable of adsorbing a maximum amount of CO molecules. Regarding the reactivity of our model system, we found only molecular desorption of CO upon thermal treatment. However, exposing the CO covered particles to low-energy electrons renders a reaction possible. A portion of the adsorbed CO gets oxidized to CO_2 via a redox mechanism, i.e., by a transfer of lattice oxygen. According to our experiments, the vanadyl oxygen does not seem to be the species that is consumed during the course of the reaction.

Studies with synchrotron radiation at BESSY II (XPS and NEXAFS)

Most of the studies were devoted to the investigations of V_2O_3(0001) surfaces discussed above. Other studies dealt with cleaved V_2O_5(001) single crystal surfaces. Here valence band, V2p, O1s core level data and angular dependent NEXAFS data were recorded, mainly to provide the group of Klaus Hermann (Theory Department) with experimental input, but also to study the reduction of V_2O_5(001) by atomic hydrogen. V_2O_5 single crystals were obtained from the Paul Drude Institute (Carsten Hucho/Peter Schilbe) via a co-operation within the Sonderforschungsbereich 546. For both, V_2O_5(001) and V_2O_3(0001), valence band spectra have been obtained in order to determine the band structure.

The spectro-microscope SMART at BESSY II

The course of the project was characterized by two aspects: (1) a technical-constructional part and (2) scientific investigations.

(1): Completion of the missing components as well as installation, test and improvement of microscope components already manufactured belong to the first point. In the summer 2001 the second version of the SMART, an energy-filtered but not yet aberration corrected photoelectron emission microscope was brought into operation at BESSY II. After adjusting and testing until November 2001 the instrument has been used for scientific investigations. Photoemission data were obtained mainly with a UV laboratory source (more than 150 days of measuring time with a Hg-short-arc-lamp) and, in addition, synchrotron radiation from a high flux beamline (62 measuring days, first with the undulator U49/1 until February 2002, thereafter with the elliptical undulator UE52) was used. On the one hand these experiments have provided scientific results and demonstrated the advantages of the measuring method, and on the other hand they were used to improve the instruments performance by examining both hardware and software in detail. Of course they also served as a training for the scientists to improve their abilities to operate the instrument. The electron optics of the SMART microscope have been designed modularly. The modules already tested and assembled are:

1. Measuring chamber with manipulator, sample holder and sample heating.
2. Objective lens with deflectors, stigmators and UHV valve.
3. Transfer optics with deflectors and contrast aperture.
4. Omega filter with magnetic quadrupoles, hexapoles and dodecapoles, a field aperture and an energy slit.
5. Projection optics with detector.

In addition two further modules are essential for the overall concept of a high-resolution spectro-microscope:

6. Photon illumination with the highest possible flux density.
7. Ultra-stable frame with vibrational damping (delivered in June 2002).

Furthermore the following components have undergone a first testing session and will be installed as soon as the production of the missing supports and supplies is finished:

8. Beam splitter.
9. Electron mirror with two electrical dodecapoles and two magnetic octupoles (together with the beam splitter this is the so-called “corrector”).
10. Electron gun with electron optics, aperture and UHV valve.

(2): The present set-up of the SMART enables the imaging of energy-filtered photo-emitted electrons. Two sources of photons were used for the *in-situ* study of the growth of organic ultra-thin films on metal substrates: a Hg-short-arc lamp with a maximum photon energy of 4.9 eV and a high flux BESSY II beamline with a tunable energy between 100 and 1500 eV and freely adjustable polarization. The two sources cause two physically different contrasts in the PEEM images: for the first case the work function contrast is dominating, whereas soft x-rays can excite core electrons which leads to elemental constrast. Additionally, utilizing the polarization in NEXAFS enables to study laterally resolved the molecular orientation of inhomogeneously grown films.

In June 2003 Dr. Engel, who was key to the technical development of the project, tragically passed away. The department is trying to ensure that the project can be sucessfully completed.

Low Temperature Scanning Tunneling Microscopy

Six month after the last visit of the Fachbeirat, the group started to move its equipment from the department of Surface Physics to the department of Chemical Physics. The two low-temperature scanning tunneling microscopes (STM) located in building F were transferred into the experimental hall of building P in the CP department. The relocation required extensive preparations. For each of the microscopes a hole of about 1,0 x 1,5 m was cut into the 0,4 m thick iron-armed concrete foundation to house the dewars for the liquid helium or nitrogen cooling of the microscopes. The STM vacuum systems were installed in two acoustic insulation chambers to reduce the noise from surrounding experiments in the hall. The electric installation had to be adapted to the new experimental set-ups. The complete reinstallation process of the STM systems took approximately six month and was finally finished at the end of 2002.

The major working field of the group in the department of Surface Physics has been the study of vibrational properties of adsorbates on noble metal surfaces. The experiments aimed to gain a better understanding of the fundamental mechanisms for vibrational excitation by tunneling electrons. For individual ammonium molecules adsorbed on a Cu(100) surface, the existence of two different reaction channels -translation and desorption- has been found, which can be controlled by tuning the energy of inelastically tunneling electrons.

After the decision of the collegium to integrate the group into the department of Chemical Physics, research was directed towards metal-oxide systems, modelling structures used in heterogeneous catalysis. In a first experiment, the atomic structure of the unit cell of a thin Al_2O_3 film on NiAl(110) has been resolved with low-temperature STM. Because of the decisive role of defects for the properties of real oxides, we have then concentrated on dislocations formed in the well-ordered Al_2O_3 layer. Theses one-dimensional defects dominate the nucleation and growth behaviour of metal particles on the oxide film. The Al_2O_3 layer on NiAl(110) grows in two reflection domains, separated by a network of antiphase (between equivalent domains) and reflection domain boundaries (between opposite domains). Antiphase domain boundaries exhibit a well-defined atomic structure, which results from the insertion of a single O row between two unaffected oxide unit cells. They form exclusively in two characteristic directions with respect to the oxide lattice, (i) along the short lattice vector and (ii) along the diagonal of the oxide unit cell. Both orientations have substantial components in the [001] direction of the NiAl support and efficiently reduce the epitaxial stress in the oxide overlayer in this direction.

Domain boundaries show almost no topographic contrast and are hardly visible in STM images taken at very low sample bias. At higher positive voltages, they are clearly imaged as pronounced white lines. The apparent height of the domain boundaries is strongly bias dependent and peaks at +2.5 V, indicating the presence of defect states in this energy range. The corresponding levels in the LDOS could also be identified with conductance spectroscopy, which revealed two dI/dV maxima at +2.5 and +3.0 V located in the vicinity of the domain boundaries. The peaks represent unoccupied defect states in the oxide band gap, induced by the disruption of the ideal oxide lattice along the domain boundaries. The experimental efforts are now extended to metal particles grown on the ultra-thin Al_2O_3 film on NiAl(110) and focus especially on the topographic and electronic properties of palladium particles. Palladium grows either in amorphous, round clusters or exhibits crystalline growth, manifested in hexagonal or triangular cluster shapes. Atomically resolved STM images of crystalline Pd particles show the hexagonal arrangement of Pd atoms in the top-most layer. Well-ordered Pd particles on Al_2O_3 thin films represent a good model system to study molecular adsorption on cluster-oxide systems. With inelastic electron tunneling spectroscopy, we aim to measure the vibrational properties of single CO molecules adsorbed on the clusters.

While the surface of metallic samples and thin oxide layers can be investigated by STM and STS, bulk oxides and thick oxide layers are mostly nonconductive and not accessible to these techniques. It is therefore highly desirable to establish an Atomic Force Microscope (AFM) at low temperatures to investigate insulating oxides on the atomic level. For this purpose, a second, new-built STM is currently supplemented with a double tuning –fork sensor for AFM measurements. The combined STM-AFM set-up has been tested successfully, and readily shows atomic resolution in the STM mode and step-resolution in the force mode on the NiAl(110) and the Ag(111) surfaces.

Scanning Probe Spectroscopies

The activities have been focused on two aspects related to the investigation of individual, oxide-supported Ag-Au alloy and Pd as well as Pt particles.

The combination of different transition metals to alloy particles often leads to a dramatic enhancement of the catalytic performance of the corresponding cluster-oxide system. The characterisation of size-dependent properties of alloy clusters in an ensemble is difficult when non-local, averaging surface science techniques are used. It often remains unclear, if the different elements completely mix to alloy particles, if they form a shell structure with different composition of inner and outer layers or if they separate to mono-elemental clusters on the surface. Since plasmon-induced light emission is sensitive to the chemical composition of the alloy particles, optical emission spectroscopy can be used to unravel details of the alloying process. Using photon emission spectroscopy combined with STM (PSTM), we have investigated Au-Ag alloy particles on an Al_2O_3 thin film grown on NiAl(110). The PSTM technique enabled experiments on individual particles selected and characterised according to size and shape. For pure Ag and Au, well-known photon emission peaks at around 320 and 510 nm were observed. The occurrence of intermediate peak positions after co-deposition of both materials indicated the formation of alloy clusters on the surface. Influences of deposition sequences of both materials (Ag → Au, Au → Ag or instantaneous deposition) and Ag-Au mass ratio in the clusters are being examined.

To improve the experimental performance of the PSTM, several changes were planned and partly implemented in the set-up to this date, such as a new control unit allowing additional spectroscopic (STS) measurements. For a better vibrational insulation an eddy current damping system has been constructed. A higher topographic resolution was obtained by applying liquid nitrogen cooling (100K). To optimise light emission yields from the tunnel junction and chemical stability of tip-sample system, the performance of W versus PtIr tips have been tested. Effects of these implementations were checked by STM topographic measurements of a well ordered silver layer epitaxially grown on NiAl(110). The intrinsic corrugation of the patches of silver atoms was readily resolved.

Energy spectroscopic characterisations of individual, oxide-supported adatoms and small clusters have been an ongoing challenge. The group has contributed to this aspect employing field emission experiments on Pd and Pt particles prepared on a well ordered, small Al_2O_3 island on the apex of a (110)-oriented NiAl field emitter tip. For both species new features in the field electron energy distributions at approximately 1eV below the Fermi energy have been measured, whereas no features were observed if particles were deposited on NiAl(110). To explain the new findings, we considered resonant electron tunneling processes through localised states of the adparticles at distinct energies. This conclusion was supported by density-functional calculations of Dr. Klüner although quantitative comparisons were not possible as yet. Because of experimental constraints particle size effects could not be established directly. However, spectroscopic measurements upon increasing Pd and Pt exposures revealed energy shifts indicative for a transition from individual adatoms to small adclusters. The field emission data also suggested a difference in the nucleation behaviour between Pt and Pd on the presumably defect-free alumina island.

Magnetic Resonance

The magnetic resonance group was engaged in two projects: the investigation of magnetic properties of metal particles on oxide surfaces and the characterization of the structure and dynamics of proteins on planar surfaces.

The first project, which utilizes ferromagnetic resonance (FMR) spectroscopy to study ferromagnetic properties of deposited metal particles, is performed within the SFB 290 “metallic thin films”. Within the project the capabilities of magnetic properties to serve as a probe for structural and chemical modifications in metal particles were explored. It was shown in the early stages of this project that the magnetic properties of particles are strongly dependent on the adsorption of gases. More importantly we could show that magnetic properties serve as a monitor for the metal substrate interface and processes that occur at this interface. Firstly, structural peculiarities at the metal substrate interface as a consequence of lattice mismatch and growth conditions modify the magnetic properties of the particles considerably. This can easily be rationalized by the strong correlation between the structure and magnetic properties. Furthermore, the sensitivity can be used to monitor chemical reaction at metal substrate interface. As an example, the reduction of CoO particles, prepared on a thin alumina film grown on top of a NiAl(110) single crystal, to ferromagnetic metal clusters were found upon annealing to 530 K. In this case aluminum originating from the NiAl substrate reduce the CoO particle resulting in an increasing thickness of the alumina film. Such a reaction is not restricted to the thin alumina film. A similar behavior was found for NiO particles prepared on a (12x4) reconstructed α-Al_2O_3 $(11\bar{2}0)$ surface. Annealing of the system results in ferromagnetic Ni particles. In this case, the reconstructed α-Al_2O_3 $(11\bar{2}0)$, characterized by an oxygen deficiency in the topmost layer, serves as the reductive agent and becomes re-oxidized in the course of the process. For both systems the efficiency of the process is reduced significantly for subsequent oxidation/annealing cycles. This is due to a limited reductive capacity in the latter example and most likely due to kinetic limitation in the former case. Beside these chemical modification of the particles also structural changes within particles can be monitored. This can readily be shown for Co particles. Annealing of these particles which were grown at room temperature to 570 K leads to an increase of the FMR intensity by a factor of 2.5. Simultaneously measured Auger spectra reveal the particle size distribution to be unchanged during this process. Thus, the increase of the FMR intensity can be interpreted as an increase of the magnetic moment of the particle, which has to be a result of structural rearrangements within the particles.

In addition, to single component particles the studies on bimetallic systems were performed. Co/Pd particles grown on a thin alumina film were investigated, which have been previously characterized in the “structure and spectroscopy” (former “deposited metal particle” group) by STM, TPD and XPS. Depending on the sequence of deposition particles with a Co core and a Pd shell and Pd crystallites decorated by Co can be prepared. Preliminary experiments exhibit significant differences of the magnetic properties for both situations. While the magnetic properties of Co particles are only slightly modified by the deposition of a Pd shell a strong increase of the FMR intensity as well as the magnetic anisotropy is observed for Co deposited on top of Pd crystallites.

In addition to magnetic measurements IRAS experiments were performed to determine available binding sites on these particles.

The second project focus on the characterization of the structure and dynamics of proteins adsorbed to planar surfaces. It is well known that the structure of proteins can be altered strongly upon adsorption to surfaces. This process usually called denaturation is usually accompanied by a loss of the proteins functionality which renders "biocompatible" surfaces an important field in science as well as technology. However, the structure determination of an adsorbed protein is hampered by a lack of methods that can address this questions. In this project we want to show that electron paramagnetic resonance (EPR) spectroscopy in combination with a site-directed spin labeling approach is capable to investigate the structure of a protein adsorbed to a planar surface. The use of planar surfaces offers the possibility to prepare and characterize well-defined model systems to elucidate the influence of changes in the chemistry and physics of the surface on the structure of the adsorbed proteins. Additionally, one can take advantage from the tensorial nature of the interaction between the paramagnetic spin label and the static magnetic field which allows a determination of the orientation of topological units with respect to the surface as long as the molecules are vectorially oriented on the surface.

As a first step fluid, planar lipid bilayers supported on a quartz surface were prepared and characterized serving as a model system for biological membranes. The lipid bilayers were functionalized with chelating head groups (Ni-NTA). This allows a selective and reversible adsorption of proteins via a short (usually 6 amino acid) n-terminal Histidine tag, which can be engineered into the proteins sequence. In addition, to the specificity and reversibility this techniques ensures a well defined adsorption site being a necessary condition for a vectorial orientation of the proteins on the surface.

T4 lysozyme a globular helical protein was chosen as an exploratory example, because it is an extensively characterized molecule particularly by EPR spectroscopy. Several single cysteine mutants were prepared in collaboration with the group of Wayne Hubbell at UCLA. The spin label, which serves as a reporter for the local structure and dynamics of protein, is selectively coupled to the single, predefined cysteine residue. Spin labels at several distinct topographic positions of the protein were investigated to characterize the structure and orientation of the protein. First, the similarity of the EPR spectra taken in viscous solution and in the adsorbed state indicate a conservation of the tertiary fold of the protein upon adsorption to the surface. This is within the expectations for the adsorption to a fluid lipid bilayer which is known to be a good model for a biological membrane. In a second step angular dependent measurements were preformed. The spectra show distinct angular dependences for several residues located at different topographic regions of the molecule. The orientation of the molecule with respect to the surface can be determined on the basis of the different angular dependences and the knowledge of the protein structure in solution.

Laser Spectroscopy and Catalysis

The relevance of surface science for technical catalysis is an actively discussed topic. Differences between the fields may originate from their specific pressure regimes and from structural differences between single crystals and supported metals. Along these lines, the activities of the Laser Spectroscopy and Catalysis group since the last Fachbeirat were two-fold. First, sum frequency generation (SFG), which was mainly utilized to study CO adsorbate structures in the past, was applied to more complex systems, i.e. the coadsorption and reaction of CO and H_2 as well as methanol decomposition on Pd model catalysts, both under ultrahigh vacuum (UHV) and ambient pressure conditions. Second, an apparatus combining polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) and X-ray photoelectron spectroscopy (XPS) was designed and setup, which allows to obtain high-pressure vibrational spectra and should thus complement our SFG studies. These two directions will be described in more detail below.

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

As an inherently surface sensitive technique, SFG allows to obtain vibrational spectra of adsorbates on model catalyst surfaces from UHV up to atmospheric pressure, being 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, which is also connected to a gas chromatograph and mass spectrometer for product analysis.

Our earlier studies, focusing on high-pressure CO adsorption, are briefly summarized here. It was shown that the high-pressure CO structures were identical to the corresponding high coverage structures observed under UHV (with “regular” on-top, bridge, and hollow bonded CO species). Pre- and post-exposure analysis by LEED and AES indicated the absence of strong changes in surface morphology and composition. By combining X-ray photoelectron spectroscopy (XPS) and SFG, a quantitative analysis of CO coverages up to 1 mbar was performed and it was shown that even at high pressure CO dissociation was absent. Even though the SFG experiments did not reveal any “high-pressure species” (different from adsorption geometries known from UHV), they clearly indicated that the resulting CO phases strongly depend on the Pd morphology. On Pd(111), a well-ordered (2x2)-3CO saturation structure was formed at

190 K and 1-1000 mbar, with CO in hollow and on-top sites. On Al_2O_3 supported Pd nanoparticles (3-7 nm mean size), a different saturation structure was observed at 1-600 mbar CO, including bridge bonded CO beside hollow and on-top CO. This dominating bridge species was attributed to specific sites at steps and edges of the Pd clusters and may be crucial for the different catalytic activity of Pd nanoparticles and Pd(111).

In the following we tried to extend the picture to the coadsorption of CO and H_2 on Pd(111) at low and mbar pressures, which is interesting from a fundamental point of view, but also of relevance for methanol synthesis and decomposition. This study was mainly motivated by the observed "inactivity" of Pd(111) for atmospheric pressure CO hydrogenation (no methanol, methane, etc was detected), even though this reaction works on Pd nanoparticles.

CO/H_2 exhibits a complex behavior due to the large number of well-ordered CO structures on Pd(111) and the various states of adsorbed and absorbed hydrogen. Sequential dosing as well as CO/H_2 mixtures were utilized to study CO/H_2 interactions on Pd(111). It turned out that it was very difficult to produce adsorbate layers where both CO and hydrogen were simultaneously present on the Pd surface. Preadsorbed CO effectively prevented the dissociative adsorption of hydrogen. Preadsorbed hydrogen was able to hinder CO adsorption at low temperature (100 K) but was replaced from the surface by CO above 130 K due to hydrogen dissolution in the Pd bulk. Using CO/H_2 mixtures below 125 K, CO and hydrogen coexisted on the surface but, of course, this temperature was too low to drive the reaction. Upon exposing CO/H_2 mixtures above 125 K, hydrogen was again replaced by CO.

When CO/H_2 mixtures were used at high-pressure (up to 55 mbar) and high temperature (300 to 550 K) (i.e. conditions similar to those used in catalytic studies on oxide supported Pd nanoparticles), CO replaced hydrogen from the surface and the resulting CO layers (~ 0.5 ML) strongly limited hydrogen adsorption. The strong blocking of hydrogen adsorption by CO explains the absence of hydrogenation products. It is therefore reasonable to assume that oxide supported Pd nanoparticles provide additional sites for CO hydrogenation (facets, step-, edge- and corner sites), on which the site blocking effects may be less pronounced. In addition, H_2-TDS spectra of Pd nanoparticles indicate a higher abundance of weakly bound hydrogen on Pd nanoparticles. Corresponding coadsorption studies on Pd-Al_2O_3 are currently performed.

We have also studied the reverse reaction, i.e. methanol decomposition, on Al_2O_3 supported Pd nanoparticles and Pd(111) in the mbar pressure range. For both types of catalysts, CO resulting from methanol decomposition was detected by SFG, but there was a very rapid deactivation due to carbon poisoning. Carbonaceous deposits on the catalysts prevented further CH_3OH adsorption and no decomposition products were detected by gas chromatography even after hours at 500 K.

Polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS):
Methanol adsorption/desorption and its time- and temperature-dependent decomposition were also examined by X-ray photoelectron spectroscopy (XPS) and polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS). Well-annealed and defect-rich (ion-bombarded) Pd(111) were used as model surfaces. Annealing CH_3OH multilayers from 100 K to 700 K mainly resulted in CH_3OH desorption. Dehydrogenation to CO was a minor path and only trace amounts of carbon or carbonaceous species (CH_x; x = 0-3) were produced, i.e. C-O bond scission was very limited. By contrast, an exposure of 5×10^{-7} mbar CH_3OH at 300 K produced CH_x (~8%) on both surfaces but the rate of formation was not enhanced by surface defects. It seems that defects generated by ion-bombardment do not exhibit the high C-O bond scission activity of steps and edges on Pd nanoparticles. Since carbon(aceous) species may either originate from C-O bond scission within methanol (or CH_xO) or from a consecutive dissociation of the dehydrogenation product CO, analogous experiments were also carried out with CO. PM-IRAS spectra up to 170 mbar CO, acquired using a UHV-high pressure cell, did not show any indications of CO dissociation, excluding CO as source of carbonaceous deposits. Our next experiments will be devoted to PM-IRAS spectroscopy on Pd nanoparticles and methanol oxidation. Special attention is also given to compare PM-IRAS and SFG spectra, since different selection rules apply to the two techniques.

Molecular Beams
The activities of the molecular beam group focus on a microscopic understanding of the reaction kinetics and dynamics on complex surfaces. In order to overcome the difficulties arising in classical reactivity studies on real catalysts, *supported model catalysts* with a reduced level of complexity are investigated employing *molecular beam techniques*, which provide detailed kinetic data under extremely well-controlled conditions. For this purpose, a molecular beam experiment has been developed and continuously improved. The system allows up to three beams to be crossed on the sample surface. Simultaneous time-resolved measurements of reaction products in the gas phase in angular-integrated and angular-resolved modes and on the surface via time-resolved IRAS (IR reflection absorption spectroscopy) are possible. As an additional facility, a single-crystal microcalorimeter has been developed in cooperation with C. T. Campbell (University of Washington, Seattle, USA), which is fully compatible with the

experimental techniques described above. The instrument is currently being set-up and tested. Complementary to the data on reaction kinetics and dynamics, it will provide thermodynamic information on adsorption and reaction processes.

In the last two years, one primary question was at the centre of the attention of the molecular beam group: How can the structure of supported particles on the one hand and catalytic activity and selectivity on the other be related at the microscopic level?

Initially, the decomposition of methanol was investigated, representing a first example of a complex multi-step and multi-pathway reaction system. Pd/alumina model catalysts were employed, which have been characterized in great detail with respect to their structure and adsorption properties by other groups in the department previously. In the molecular beam group, systematic transient and steady-state measurements and in-situ TR-IRAS have been performed in order to unravel the mechanism and kinetics in detail. One specific issue concerns the fact that methanol decomposition proceeds via two competing pathways, dehydrogenation to CO on the one side and C-O bond scission leading to formation of adsorbed carbon species on the other. In cooperation with K. M. Neyman and N. Rösch (TU München) as well as groups from the Chemical Physics Department including the Catalysis / Laser Spectroscopy Group a spectroscopic assignment of adsorbed CO to specific sites on the supported particles was possible. As a result, the occupation of different adsorption sites could be analysed and reaction rates for the two pathways could be determined combining molecular beam experiments and TR-IRAS. In this way, it was shown that there are different sites on the particle which are responsible for the two reaction pathways and, consequently, the structure of the particle controls the selectivity in this reaction system.

A second reaction system which has been investigated in detail was the decomposition and reduction of NO on the same Pd model catalyst. Recently, this reaction has attracted considerable attention in environmental catalysis due to open questions concerning the NO_x reduction. The work performed here is part of a joint project in collaboration with C. S. Gopinath (National Chemical Laboratory, Pune, India). We have focussed on two aspects so far: the kinetics of NO dissociation and the interaction with the alumina support.

Concerning the second issue, we have observed a slow NO decomposition at low surface temperature, resulting in the formation of variety of nitrogen-oxo surface species. The process involves strong structural transformations of the support and is shown to be initiated at oxide defect sites.

With respect to the first issue, i.e. N-O bond scission, the work of the group was directed towards a microscopic understanding of the activity of different sites on the supported catalyst particles. In contrast to methanol decomposition, the distribution of reactants and products over the different particle sites can be monitored under reaction conditions in the NO case, without the necessity to use any additional probe molecule. An enhanced decomposition activity is found for the supported Pd nanocrystallites, indicating preferential N-O bond scission at particle edges and steps. It is observed that atomic nitrogen and oxygen species are preferentially located in the vicinity of such edge and defect sites and it is demonstrated that the presence of these atomic coadsorbates critically controls the NO dissociation activity.

In addition to structure, size and support dependent effects, which are related to the presence of specific reactive sites or the modification of the adsorption or reaction parameters, there are also kinetic phenomena which exclusively arise as result of the limited size of the reaction system. We have recently started to investigate some of these nanoscale effects, among which are e.g. limitations of *surface diffusion* of adspecies due to the limited particle size or the occurrence of *kinetic bistabilities*, which show a pronounced particle size dependence.

In these studies it turned out to be essential to extend the experimentally accessible particle size range towards larger particles. This has been achieved by using supported Pd model catalysts prepared by electron beam lithography (in collaboration with A. W. Grant and B. Kasemo, Chalmers Univ. of Technology, Göteborg, Sweden) in addition to the typical model catalysts prepared in the Chemical Physics Department by metal vapour deposition and growth.

In order to investigate the diffusion rates of adsorbates under reaction conditions, multi-molecular beam experiments and angular-resolved detection of products were combined on both types of model systems, using CO oxidation as a simple test reaction. It was shown experimentally that regions with different local coverage can develop on particles above a critical particle size and that the reaction rates on these particles depend on the direction of the incident reactants.

As a second phenomenon, kinetic bistabilities occurring during CO oxidation have been investigated systematically. Molecular beam experiments were performed on the transient and steady-state kinetic behaviour as a function of sample temperature, adsorbate fluxes and particle size. Whereas on larger particles well-defined bistability regions are observed, all macroscopic bistabilities vanish with decreasing particle size as a result of fluctuation induced transitions between the two reactive states. The influence of defects on these transitions is investigated via a comparison with quantitative microkinetic simulations.

Photon-Induced Processes

The activities of the group are focused on the investigation of surface processes on clean or modified oxide surfaces as well as on supported metal aggregates by inducing and probing these processes by fs-laser pulses. For photon stimulated desorption experiments a novel set up was developed, which combines time resolved two-photon photo-emission spectroscopy and quantum state resolved detection of the photo-desorbed molecules via resonant multi-photon ionization. For experiments requiring a tunable wavelength, a nonlinear optical parametric amplifier has now been implemented.

One goal of the group is to probe the intermediate state of the photodesorbing molecule by manipulating the propagating wave packet via pump probe delays. We started one-color experiments on the NO/NiO(100) system where we had a rather detailed understanding of the photo-chemical processes from investigations by our theory group. The 2PPE spectra revealed an enhancement above the NiO-valence band edge if NO was adsorbed, allowing us to identify an unoccupied state at 1,9 eV above the Fermi level. This state can be assigned as the empty π^* orbital of NO, indicating that the detected photoelectron is detached from an NO^- intermediate.

The investigation of the NO photo desorption from NiO yielded a linear DIET process with a cross section of $2\text{x}10^{-17}$ cm^2, and a bimodal velocity distribution of the desorbing NO. The coupling of translation and rotation was observed and the findings agreed with those seen by our group so far for other oxides.

In order to determine the alignment of the desorbing NO we measured the quadrupol moment depending on the rotational quantum number. There is a preferred alignment, but due to the spin of the single electron a quantitative evaluation of the data is only possible by a quantum state treatment, which is under way.

The investigation of photon induced processes on nanostructured metal surfaces began with Ag-aggregates deposited on alumina films on NiAl, a system for which plasmon excitation has been studied in detail by cathodoluminescense and STM. The measured 2PPE spectra confirm the same resonance behaviour, but display a wider line width due to inhomogeneous broadening. The 2PPE rate at resonance exhibits a $\sin^4$ dependence on the polarisation angle of the laser light indicating a two plasmon excitation of the Ag clusters. Even at a photon energy of 3.2 eV, where the emission rate has dropped to less than 10 %, this dependence is still observed. Most of the photo desorption experiments were performed at this energy for laser intensity reasons. In the same way as the corresponding 2PPE intensity, the measured NO photo desorption yield depends on the polarisation angle, suggesting that primarily a two plasmon excitation induces the NO desorption. This is further confirmed by the quadratic dependence of NO desorption rate on laser power. The efficiency of the photo desorption from the clusters is much higher than from Ag(111), as expressed by a cross section of $5x10^{-17}$ cm^2 at a light intensity of 4 mJ/cm^2.

The quantum state resolved detection yields a mono modal velocity distribution of nonthermal nature for the desorbing NO. The velocity dependence on the probed rotational moment reveals the linear coupling between mean translational energy and the corresponding rotational energy. However the observed occupation of vibrational states at $\boldsymbol{\nu}$ =1 and 2 does not correlate energetically with the rotational quantum number, and the derived effective temperature of 3500 K is discussed in terms of the lifetime of the NO^- intermediate.

Due to the underlying DIET mechanism time resolved measurement of the NO desorption rate in a pump/probe experiment reveals, not only a dominating fast process in the fs range, but also a slow one in the ps range, which can be interpreted within the DIMET or friction model.

In order to observe the relaxation dynamics of coherent plasmon excitation of nanoparticles, a photoelectron emission microscope (PEEM) was attached to our pump and probe laser facility. This time resolved PEEM, us to study the nonlinear optical behaviour of surfaces in two dimensions at a spatial resolution of 500nm.

We looked for ultra fast giant fluctuations of the local electric field strength after plasmon excitation by a fs laser pulse, which should be visible as temporary hot spots in the PEEM image. As a first step, time resolved (TR) measurements were accomplished for a regular array of square Ag aggregates at a size of 500 nm by 500 nm lithographically prepared on a SiO_2/Si substrate. The PEEM images in the 2PPE mode show even at the highest magnification a very high contrast, although the Ag islands appear by a factor of three bigger due to the electron optical properties of the system. The data of the TR investigation corresponded with the expected silver plasmon life time. In a next step, an array of randomly distributed Ag nanoparticles prepared at otherwise same conditions was analysed with the PEEM, with the same result as before. The above described dynamic effect was therefore not observed. An investigation for a random distribution of much smaller Ag cluster is under way.

Theory

The theoretical investigation of the electronic structure and nuclear dynamics of small molecules on surfaces continued to be the main focus of the Theory group. In particular, laser induced desorption of molecules from transition metal oxide surfaces was studied in close collaboration with experimental groups of the Chemical Physics department. The first-principles investigation of complex phenomena such as surface photochemistry requires the development, implementation and application of new theoretical methods and efficient algorithms. In particular, three different aspects of surface photochemistry have been studied:

In the first project high-dimensional wave packet calculations on ab initio potential energy surfaces have been performed in order to investigate vectorial effects in laser induced desorption such as rotational alignment of the desorbate. Experimentally, a correlation between rotational excitation and the orientation of the angular momentum vector J with respect to the surface normal n was observed for the system $CO/Cr_2O_3(0001)$. For small rotational quantum numbers a preferential helicopter motion $(J \parallel n)$ was obtained while for large rotational excitation a preferential cartwheel motion $(J \perp n)$ was found.

In order to provide a microscopic understanding of this phenomenon, global four dimensional potential energy surfaces (PES's) for the electronic ground state as well as for a CO internal ($5\sigma \rightarrow 2\pi^*$)-excited state were calculated on the Configuration Interaction (CI) level of theory. The adsorbate-substrate complex was simulated by a cluster embedded in a semi-infinite array of point charges taking into account the desorption coordinate Z, two angular degrees of freedom (the polar and azimuthal angle), and a lateral translation coordinate X. These PES's provide the prerequisite for stochastic quantum dynamical wave packet calculations allowing for a direct comparison of our theoretical results with experimental data. It should be noted that the ab initio calculation of high-dimensional PES's represents a true challenge especially for electronically excited states.

The experimental results could be reproduced qualitatively by three-dimensional wave packet simulations in which the lateral translation coordinate was omitted. While a microscopic understanding of stereodynamic effects could be derived, deviations for small rotational quantum numbers remain. Nevertheless, the influence of surface temperature on rotational alignment was investigated and effects of rotational preexcitation on the observables of interest were predicted stimulating new experiments. Additionally, a complete quantum mechanical investigation of the angular momentum distribution of molecules desorbing from a surface has been performed for $CO/Cr_2O_3(0001)$. For the first time, we also performed four-dimensional stochastic quantum dynamical calculations on ab initio PES's in order to simulate lateral velocity distributions which were experimentally obtained by detection of Doppler profiles. Excellent agreement between experiment and theory was obtained, and a Doppler split profile was predicted theoretically suggesting a reinvestigation of the experimental data with an improved signal to noise ratio. A prerequisite for the quantum dynamical simulations was the efficient implementation of our wave packet code on massively parallel supercomputers. Recently, the code has been generalized utilizing the platform independent message passing interface (MPI) with an outstanding linear speedup with respect to the number of processing elements used.

In the second project scalar observables such as desorption velocity distributions were investigated for the system NO/NiO(100). In the stochastic wave packet calculations performed so far, the resonance lifetime of the electronically excited state enters the theory as a semi-empirical parameter. In order to gain microscopic insight into the physical mechanism determining the lifetime of the intermediate a new theory has been developed and implemented which explicitly takes quantum dissipative effects such as energy relaxation and dephasing during the time evolution of a wave packet into account. In close collaboration with Prof. Dr. R. Kosloff (Hebrew University Jerusalem, Israel) this “Surrogate Hamiltonian” method was used to model the interaction of the excited state with a bath of electron hole pairs within the surface after excitation of the adsorbate substrate system by ultrashort laser pulses. This interaction is responsible for the ultrashort lifetime of the intermediate. It was possible to obtain a complete microscopic picture of the electronic relaxation process, and a lifetime of 25 fs was predicted in agreement with previous stochastic wave packet calculations.

Currently, a multi-dimensional extension of the method is implemented and four-dimensional PES’s for the NO/NiO(100) system are constructed on the CASPT-2 and CI level of theory. A multidimensional “Surrogate Hamiltonian” treatment will eventually lead to complete microscopic insight into femtosecond laser induced desorption and will help to interpret the results of currently performed experiments.

In the third project the group continued to develop new methods in electronic structure theory. In close collaboration with Prof. Dr. E.A. Carter (University of California, Los Angeles, USA) an ab initio embedded cluster approach has been developed in which a local region of interest, e.g. an adsorption site on a metal surface, is described by accurate conventional quantum chemical cluster calculations (Configuration Interaction, Complete Active Space Self Consistent Field, and Møller-Plesset Perturbation Theory). The infinite solid is taken into account by an effective one-electron embedding operator obtained from periodic slab calculations within Density Functional Theory (DFT). Accurate adsorption energies and vertical excitation energies of CO adsorbed on Pd(111) could be calculated. Recently, a formal extension of the embedding theory has been derived and is currently been implemented. This extension lifts the approximation of a frozen background density inherent to the present implementation of the embedding formalism. This new approach will be tested on the system CO/Pt(111) for which all currently available electronic structure methods fail to predict the correct adsorption site.

In addition to these main research projects the group performed ab initio calculations on various systems often in collaboration with experimental groups of the department:

- The structure and energetics of Pd nanodeposits on a thin FeO(111) film grown on a Pt surface has been investigated. STM images have been simulated in order to compare the structural predictions with recently performed experiments. Currently, adsorption phenomena on these nanodeposits are studied by DFT calculations (collaboration with the Structure and Spectroscopy group of the CP department)
- Infrared and Raman frequencies and intensities of CO adsorbed on Pd surfaces have been calculated and analysed as a probe to characterize the surface chemical bond. Again, a direct collaboration with experimental groups was established (collaboration with Magnetic Resonance and Laser Spectroscopy and Catalysis groups of the CP department).
- Excitation spectra and ground-state properties for the inverted band-structure systems β-HgS, HgSe and HgTe have been calculated and compared to experiment (collaboration with the ICTP, Trieste, Italy).

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Klimenkov, M., H. Kuhlenbeck and S. A. Nepijko: Growth mode of Pt clusters deposited on g-Al_2O_3(111)/NiAl(110): A TEM study. Surface Science **539**, 31-36 (2003).

Koch, C. P., T. Klüner, H.-J. Freund and R. Kosloff: Femtosecond photodesorption of NO from NiO(100): A theoretical investigation from first principles. Virtual Journal of Ultrafast Science **2**, Issue 4 (2003).
- Surrogate Hamiltonian study of electronic relaxation in the femtosecond laser induced desorption of NO/NiO(100). Virtual Journal of Ultrafast Science **2**, Issue 8 (2003).

Koch, C. P., T. Klüner, H.-J. Freund and R. Kosloff: Femtosecond photodesorption of small molecules from surfaces: A theoretical investigation from first principles. Physical Review Letters **90**, 117601-1–117601-4 (2003).

Koch, C. P., T. Klüner and H.-J. Freund and R. Kosloff: Surrogate Hamiltonian study of electronic relaxation in the femtosecond laser induced desorption of NO/NiO(100). Journal of Chemical Physics **119**, 1750-1765 (2003).

Kulawik, M., N. Nilius, H.-P. Rust and H.-J. Freund: Atomic structure of antiphase domain boundaries of a thin Al_2O_2 film on NiAl(110). Physical Review Letters, submitted.

Kulawik, M., M. Nowicki, G. Thielsch, L. Cramer, H.-P. Rust and H.-J. Freund, T. P. Pearl and P. S. Weiss: A double lamellae drop-off etching procedure for tungsten tips attaches to tuning fork AFM/STM Sensors. Review of Scientific Instruments **74**, 1027-1030 (2003).

Lemire, C., R. Meyer, Sh. K. Shaikhutdinov and H.-J. Freund: Do quantum size effects control co adsorption on au nanoparticles? Angewandte Chemie, submitted.

Magg, M., J.B. Giorgi, A. Hammoudeh, T. Schröder, M. Bäumer and H.-J. Freund: Model catalyst studies on vanadia particles deposited onto a thin-film alumina support: Second interaction with carbon monoxide. Journal of Physical Chemistry B, accepted.

Mayer, R. W., M. Melzer, M. Hävecker, A. Knop-Gericke, J. Urban, H.-J. Freund and R. Schlögl: Comparison of oxidized polycrystalline copper foil with small deposited copper clusters on their behaviour in the ammonia oxidation: An investigation by means of in-situ NEXAFS spectroscopy in the soft X-ray range. Catalysis Letters **86**, 245 (2003).

Meyer, R., C. Lemire, Sh. Shaikhutdinov and H.-J. Freund: Surface chemistry of catalysis by gold. Gold Bulletin, submitted.

Morkel, M., H. Unterhalt, M. Salmeron, G. Rupprechter and H.-J. Freund: SFG spectroscopy from 10^{-8} to 1000 mbar: Less-ordered CO structures and coadsorption on Pd(111). Surface Science **532-535**, 103-107 (2003).

Morkel, M., G. Rupprechter and H.-J. Freund: UHV and high-pressure coadsorption of CO and H_2 on Pd(111): A combined SFG, TDS and LEED study. Journal of Chemical Physics, in press.

Nilius, N.: From single atoms to nanoparticles, spectroscopy on the atomic level. Proceedings “STM 2003”, American Institute of Physics, submitted.

Pacchioni, G., C. Di Valentin, D. Dominguez-Ariza, F. Illas, T. Bredow, T. Klüner and V. Staemmler: Bonding of NH_3, CO and NO to NiO and Ni-doped MgO: a problem for DFT. Journal of Physics: Condensed Matter, accepted.

Pascual, J. I., N. Lorente, Z. Song, H. Conrad and H.-P. Rust: Selectivity in vibrationally mediated single-molecule chemistry. Nature **423**, 525-528 (2003).

Richter, B., H. Kuhlenbeck, P. S. Bagus and H.-J. Freund: Core-level binding-energy shifts for supported clusters: lattice strain and initial state effects. Physical Review Letters, submitted.

Risse, T., M. Mozaffari-Afshar, H. Hamann and H.-J. Freund: Structural changes in nanoparticle catalysts as monitored by their magnetic properties. Angewandte Chemie International Edition, accepted.
- Magnetische Eigenschaften als Sonden für strukturelle Modifikationen nanoskopisch strukturierter Modellkatalysatoren. Angewandte Chemie, accepted.

Risse, T., W. L. Hubbell, M. Isas and H. T. Haigler: Structure and Dynamics of Annexin 12 bound to a plasma bilayer, Physical Review Letters, in press.

Risse, T., A. Carlsson, M. Bäumer, T. Klüner and H.-J. Freund: Using IR intensities as a probe for studying the surface chemical bond. Surface Science Letters, accepted.

Rodriguez de la Fuente, O., M. Borasio, P. Galletto, G. Rupprechter and H.-J. Freund: The influence of surface defects on methanol decomposition on Pd(111) studied by XPS and PM-IRAS. Surface Science, submitted.

Rupprechter, R., H. Unterhalt, M. Morkel, P. Galletto, T. Dellwig and H.-J. Freund: Extending UHV studies to the mbar range: Vibrational SFG spectroscopy of high-pressure CO adsorption on Pt(111) and Pd(111). Vacuum **71**, 83-87 (2003).

Schauermann, S., V. Johánek, M. Laurin, J. Libuda and H.-J. Freund: Low temperature decomposition of no on ordered alumina films. Chemical Physics Letters, submitted.
- Interaction of NO with alumina supported palladium model catalysts. Physical Chemistry Chemical Physics, submitted.

Shaikhutdinov, Sh., R. Meyer, D. Lahav, M. Bäumer, T. Klüner and H.-J. Freund: Determination of the atomic structure of the metal-oxide interface: Pd nanodeposits on an FeO(111)/Pt(111)-film. Physical Review Letters **91**, 076102-1-4 (2003).

Shaikhutdinov, Sh., R. Meyer, M. Naschitzki, M. Bäumer and H.-J. Freund: Size and support effects for CO adsorption on gold model catalysts. Catalysis Letters **86**, 211-219 (2003).

Shaikhutdinov, Sh., R. Meyer, M. Bäumer and H.-J. Freund: Two dimensional growth of Pd on a thin FeO(111) film. Surface Science Letters, submitted.

Shaikhutdinov, Sh., R. Meyer, C. Lemire and H.-J. Freund: Size and support effects of gold catalysts. Proceedings to “Gold 2003” Symposium, 28.09.-01.10.03, Vancouver, Canada, submitted.

Shaikhutdinov, Sh., R. Meyer, M. Naschitzki, M. Bäumer and H.-J. Freund: Size and support effects for CO asorption on gold model catalysts. Catalysis Letters **86**, 211-219 (2003).

Yudanov, I. V., R. Sahnoun, K. M. Neyman, N. Rösch, J. Hoffmann, S. Schauermann, V. Johánek, H. Unterhalt, G. Rupprechter, J. Libuda and H.-J. Freund: CO adsorption on Pd nanoparticles: density functional and vibrational spectroscopy studies. Journal of Physical Chemistry B **107,** 255-264 (2003).

Dissertation:

Hoffmann, J.: Methanol-Oxidation an getragenen Pd-Modellkatalysatoren. FU Berlin 2003.

Habilitation:

Libuda, Jörg: Molekularstrahlexperimente an Modellkatalysatoren. HU Berlin 2003.

Invited Talks of the Members of the Department of Chemical Physics

Marcus Bäumer

2001	*Auf dem Weg vom Einkristall zum Realkatalysator:* *Adsorption und Reaktion an Nanopartikeln auf Oxidoberflächen* Institutsseminar, Universität Ulm 04.10.2001, Ulm
2002	*Nanoparticles on Oxide Supports* Frühjahrstagung der Deutschen Physikalischen Gesellschaft, Symposium: "Cluster auf Oberflächen" 14.03.2002, Regensburg
	Nanoparticles on Oxide Surfaces Spring Meeting of the European Materials Research Society, Symposium J: "Growth and Evolution of Ultrathin Films: Surface and Interface Geometric and Electronic Structure" 21.06.2002, Strassbourg, France
	Nanoparticles on Oxide Supports: Model Systems for Heterogeneous Catalysts Workshop: "Nanostrukturierte Oberflächen: Herstellung, Charakterisierung und Anwendung: Nano2002" 20. - 24.10.2002, Porquerolles, France

Stefan Borowski

2002	*Parallel Quantum Dynamics: Small Molecules on Surfaces* Institute of Chemistry, Free University Berlin 11.06.2002, Berlin, Germany
	Parallel Quantum Dynamics: Small Molecules on Surfaces John von Neumann Institute, Forschungszentrum Jülich 24.09.2002, Jülich, Germany
2003	*Rotational and Lateral Dynamics in Laser Induced Desorption of CO from* $Cr_2O_3(0001)$ Institute of Chemistry, Free University Berlin 01.07.2003, Berlin, Germany

Hans-Joachim Freund

2001	*Model Systems for Catalysis: The Atomic Dimension* Malaysian Conference on Catalysis, Universiti Putra Malaysia 2.11.-13.11.2001, Kuala Lumpur, Malaysia

Modellsysteme für heterogene Katalysatoren: Die Brücke zu Surface Science
GdCH-Vortrag, Universität Hamburg
22.11.2001, Hamburg, Germany

Modellsysteme für die Katalyse: Die atomare Dimension
GdCH-Vortrag, Universität Köln
23.11.2001, Köln, Germany

2002

Modelle für die Katalyse: Ethenhydrierung auf deponierten Pd-Nanoteilchen
BASF Aktiengesellschaft Ludwigshafen
09.01.2002, Ludwigshafen, Germany

Nanocluster auf Oberflächen: Struktur, Adsorption und Katalyse
Ringvorlesung, TU Darmstadt
10.01.2002, Darmstadt, Germany

Modelle für die Katalyse: Die atomare Dimension
Hauptvortrag zum Tag der Chemie, RWTH Aachen
25.01.2002, Aachen, Germany

Increasing Complexity: Oxide Clusters on Oxide Surfaces
Workshop „Oxidic Interfaces“
15.02.-17.02.2002, Wittenberg, Germany

Chemical Reactivity of Oxide Supported Metal Clusters
Kick-off-Meeting of the COST D19/005/01 Working Group “Chemical Reactivity of Metal Oxide Nanoclusters”
15.03.-16.03.2002, Vienna, Austria

Deposited Nanoclusters: Models for Heterogeneous Catalysts
Seminar, Department Interfasechemie, Katholieke Universiteit Leuven
26.03.2002, Leuven, Belgium

Bridging the Materials and Pressure Gaps Between Surface Science and Catalysis
ACS-Spring Meeting, Symposium „Nanoscale Studies of Surface Science“
07.04.-11.04.2002, Orlando, USA

Die Dynamik desorbierender Moleküle: Wie bricht eine Oberflächen-Molekül-Bindung?
Festvortrag zum Abschied von G. Hohlneicher, Universität Köln
15.04.2002, Köln, Germany

Basic Principles of X-ray Diffraction
Lecture for COMBICAT-groups, University of Malaya
02.05.2002, Kuala Lumpur, Malaysia

Basic Principles of Adsorption
Lecture for COMBICAT-groups, University of Malaya
03.05.2002, Kuala Lumpur, Malaysia

Chemical Reactivity of Supported Metal Clusters
Surface Science Canada 2002, University of Ottawa
13.05.-15.05.2002, Ottawa, Canada

Reactivity of Clean and Metal Modified Oxide Surfaces: Model Systems for Heterogeneous Catalysis
Euroconference „Fundamental Aspects of Surface Science“
01.06.-06.06.2002, Aquafredda di Maratea, Italy

Oxide Clusters on Oxide Surfaces: Increasing Complexity in Model Systems
Irsee II, Kloster Irsee
07.06.-09.06.2002, Irsee, Germany

Model Systems for Catalysis: The Atomic Dimension
Gordon Research Conference on Catalysis, Colby Sawyer College,
23.06.-28.06.2002, N.H., USA

Catalysis and Surface Science: How to Bridge the Gap?
4th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT 4)
14.07.-19.07.2002, Plenary Lecture, Tokyo, Japan

Heterogenizing Homogeneous Catalysts: Ziegler-Natta-Catalysis of Ethene Polymerization as an Example of an in-situ Study
National Institute of Advanced Industrial Science and Technology (AIST),
Research Institute for Green Technology
18.07.2002, Tsukuba, Japan

Nanostructures in Catalytic Environments:
1. Heterogenizing Homogeneous Catalysts: Ziegler-Natta-Catalysis of Ethene Polymerization as an Example of an in-situ Study
2. Deposited Nanoclusters on Oxide Supports: The Atomic Dimension of Heterogeneous Catalysis
2 Lectures under the General Title „Metal-Ligand-Interactions in Molecular, micro-, and macro-systems in complex environments“,
NATO-Advanced Study Institute, Grand Hotel San Michele
01.09.-12.09.2002, Cetraro, Italy

Complex Surfaces: From Clean Oxides to Nanomaterials and Real World Catalysts
Advanced School on Material Science
01.09.-03.09.2002, Torino, Italy

Modelsystems in Catalysis: The Atomic Dimension
Perspectives and Prospects in Catalytic Sciences, The Royal Institution
03.09.-05.09.2002, London, U.K.

Deposited Clusters on Oxide Supports: Catalysis and the Atomic Dimension
International Symposium on Small Particles and Inorganic Clusters (ISSPIC) 11, Council of Europe
01.09.-13.09.2002, Straßburg, Frankreich

Model Systems for Catalysis with Increasing Complexity
Minerva School “Computational Quantum Chemistry”, Schloß Blankensee
26.09.2002, Blankensee, Germany

Chemical Reactivity of Metal Oxides and Deposited Nanostructures
COST General Meeting, TU Wien
27.09.2002, Wien, Österreich

Deposited Metal Nanoparticles as Model Catalysts: Can Surfaces Science and Catalysis Merge?
William Draper Harkins Lecture, Department of Physics, University of Chicago
06.10.2002, Chicago, USA

Probing the Optical Properties of Individual Deposited Metal Particles with the Photon Emission STM
Colloquium, James Frank Institute, University of Chicago
08.10.2002, Chicago, USA

Model Systems for Catalysis with Increasing Complexity
Workshop on “Interfacial Chemistry and Catalysis” (COST D15)
10.10.-13.10.2002, Ysermonde, Nieuwpoort, Belgium

Deposited Clusters on Oxide Supports: Catalysis and the Atomic Dimension
Kolloquium, Max-Born-Institut
16.10.2002, Berlin, Germany

X-Ray Photoelectron Spectroscopy on Model Catalysts
International Conference on X-Ray in Research and Industry (ICRXI-2002)
30.10.-31.10.2002, Kuala Lumpur, Malaysia

Models for Heterogeneous Catalysts: The Atomic Dimension
Symposium des Institut Universitaire de France
12.11.2002, Paris, France

Lectures at the Université Paul et Marie Curie, Laboratoire des Matériaux Microscopices et Nanométriques
1. Structure and Morphology of Deposited Metal Particles
2. Electronic Structure of Ensembles and Individual Particles
3. Adsorption and Reaction on Models for Heterogeneous Catalysis
4. In-situ Experiments in Model Catalysts
5. Towards Ultrafast Spectroscopy of Reactions at Surfaces
13.-14.11. 2002, Paris Frankreich

Model Systems in Catalysis: The Atomic Dimension
Seminar, UF San Carlos
22.11.2002, San Carlos, Brasilien

Model Systems in Catalysis: The Atomic Dimension
Colloquium, COPPE
26.11.2002, Rio de Janeiro, Brasilien

Deposited Metal Clusters: Models for Heterogeneous Catalysis
Seminar, Institute of Physics, Lund University
04.12.2002, Lund, Sweden

Modellsysteme für die Katalyse: Die atomare Dimension
GdCh-Vortrag, Universität Kiel
05.12.2002, Kiel, Germany

2003

Vanadium Oxide Surfaces and Deposited Vanadium Oxide Clusters
International Workshop on Oxide Surfaces (IWOX-3)
26.01.-31.01.03, Sapporo, Japan

Model Systems for Catalysis: The Atomic Dimension
Surface Science Symposium, University of California at Riverside
13.02.-14.02.03, Los Angeles, USA

Adsorption and Reaction on Deposited Nanoclusters: Models for Heterogeneous Catalysts
Inauguration of the Cracow Research Centre for Molecular Catalysis and Soft Matter Chemistry
31.03.-01.04.03, Cracow, Poland

STM and Photon-STM Investigations on Deposited Metal Aggregates
2nd Latin American Symposium on Scanning Probe Microscopy
06.04.-09.04.03, Buzios, Rio de Janeiro, Brazil

Surface Science and Catalysis: Quo Vadis?"
Workshop in honor of Prof. D. Menzel, TU München
28.04.03, Garching, Germany

Models for Heterogeneous Catalysts: Can Surface Science and Catalysis Merge
Kolloquium der Chemisch-Physikalischen Gesellschaft Wien
13.05.03, Wien, Austria

Sites, Edges and Corners on Nanoclusters Deposited on Oxide Surfaces: Selectivity in Model Catalysis.-Models of Metal-oxide Catalysts and Inverse Catalysts -
ESF Workshop
16.05.-18.05.03, Brixen, Italien

Chemistry on Deposited Nanostructures in Relation to Heterogeneous Catalysis"
Gordon Research Conference on Clusters, Nanocrystals and Nanostructures,
Connecticut College
03.08.-08.08.03, New London, Connecticut, USA

"Atomic-scale Description and Control of Complex Surfaces Structures"
Symposium on "Molecular Design of New Catalysts and Nanoporous Materials by Self-Assembling & Combinatorial Methods", II. International ASTATPHYS-MEX-2003 Conference, Aug. 25-29, 2003, Plenary Lecture
29.08.03, Puerto Vallarta, Mexico

Clusters, Facets and Edges: Site Dependent Selective Chemistry on Model Catalysts
ACS New York, Annual Meeting of the American Chemical Society, Symposium on "Chemistry on Size Selected Metal Clusters"
07.09.-11.09.03, New York, USA

Model Catalysts for Selective Oxidation: Preparation and Characterization
ACS New York, Annual Meeting of the American Chemical Society, Symposium on "Selective Catalytic Oxidation: Fundamentals, Applications and Environmental Impact"
07.09.-11.09.03, New York, USA

Atomic Scale Description and Control of Complex Surface Structures
1st Nanocat Summerschool “Highlights in Nanoscale Catalyst Design and Engineering
14.09.-21.09.03, Torino, Italy

The Surface Chemistry of Catalysis by Gold
Gold 2003
28.09.-01.10.03, Vancouver, Canada

Modelling Catalysts: Chemistry of Nanostructures at the Atomic Scale
Open Ceromeny of the “Hebrew University Center for Nanoscience and
Nanotechnology (HUCNN)”, Hebrew University
03.11.-05.11.03, Jerusalem, Israel

Markus Heyde

2003 *Design of a Low Temperature UHV STM/DFM & Dynamic Surface*
University of Münster, Institute of Physics
28.05.2003

Kerstin Jacobsen

2003 *EPR-Spectroscopic Investigation of the Interfacial System „Model Membrane -Adsorbed Protein"*
14.01.2003, FU-Berlin, Department of Physics, Berlin, Germany

Thorsten Klüner

2002 *Theory of Electronic Structure*
Young researcher meeting, Centre of Physics
09.01.-12.01.2002, Les Houches, France

Theoretical Investigation of Photochemical Reactions on Surfaces: A First Principles Approach
International Workshop on Oxidic Interfaces, University of Halle
14.02.-17.02.2002, Halle, Germany

Theoretical Investigation of Photochemical Reactions on Surfaces: A First Principles Approach
Laboratoire de Physique des Lasers, Atomes et Molecules, Université de Lille
15.03.2002, Lille, France

Theoretische Beschreibung Photochemischer Reaktionen an Festkörperoberflächen
Institute of Chemistry, Humboldt-University Berlin
23.05.2002, Berlin, Germany

Rapporteur of the session "Ab initio Molecular Dynamics"
Search Conference of the Volkswagenstiftung "Development of Theoretical Methods for Complex Systems", Schloss Reisensburg
16.-18.06.2002, Günzburg, Germany

Theoretische Beschreibung Photochemischer Reaktionen an Festkörperoberflächen
Institute of Chemistry, RWTH Aachen
10.07.2002, Aachen, Germany

Theoretical Investigation of Photochemical Reactions on Surfaces: A first principles approach
Institute of Chemistry, Carl von Ossietzky University Oldenburg
11.11.2002, Oldenburg, Germany

Introduction to ab initio Electronic Structure Calculations
Department of Physics, Free University Berlin
15.11.02, Berlin, Germany

2003 *Ab initio Simulation of Photochemistry at Surfaces*
Institute of Chemistry, University Regensburg
08.01.2003, Regensburg, Germany

Theoretical Simulation of Photochemical Reactions on Surfaces: A first Principles Approach
Institute of material physics, University Vienna
13.01.2003, Vienna, Austria

Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from a First-principles Embedding Approach
Workshop "Modelling Statistics and Dynamics in Catalysis: from ab initio potentials to rare events", Schloss Ringberg
12.09.03, Tegernsee, Germany

Christiane Koch

2002 *Quantum Dissipative Dynamics with a Surrogate Hamiltonian. The Method and Applications*
CNRS Laboratoire Aimé Cotton
24.10.2002, Orsay, France

Quantum Dissipative Dynamics with a Surrogate Hamiltonian. The Method and Applications
Evaluation of the Fritz-Haber Minerva Center, Administrative Headquarters of the Max Planck Society Munich
18.11.2002, Munich, Germany

Helmut Kuhlenbeck

2002 *Spectroscopy of* V_2O_5*(001) Single Crystal Surfaces and* V_2O_3*(0001) Supported on W(110) and Au(111)*
JRP Workshop
20.10.-23.10.2003, Stadtschlaining, Austria

2003 *Spectroscopy of* V_2O_3*(001) Films: Termination and Adsorbate Interactions*
ESF workshop “Nano-oxides: perspectives and applications of oxide based ultrathin films and nanoparticles”
16.05.–18.05.2003, Brixen, Italy

Jörg Libuda

2002 *Molekularstrahlexperimente an Modellkatalysatoren*
Universität Oldenburg
27.05.2002, Oldenburg, Germany

Molecular Beam Studies on Model Catalysts
NATO-Advanced Study Institute “Metal-Ligand-Interactions in Molecular, Micro-, and Macro-Systems in Complex Environments”
01.09. - 12.09.2002, Cetraro, Italy

Nanostructured Model Catalysts: Methods - Mechanisms – Kinetics
2nd Annual Nanoscale Science and Technology Workshop, Center for Nanotechnology and University of Seattle
18.09. - 19.09.2002, Seattle, USA

2003 *Reaction Kinetics on Complex Surfaces*
TU München
16.05.2003, München, Germany

Reaktionskinetik an komplexen Oberflächen
TU Wien
17.06.2003, Vienna, Austria

Niklas Nilius

2003
From Single Atoms to Nanoparticles, Spectroscopy on the Atomic Level
Plenary Talk, STM 2003, Eindhoven University of Technology
23.07.2003, Eindhoven, The Netherlands

Thomas Risse

2002
Small Metal Particles as Model Systems for Heterogeneous Catalysis
European Workshop on mirco and nanotechnologies
23.02.2002, Grenoble, France

Clusters on Oxide Surfaces: From Structure to Magnetism
IWSITFP Workshop
01.06.2002, Beijing, China

2003
Investigation of the Structure and Dynamic of Proteins on Surfaces by EPR Spectroscopy
Nanoscience Seminar, University of Washington
11.02.2003, Washington, USA

Characterization of a Model Ziegler-Natta Catalyst by EPR and IR Spectroscopy
Gordon Research Conference
20.03.2003, Ventura, USA

Günther Rupprechter

2002
Vibrational Sum Frequency Spectroscopy on Pd Model Catalysts
EU-TMR Research Conference on Surface Photoprocesses, Les
January 2002, Houches, France

High Pressure CO Adsorption on Pd Model Surfaces: An SFG Study
European Union COST Chemistry Action, Working Group Meeting, University Aix-Marseille
January 2002, Aix-Marseille, France

Palladium Model Catalysts Probed By Vibrational Sum-Frequency Spectroscopy
Workshop “Catalysis from First Principles”
February 2002, Vienna, Austria

Summenfrequenz-Schwingungsspektroskopie an Palladium-Modellkatalysatoren: CO Adsorption und Ethylen Hydrierung im Ultrahochvakuum und bei Atmosphärendruck
Technical University Berlin
May 2002, Berlin

Sum Frequency Spectroscopy on Pd Nanoparticles and Pd(111) from UHV to 1 bar
Physikalisch-Chemisches Institut der Universität Heidelberg
July 2002, Heidelberg

Vibrational SFG spectroscopy on model catalysts from UHV to atmospheric pressure
NATO-Advanced Study Institute "Metal-Ligand-Interactions in Molecular, Micro-, and Macro-Systems in Complex Environments"
September 2002, Cetraro, Italy

High Pressure SFG Spectroscopy on Pd Model Catalysts
Symposium of the "Gas-solid interactions" priority program of the Austrian Science Foundation
October 2002, Schlaining, Austria

2003 *Vibrational SFG Spectroscopy on Pd Nanoparticles and Pd(111): Adsorption and Reactions from UHV to Atmospheric Pressure*
University of California at Berkeley and E.O. Lawrence Berkeley National Laboratory, Surface Science and Catalysis Seminar
February 2003, Berkeley, USA

The Catalytic Activity of Supported Pd Nanocrystals
International Workshop on "Catalysis by Oxide-Supported Nanoclusters", University of California at Santa Barbara, USA,
February 2003, Santa Barbara, USA

Summenfrequenz-Spektroskopie an Pd-Nanoteilchen und Pd(111): Adsorption und Reaktion im Ultrahochvakuum und bei Atmosphärendruck
Technical University Vienna
June 2003, Vienna, Austria

Department of Molecular Physics Director: G. Meijer

(until: 31st July 2002: Department of Surface Physics)

Staff scientists:

Dr. K. Asmis	
Prof. Dr. U. Becker	(Habilitation)
Dr. H. Conrad	(Habilitation)
Dr. B. Friedrich	(Habilitation)
Dr. G. von Helden	
Prof. Dr. K. Horn	(Habilitation)
Dr. J. Küpper	
Dr. G. Prümper	
Dr. W. Vogel	

Scientists paid from external funds:

- Dr. M. Braune
- Dr. U. Hergenhahn
- Dr. A. Reinköster
- Dr. J. Viefhaus

Guest scientists, staying for at least six months:

- Prof. N. Kabachnik
- Prof. Dr. H. Kleinpoppen
- Dr. J. W. Kim

Graduate students:	11
Technicians:	10

Recent Developments in the Department of Molecular Physics (formerly Surface Physics)

Director: Gerard Meijer

In view of the restructuring of the Department within the last two years, in connection with the appointment of a new director, this report is split into two parts. Part I presents the current and future research in the field of molecular physics, and describes to which extent this will be transferred from the FOM-Institute "Rijnhuizen" in Nieuwegein, The Netherlands, to the FHI. Part II deals with the activities and future plans of the research groups that have been active within the FHI for much longer, within the former Surface Physics Department. Part II includes activities both in the field of atomic and molecular physics and in surface- and interface-science.

Part I

Molecular physics studies at the FOM-Institute ……

The research in the field of molecular physics at the FOM-Institute has concentrated on two different subjects. In the research program on **Cold Molecules** the aim 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 particular, time-varying electric fields are used to slow down, store and trap neutral polar molecules. With the successful demonstration of the so-called Stark decelerator, the equivalent of a LINear ACcelerator (LINAC) but for neutral particles, a whole new field has been opened up. Both confinement of slow neutral molecules in a prototype electrostatic storage ring and in a three-dimensional electrostatic trap have been demonstrated.

In the research program referred to as **Molecular Physics Studies with FELIX,** connected to the Free Electron Laser for Infrared eXperiments (FELIX), the IR optical properties and dynamics of molecules, clusters and nano-crystals, isolated in the gas-phase, are studied. The development of laser excitation and probing schemes that enable IR spectroscopic characterization of transient species that are only present at low density in the gas-phase is an integral part of this research program.

…..to be transferred to the FHI

The research on **Cold Molecules** is currently supported by FOM under FOM-program #50 for the 2000-2004 period, and receives additional support from three separate so-called "FOM-Projectruimte" projects (FOM is the Dutch funding agency for fundamental physics, and the abbreviation stands for "Fundamenteel Onderzoek der Materie", i.e. fundamental research on matter; for more information see: http://www.fom.nl). It is also embedded in a European network on Cold Molecules for the period 9.2002 – 8.2006. The experimental set-ups that have been developed for this research line will be transferred to the FHI as soon as the renovation of building C is completed, which we expect to happen before the end of this year. At the same time a group of three graduate students and five post-docs will come from the FOM-Institute to the FHI. The latter include *Jochen Küpper*, who has been appointed since October 2002 at the FHI as “Habilitand” but who has been stationed at the FOM-Institute thus far, and *Wieland Schöllkopf*, who is currently appointed by FOM but who will be appointed as “Habilitand” at the FHI starting from January 2004. The three other post-doctoral scientists, *Rick Bethlem* (FOM/EU), *David Carty* (FHI) and *Nicolas Vanhaecke* (FHI), will join for a short period of time. The three graduate students, *Bas van de Meerakker*, *Jacqueline van Veldhoven* and *Sophie Schlunk*, will remain employed by the FOM, but they will be stationed at the FHI. The individual projects that this group of researchers has been working on during the last years, and that will be actively pursued further at the FHI, are described in the next section and in the poster abstracts. The Cold Molecules research at the FHI is further strengthened by the appointment of *Bretislav Friedrich* on a permanent-staff scientist position per September 2003. He will start a research line on the use of various combinations of external fields to manipulate molecules, with a focus on optical manipulation. *Horst Conrad*, whose recent contributions in the area of surface science are highlighted in Part II, will redirect a large fraction of his research efforts to an experimental study of the possibilities of using micro-structured electrostatic devices for manipulation and trapping of molecules, a new research line popularly referred to as “molecules on a chip”. 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, will be pursued at the FHI.

The **Molecular Physics Studies with FELIX** are supported by FOM as FOM program #59 for the 2003-2008 period. It receives additional support by a “FOM-Projectruimte” project and by three separate projects from the chemical sciences (CW/NWO) and part of it is embedded in a European network on Cluster Cooling (10.2000-10.2004). The experimental set-ups used for these experiments will largely remain at the FOM-Institute, and the experiments will also be continued there. A formal contract between the FHI and the FOM-Institute will arrange for the appropriate beam-time allocation, etc. Here it is important to mention that the exploitation costs for FELIX are covered under a separate FOM-program until 2012, and that an investment grant to upgrade the FELIX facility with intra-cavity capabilities has been secured. After the completion of this so-called FELICE (Free Electron Laser for Intra-Cavity Experiments) project, planned for 2006, the already unique possibilities for gas-phase molecular physics studies at this IR user-facility will be greatly enhanced. *Gert von Helden*, as former staff-scientist at the FOM-Institute responsible for the day-to-day supervision of the various molecular physics research projects, has accepted a position as permanent-staff scientist at the FHI per September 2003. Together with *Knut Asmis*, an experienced FELIX-user who is employed at the FHI as “Habilitand” per July 2003, he will continue to supervise the ongoing molecular physics studies at the FOM-Institute. At the same time they will design and set up a dedicated molecular beam machine at the FHI, coupled to a commercially available pulsed IR laser system, to perform conformer-specific vibrational spectroscopic studies of (bio-) molecules and clusters in the gas-phase. The experimental apparatus will be designed such that it can be transported to the FELIX facility for specific studies in the long-wavelength range, as well as to other IR facilities that might become available in the near future.

Cold Molecules

The ability to cool and slow atoms with light for subsequent trapping allows investigations of the properties and interactions of the trapped atoms in unprecedented detail. This has led to exciting and sometimes unforeseen results, and the pay-offs have included atom interferometry, precision spectroscopy, Bose-Einstein condensates, and atom lasers. In principle, all these experiments could be performed with molecules as well. Molecules would add a new dimension to these experiments as they can be prepared in a wide variety of selected rotational and vibrational quantum states and as they can be spatially oriented. The experimental challenges – formidable enough for atoms – loom even larger for molecules, however, and the complex structure of molecules has thus far excluded the type of laser manipulation that has been so crucial for the success in the field of cold atoms. Nevertheless, a number of research groups have entered the quest with the goal of bringing molecules to sub milliKelvin temperatures, slow enough to be trapped or otherwise manipulated.

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 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 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.

To exemplify the similarity with charged particle physics, we mention here the construction of a buncher, an element well-known in charged particle physics, to manipulate the velocity distribution of the packet of neutral molecules leaving the Stark decelerator. The buncher is built as an enlarged section (total of 4 stages) of the conventional Stark decelerator and is mounted some 15 cm downstream from the Stark decelerator. It is effectively a lens for the packets of molecules in the longitudial direction (i.e., along the molecular beam axis), allowing the preparation of either a parallel beam with a strongly reduced velocity distribution or a converging beam with a strongly reduced spatial distribution at a specific position downstream. Beams of ND_3 molecules with a longitudinal velocity spread corresponding to a temperature of 0.25 mK as well as beams focussed down to 0.3 mm at a distance of 20 cm behind the decelerator have been produced.

In a series of detailed experiments on molecular beams of ammonia seeded in Xe, the characteristics of the combination of the Stark decelerator, the buncher and an electrostatic trap have been thoroughly investigated. Densities of trapped ammonia molecules of $\geq 10^7$ mol/cm^3 at temperatures of around 25 mK have been obtained. The temperature of the trapped cloud is deduced from the measured spatial distribution of the cloud in the trap. The shape of the trapped cloud is that of a pancake, with about 1 mm diameter and 0.5 mm thickness, containing a total of (only) 10^4 state-selected ammonia molecules. As the experimental technique relies on the Stark effect that a certain molecule experiences in the fields of the decelerator, different molecules can be decelerated simultaneously; we have explicitly demonstrated this by decelerating and trapping two different isotopomers of ammonia.

In the cold regime, spectroscopic investigations of molecules can be carried out in a much greater detail. In many molecular beam spectroscopic studies on isolated gas-phase molecules the ultimate resolution is determined by the finite interaction time of the (moving) molecules with the measurement apparatus. By slowing down the molecular beam, i.e. even without trapping the molecules, the spectroscopic resolution can be significantly improved. To test this, we have set up a separate molecular beam machine in which transitions between the upper and lower component of the tunneling doublet in ND_3 have been studied. In the first experiments, the spectral resolution in these microwave measurements has been in the kHz range, limited by transit time broadening. These measurements have nevertheless allowed us to unravel, for the first time, the complete hyperfine splitting in ND_3. Information on the details of the hyperfine splitting in ND_3 is crucial for future evaporative cooling experiments with ND_3, as well for the production of molecular beams in selected hyperfine levels of the high-field seeking component of the tunneling doublet.

During the last year we have made important progress in the production of pulsed beams of diatomic radicals such as OH and NH with which we plan to do deceleration and trapping experiments in the near future. Here, the production of an intense pulsed beam of NH radicals in the electronically excited, metastable $a^1\Delta$ state should be mentioned. Molecules in the lowest rotational J=2 level in this metastable state can be readily decelerated with a "standard" Stark decelerator. After decelerating the molecules to a near standstill, they can be optically pumped to the electronic ground state via a spin-forbidden transition. We have recently observed this transition, and found that the rotational structure and the overall intensity of this transition is indeed adequate for efficient optical pumping. Once in the electronic ground-state, the NH radicals can be magnetically trapped. One of the main advantages of this particular deceleration and trapping scheme is that it allows accumulation of successive bunches of decelerated molecules in the magnetic trap, thereby increasing the number density of trapped ground-state molecules.

By bending a hexapole in the shape of a torus, a prototype storage ring for neutral molecules has been constructed. By injecting velocity compressed bunches of molecules into the 25 cm diameter storage ring, the spreading out of the stored package in the tangential direction can be minimized. This makes it possible to observe many round trips of the molecules in the storage ring and to study the stability of the trajectories in the storage ring as a function of external parameters. We were able to detect the molecules after 50 round trips (corresponding to more than 40 meters in circular orbit!), and deduced from the width of the spatial distribution of the stored bunch of molecules a longitudinal temperature of approximately 0.30 mK.

Molecular Physics Studies with FELIX

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 5 - 250 μm, e.g. (almost) the full “molecular fingerprint” region, and the possibility of user-controlled wavelength scanning. But 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.

As building blocks for all living materials, proteins form a class of molecules of great importance. Many, if not all, of their functional characteristics are strongly dependent on their specific shape. Although the individual amino acids that make up the protein are strongly bound to each other by the peptide bond, numerous degrees of freedom are still present allowing for different shapes. While the functionality of a protein is determined by its “right” shape, a “wrong” conformation can have dramatic results and even lead to diseases, such as Alzheimer’s disease and BSE. This so-called secondary structure of a protein is determined by interactions within the molecule, but also by interactions with its environment. It is thus of interest to investigate those interactions in the gas phase on a fundamental level. Making use of the IR radiation produced by FELIX, a study is performed on different conformations of the amino acid tryptophan. For three conformers the IR absorption spectrum is recorded in the region between 5 and 30 micron. These first ever studies in this wavelength range reveal that the spectra for individual conformers exhibit clear differences that can, especially in the long wavelength region, be quite dramatic. This is in agreement with the notion that short wavelengths are characteristic for vibrational structure localized to individual atoms, whereas the long range interactions, involving whole groups, are found in the longer wavelength range. The experimental results can be compared to predictions from quantum chemical calculations, allowing detailed insight in the structure and dynamics of those molecules. It is expected that this technique can be extended successfully to even longer wavelengths and more complex systems, yielding fundamental knowledge about intramolecular interactions.

In the infrared emission spectra of many interstellar and circumstellar objects, strong bands are observed at wavelengths that correspond roughly to typical vibrational modes of polycyclic aromatic hydrocarbons (PAHs). For that reason, such PAH molecules, and in particular their positive ions, are believed to be the carriers of these interstellar emission bands. Verification of the PAH hypothesis requires laboratory spectra of ionic PAHs in the gas phase. However, ionic species are difficult to study in the gas phase, since they can only be generated in small quantities due to their mutual Coulombic repulsion. Standard infrared techniques fail to record a spectrum of such low-density samples. We have developed a method to record the infrared spectra of large gas phase molecular ions and have applied this method to a variety of PAHs and PAH-related compounds. In a vacuum chamber, the PAH vapor is ionized with a UV laser. The ions are then stored in an rf-driven ion trap consisting of a ring electrode sandwiched between two hyperbolically shaped endcap electrodes. In the trap, the ions are irradiated with the intense and narrow-band infrared laser light from FELIX. When the wavelength of the laser radiation matches an infrared absorption of the ion, multiple photons are absorbed, which effectively heats the ion to internal energies beyond the dissociation threshold. The ion dissociates into lower mass fragments, which are detected in a mass spectrometer. Thus, recording the fragment yield as a function of infrared wavelength gives the spectrum of the ionic PAH. One of the highlights is the recording of the spectrum of the highly symmetric coronene ion $C_{24}H_{12}^+$. It is, to our knowledge, the largest gas phase ion of which the infrared spectrum has ever been recorded. Currently, we focus on ionic PAH-related species, which have no stable neutral counterpart, such as closed-shell ions. Although such species hardly occur in our atmosphere, they may be fairly stable under the low-density conditions of interstellar clouds. As an example, we recently recorded the infrared spectrum of the benzoyl cation $C_6H_5CO^+$, which possesses an even number of electrons. Therefore, its neutral counterpart, the benzoyl radical, is unstable under normal terrestrial conditions.

The energy flow dynamics in molecules and molecular complexes has been in the focus of scientific research for a number of years. In most experiments, the energy flow dynamics is followed on some electronically excited potential energy surface. Using FELIX, experiments can also be performed on the electronic ground state surface, which is more relevant and easier to compare to theoretical predictions. Here, we study the dissociation dynamics of vibrationally excited Van der Waals (VdW) complexes. For the complex to dissociate, energy has to be transferred from the light absorbing (intra-molecular) mode to the inter-molecular VdW bond. The lowest energy intra-molecular modes are typically several hundreds of wavenumbers in energy. The VdW modes in contrast have typical vibrational energies of a few tens of wavenumbers. The energy transfer mechanisms between such modes are presently not well understood. In the experiment this energy transfer is measured in a gas phase pump-probe setup. This is accomplished by exciting the complex using a single (ps) IR pulse of FELIX and then probing the dissociating complex using a short pulse (ns or ps) UV laser. In the experiment, aniline–argon or aniline–neon complexes are excited with 422 cm^{-1} photons. The dissociation is observed to be surprisingly slow, and experiments indicate a lifetime of 151 ns and 38 ns, respectively. This is many orders of magnitude slower than expected from statistical models. Simple modelling indicates that the rate limiting step is the internal vibrational redistribution of the energy from the intramolecular mode to the VdW modes.

One fundamental approach to understand the properties of nanosized materials or isolated surface sites is to elucidate the structures of their gas phase clusters. Our recent work on resonant ionization of clusters using intense infrared radiation demonstrates that infrared spectra of strongly bound clusters can be obtained via resonant ionization spectroscopy and structural information can be derived from these spectra. Recently, we applied a technique, where the clusters are resonantly heated via absorption of multiple infrared photons and the induced dissociation of clusters is used to monitor their infrared absorption spectrum. Structural determination is achieved by comparing the experimental infrared spectra to spectra that have been calculated using quantum chemical methods. Using this technique we studied the structures of transition metal oxide clusters, with the main emphasis on oxides of vanadium, niobium and tantalum. In the experiment, the structures of for example some niobium oxide cluster cations, such as $Nb_2O_6^+$ or $Nb_3O_8^+$, could be clearly identified. The complexes of some of those oxides with hydrocarbons are relevant in heterogeneous catalysis. The oxide clusters are reactive towards hydrocarbons and different mechanisms for hydrocarbon oxidation are under discussion. We have preliminary results on IR spectra of ethene - metal oxide cluster adducts, which might help to identify the binding sites of the hydrocarbon.

Part II

The study of **fullerenes in the gas phase** continues in the group of *U. Becker*. Strong oscillations in the cross-sections of the valence photoionization of C_{60} as a function of photon energy were interpreted in terms of a simple refractive model. Refined measurements have now shown that more frequencies than the main one, which is determined by the cage diameter, exist. The Fourier spectrum of the cross sections for the HOMO and HOMO-1 orbitals displays additional side bands, representing the length difference between the outer and inner spherical shells of the delocalized part of the electron cloud. The method may be considered as sort of imaging of delocalized electron clouds in reciprocal Fourier space.

A second field of interest is coincidence spectroscopy of atoms and molecules, in particular angle-resolved electron-electron and electron-ion coincidence spectroscopy. The COLTRIMS method has now been implemented into synchrotron radiation research. A complementary method, concentrating on high-resolution coincidence spectroscopy, has been pioneered by the group. Electron-electron experiments by *J. Viefhaus* *and S. Cvejanovic* explore the double Auger process; whereas the electron-ion experiments by *G. Prümper and U. Hergenhahn* are aimed at studying photoelectron scattering and diffraction in the gas phase. The related activities center around three major topics:

(i) Double Auger decay as a show-case for electron correlation. This process is completely mediated via electron–electron correlations as in double photoionization, but reflects this correlational behavior in a different way, because no photon with an angular momentum of unity is involved. Electron-electron coincidence studies of the double Auger process in rare gas atoms provide additional information on its dynamical properties.

(ii) Resonant Auger decay in dissociating molecules with Doppler-marking of the emitter atom. In multi-electron ejection processes, the main subject of interest is the interaction between the electrons. In molecular single ionization the interaction between the emitted electron and the ionized molecule fragment results in the scattering of a photo- or Auger electron on its way out of the original molecular environment. In a static situation, this intra-molecular scattering leads to electron diffraction. In dissociating molecules, the scattering behavior reflects the effect of the molecular dynamics on the diffraction pattern. The present experiment disentangles for the first time three elementary processes in molecular photoemission: forward and backward emission, forward and backward scattering and interatomic electron transfer. These processes completely determine the electron emission pattern of fixed-in-space molecules.

(iii) Photoelectron diffraction and/or interference in hetero- and homo-nuclear diatomic molecules as a prototype system for localized and delocalized core holes. In contrast to hetero-nuclear molecules such as CO, where the core holes are completely localized, this localization problem in homo-nuclear molecules such as N_2 is still open. New experiments by *G. Prümper* and *U. Hergenhahn* disclosed that these orbitals are indeed coherent electron emitters from two locally separated positions. This demonstrates that they are not localized, and that there is no coincidence experiment that could break the genuine mirror symmetry. However, another question immediately arises: Is it possible to break this symmetry, caused by the identity of the two centers, on a nuclear level in order to force core hole localization, or should this perturbation take place on an electron orbital level in order to become effective for measurable changes in the photoelectron properties? The problem is related to the transition from identity to individuality in quantum mechanics. It seems that the transition is sudden but its appearance is smooth, depending on the mixing and coherence properties of the *gerade* and *ungerade* core-hole states.

Turning to surface and interface studies, work using the **low temperature STM** in the group of *Horst Conrad, Ignacio Pascual,* and *Hans-Peter Rust* dealt with the field of mode-selective chemistry, i.e. steering chemical reactions by exciting specific molecular vibration modes, influencing thus both velocity and product distributions of chemical reactions. In applying these ideas to single adsorbed molecules, specific eigenmodes of an adsorbed molecule can be excited with tunneling electrons. For the system NH_3 adsorbed on a Cu(100) surface, the chemisorption bond is sufficiently strong to provide imaging of single molecules. If the tip is positioned exactly above a single ammonia molecule, ramping of the bias voltage induces the cleavage of the Cu-NH_3 bond if certain threshold voltages are exceeded. A subsequent examination of the related area revealed two possible processes, either translation or desorption of the target molecule. A statistical analysis of a number of such events showed that the thresholds correspond to excitations of the N-H stretch vibration or the N-H bending (umbrella) mode of the adsorbed ammonia molecule. By varying the tunneling current, it is possible to switch between the corresponding reaction pathways. At low current, excitation of the N-H stretch mode occurred exclusively as proven by observing the corresponding isotopic shift in the threshold value for deuterated ammonia.

By analyzing the reaction yield (probability of reaction per tunneling electron) as a function of tunneling current, one can determine the number of excitations necessary to induce the various processes. Three operative mechanisms were identified: a single excitation of the N-H stretch mode only induces a translation, since the binding energy of ammonia is higher than that of the vibrational quantum, while the diffusion barrier is smaller. At higher current, a double excitation of the N-H stretch leads predominantly to desorption. Excitation of the umbrella mode induces desorption in a three-step ladder-climbing process. Intermode coupling redistributes the N-H- stretch energy to the umbrella mode excitation, which results either in the translation or, if the energy is high enough, via the NH_3 inversion to desorption.

The investigation of the **initial stages of oxide formation on a Ru(0001) surface** has focused on the precursor states of oxygen. By means of various surface science technique two oxygen species prior to the onset of oxide formation were identified. In collaboration with the groups of *H. Niehus* at the Humboldt University and *M. Kiskinova* at ELETTRA, Trieste, a precursor oxygen state was identified, which corresponds to an additional oxygen incorporation up to about 0.5 MLE (monolayer equivalent). An additional species, that increased the oxygen load further by about 1.5 to 2 MLE, is directly connected with the number of defects on the surface, as shown by a controlled increase of the defect density. The preparation condition of these species required high oxygen pressure (10^{-3} to 1000 mbar) at low temperatures (350 to 600 K). Both precursor species are definitely not oxidic but are formed in thermally activated processes; both show an increased reactivity for the CO oxidation reaction. Laterally resolved XPS measurements at the ESCAMICROSCOPY beam line at ELETTRA confirm the correlation of the second oxygen species with defect structures. Moreover, a substantial change of the pre-existing defects, even of the general morphology of the surface, occurred during the oxygen exposure.

Surface- and interface-related experimental investigations make an increasingly important contribution to fundamental problems in general solid state physics, and the electronic structure of novel systems continues to attract interest also from outside the surface community. Work in the group of *Karsten Horn* has centered on **electronic structure studies of quantum wells and low-dimensional metallic systems**, and on the valence level structure of complex alloys such as the quasicrystals. These studies have been carried out by means of angle-resolved photoemission, and through scanning tunneling microscopy and spectroscopy. Low dimensional systems offer a wealth of interesting physics, and are also of interest for applications. We have investigated several **systems with one-dimensional character**: chains of barium on Si(111) surfaces, and step structures on vicinal surfaces of Cu. The Ba/Si(111) system shows a (3x1) superstructure in LEED, and based on electron counting arguments a metallic surface is expected, whereas photoemission showed a semiconducting surface. In an STM study we showed that linear chains of Ba have a local (3x2) structure, which explains the semiconducting nature of the surface. These chains exhibit random shifts in their registry normal to the chains, giving rise to a (3x1) LEED pattern which explains the apparent discrepancy between geometric and electronic structure. The electronic structure of vicinal Cu was studied by means of STM at low temperatures (4.2 K), and the results indicate a terrace-width dependent transition from predominantly one-dimensional behavior of the Cu surface state, to a 2D extended state for larger terrace widths. Work on **quantum wells** continued with studies of Mg quantum wells on Si(111), where perfect epitaxial growth was found in spite of the fact that this system exhibits a strong interface reaction. This system was also used to study the optical response of quantum well states in the region of the bulk-like and multipole plasmon energies. With the availability of low energy photons at BESSY II, we have returned to quantum well studies, using an electron analyser that permits to record momentum distribution images in a display mode, developed on our initiative by the SPECS company. This instrument is currently being augmented with a six-axis manipulator to permit the recording of complete Fermi surface maps. An interesting interplay between electronic structure and film morphology was recently found in a study of Pb/Cu(111): from the energies of quantum well states we were able to show that certain thicknesses are preferred over others when brought into thermal equilibrium by annealing. This effect is related to total energy minimisation, since the stable layers exhibit quantum well states that are further removed in energy from the Fermi level than the less stable ones.

Work on quasicrystals has progressed towards a semi-quantitative understanding of emission patterns from **quasicrystals**, in a collaboration between scientists form the Advanced Light Source (*E.Rotenberg*) and the Freie Universität Berlin (*W.Theis*). These were analysed in terms of free-electron-like states, based on the concept of quasi-Brillouin zones; here the reciprocal lattice vectors that give rise to prominent structures were identified in a semi-quantitative manner in terms of their (high-dimensional) Miller indices. Other studies have concentrated on the near-surface structure of icosahedral Al-Pd-Mn using photoelectron diffraction, and the electronic structure of *i*-Al-Pd-Mn using resonant photoemission and photoabsorption. We are currently in the process of analyzing the *d*-level dispersion and state distribution near the Fermi level in decagonal Al-Ni-Co in order to attempt a connection between the electronic structure and the unusual conductivity of quasicrystals. Work is also under way to identify possible magnetic moments in the class of MgZn-rare earth icosahedral quasicrystals.

Research of the structural properties of surface systems has been conducted in the **photoelectron diffraction (PhD)** group (*M.Polcik* and *D.P. Woodruff*) in collaboration with *C.L.A. Lamont* (University of Huddersfield, UK) by the use of photoelectron diffraction. The technique of scanned-energy mode photoelectron diffraction (PhD) offers the possibility to derive quantitative local structural information for adsorbates on well-characterised surface in both an element-specific and chemical-state-specific fashion. The Warwick-Berlin (FHI) collaboration has developed this technique into an established methodology, using a combination of direct data inversion and multiple scattering simulations to refine the detailed local structural parameters. This collaboration, based on experiments performed using BESSY, has resulted in detailed structure determinations of many atomic and molecular adsorption structures. Especially significant has been the ability to study molecular adsorbates containing C, N and O, relevant to model studies of heterogeneous catalysis.

The full potential of this technique involves exploiting the **‘chemical shifts’** in photoelectron binding energies associated with atoms of the same element in different local environments, such as the methyl and carboxyl C atoms in the acetate species (CH_3COO-), in coadsorbed fragments resulting from a surface chemical or photochemical reaction (e.g. P in coadsorbed PF_3, PF_2 and PF), or even in coadsorbed species adsorbed in locally inequivalent sites (such as CO in bridge and atop sites). This extension to chemical shift PhD (CSPhD) requires *both* high spectral resolution and high photon flux at the sample. The group are now reaping the benefit of the combination of high flux and high resolution provided by BESSY II undulators which allows us to make far more extensive use of the unique potential of the CS-PhD technique, and this is one of the primary objectives of our continuing program. In particular they have been able to resolve the problem of the adsorption geometry of methanethiolate, CH_3S-, on the unreconstructed surface of Cu(111), exploiting the inequivalence of the two N atoms of N_2 on Ni(100), and to determine the local adsorption geometry of the carbonate species, CO_3, on Ag(110).

Our experimental determination of the local geometry of CO chemisorbed on Ni(100) in atop and bridge sites, with and without coadsorbed hydrogen, shows that while changes in chemisorption bond order lead to changes in the associated bond lengths closely consistent with simple Pauling rules, large changes in the chemisorption energy have a far more modest influence on the bond length. Similar data for the weakly chemisorbed isoelectronic N_2 species on Ni(100) reinforce the view that weak chemisorption does not lead to substantial increase in bond length, contrary to prior suggestions.

In continuation of previous studies of cluster-like Ru_x particles a chalcogenide compound $RuSe_x$ was prepared via the carbonyl precursor and studied in situ by **X-ray diffraction** in the group of *Walter Vogel*. Whereas Ru_x particles are highly sensitive to oxygen, the chemical stabilization, against oxidation, of such metallic centers is obtained by the coordination to selenium atoms. Besides the very good resistance against oxidation of the chalcogenide particles, the study puts in evidence the remarkable thermal stability of these particles. Ruthenium-based catalyst cluster materials are effective cathodes for the molecular oxygen reduction and have the advantage of being very selective in the presence of methanol. Our results confirm the coexistence of Se and Ru atoms on the surface of the particles. A minority of amorphous-like ruthenium oxide is formed after exposure to oxygen at 1 bar and 320 C. In collaboration with two Indian groups we have performed structural studies by X-ray diffraction on semiconductor ZnS nanoparticles, rutile phase nanoparticles of TiO_2, and Cu and Cu_2O nanoparticles prepared by chemical roots. We took part in studies of microbially synthesized PbS and CdS nanoparticles, and silver particles prepared by extracellular synthesis of silver tolerant yeast.

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Dissertationen (Doctoral Theses)

Ch.-H. Chen: Electronic structure investigations of group III-nitride surfaces and interfaces. TU 2003.

V.S. Efstathiou: Infrared spectroscopic studies of organic molecules adsorbed on copper surfaces. University of Warwick, UK 2003.

J.T. Hoeft: Structure investigation of adsorbates on surfaces using photoelectron diffraction. University of Warwick, UK 2003.

Invited Talks of the Members of the Department of Surface Physics/Molecular Physics

Gerard Meijer

Aug 2002	17th Int. Symposium on Gas Kinetics, Essen, Germany: *Deceleration and trapping of neutral dipolar molecules*
Sep 2002	European Conference "MOLEC XIV", Istanbul, Turkey: *Deceleration and trapping of neutral dipolar molecules*
Sep 2002	Symposium "Interactions in Ultracold Gases: From Atoms to Molecules", Heidelberg, Germany: *Deceleration and trapping of neutral dipolar molecules*
Sep 2002	CCP6 Workshop on Interactions of Cold Atoms and Molecules, Durham, UK: *Deceleration and trapping of neutral dipolar molecules*
Sep 2002	Eur. Res. Conf. on Quantum Optics, Sant Feliu des Guixols, Spain: *Deceleration and trapping of neutral dipolar molecules*
Sep/Oct 2002	7th Int. Workshop on Atom Optics and Interferometry, Lunteren, The Netherlands: *Deceleration and trapping of neutral dipolar molecules*
Nov 2002	Ehrenfest Colloquium, Univ. of Leiden, Leiden, The Netherlands: *Cold Molecules*
Nov 2002	Physics Colloquium, University Mainz, Germany: *Deceleration and trapping of polar molecules*
Dec 2002	IXth Int. Meeting on Stereodynamics of Chemical Reactions, Schoorl, The Netherlands: *Deceleration and trapping of polar molecules*
Jan 2003	33rd Winter Colloq. on the Physics of Quantum Systems, Snowbird, Utah, USA: *Deceleration and trapping of polar molecules*
Jan 2003	SFB450-Meeting, Free University, Berlin, Germany: *Molecular physics studies with an infrared free electron laser*
Jan 2003	Physics Colloquium, Oxford University, Oxford, UK: *Cold Molecules*
Feb 2003	Colloq. "3ème Cycle en Chimie", Univ. Fribourg, Switzerland: *Infrared spectroscopic studies on PAH cations and on strongly bound metal clusters*
Feb 2003	Colloq. "3ème Cycle en Chimie", University Geneva, Switzerland: *Molecular physics studies with infrared free electron lasers and molecular beam decelerators*

Feb 2003	Colloq. "3ème Cycle en Chimie", University Basel, Switzerland: *Cold Molecules*
Feb 2003	Colloq. "3ème Cycle en Chimie", University Bern, Switzerland: *Deceleration and trapping of neutral polar molecules*
Feb 2003	Colloq. "3ème Cycle en Chimie", LCPM-EPFL, Lausanne, Switzerland: *Cold Molecules*
Feb 2003	Physics Colloquium, Free University Berlin, Germany: *Cold Molecules*
March 2003	Physics Colloquium, Charles University, Prague, Czech Republic: *Deceleration and trapping of neutral polar molecules*
Apr 2003	Meeting on "Manipulation of electrons, atoms and molecules", University Nottingham, UK: *Deceleration and trapping of polar molecules*
May 2003	Tulip Summer School on Modern Developments in Spectroscopy, Noordwijk, The Netherlands: *Cold Molecules*
June 2003	XXth Int. Symposium on Molecular Beams, Lisbon, Portugal: *Deceleration and trapping of polar molecules*
June 2003	XVIIIth Europ. Conf. on Molecular Energy Transfer (COMET), San Lorenzo de El Escorial, Spain: *Deceleration and trapping of polar molecules*
June 2003	Workshop: CLEO/Europe-EQEQ 2003, Munich, Germany: *Deceleration and trapping of polar molecules*
July 2003	SFB546-Meeting, Humboldt University, Berlin, Germany: *Molecular physics studies with an infrared Free Electron Laser*
July 2003	XIXth Conf. on the Dynamics of Molecular Collisions, Lake Tahoe, Calif., USA: *Deceleration and trapping of polar molecules*

Uwe Becker

Sep 2001	Synchrotron Radiation Users' Meeting, CLRL, Daresbury, UK: *New trends in atomic and molecular physics with synchrotron radiation*
Nov 2001	Workshop "Atomic and Molecular Physics at 4GLS", CLRL, Daresbury, UK *Perspectives of atomic and molecular physics at the TTF and BESSY-FEL*
Dec 2001	Workshop "Atomic Physics and X-Ray Free Electron Laser-Related Dynamics", MPI für Physik komplexer Systeme, Dresden, Germany: *Atomic and molecular physics planned at the DESY and BESSY-FEL*

Jan 2002	Seminar "Atomare Stoßphysik am MPI für Kernphysik", Heidelberg, Germany: *Atom- und Molekülphysik an Synchrotronstrahlungsquellen der 3. und 4. Generation*
Apr 2002	Seminar, FOM Institute, Amsterdam, The Netherlands: *Molecular photoionization dynamics studied by synchrotron radiation excitation*
Apr 2002	Colloquium, Hahn-Meitner-Institut, Berlin, Germany: *VUV and XUF free electron lasers: research perspectives at 4th generation light sources*
May 2002	Seminar, LCAM-Institut, Orsay, France: *Molecular photoionization dynamics studied by synchrotron radiation excitation*
June 2002	WEH-Seminar on Highly Correlated States in Molecules, Atoms and Nuclei, Bad Honnef, Germany: *Dichroism in the photoionization of atoms and molecules*
June 2002	LURE Users' Meeting: Orsay, France: *Advances in synchrotron radiation-based atomic and molecular physics*
July 2002	Workshop INFM, Rome, Italy: *Perspectives in synchrotron radiation and FEL-based atomic and molecular physics*
July 2002	Workshop "Decimo Convegno SILS", Rome, Italy: *Electron correlation and structural properties of atoms and molecules probed by VUV and soft x-ray photoionization*
Aug 2002	Physics Colloquium, Zheijang University, Hangzhou, PR China: *Research perspectives at VUV and XUV Free Electron Lasers*
Sep 2002	2nd Conf. on "Elementary Processes in Atomic Systems", Gdansk, Poland: *Photoexcvitation and photoionization spectroscopy of atoms and molecules*
Oct / Nov 2002	Workshop, HASYLAB, DESY, Hamburg, Germany: *High-resolution photoion and photoelectron spectroscopy with circularly/linearly polarized photons in the energy range 200 eV – 2500 eV*
Dec 2002	Int. Workshop on Atomic Physics, MPI für Physik komplexer Systeme, Dresden, Germany: *Coherence and scattering in photoionization*
July 2003	Int. Symposium "ISACC 2003", St. Petersburg, Russia: *Imaging delocalized electron clouds: photoionization of fullerenes in Fourier reciprocal space*
Jul/Aug 2003	Int. Symposium, Königstein, Germany: *Coherence and scattering of photo- and Auger electrons*

Bretislav Friedrich

Sep 2003	Workshop & Training School "Theoretical concepts and recent experiments on ultracold molecules", Volterra, Italy: *Cool molecular micro-beams, frigid cluster salts, molecular diffraction images, and other heart-warming exploits*

Gert von Helden

Sep 2003	226th ACS National Meeting, New York City, USA: *Infrared spectroscopy on size-selected gas-phase clusters and cluster adducts*
Oct 2003	Wilhelm und Else Heraeus Seminar "Freie und deponierte Cluster", Brand, Austria: *Infrarotspektroskopie an Clustern*

Uwe Hergenhahn

Oct 2001	3ème Cycle Interuniversitaire en Physique Atomique et Moléculaire, Université de Liège, Belgium: *Two Lectures on Fundamentals of and Current Problems in Molecular Photoionization*
Nov 2001	Seminar, AK Theoretische Chemie, Universität Heidelberg, Germany: *Altes und neues von der K-Schalen-Photoionisation kleiner Moleküle*
Apr 2002	Physics Faculty Seminar, University of Windsor, Canada: *Inner shell photionization of small molecules*
July 2002	Free University Germany: *Die Photoionisation der inneren Schalen kleiner Moleküle*
Jan 2003	SFB276-Seminar, Universität Freiburg, Germany: *Innerschalen-Photoionisation chiraler Moleküle*
Mar 2003	Hasylab-Seminar, DESY, Hamburg, Germany: *New directions in inner-shell photoionisation of molecules*
Aug 2003	Seminar, IPP, Bereich Plasmadiagnostik, Berlin, Germany: *Neue Ergebnisse zur Photoionisation kleiner Moleküle*
Sep 2003	Workshop on free, neutral clusters studied by synchrotron radiation, Sigtuna, Sweden: *Energy and charge transfer in weakly bound systems*

Karsten Horn

Oct/Nov 2001	Plenary talk, 15th Int. Vacuum Congr, 48th AVS Symposium and 8th Int. Conf. on Solid Surfaces, San Francisco, USA: *Surface preparation and electronic properties of d-AlNiCo*
May 2002	Colloquium, Donostia Int. Physics Center, University San Sebastian, Spain: *Electronic structure in low-dimensional systems and complex quasicrystalline alloys*
June 2002	Plenary talk, Spring Meeting of the European Materials Research Society, Strasbourg, France: *Electronic structure of quasicrystals*
June 2002	Seminar, Physikal. Institut, University Karlsruhe, Germany: *Experimente zur Charakterisierung von elektronischen Bändern in dünnen Schichten und Festkörpern*
Sep 2002	Plenary talk, 12. Arbeitstagung Angewandte Oberflächenanalytik, Kaiserslautern, Germany *Elektronische Strukturuntersuchungen mittels Photoemission: von dünnen Schichten bis zu komplexen Legierungen*
Oct 2002	Seminar, Advanced Light Source, LBL, Berkeley, California, USA: *Influence of collective excitations on valence level photoemission*
Nov 2002	Colloquium, Dept. of Physics, University Delft, The Netherlands: *Electronic structure investigations by photoemission: from metallic quantum wells to complex alloys*
Jun/Jul 2003	Plenary talk, 9th Int. Conference on Electron Spectroscopy and Structure (ICESS9), Uppsala, Sweden: *Electronic structure of quasicrystals*
Sep 2003	Plenary talk, 9th Int. Conf. on the Formation of Semiconductor Interfaces (ICFSI-9), Madrid, Spain *Quantum well states in metals on semiconductors*

Jochen Küpper

Mar 2003	Spring Meeting of the German Phys. Society (DPG), Hannover, Germany: *Bestimmung der geometrischen Strukturen elektronisch angeregter Aromaten*
Apr 2003	Atoms Day, FOM Institute, Amsterdam, The Netherlands: *Cold Molecules*

Oliver Kugeler

Dec 2002	Seminar "Science on the Fly", BESSY Users' Meeting, Berlin, Germany: *Photoelektron-Auger-Elektron Koinzidenzmessungen der N 1s Photoionisation von* N_2O

Simon Marburger

Sep 2003	Workshop on free, neutral clusters studied by synchrotron radiation, Sigtuna, Sweden: *Interatomic Coulombic decay studied in Ne clusters*

Georg Prümper

Jun/Jul 2003	9th Int. Conf. on Electronic Spectroscopy and Structure (ICESS9), Uppsala, Sweden: *A new apparatus for high resolution electron-ion coincidence spectroscopy*

Daniel Rolles

May 2003	Seminar "Science on the Fly": BESSY Users' Meeting, Berlin, Germany: *Photoelectron diffraction in free molecules – coherent vs. incoherent emission*

Jens Viefhaus

June 2002	Berliner Physikalisches Colloquium, Berlin, Germany: *Dichroismus in der Photoionisation – vom Ursprung des Lebens bis zum 3-Körper-Coulomb-Problem*
Jul/Aug 2003	Int. Symposium, Königstein, Germany: *Double Auger decay*
Jun/Jul 2003	9th Int. Conf. on Electronic Spectroscopy and Structure (ICESS9), Uppsala, Sweden: *Double photo- and Auger electron emission studied by electron-electron coincidence spectroscopy*

Walter Vogel

May 2003	2nd Workshop on Nanomaterials, Toulouse, France: *X-ray diffraction from clusters*

D. P. Woodruff

Feb 2002	Seminar, Chemistry Department, University Nottingham, UK: *Surface structural studies of molecular adsorbates: chemically significant bondlength changes at surfaces*
Juy 2002	INFM Workshop on Fisica Atomica e Moleculare con Luce di Sincrotrone,

	Rome, Italy: *Non-dipole asymmetry parameters in photoemission: consequences for, and measurements by, x-ray standing waves in solids*
Aug 2002	EPSRC Surface Science Summer School, University of Warwick, UK: *Surface structure determination: adsorbates on metals*
Aug 2002	XIX Congress and General Assembly of the Int. Union of Crystallographies, Geneva, Switzerland*:* *Photoemission-monitored normal incidence x-ray standing waves: structural studies of low-Z molecular adsorbates with chemical-state specificity*
Aug 2002	ICMSC Conf. on Applied Surface Modelling: Experiment, Theory and Simulations, Cleveland, Ohio, USA: *Some structural issues in surface alloys and alloy surfaces: rumpling, stacking faults and disorder*
Sep 2002	2nd Int. Workshop on Ion Beam Techniques for the Analysis of Composition and Structure with Atomic Layer Resulution, Kyongju, South Korea*:* *Structural studies at metallic surfaces and interfaces using MEIS*

Department of Physical Chemistry Director: G. Ertl

Staff Scientists:	Dr. M. Eiswirth	
	Dr. T. Hertel	
	Prof. Dr. J.F. Holzwarth	(Habilitation FU)
	Prof. Dr. K. Jacobi	(Habilitation TU)
	Prof. Dr. A.S. Mikhailov	
	Dr. B. Pettinger	
	Prof. Dr. H.H. Rotermund	(Habilitation TU)
	Dr. W. Schulze	
	Dr. R. Schuster	(Habilitation FU)
	Dr. M.-S. Zei	

Scientists on temporary positions from external funds:

Dr. Ch. Frischkorn
Dr. U.A. Paulus
Dr. O. Rudzick
Dr. W.D. Schöne
Dr. Y. Wang
Dr. J. Wolff

Visiting scientists (> 6 months):

Dr. S. Azouani-Couderc
Dr. R. Dudek
Dr. M. T. Giacomini
Dr. S.L. Horswell
Dr. H. Kori
Dr. A. Kudelski
Prof. A.C. Luntz
Dr. B. Ren
Dr. T. Suzuki
Dr. M.C. Xu

Graduate students: 15

Technicians: 9

Recent Developments in the Department of Physical Chemistry

Director: G. Ertl

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

- Dr. K. Doblhofer retired.
- Dr. W. Ekardt deceased.
- Dr. T. Hertel accepted an offer as Associated Professor at the Vanderbilt University, Nashville (USA) and will leave the institute in 2004.
- Prof. K. Jacobi retired officially, but continues part-time until October 2004.
- Dr. K. Krischer became Professor of Physics (C3) at the Technische Universität München.
- Dr. H. Over became Professor of Physical Chemistry (C3) at the University of Giessen.
- Dr. H.H. Rotermund became Adjunct Professor of Physics at the Dalhousie University, Halifax (Canada).
- Dr. J. Wintterlin became Professor of Physical Chemistry (C3) at the University of München.

Apart from the director of the department, several other staff scientists (J.F. Holzwarth, W. Schulze, M.S. Zei) will retire prior to the next meeting of the Fachbeirat in 2005.

Despite this ongoing internal reorganization research in the department continues to focus on the dynamics and reactivity of solid surfaces in contact with gaseous and liquid phases, including carbon nanotubes, metal clusters, colloidal systems, electrochemical microstructuring, and in particular phenomena of nonlinear dynamics in complex systems.

As in previous years, members of the department were actively involved in the following DFG-Sonderforschungsbereiche:

Sfb 296: Wachstumskorrelierte Eigenschaften niederdimensionaler Halbleiterstrukturen
Sfb 450: Analyse und Steuerung ultraschneller photoinduzierter Reaktionen
Sfb 555: Komplexe nichtlineare Prozesse.

Apart from that there exist worldwide cooperations (in part associated with external fundings) with numerous other groups.

1. Electronic excitations and ultrafast dynamics at surfaces

Electronic excitations are the key for elementary processes in surface reactions as well as for a number of physical properties. While their lifetimes in confined systems (molecules) may become long enough to enable optical decay, this channel will be efficiently quenched as soon as the electronic structure becomes delocalized (i.e. band-like). The transition between molecular and metallic state with increasing number of atoms becomes evident in studies on the agglomeration of small metal clusters in noble gas matrices. As found previously, aggregation of Ag_n (or Cu) clusters with $3 \leq n \leq 20$ may be associated with the emission of visible light which was identified with the optical decay of electronically excited monomers, dimers or trimers. The yield of chemiluminescence was investigated as a function of deposition rates of the metal and the noble gas, as well as the temperature of the matrix, and rather complex correlations were found. There are indications that this effect might be quite universal as suggested by recent observations with Mg.

Direct determination of the lifetimes of electronic excitations may be performed by time-resolved photoemission employing femtosecond laser techniques. In this context, previous studies with graphite and single-wall carbon nanotubes (SWNT) were extended to MgB_2, a recently discovered strongly coupled phonon-mediated superconductor. These experiments enabled determination of the electron-phonon mass enhancement parameter λ, which for MgB_2 was found to be more than three orders of magnitude larger than that for graphite or metallic SWNT and about one order of magnitude larger than in copper. Similarly, the dynamics of photoexcited holes in the surface state of Ag(111) and their coupling to phonons was investigated.

Rapid heating of the electron gas at a metal surface by absorption of an intense femtosecond laser pulse in the infrared may create a short-lived nonequilibrium situation initiating non-adiabatic surface reactions. The associative desorption of hydrogen from a Ru(0001) surface was investigated in this way. The molecules coming off the surface are ‘hot’ (i.e. > 1000 K) in all degrees of freedom, and their formation was identified as due to non-adiabatic coupling of the nuclear motion to transiently excited hot substrate electrons. A pronounced isotope effect in the yields of desorbing H_2 and D_2 is caused by different coupling times, which control the energy flow and give rise to a novel dynamic promoter effect.

If a STM tip of Ag or Au is approached to a surface, irradiation with visible light causes the excitation of localized surface plasmons within the gap of about 1 nm. For tip radii below 100 nm the enhanced electromagnetic field is confined to a surface area of less than 15 nm enabling localized Raman spectroscopy (tip enhanced Raman spectroscopy

= TERS) with promising avenues towards single molecule spectroscopy. So far, this effect has been studied for dyes and CN^- ions adsorbed on Au (and Ag, Pt) films. In the STM mode of operation tunneling electrons may in turn excite optical resonances, and their spectral investigations reflect mode structure of the localized surface plasmons, depending on the local geometry (Frischkorn, Hertel, Pettinger, Schulze, Wolf).

2. Structure and reactivity of surfaces

Carbon monoxide oxidation on ruthenium served for long times as a striking example for the existence of a ‘pressure gap’ in heterogeneous catalysis: While Ru under UHV conditions is practically inert, it exhibits high catalytic activity if operated under atmospheric pressure conditions. The puzzle was solved by the discovery that a Ru(0001) surface transforms under high oxygen exposures (and at elevated temperatures) into the (110) surface of RuO_2, whose structure and reactivity have in the meantime also been studied in detail by members of the Theory department. This transformation as well as the surface structures formed at high pressures may now be studied *in situ* by a newly constructed high pressure scanning tunneling microscope (STM), which may be operated at pressures up to 1 bar. After completion this instrument was successfully tested with the RuO_2(110) system and will soon be transferred to J. Wintterlin’s laboratory at the University of München.

The reactivity of the RuO_2(110) surface is studied, in addition, in detail particularly by vibrational spectroscopy (HRELS) in conjunction with mass spectroscopy. The role of the two oxygen surface species (O-cus and O-bridge) could be identified, and the kinetics of CO oxidation was analyzed and compared with high-pressure data. The interaction with H_2 gives rise to a rich scenario of surface coordination chemistry, which was explored in collaboration with members of the Theory department. Current experiments concern interactions with NO, C_2H_4, NH_3, etc.

Another technique for vibrational spectroscopy of adsorbates is offered by broadband sum-frequency spectroscopy (SFG), which, by applying femtosecond laser pulses, offers the additional possibility of extreme temporal resolution. The structure of adsorbed water was one of the topics studied in this way.

Studies on the adsorption of a variety of molecules on single-wall nanotubes in comparison with the properties of graphite surfaces provide information on fundamental questions concerning adsorbate–surface interactions and the surface properties of these systems.

Structures formed at electrode surfaces in contact with an electrolyte are not directly accessible to the standard surface science techniques. For this purpose an apparatus is used in which an electrochemical cell is attached through a transfer system to an UHV system containing facilities for LEED, RHEED and Auger electron spectroscopy. Current studies concern the characterization of modified Pt-Ru electrodes in connection with fuel cell reactions.

A quite different activity concentrates on the investigation of the aggregation processes of surface active compounds (surfactants) in aqueous solution. Small-angle neutron scattering, microcalorimetry, and spectroscopic techniques are the tools providing information on the molecular level. Stopped-flow and laser temperature jump methods yield kinetic data from nanoseconds to seconds (Hertel, Holzwarth, Jacobi, Wintterlin, Wolf, Zei).

3. Nonlinear dynamics and complex surface reactions

Activities in this area are embedded to a large extent in the Sonderforschungsbereich 555 “Komplexe nichtlineare Prozesse” and are characterized by a strong interplay between experiment and theory. Processes of spatio-temporal self-organization are studied in different areas, from single enzyme molecules and nanoscale structures to macroscopic concentration patterns in catalytic and electrochemical surface reactions.

CO oxidation on a Pt(110) surface has been further explored as a prototype system for complex surface reactions. While most observed features can be successfully modeled by deterministic equations based on experimental observations, certain features (such as the so-called ‘raindrop’ patterns) are likely to be stochastic in nature. A rescalable stochastic model was developed and successfully analyzed. Further attention was concentrated on the analysis of pacemaker structures. These are not only created by inhomogeneities of the oscillatory medium but may, under certain conditions, also develop spontaneously in uniform systems.

The control of spatiotemporal chaos by novel global feedback techniques leads to a wealth of new (periodic) structures and may be considered as a general strategy for pattern stabilization in complex systems. In experiments with an ultrathin Pt single crystal foil thermal effects come additionally into play. Periodic deformations as a consequence of the interplay between chemical reaction, evolution of heat and mechanical deformation could be observed and modeled. *Local* variation of the surface reactivity can be achieved by directing a laser spot onto a certain small area of the surface where thereby the temperature is increased and whose position can be controlled from outside.

Based on the analysis of experimental data provided by fluorescence correlation spectroscopy, kinetic models for single enzyme molecules as cyclic protein machines have been developed, and spontaneous emergence of collective synchronous activity in molecular networks formed by such interacting protein machines could be identified.

Theoretical studies on self-organization on nanoscale were performed for systems characterized by an interplay between chemical reactions and phase transitions. Two-component phase-separating reactive Langmuir monolayers exhibit the spontaneous development of traveling waves. With catalytic reactions involving adsorbate-driven surface reconstruction (such as CO oxidation on Pt(110)), on the other hand, localized reactive non-equilibrium nanostructures may emerge.

For three-dimensional chemical excitable media it was shown that the Winfree turbulence of scroll waves can be tamed – either induced or suppressed – by applying an appropriate weak periodic forcing. Since similar processes are considered to be responsible for the development of fibrillation in the cardiac tissue, the results of this study caused considerable interdisciplinary interest.

The theoretical understanding of spatio-temporal self-organization in electrode reactions has made significant progress in recent years, essentially through application of potential theory and derivation of reaction-migration equations describing the interplay between chemical reactions and electrical effects. Recently, particular emphasis was put on the study of edge effects at insulator–conductor interfaces. Edges may play an important role for the dynamics, in particular since the spatial (migrational) coupling diverges at the edges. Experiments were performed with formic acid oxidation at ring and ribbon electrodes, which clearly demonstrate the effect of geometry on pattern formation.

In another set of experiments small parts of a Pt ring electrode were covered with insulating layers. For conditions under which an unperturbed ring exhibits a pulse wave propagating with constant velocity, such pulses were still created, but were considerably accelerated near an insulating section across which they then jumped. This phenomenon is reminiscent of the saltatory conduction in myelinated axons (where the excitation jumps from one node of Ranvier to the next) and can readily be rationalized by the increase of coupling near the edges (Eiswirth, Mikhailov, Rotermund).

4. Microstructuring of surfaces

Deposition of material onto a surface usually leads to the formation of an overlayer via nucleation and growth. This strategy was applied to study the formation of InAs quantum dots (QD) on differently oriented GaAs single crystal surfaces by combining molecular beam epitaxy (MBE) with *in situ* scanning tunneling microscopy. The previous surprising finding that on GaAs(001) the InAs QD are mostly terminated by the open (137) surface and not by expected low-index (110) or (111) planes was further confirmed. From continuing studies with a large series of other GaAs surfaces several general conclusions could be drawn:

- The QD are fairly flat. This is achieved by terminating the QD with high-index surfaces if grown on low-index substrates and vice versa. The crucial aspect is the high stability of the high-index (137) and (2511) surfaces discovered in this group.
- The shape of the QD reflects the symmetry of the substrate.
- Nucleation is governed by kinetics while formation of the shape is near to thermodynamic equilibrium.
- The size distribution is bimodal: A small number of large QD presumably incorporate dislocations and are optically dead, while growth of the majority is limited by strain leading to quite uniform size.

If the (nominal) composition of a binary system is far inside the miscibility gap, another mechanism for phase separation will be operating if the change of the state occurs rapidly enough to suppress nucleation growth through surface diffusion. This spinodal decomposition has so far been observed by quenching binary alloys or polymeric melts, but was experimentally not accessible for epitaxial metallic monolayers. This demanding task could be solved with an electrochemical system for which very fast change of the state could be achieved.

By the application of a single microsecond voltage pulse to the tip of a STM, scanning a Au(111) surface, about half a monolayer of Au atoms was randomly removed from the topmost surface layers. Due to the fast change of the thermodynamic state of the surface system within microseconds, the remaining Au atoms ordered into labyrinthine island patterns, indicative of spinodal decay of an unstable two-dimensional adatom gas. This morphology contrasts the compact island patterns usually obtained by nucleation and growth processes, e.g., upon metal on metal deposition in UHV. The characteristic length scale of the labyrinthine patterns could be quantitatively explained within the theoretical framework of Cahn and Hilliard. Additionally the self-similar coarsening of the island structures was *in situ* followed by STM.

Ultrafast charging of an electrochemical double layer is also the principle underlying development of a technique for micromachining of metal and semiconductor surfaces, which was further improved and patented. In particular, the electrochemical behavior of passivating materials such as stainless steel upon application of short voltage pulses was studied in order to get further insights into the differences between conventional electrochemical machining methods and the novel technique. In addition, complex electrochemical reactions such as the electropolymerization of polypyrrol could be successfully localized by application of short voltage pulses. Further technical improvement could be achieved by shortening the voltage pulses down to 300 ps duration leading to spatial resolution of better than 50 nm. First attempts to parallelize the technique were undertaken: In collaboration with the University of Virginia, complex structures with elements as small as 100 nm could be imprinted onto a surface in a single step (Jacobi, Schuster).

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Hildebrand, M., M. Ipsen, A.S. Mikhailov and G. Ertl: Localized nonequilibrium nanostructures in surface chemical reactions. New J. Phys. **5**, 61.1–61.28 (2003).

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Kim, S.H., U.A. Paulus, Y. Wang, J. Wintterlin, K. Jacobi and G. Ertl: Interaction of CO with the stoichiometric RuO_2(110) surface. J. Chem. Phys. (resubmitted).

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Krischer, K.: Nonlinear dynamics in electrochemical systems. Chapter 2. In: Advances in Electrochemical Science and Engineering. Vol. 8. (Eds.) R.C. Alkire, D.M. Kolb. Wiley-VCH, Weinheim 2003, 89-208. ISBN 3-527-30211-5.

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Electrochim. Acta. (in print).

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Paulus, U.A., Y. Wang, H.P. Bonzel and K. Jacobi: Adsorption of ethylene on stoichiometric RuO_2(110). Surf. Sci., for ECOSS Prague (submitted).

Paulus, U.A., Y. Wang, K. Jacobi and G. Ertl: CO adsorption on the reduced RuO_2(110) surface. Surf. Sci. (submitted).

Pettinger, B., C. Bilger and J. Lipkowski: SHG studies on halide adsorption at Au(111) electrodes. In: Solid–Liquid Interfaces: Macroscopic Phenomena – Microscopic Understanding. (Eds.) K.Wandelt, S. Thurgate. Topics in Applied Physics, Vol. 85. Springer, Berlin-Heidelberg 2003, 223-240. ISBN 3-540-42583-7.

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Schulze, W., I. Rabin and G. Ertl: Formation of light-emitting Ag_2 and Ag_3 species in the course of condensation of Ag atoms with Ar. ChemPhysChem. (submitted).

Schuster, R. and G. Ertl: Electrochemical nanostructuring of surfaces. Chapter 6.
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Temko, Y., T. Suzuki, M.C. Xu and K. Jacobi: InAs quantum dots on the GaAs($\bar{5}\ \bar{2}\ \bar{1}\bar{1}$)B surface. Appl. Phys. Lett. (submitted).

Thron, D., M. Binetti, M. Kock, M. Giacomini and R. Schuster: Electrochemical microstructuring with scanning probes. In: Proceedings of the Workshop on SPM, Cracow 2003. (in print).

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Appl. Phys. Lett. **82**, 3327-3329 (2003).

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Ulbricht, H., G. Moos and T. Hertel: Interaction of molecular oxygen with single-wall carbon nanotube bundles and graphite. Surf. Sci. **532-535**, 852-856 (2003).

Ulbricht, H., G. Moos and T. Hertel: Wetting of single-wall carbon nanotube ropes and graphite. In: Proc. of Int. Winterschool on Electronic Properties of Novel Materials. (submitted).

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Wang, Y., K. Jacobi and G. Ertl: Interaction of NO with the stoichiometric RuO_2(110) surface. J. Phys. Chem. B (submitted).

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Angew. Chem. Int. Ed. **42**, 2850-2853 (2003).

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Wolff, J., A.G. Papathanasiou, H.H. Rotermund, G. Ertl, X. Li and I.G. Kevrekidis: Gentle dragging of reaction waves. Phys. Rev. Lett. **90**, 018302(4) (2003).

Wolff, J., A.G. Papathanasiou, H.H. Rotermund, G. Ertl, X. Li and I.G. Kevrekidis: Local manipulation of catalytic surface reactivity. J. Catal. **216**, 246-256 (2003).

Wolff, J. and H.H. Rotermund: Local periodic forcing of CO oxidation on a Pt(110) surface. New J. Phys. **5**, 60.1–60.12 (2003).

Xia, X.H., L.C. Nagle and R. Schuster: Assembly of Au-cluster superstructures by steering the phase transitions of electrochemical adsorbate structures. In: Solid–Liquid

Interfaces: Macroscopic Phenomena – Microscopic Understanding. (Eds.) K. Wandelt, S. Thurgate. Topics in Applied Physics, Vol. 85. Springer, Berlin-Heidelberg 2003, 323-331. ISBN 3-540-42583-7.

Zacharia, R., H. Ulbricht and T. Hertel: The interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons. Phys. Rev. B (submitted).

Zanette, D.H. and A.S. Mikhailov: Dynamical clustering in oscillator ensembles with time-dependent interactions. Phys. Rev. Lett. (submitted).

Zei, M.S., T. Lei and G. Ertl: Spontaneous and electrodeposition of Pt on Ru(0001). Z. Phys. Chem. **217**, 447-458 (2003).

Dissertationen

Janakiraman, Umamaheswari: Analysis of electrogenerated chemiluminescence of PPV type conducting polymers. HU Berlin 2003.

Kim, Sang Hoon: Study of Reaction Mechanisms on Single Crystal Surfaces with Scanning Tunneling Microscopy: Atomically resolved CO oxidation on Pd(111) and RuO_2(110). HU Berlin 2003.

Li, Yong-Jun: Adsorption processes and spatiotemporal pattern formation during electrochemical reactions on Au(111) film electrodes – A surface plasmon resonance study. FU Berlin 2003.

Moos, Gunnar: Zur Dynamik niederenergetischer Elektronen in metallischen Festkörpern. FB Physik, FU Berlin 2003.

Picardi, Gennaro: Raman spectroscopy and light emission at metal films enhanced by the optical near-field of a scanning tunneling tip. FU Berlin 2003.

Plenge, Florian: Theory of electrochemical pattern formation under global coupling. TU Berlin 2003.

Rößler, Mario W.: Rastertunnelmikroskopie bei hohen Drücken – Ein Ansatz zur Überbrückung des *pressure gaps* in der Katalyseforschung. FU Berlin 2003.

Stich, Michael: Target patterns and pacemakers in reaction-diffusion systems. TU Berlin 2003.

Department of Physical Chemistry

Invited lectures at conferences

M. Eiswirth

“Thermodynamic efficiency of periodic processes”.
Winterseminar Komplexe Systeme, Zeinisjoch, Austria, Feb. 2002.

“Edge effects in electrochemical systems”.
2nd Int. Symposium on Engineering of Chemical Complexity, Berlin, June 2002.

“Stochastic effects in the CO oxidation on Pt”.
XXII Dynamics Days Europe, Heidelberg, July 2002.

“Nucleation and propagation failure in CO oxidation on Pt”.
7. Herbstseminar Strukturbildung, Salzwedel, Sep. 2002.

“Diffusion-induced instabilities”.
Symposium Stoichiometric Network Analysis, Berlin, Dec. 2002.

“Pulse propagation in an electrochemical sysem”.
Workshop Complex Nonlinear Processes, Berlin, Sep. 2003.

G. Ertl

“Reactions at surfaces: From atoms to complexity“.
37th Winter-Seminar, Klosters, Switzerland, Jan. 2002.

“Dynamics of surface reactions”.
Spiers Memorial Lecture, Faraday Discussion 121, Berlin, April 2002.

“Reactions at surfaces: From elementary processes to complexity”.
NANO-7/ECOSS-21 Conference, Malmoe, Sweden, June 2002.

“Catalysis on the atomic scale”.
Perspectives and Prospects in Chemistry. The Royal Society of Chemistry,
London, UK, Sep. 2002.

“Dynamics of reactions at surfaces”.
Hayama Conference, Japan, Sep. 2002.

“Electrochemical nanostructuring”.
84th Int. Bunsen Colloquium, Ulm, Germany, Nov. 2002.

"Elementary processes in the surface chemistry of Pt and Ru catalysts".
Euchem Conference on Environmetal Catalysis, Hindas, Sweden, Nov. 2002.

"Dynamics of reactions at surfaces".
Royal Society of Chemistry, Theoretical Chemistry Group, London, UK, Dec. 2002.

"Controlling surface reactions".
Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, USA, Feb. 2003.

"Reactions at surfaces: From atoms to complexity".
83rd Meeting of the Chemical Society of Japan, Tokyo, March 2003.

"Dynamics of reactions at surfaces".
Femtochemistry VI, Paris, France, July 2003.

"Interface reactions associated with fast charge transfer".
R.A. Marcus Symposium, München, July 2003.

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

C. Frischkorn

"Promoting surface reactions by spectators in excited adsorbate layers".
Workshop on Ultrafast Photoinduced Reactions, Berlin, March 2003.

T. Hertel

"Carbon Nanotubes: Promise and Challenge".
Symposium of DFG SFB 288, Marienthal, Germany, Feb. 2002.

"Ultrafast charge-carrier dynamics in carbon nanotubes".
Workshop on Energy and Information Transfer in Biological Systems,
Catania, Italy, Sep. 2002.

"Gas-surface interactions and charge-carrier dynamics in single-wall carbon nanotubes".
American Physical Society, Austin, USA, March 2003.

"Carbon nanotubes: Electronic structure, charge carrier dynamics and adsorbate kinetics".
Symposium on Physical Chemistry, TU München, May 2003.

“Gas-surface interactions and charge-carrier dynamics in single-wall carbon nanotubes”.
SPIE Meeting on Nanotechnology, Gran Canaria, Spain, May 2003.

“Electron-phonon interactions probed by time-resolved photoemission”.
Symposium on ultrafast dynamics, Telluride, USA, June 2003.

J.F. Holzwarth

“Aggregation thermodynamics and thermodynamics of functional block-copolymers in aqueous solutions influenced by surfactants”.
Int. Discussion Meeting on Surfactants, Massa Marittima, Italy, April 2002.

“Aggregation thermodynamics and thermodynamics of functional block-copolymers in aqueous solutions influenced by surfactants”.
International Meeting on: Surfactants in Solution, Barcelona, Spain, June 2002.

“Synergistic effects caused by the binding of surfactants to polymers”.
“Laser temperature jump experiments with nanometer space resolution using rhodamine 101 anti-stokes fluorescence”.
FRIS 2002, Discussion Meeting of the Royal Society of Chemistry, Istanbul, Turkey, Sep. 2002.

“Laser temperature jump experiments with nanometer space resolution”.
Spring Meeting of the American Chemical Society, New Orleans, USA, March 2003.

“Laser temperature jump experiments with nanometer space resolution using rhodamine 101 anti-stokes fluorescence as a probe for dynamics in proteins and surfactant aggregates”. Royal Society of Chemistry, London, UK, April 2003.

“Laser temperature jump experiments with nanometer space resolution using rhodamine 101 anti-stokes fluorescence from nanoseconds to milliseconds for precise measurements of temperature changes in liquid micro-environments”.
Symp. on Modern Lasers in Solution Dynamics, Didcot, UK, May 2003.

“Interaction of surfactin with model membranes and micelles”.
FRIS 2003, Discussion Meeting of the Royal Society of Chemistry.
Halle, Germany, Aug. 2003.

“Surfactant polymer interactions investigated by electromotive force and calorimetry experiments”.
Int. Meeting on Surfactant Polymer Interactions, Wrexham, UK, Sep. 2003.

“Surfactant polymer interactions investigated by electromotive force light scattering and calorimetry methods”.
Chinese Academy of Sciences, Beijing, China, 2003.

K. Jacobi

“Atomic structure of self-organized quantum dots”.
LEOS 2001, San Diego, USA, Nov. 2001.

“Atomically resolved shape of InAs quantum dots”.
ISE 2002, Toulouse, France, Jan. 2002.

“Atomic structure of InAs quantum dots on GaAs”.
SSP-9, Trest, Tschechien, Sep. 2002.

“Atomic structure of InAs quantum dots on GaAs substrates”.
MRS, Fall Meeting, Boston, USA, Dec. 2002.

K. Krischer

“From coherent patterns to turbulence: An experimental and theoretical study of spatiotemporal phenomena during the oscillatory oxidation of H_2 on Pt electrodes”.
2nd Int. Symp. on Engineering of Chemical Complexity, Berlin, June 2002.

“Nonlinear phenomena in electrochemical systems”.
First Italian German Workshop of Electrochemistry, Neu-Ulm, Germany, June 2002.

“Spontaneous formation of reactivity patterns during the oxidation of H_2 on Pt: From electrochemical turbulence to highly ordered cluster patterns”.
2nd Gerischer Symposium, Berlin, June 2002.

“Spatiotemporal patterns during bulk CO electrooxidation on Pt”.
ISE, 53rd Annual Meeting, Düsseldorf, Sep. 2002.

“Self-organized patterns during bulk CO electrooxidation on Pt”.
225th ACS National Meeting, New Orleans, USA, March 2003.

A.S. Mikhailov

“Nonequilibrium pattern formation in reactive two-component Langmuir monolayers”.
2nd Int. Symp. on Engineering of Chemical Complexity, Berlin, June 2002.

“Nonlinear science and molecular biology”.
Workshop on Spatiotemporal Chaos, Trieste, Italy, July 2002.

“Coherent collective dynamics of protein machines”.
XXII Dynamics Days Europe, Heidelberg, July 2002.

“Coherent collective dynamics of protein machines”.
Int. Workshop on Protein Dynamics, Florence, Italy, Feb. 2003.

“Nonequilibrium nanostructures in reactive soft matter”.
Symposium on Nonequilibrium Nanostructures, Tokyo, Japan, March 2003.

“Taming Winfree turbulence of scroll waves in excitable media”.
Workshop on Trends in Pattern Formation, Dresden, Sep. 2003.

B. Pettinger

“Tip-enhanced Raman spectroscopy at smooth metal films”.
69. AGEF Seminar, Jülich, Jan. 2002.

“Tip-enhanced Raman spectroscopy on adsorbates at smooth metal films”.
Spring School on Single Molecules in Physics, Chemistry and Biology,
Hofgeismar, April 2002.

“STM-tip enhanced Raman spectroscopy on adsorbates at smooth metal films”.
XVIIIth Int. Conf. on Raman Spectroscopy – ICORS 2002, Budapest, Hungary, Aug. 2002.

“Tip-enhanced Raman spectroscopy and STM-induced light emission from Au surfaces”.
7th Int. Symp. on Reactivity of Metastable Materials, Warsaw, Poland, Aug. 2003.

H.H. Rotermund

“Spatio-temporal addressing of surface activity”.
2nd Int. Symp. on Engineering of Chemical Complexity, Berlin, June 2002.

“Real time imaging and manipulating pattern formation during catalytic surface reactions”. Gordon Conference for Oscillations and Dynamic Instabilities in Chemical Systems, Oxford, UK, July 2002.

“Control of catalytic surface reactions by local laser heating”.
Workshop on Nonlinear Phenomena in Chemistry”, Budapest, Hungary, Jan. 2003.

“Putting surface reactions under a magnifying glass:
Real time imaging of catalytic reactions”.
Conference on Surfaces, Les Treilles, France, July 2003.

“Spatio-temporal addressing of surface activity”.
Symposium of the DFG SFB 555”, Berlin, Sep. 2003.

"Control of catalytic surface reactions by local laser heating".
Workshop on Reaction, Diffusion and Transport in Inhomogeneous and Stochastic Media, Leipzig, Oct. 2003.

R. Schuster

"Electrochemical microstructuring".
Gordon Research Conference on Electrodeposition, New London, USA, Aug. 2002.

"Electrochemical microstructuring".
Workshop on SPM, Krakow, Poland, Feb. 2003.

J. Wintterlin

"Spatio-temporal pattern formation viewed on the atomic scale".
VIIth European Conf. on Surface Crystallography and Dynamics,
Leiden, The Netherlands, Aug. 2001.

"Dynamic spatial patterns in a surface reaction – the microscopic and mesoscopic scales".
IUVSTA 15th Int. Vacuum Congress, San Francisco, USA, Oct. 2001.

"Non-uniformities and spatial patterns in catalytic reactions".
Yamada Conf. LVII, Tsukuba, Japan, Nov. 2001.

"Scanning tunneling microscopy of atomic processes in propagating reaction fronts".
2nd Int. Symp. on Engineering of Chemical Complexity, Berlin, June 2002.

Invited seminars and colloquia (selection)

G. Ertl

K. University of Leuven, Belgium, Jan. 2002

Phys. Kolloquium, München, Jan. 2002

University of Stockholm, Sweden, Max 2002

Universität Magdeburg, GDCh, June 2002

Universität Bochum, GDCh, Oct. 2002

Princeton University, FMC Lectures, Nov. 2002

Mülheim/Ruhr, Karl Ziegler Lecture, Nov. 2002

Universität Giessen, GDCh., Jan. 2003

Merseburg-Leuna, GDCh, April 2003

Chalmers University of Technology, Gothenburg, Sweden, May 2003

Universität Freiburg, GDCh, June 2003

Universität Dortmund, GDCh, June 2003

Universität Stuttgart, GDCh, July 2003

Universität Leipzig, Ostwald Symp., Sep. 2003

Leopoldina, Halle, Sep. 2003

University of Aarhus, Sep. 2003

Siemens Stiftung, München, Oct. 2003

Berlin-Brandenburgische Akademie, Berlin, Nov. 2003

Nordrhein-Westfälische Akademie, Düsseldorf, Nov. 2003.

T. Hertel

Trinity College, Dublin, March 2002

TU München, Garching, June 2002

IBM Yorktown Heights, Oct. 2002

Columbia University, New York, Oct. 2002

Penn State University, University Park, Oct. 2002

University of Pennsylvania, Philadelphia, Oct. 2002

Universität Giessen, Dec. 2002

Vanderbilt University, Nashville, April 2003

Universität Marburg, May 2003

Universität Würzburg, July 2003

Brookhaven National Laboratories, Upton, July 2003

EPFL Lausanne, Sep. 2003

MPI für Festkörperforschung, Stuttgart, Nov. 2003.

J.F. Holzwarth

University of Santiago de Compostela, May 2002

University of Vigo, Spain, June 2002.

K. Jacobi

Kansas State University, Manhattan, Dec. 2001

Brown University, Providence, Dec. 2002

TU Berlin, Feb. 2003

TU Ilmenau, May 2003

FU Berlin, June 2003.

K. Krischer

Luis-Pasteur University, Strasbourg, France, May 2002

University of Bologna, Bologna, Italy, May 2002

University of Modena, Modena, Italy, May 2002

Kolloquium Münchner Physiker, München, Dec. 2002

Paul- Scherrer-Institut, Villingen, Switzerland, Jan. 2003

Universität Bremen, Feb. 2003

Universität Magdeburg, DPG, June 2003

Technische Universität Clausthal, GDCh, Clausthal-Zellerfeld, July 2003.

A.S. Mikhailov

University of Kyoto, Japan, April 2002

University of Tokyo, Japan, April 2002

Nanotechnology Res. Inst., Tsukuba, Japan, April 2002

University of Hiroshima, April 2002

Universität Hannover, May 2002

Université Libre de Bruxelles, Belgium, Oct. 2002

MPI f. Mathematik in Naturwissenschaften, Leipzig, Nov. 2002

FU Berlin, Dec. 2002

University of Tokyo, Japan, March 2003

University of Sapporo, Japan, March 2003

Nanotechnology Res. Inst., Tsukuba, Japan, March 2003.

R. Schuster

University of Virginia, Charlottesville, Dec. 2001

Universität Essen, GDCh, Dec. 2001

Universität Giessen, Oct. 2002

Universität Darmstadt, Dec. 2002

Universität Karlsruhe, May 2003

FU Berlin, June 2003

TU Braunschweig, July 2003.

J. Wintterlin

TU Chemnitz, GDCh, Jan. 2002

LMU München, April 2002

Université de Strasbourg, France, Sep. 2002

University of Aarhus, Denmark, Oct. 2002.

Department of Physical Chemistry

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:

- M. Eiswirth was in charge of the Chair of Experimental Physics at the University of Magdeburg during Winter 2002/2003.
- J.F. Holzwarth is the European Editor of Langmuir.
- A.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 Publishing Co., and organized the Second Int. Symposium “Engineering of Chemical Complexity”, Berlin 2002.

Theory Department Director: M. Scheffler

Staff scientists:

Dr. Johan Carlsson	
Dr. Ricardo I. Gómez Abal	
Prof. Dr. Klaus Hermann	(Habilitation)
Dr. Peter Kratzer	(Habilitation)
Dr. Karsten Reuter	
Dr. Patrick Rinke	

Scientists (temporary) paid from external funds:

Hazam O.A. Abu-Farsakh(IG)	
Dr. Abdullah Al-Sharif(IG)	
Prof. Dr. Randall Feenstra(IG)	(AvH Award)
Dr. Martin Friák	
Dr. Bothina Hamad	(AvH Fellowship)
Dr. Magnus Hedström	
Dr. Hiroyuki Kageshima	
Dr. Christine Kolczewski	
Dr. Seung Mi Lee	
Dr. Bernhard Lehner	(AvH Fellowship)
Nicholas Wambua Makau	
Prof. Dr. Mats Persson	
Prof. Dr. Abdallah Qteish(IG)	
Dr. Sladjana Stojkovic	(AvH Fellowship)
Dr. Qiang Sun	
Dr. Chris Van de Walle(IG)	(AvH Award)
Dr. Deng-Ke Yu	

Guest scientists, staying for at least six months:

Dr. Joel Ireta(IG)
Dr. Weixue Li
Dr. Evgeni Penev
Dr. Catherine Stampfl
Dr. Ligen Wang
Dr. Hua Wu

Graduate students: 15

Diploma students: 1

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

Recent Developments in the Theory Department

Director: M. Scheffler

I. General Remarks

The main research projects of the *Theory Department* continue to be concerned with fundamental aspects (starting from the electronic structure) of catalysis and chemical and physical properties of surfaces, interfaces, clusters and nanostructures. Some work is done in the field of biophysics. Basically all calculations employ density-functional theory (DFT). It has often been argued that DFT is a zero-temperature, zero-pressure technique and that the applicability of the results to high-pressure phenomena, such as catalysis, may be limited. This assessment is, however, not correct, and already in the mid 80's the method of "*ab initio* atomistic thermodyna-mics" was developed and applied in the *Theory Department,* at that time to study defects and interfaces. The approach was recently complemented by the concept of a *constrained equilibrium* in order to study environmental gas phases containing more than one (reactive) component. This allows to identify regions in (T, p)-space that may show an enhanced dynamics and chemical activity.

In addition to this computational method for studying equilibrium (or quasi equilibrium) surface compositions and structures, scientists in the *Theory Department* are also using "*ab initio* statistical mechanics". In particular they are developing and implementing kinetic Monte Carlo simulations to describe the time evolution of non-equilibrium surfaces. Again, this is done with DFT determined input, which implies that one does not get along with just few effective parameters, but it is necessary to include many processes, which all have a well-defined physical meaning.

Emphasis is also put on the analysis of DFT-LDA (or DFT-GGA) errors both in ground state and excited state calculations. Keywords along this line are *optimized effective potentials* (or exact exchange), the *GW* approach, and the *quantum Monte Carlo* approach.

Application of the methods mentioned above extend from quantifying the composition and geometry of metal, metal oxide, and semi-conductor surfaces to elucidating the structures of adsorbed layers to describing the kinetics and dynamics of growth, adsorption, and catalysis at surfaces.

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. The work done in collaboration with J. Neugebauer, e.g. biophysics, is not presented here, but will be discussed in his Chapter.

II. Personnel and Related Activities

Since the last visit of the *Fachbeirat* in November 2001 the important changes among the scientists on longer-term positions are:

- Dr. Klaus-Peter Charlé deceased (December 2002),
- Prof. Dr. Klaus Hermann became head of the *Network Center* (Gemeinsames Netzwerkzentrum der Berlin-Brandenburgischen Max-Planck-Einrichtungen) which is a half-time commitment (June, 2002).
- Dr. Catherine Stampfl obtained a professorship in Sydney (March 2003), and is now an *associate member* of the department.
- Dr. Arno Schindlmayr accepted a position at the *Forschungszentrum Jülich* (April 2003). The collaboration on several projects, that deal with excited states projects, continues.
- Dr. Karsten Reuter took a one-year leave of absence to work in Daan Frenkel's group in Amsterdam. He is back in Berlin since September 1, 2003
- With Dr. Jörg Neugebauer's move to a professorship in Paderborn, his *Independent Junior Research Group (IG)* was officially terminated. He is now an *associate member* of the department, continuing to work with his students, who remain in Berlin, on group-III-nitrides (cf. also his report).

With the forthcoming increase of scientific staff positions in the *Theory Department* (it will rise to 8 positions by the end of next year) it is possible and appropriate to install a group structure. Effective October 1 this year the following 4 groups were established:

- Johan Carlsson: Nanoporous carbon
- Klaus Hermann: Cluster studies on metal oxides and surface crystallography
- Peter Kratzer: Morphology and growth of semiconductor surfaces

- Karsten Reuter: Catalytic reactions at surfaces

Additional groups on excited states (*GW*/TD-DFT), *ab initio* biophysics, and electrochemistry and fuel cells are envisaged for the future.

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. And they take part in DFG Priority Programs (Schwerpunktprogramme, SPP) and various other activities:

- Sfb 290: M. Scheffler, P. Fumagalli, J. Paggel (Metallic Thin Films: Structure, Magnetism, and Electronic Properties (B10))
- Sfb 296: P. Kratzer, M. Scheffler (Growth-Correlated Properties of Low-Dimensional Semiconductor Structures (A5))
- Sfb 546: K. Hermann (Structure, Dynamics, and Reactivity of Aggregates of Transition-Metal Oxides (C6))
- DFG – Bilateral Exchange with Poland (436 POL 113/0-1): K. Hermann, M. Witko (Theoretical Studies on Transition-Metal Oxides for Catalytic Applications Me_2O_3, Me = Ti, V, Cr)
- DFG – Bilateral Exchange with Poland (436 POL 113/104/0-1): M. Scheffler, A. Kiejna (First Principles Studies of Adsorbate Structures at Metal and Oxide Surfaces)
- SPP-1091: M. Scheffler, K. Reuter (Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis)
- European Commission – Research Training Network: M. Scheffler (Nano-scale Photon Absorption and Spectroscopy with Electrons (NANOPHASE))
- ESF-PESC: M. Scheffler (Electronic Structure Calculations for Elucidating the Complex Atomistic Behavior of Solid and Surfaces (STRUC-Ψ_k)), until 12.2002
- ESF-PESC: M. Scheffler (Towards Atomistic Materials Design (Psi-k))
- NIST Database # 42 Project: K. Hermann, M. Van Hove, P. Watson (Surface Structure Database)
- Volkswagen-Stiftung$^{(IG)}$: M. Scheffler, J. Neugebauer, A. Qteish (Structural and Electronic Structure Properties of Solid: Implementation and Analysis of the Exact-Exchange Functional in Density-Functional Theory), until 12.2003

- Volkswagen-Stiftung – Partnership Program: P. Kratzer, A. Chakrabarti (Thin Ternary Films and Quantum Dot Formation in III-V Compound Semiconductor Materials)
- NTT corporation (Japan): H. Kageshima, M.Scheffler, P. Kratzer (Growth Simulations of SiO_2)
- Toshiba corporation (Japan): K. Nishitani, M. Scheffler, P. Kratzer (High-k Dielectrics)

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

Scientists of the *Theory Department* were also involved in various services to the surface-science and electronic-structure communities worldwide. For example, they organized or co-organized conferences on topics in surface science, and ran several international workshops on methods for electronic structure calculations that have touched numerous students aspiring to be theoretical surface scientists. Examples from the last two years include:

- CECAM Workshop on *ab initio* Theoretical Approaches to the Electronic Structure and Optical Spectra of Materials, Lyon, 23-25 September 2002 (A. Schindlmayr)
- CECAM Tutorial on kinetic Monte Carlo, Lyon, 14-17 October 2002 (P. Kratzer)
- Growth, electronic and optical properties of low-dimensional semiconductor quantum structures, Ringberg Castle, 12-15 February 2003 (P. Kratzer, K. Jacobi)
- Oxide formation on Metal Surfaces: Stability, Reactivity and High Pressures, Lund, 3/4 July 2003 (K. Reuter)
- Modelling Statistics and Dynamics in Catalysis: from ab-initio Potentials to Rare Events, Ringberg Castle, 10-13 September 2003 (K. Reuter)
- Ab initio Electrons Excitations Theory: Towards Systems of Biological Interest, San Sebastian, 21-24 September 2003 (A. Schindlmayr)
- Workshop on Application of Density-Functional Theory in Condensed-Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, 21-30 July 2003
  (P. Kratzer, J. Neugebauer, R. Gomez Abal, C. Stampfl, A. Schindlmayr)

The latter noted workshop featured detailed presentations on basic aspects of DFT, time-dependent DFT, and many-body schemes, that were supplemented by practical sessions at computer terminals, in which the use of the new version of the FHI *ab initio* pseudopotential computer code was taught (cf. also the report by J. Neugebauer). The effort undertaken by all members of the *Theory Department* and the *Junior Research Group* was significant, but the result was most gratifying. The workshop program, the lectures, and some slides can be found at the website: www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/

The computer situation of the department right now is good. In Berlin we are running a Linux cluster and at the RZG (Rechenzentrum Garching) of the MPG we have access to the IBM SP4 computer (Regatta) with 22 compute nodes (32 processors each) which is operational since January 2003, though the fast inter-node communication is still missing.

III. New Concepts, Methods, and Techniques

III.1 Beyond today's Density-Functional Theory

At present, DFT is the best approach for describing the electronic, magnetic, structural, and vibrational properties of poly-atomic systems. If combined with the super-cell approach, one can ensure that the treatment of the exchange-correlation (xc) functional remains the only relevant approximation. Although recent years have brought improved xc functionals, it is still our view that actual DFT calculations give a somewhat blurred or even distorted picture of reality. This, however, is not necessarily a weakness, i.e., it may even help to disclose important physics. 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 trust neither of them.

Several co-workers in the department are presently developing a more constructive approach for dealing with the problem. Three different routes are being considered:

- "Optimized effective potentials", also often called "exact exchange", apparently cure certain shortcomings of commonly used, jellium-based xc functionals (cf. the report by J. Neugebauer).
- In collaboration with Rex Godby (University of York) we are working with a pseudopotential plane-wave formulation of the *GW* approach to evaluate the quasi-particle bandstructure of surfaces and of surface defects. We also started

developing an all-electron *GW* scheme, based on the APW+lo formulation of the WIEN2k package. It is planned to combine the “exact exchange” approach with *GW*, for example to check on the size of the discontinuity of the xc potential.
(P. Eggert, Ch. Freysoldt, M. Friak, R. Gómez-Abal, P. Rinke, A. Schindlmayr)

- Exploiting the “nearsightedness”: There is some evidence that what is incorrect in actual DFT-LDA or DFT-GGA calculations stems from a rather localized contribution, e.g. largely from the self-interaction that is not properly corrected in neither the LDA nor GGA. Therefore a two-step approach is taken. We start by calculating geometries and energies using the DFT super-cell 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. using the quantum Monte Carlo (QMC) approach. For energy barriers, the cluster edge effects cancel and the difference of the cluster results obtained by DFT and QMC as function of cluster size show converging behavior giving the correction that ought to be added to the super-cell results. (C. Filippi, P. Kratzer)

III.2 Lattice Gas Hamiltonians for Adsorbate Systems

For systems with an underlying lattice structure adsorption can be described by a lattice-gas Hamiltonian (LGH). This determines the partition function which in turn determines all thermodynamic properties of the system. The LGH parameters can be obtained from DFT calculations, and this was done in the department five years ago to analyze phase transitions and thermal desorption spectra of O/Ru(0001), as well as substrate-mediated adsorbate interactions for studying the diffusion and growth of Ag/Ag(111). Present work employs a more automated approach to parameterize LGHs from DFT data than what we had done previously. This new scheme is applied for calculating the low-coverage phase diagram of H on Pd(111). (C. Lazo and K. Reuter)

III.3 The Stockholm-Berlin (StoBe) Cluster Code

The StoBe code (Stockholm-Berlin version of deMon), developed by K. Hermann and L. G. M. Pettersson (University of Stockholm), for the calculation of chemical/ physical properties of large molecules and (surface) clusters has been further improved. Recently implemented features include: advanced X-ray spectroscopy (NEXAFS, XES) options with higher moment (quadrupole) transitions, evaluation of vibrational excitations based on the full molecular symmetry with and without geometric constraints, enhanced geometry optimizers, new analysis tools (e.g. topological Bader analyses, molecular symmetry finders/generators). The package has been complemented with an extensive documentation including a full set of examples for learning and testing. The StoBe software is available for MS Windows 2000/NT4/XP and Linux/Unix systems and is distributed by the Fritz-Haber-Institute, see also w3.rz-berlin.mpg.de/~hermann/StoBe/index.html. (K. Hermann)

III.4 Dmol^3 Developments

The APW+lo approach, as implemented in the WIEN2k package, is probably the most accurate method for evaluating the Kohn-Sham equation and total energy. Despite noticeable advances in programming the forces, molecular dynamics, code speed-ups, and code parallelization (the latter is being done in collaboration with R. Dohmen and J. Pichlmeier of the RZG) the approach is still annoyingly slow for big systems. Recently we started a collaboration with Bernard Delley, who originated the Dmol^3 code, an all-electron, atom-centered basis-set approach that is not only significantly faster that the APW+lo approach but even noticeably faster than our pseudopotential plane-wave code (by about a factor of 5). However, Dmol^3 still suffers from some limitations, which we are working on to remove. Recently we implemented a spin-constrained DFT method which enables us to investigate the non-adiabaticity of the dissociative adsorption of O_2 at Al(111) (cf. also section IV.1). (J. Behler, K. Reuter)

IV. Applications – Some Highlights

IV.1 Oxygen-Metal Interactions and Metal-Oxides

The interaction of oxygen with metal surfaces is being studied in the department since several years, and the contacts and collaboration with the *PC* and *AC Departments* were and are most pleasing. Our initial theoretical work had concentrated on overlayers and subsurface oxygen at Ru and Rh. For Ru it was recently shown experimentally that in an oxygen-rich environment the surface is covered with ruthenium-oxide, $RuO_{2,}$, and this transition was then analyzed theoretically. The recent work on Pd and Ag in an oxygen-rich environment shows that for these systems *surface oxides* are formed that differ from the known bulk phases. (W. Li, K. Reuter, J. Rogal, C. Stampfl, M. Todorova)

A particular puzzle is the O_2 dissociation at Al(111). For this very elementary system and process in surface science, the lack of understanding could hardly be more dramatic: Numerous experiments have shown that the initial sticking probability of thermal oxygen molecules impinging onto Al(111) is about one percent. However, DFT studies were hitherto unable to explain this and predicted a sticking coefficient close to unity. A detailed analysis of the six-dimensional potential-energy surface, of the dissociation dynamics, and, in particular, of non-adiabatic effects (actuated by the triplet state of the free O_2 molecule) provides the so far missing explanation. (J. Behler, K. Reuter)

For metal surfaces exposed to an environment containing O_2 as well as CO it is important to note that CO may reduce the surface-oxide. Using first-principles kinetic Monte-Carlo (kMC) simulations, i.e., using rates derived from DFT, this is presently studied for the RuO_2 surface. The kMC results enable us to monitor the mesoscopic turnover rates over the whole range of experimentally accessible gas phase conditions. The highest steady-state turnover rates are found to occur when a phase coexistence at the surface enables a specific new reaction mechanism between O and CO, both adsorbed at “cus” sites, that is not operational at other temperature and pressure conditions, including ultra-high vacuum. (K. Reuter)

Similarities between bond formation in transition metal complexes and chemisorption on solid surfaces form the basis for possible relationships between homogeneous and heterogeneous catalysis. This has been explored in close collaboration with the *PC Department* (J. Wang, C.Y. Fan, K. Jacobi, G. Ertl) studying the O and H interaction with the RuO_2(110) surface. The combination of low-temperature ultrahigh vacuum experiments in conjunction with DFT calculations provided detailed insight into the complex coordination chemistry of a solid surface, which exhibits a remarkable correlation with the chemistry of single-atom transition-metal complexes. (Q. Sun, K. Reuter)

The oxidation of CO as well as OH and H_2O formation (after hydrogen exposure) at the V_2O_5(010) surface are studied in detail using the cluster code StoBe (see III.3). These studies form part of an effort to understand catalytic reactivity at metal oxide surfaces on a microscopic scale. The results show that CO_2 formation involving CO adsorbate and surface oxygen proceeds via a bent CO_2-type transition state and is connected with a reaction barrier of only 0.4 eV if the surface is excited electronically. This is consistent with recent experimental findings. (Ch. Friedrich, K. Hermann)

The V_2O_5(010) surface contains 1-, 2-, and 3-fold coordinated oxygen centers which can behave differently as active sites in specific surface reactions. Therefore, discrimination between the different centers by experimental methods is important for an understanding of reaction details. Using DFT cluster calculations angle-resolved NEXAFS spectra of 1*s* core excitation at differently coordinated oxygen sites at the V_2O_5(010) surface were calculated. A comparison of the theoretical results with experimental NEXAFS data yields very good agreement and allows an assignment of spectral details to differently coordinated oxygen centers.
(K. Hermann, Ch. Kolczewski)

For the V_2O_3(0001) surface six different terminations were studied using large cluster models. The terminations are suggested either by the intrinsic bulk stacking or have been proposed from experiments where excess oxygen is present at the surface. The different terminations show pronounced differences in their atomic relaxation where the half metal termination V'OV reveals a relaxation scheme close to that observed for Cr_2O_3(0001). Charge analyses show that relaxation leads always to increased ionicity near the surface. Vanadyl groups due to oxygen excess are found to broaden the O 2*p* valence region of the V'OV terminated surface due to the appearance of singly coordinated oxygen. This can explain recent photoemission experiments for thin films of (0001) oriented V_2O_3. Further, oxygen added in bridging sites at the metal terminated surface results in lateral relaxation which can explain the geometry of V_2O_3 films on Cu_3Au(001) suggested by scanning tunneling microscopy. (I. Czekaj, K. Hermann, M. Witko)

IV.2 Nanoporous Carbon

Dehydrogenation of ethylbenzene to form styrene is an important reaction in the chemical industry. In collaboration with the *AC Department* we had investigated the composition of iron oxide. The theoretical results suggested further experimental work which then showed that the surface of the iron oxide catalyst becomes covered by a carbon layer after a short period of use. Previously this was believed to kill the catalyst, but now it is established that nanoporous carbon is in fact the actual catalytic material. Consequently, the atomic structure and electronic properties of characteristic motives of nanoporous carbon are now being investigated by DFT. (J. Carlsson)

IV.3 Modeling Diffusion, Nucleation, and Growth

Recent theoretical and experimental studies showed that indirect substrate-mediated interactions can be significant enough to influence the formation of nanostructures at surfaces. Our previous DFT studies of these interactions have now been complemented by kinetic Monte Carlo simulations to study the nucleation and growth. For Ag/Ag(111) and Cu/Cu(111) it is found that these interactions lead to the formation of repulsive barriers surrounding small adsorbate islands, and that they depend on the island size and shape. The calculations suggest that these interactions can be tuned by straining the surface which opens possibilities for creating well-defined nanostructures at surfaces. (K. Fichthorn, M. Merrick [The Pennsylvania State University])

In collaboration with colleagues from the Humboldt University a combined theoretical and experimental study of island nucleation and growth in the deposition of Co on Cu(001) was performed – a prototype for understanding heteroepitaxial growth involving intermixing. Both, our kinetic Monte Carlo study to simulate the heteroepitaxial growth, and the experiments show a unique *N*-shape- (non Arrhenius) dependence of the island density on temperature that stems from the interplay and competition of the different processes involved. (K. Fichthorn [The Pennsylvania State University], R. Pentcheva)

IV.4 Semiconductor Quantum Dots

The self-assembly of semiconductor nanostructures continues being investigated in collaboration with the *PC Department* and other groups in Berlin. In recent calculations we analyzed, for example, the alloying and strain driven reconstructions of the wetting layer, and determined the diffusion. Presently it is attempted to take strain effects on the diffusion and nucleation into account, which calls for new developments for kMC calculations. (T. Hammerschmidt, E. Penev, P. Kratzer)

Though strain plays an important role in the QD formation, very few studies have addressed its influence in the QD bound states for electrons and holes. We analyzed this in collaboration with B. Koiller from the University of Rio de Janeiro, using an sp^3s^* empirical tight-binding model. Koiller's approach enables us to calculate single-particle bound-state energies (with respective wave functions) and charge localization of single

QDs, containing several thousands of atoms, as well as of QD arrays. (P. Kratzer, R. Santoprete)

IV.5 Spin-Electronics

Considerable effort has recently been made to identify material systems that could serve as candidates for spintronics devices. Since both metallic Mn and Mn-Si compounds have interesting magnetic properties and are closely lattice-matched with Si, we choose to investigate magnetism in thin films of these materials. Corresponding experiments are being performed at the Free University. Investigating numerous structures as well as Mn diffusion, we find, for example, that Mn atoms can reach the subsurface region of the Si(001) surface without a substantial energy barrier. This may lead to a Si-Mn sandwich structure capped by a Si layer, which has interesting properties. (M. Hortamani, P. Kratzer, H. Wu)

A very different material, also of interest to spintronics, is magnetite (Fe_3O_4). It is ferrimagnetic with a unique combination of several interesting properties. For example, it has an unusually high Curie temperature (858 K). We studied the behavior of this system as a function of uniaxial and biaxial stress, pressure, and atom substitution. Particular focus is put on the conditions that induce a halfmetal-to-metal transition, i.e., a loss of the material's desirable halfmetallic properties. (M. Friak)

IV.6 Surface Structure Database (SSD Version 5, SSDIN)

The Surface Structure Database (SSD, NIST database no. 42) is presently the only existing and periodically updated electronic database collecting quantitatively known surface crystallographic structures. It has been established since 1990 in a joint effort with the Lawrence Berkeley Laboratory, UC Berkeley (M. A. Van Hove), the Oregon State University, Corvallis (P. R. Watson), and the National Institute of Standards and Technology (NIST), Washington. Version 5 of SSD contains almost 1400 structures published up until Dec. 2002 and is due to appear by Dec. 2003. The database has been developed as a MS Windows® 98/NT/2000/XP application featuring extended search algorithms with a versatile query language as well as analysis tools based on numerical listings as well as interactive graphics. (K. Hermann)

The input software, SSDIN (new Version 5), has been further improved to assist contributors of surface structures in submitting their data to the SSD developers. The software is written as an interactive MS Windows® 98/NT/2000/XP application and offers interactive visualization as well as extensive symmetry handling. The new Version 5 of SSDIN includes a LEED pattern symmetry analyzer (LEEDpat) as well as a separate surface visualizer (SURVIS), see the website: w3.rz-berlin.mpg.de/~hermann/ssdin5/index.html. (K. Hermann)

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Stampfl, C. and M. Scheffler: Energy barriers and chemical properties in the coadsorption of carbon monoxide and oxygen on Ru(0001) (11 pages). Phys. Rev. B **65**, 155417 (2002).

Todorova, M., W.X. Li, M.V. Ganduglia-Pirovano, C. Stampfl, K. Reuter and M. Scheffler: Role of sub-surface oxygen in oxide formation at transition metal surfaces. Phys. Rev. Lett. **89**, 096103 (2002).

Van Hove, M.A., K. Hermann and P.R. Watson: Adsorbate-induced changes in surface structure on metals and semiconductors. In: Physics of Covered Solid Surfaces, Subvolume A: Adsorbed Layers on Surfaces, Part 2: Measuring Techniques and Surface Properties Changed by Adsorption, Chapter 4: Adsorbate-Induced Changes of Substrate Properties. (Ed.) Hans P. Bonzel. Springer, Berlin-Heidelberg-New York 2002. Title of Series: Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Group III: Condensed Matter, Vol. 42A (Part 2), 4.1./1-4.1./122.

Van Hove, M.A., K. Hermann and P.R. Watson: The NIST surface structure database – SSD version 4. Acta Cryst. B **58**, 338-342 (2002).

Wang, X.-G., J.R. Smith and M. Scheffler: Effect of hydrogen on Al_2O_3/Cu interfacial structure and adhesion (4 pages). Phys. Rev. B **66**, 073411 (2002).

Dissertationen (Doctoral Theses)

Da Silva, J. L.F.: The nature and behavior of rare-gas atoms on metal surfaces. TU Berlin 2002.

Penev, E.: On the theory of surface diffusion in InAs/GaAs(001) heteroepitaxy. TU Berlin 2002.

Diplomarbeiten (Master Theses)

Ismer, L.: Protonentransport in Wasserstoffbrückenbindungen. TU Berlin 2002.

Rogal, J.: Elektronenstruktur und Stabilität von Pd und PdO (Dichtefunktionaltheorieberechnungen). FU Berlin 2002.

Wahn, M.: Implementation und Analyse des exakten Austauschfunktionals in der Dichtefunktionaltheorie. TU Berlin 2002.

2003

Czekaj, I., K. Hermann and M. Witko: Ab initio DFT studies on oxygen stabilization at the V_2O_3(0001) surface. Surf. Sci., in print.

Czekaj, I., K. Hermann, M. Witko: Relaxation and electronic structure of the V_2O_3(0001) surface: ab initio cluster model studies. Surf. Sci. **525**, 33-45 (2003).

Czekaj, I., M. Witko, K. Hermann: Structure and electronic properties of the V_2O_3(0001) surface: ab initio density functional theory cluster studies. Surf. Sci. **525**, 46-56 (2003).

Da Silva, J. L.F., C. Stampfl and M. Scheffler: Adsorption of Xe atoms on metal surfaces: New insights from first-principles calculations. Phys. Rev. Lett. **90**, 066104 (2003).

Domínguez-Ariza, D., C. Sousa, N.M. Harrison, M.V. Ganduglia-Pirovano, F. Illas: Effect of surface model on the theoretical description of the chemisorption of atomic hydrogen on Cu(0 0 1). Surf. Sci. **522**, 185-197 (2003).

Fichthorn, K.A., M.L. Merrick and M. Scheffler: Nanostructures at surfaces from substrate-mediated interactions (4 pages). Phys. Rev. B **68**, 041404(R) (2003).

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Hermann, K. and K. Reuter: Theoretische Bausteine zum Verständnis katalytischer Reaktionen an Übergangsmetall-Oxidoberflächen. MPG Jahrbuch 2003, in print.

Ireta, J., J. Neugebauer, M. Scheffler, A. Rojo and M. Galván: Density functional theory study of the cooperativity of hydrogen bonds in finite and infinite α-helices. J. Phys. Chem. B **107**, 1432-1437 (2003).

Kolczewski, C. and K. Hermann: Ab initio DFT cluster studies of angle-resolved NEXAFS spectra for differently coordinated oxygen at the V_2O_5(010) surface. Surf. Sci., submitted.

Kolczewski, C. and K. Hermann: Identification of oxygen sites at the V_2O_5 surface by core-level electron spectroscopy: Ab initio cluster studies. J. Chem. Phys. **118**, 7599-7610 (2003).

Kratzer, P.: Atomistic simulations of processes at surfaces. In: Challenges in Predictive Process Simulations. (Ed.) J. Dabrowski. Springer Verlag 2003.

Kratzer, P., E. Penev and M. Scheffler: Understanding the growth mechanisms of GaAs and InGaAs thin films by employing first-principles calculations. Appl. Surf. Sci. **216**, 436-446 (2003).

Li, W.X., C. Stampfl and M. Scheffler: Insights into the function of silver as an oxidation catalyst by ab initio, atomistic thermodynamics. Phys. Rev. B, in print.

Li, W.X., C. Stampfl and M. Scheffler: Subsurface oxygen and surface oxide formation at Ag(111): A density-functional theory investigation (16 pages). Phys. Rev. B **67**, 045408 (2003).

Li, W.X., C. Stampfl and M. Scheffler: Why is a noble metal catalytically active? The role of the O-Ag interaction in the function of silver as an oxidation catalyst. Phys. Rev. Lett. **90**, 256102 (2003).

Márquez, J., P. Kratzer and K. Jacobi: Structure and morphology of the As-rich and the stoichiometric GaAs(114) surface. J. Appl. Phys., submitted.

Neugebauer, J., T.K. Zywietz, M. Scheffler, J.E. Northrup, H. Chen, and R.M. Feenstra: Adatom kinetics on and below the surface: The existence of a new diffusion channel. Phys. Rev. Lett. **90**, 056101 (2003).

Penev, E., P. Kratzer and M. Scheffler: Thermodynamics of the wetting layer in InAs/GaAs(001) heteroepitaxy. Phys. Rev. Lett., submitted.

Pentcheva, R., K.A. Fichthorn, M. Scheffler, T. Bernhard, R. Pfandzelter and H. Winter: Non-Arrhenius behavior of the island density in metal heteroepitaxy: Co on Cu(001). Phys. Rev. Lett. **90**, 076101 (2003).

Reuter K. and M. Scheffler: Composition and structure of the RuO_2(110) surface in an O_2 and CO environment: Implications for the catalytic formation of CO_2 (11 pages). Phys. Rev. B **68**, 045407 (2003).

Reuter K. and M. Scheffler: First-principles atomistic thermodynamics for oxidation catalysis: Surface phase diagrams and catalytically interesting regions. Phys. Rev. Lett. **90**, 046103 (2003).

Reuter K. and M. Scheffler: Oxide formation at the surface of late 4*d* transition metals: Insights from *first-principles atomistic thermodynamics*. Appl. Phys. A, submitted.

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Scharoch, P., J. Neugebauer and M. Scheffler: Al(111)-($\sqrt{3} \times \sqrt{3}$)R30: On-top versus substitutional adsorption for Rb and K (5 pages). Phys. Rev. B **68**, 035403 (2003).

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Sun, Q., K. Reuter and M. Scheffler: Effect of a humid environment on the surface structure of RuO_2(110) (7 pages). Phys. Rev. B **67**, 205424 (2003).

Todorova, M., E. Lundgren, V. Blum, A. Mikkelsen, S. Gray, J. Gustafson, M. Borg, J. Rogal, K. Reuter, J.N. Andersen, M. Scheffler: The Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-O surface oxide revisited. Surf. Sci. **541**, 101-112 (2003).

Tokarz-Sobieraj, R., R. Grybos, M. Witko, and K. Hermann: Oxygen sites at molybdena and vanadia surfaces: thermodynamics of the reoxidation process. Collected Czech. Chemical Communications, submitted.

Wang, J., C.Y. Fan, Q. Sun, K. Reuter, K. Jacobi, M. Scheffler and G. Ertl: Surface coordination chemistry: Dihydrogen versus hydride complexes on RuO_2(110). Angew. Chem. **115**, 2201-2204 (2003); Angew. Chem. Int. Ed. **42**, 2151-2154 (2003).

Wang, X.-G., J.R. Smith, M. Scheffler: Adhesion of copper and alumina from first principles. J. Am. Ceram. Soc. **86**, 696-700 (2003).

Invited Talks of the Members of the Theory Department

Jörg Behler

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
Dmol^3*– A Standard Tool for Density-Functional Calculations*

Christoph Friedrich

Jul 2003 Forschungszentrum Jülich, IFF, Jülich, Germany
Reaction of CO, H, and H_2 *at the* $V_2 O_5(010)$ *Surface: Ab-Initio DFT Cluster Models*

Martin Fuchs

May 2002 Forum on Electron Density, Density Matrices and Density Functional Theory, Oxford, U.K.
Towards van der Waals Interactions, Chemical Accuracy, and Proper Molecular Dissociation within Density-Functional Theory: Use of the Adiabatic-Connection Fluctuation-Dissipation Approach

Nov 2002 1st ABINIT Developers Workshop, Louvain-la-Neuve, Belgium
Constructing Pseudopotentials for Abinit: On the Use of the fhi98PP Package

Nov 2002 1st ABINIT Developers Workshop, Louvain-la-Neuve, Belgium
Density Functionals from Linear Response Theory: Implementation in Abinit and Results for H_2 *and* Be_2

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
Pseudopotentials for Ab Initio Electronic Structure Calculations

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
Density-Functionals for Exchange and Correlation: From LDA to GGA and Beyond

M. Verónica Ganduglia-Pirovano

Jan 2002 Kolloquium am Institut für Experimentalphysik, Karl-Franzens-Universität Graz, Austria
Interaction of Oxygen with Metal Surfaces: From Adlayers to Surface-Oxide Formation

Mar 2002	Université de Bourgogne, Laboratoire de Physique et Centre de Dynamique des Systemes Complexes, Dijon, France *On the Role of Subsurface Oxygen in the Oxide Formation on Transition Metal Surfaces*
Apr 2003	The Department of Chemistry, Imperial College of Science, Technology and Medicine, London, U.K. *On the Atomistic Understanding of Oxide Formation on Transition Metal Surfaces*
Jul 2003	Workshop on Oxide Formation on Metal Surfaces: Stability, Reactivity and High Pressures, Lund, Sweden *On the Role of Sub-Surface Oxygen in the Oxide Formation at 4d Transition Metal Surfaces*

Klaus Hermann

Dec 2001	Kolloquium, Physik-Department, Universität Stockholm, Stockholm, Sweden *Local Models of the Geometric and Electronic Structure of Vanadium Oxide Surfaces*
Mar 2002	DPG Frühjahrstagung, Regensburg, Germany *CO-Adsorption und Oxidation auf der* V_2O_5*(010)-Oberfläche: ab-initio Clustermodelle*
Apr 2002	3rd deMon Developers Workshop, Geneva, Switzerland *Towards a Concise Basis Set Library for deMon/StoBe: Results and Frustrations*
Apr 2002	3rd deMon Developers Workshop, Geneva, Switzerland *News from the deMon/StoBe Scene: Properties and More*
Jun 2002	International Conference on Current Trends in Theoretical Chemistry, ICTAC-IV, Cracow, Poland *Electronic Structure and Reactions at Complex Transition Metal Oxides: Ab Initio DFT Cluster Studies for CO Oxidation at* V_2O_5 *Surfaces*
Sep 2002	North Carolina State, Chemistry Department, Raleigh, U.S.A. *Local Models of the Geometric and Electronic Structure of Vanadium Oxide Surfaces*
Dec 2002	University of Virginia, School of Chem. Engineering, Charlottesville, U.S.A. *Local Models of the Geometric and Electronic Structure of Vanadium Oxide Surfaces*
Jan 2003	Universität Hannover, Hannover, Germany Zur elektronischen und geometrischen Struktur von Oberflächen der Übergangsmetalloxide: DFT-Untersuchungen für Vanadiumoxide

Feb 2003	Universität Erlangen-Nürnberg, Erlangen, Germany *Lokale Modelle zur geometrischen und elektronischen Struktur von Vanadiumoxid-Oberflächen*
Feb 2003	Seminar on Advanced Synchrotron Light Source, Lawrence Berkeley Laboratory, Berkeley, U.S.A. *Computation of NEXAFS/XES Spectra of Free and Adsorbed Mole-cules Using Quantum Chemical Tools*
Feb 2003	Colloquium at Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, U.S.A. *Adsorption and Reaction at Clean and Defected Vanadium Oxide Surfaces: Ab Initio DFT Cluster Studies*
Apr 2003	4th deMon Developers Workshop, Stockholm, Sweden *DFT Calculations of X-Ray Spectra*
May 2003	ESF Workshop on Nano-Oxides: Perspectives and Applications, Bressanóne, Italy *Electronic Structure and Spectroscopy at Transition Metal Oxide Surfaces with and without Defects: Theoretical DFT Studies on Vanadium Oxide Surfaces*
Jun 2003	Kolloquium am Fachbereich Chemie, Technische Universität Dresden, Dresden, Germany *Strukturelle und elektronische Eigenschaften von Vanadiumoxid-Oberflächen: Theoretische DFT-Clusteruntersuchungen*

Peter Kratzer

Feb 2002	Workshop on Catalysis from First Principles, Vienna, Austria *Performance of Density Functionals Compared to the Quantum Monte Carlo Method: Case Study of H_2 Adsorption on Silicon*
Mar 2002	International Seminar on Models of Epitaxial Crystal Growth, *MPI für Physik komplexer Systeme, Dresden, Germany* *From First-Principles Calculations to Growth Simulations: Molecular Beam Epitaxy of GaAs*
Aug 2002	Sandia Workshop on Quantum Mechanical Techniques: Exchange Correlation Functionals in Density-Functional Theory, Albuquerque, U.S.A. *Performance of Density Functionals Compared to the Quantum Monte Carlo Method: Case Study of H_2 Adsorption on Silicon*
Sep 2002	9th Symposium on Surface Science, Třešt, Czech Republic *Surface Diffusion and Growth of III-V Semiconductors and the Formation of Quantum Dots*

Sep 2002	WE-Heraeus Summer School on Computational Materials Science, Halle (Saale), Germany *Dichtefunktionalmethoden zur Untersuchung der atomaren und elektronischen Struktur von Oberflächen*
Sep 2002	WE-Heraeus Summer School on Computational Materials Science, Halle (Saale), Germany *Kinetische Simulationen von Epitaxie und Kristallwachstum*
Oct 2002	Fourth International Symposium on Control of Semiconductor Interfaces (ISCSI-4), Kariuzawa, Japan *Understanding the Growth Mechanisms of GaAs and InGaAs Thin Films Employing First-Principles Calculations*
Nov 2002	MPI für Festkörperphysik, Stuttgart, Germany *Surface Diffusion and Growth of III-V Semiconductors and the Formation of Quantum Dots*
Mar 2003	Institut Français de Pétrol, Rueil, France From First-Principles Calculations to Growth Simulations: Molecular Beam Epitaxy of GaAs
Jul 2003	Gordon Conference on Chemistry of Electronic Materials, New London, Connecticut, U.S.A. *First Principles Calculations of the Energetics and Kinetics of Surface Chemical Reactions*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Fast Guide to Density-Functional Calculations*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Prerequisites for Reliable Modeling with First-Principles Methods*
Sep 2003	Workshop on Modelling Statistics and Dynamics in Catalysis: from ab-initio potentials to rare events, Schloss Ringberg, Rottach-Egern, Germany *Kinetic Monte Carlo Simulations of Epitaxial Growth Based on First-Principles Calculations*

Evgeni Penev

Dec 2001	Bulgarian Academy of Sciences, Sofia, Bulgaria *Effect of Strain on Surface Reconstruction and Surface Diffusion in InAs/GaAs(001) Heteroepitaxy*

Feb 2003	Workshop on Growth, Electronic and Optical Properties of Low-Dimensional Semiconductor Quantum Structures, Schloss Ringberg, Rottach-Egern, Germany *Computer-Aided Understanding of QD Growth Kinetics*
Jun 2003	NATO ARW “Quantum Dots: Fundamentals, Applications, Frontiers”, Amoudara, Crete, Greece *Probing InAs/GaAs(001) Heteroepitaxy from First Principles*
Sep 2003	International Workshop on Fundamentals and Practical Applications of Surface Diffusion, Třešt Castle, Czech Republic *Surface Diffusion in Semiconductor Epitaxial Growth: Gaining Knowledge from First Principles*

Rossitza Pentcheva

Jul 2002	Third International Alloy Conference (IAC-3), Estoril/Cascais, Portugal *Heteroepitaxial Metal Growth with Intermixing: A DFT - kMC Approach*
Jun 2003	Seminar at Faculty of Applied Physics, University of Twente, Enschede, The Netherlands *Surface Phase Diagrams and Growth Kinetics from First Principles*
Sep 2003	International Workshop on Surface Physics 2003: Metals on Surfaces (IWSP-2003), Polanica Zdrój, Poland *Non-Arrhenius Behavior of Island Density in Metal Heteroepitaxy: Co on Cu(001)*

Karsten Reuter

Nov 2001	6th Workshop of the Joint Research Programme “Gas-Surface Interactions”, Graz, Austria *Oxidation Catalysis on Ru: From UHV to High Pressure*
Nov 2001	Seminar an der Universität Erlangen-Nürnberg, Erlangen, Germany *Oxidationskatalyse auf Ru: vom UHV zur Realität*
Dec 2001	Seminar at AMOLF/FOM Institute, Amsterdam, The Netherlands *Oxidation Catalysis on Ru: From UHV to High Pressure*
Feb 2002	Workshop on Catalysis from First Principles, Vienna, Austria *CO Oxidation Catalysis on Ru: From UHV to High Pressures*
Jun 2002	European Conference on the Structure of Surfaces (ECOSS-21/ NANO-7), Malmö, Sweden *Surface Knowledge from Ultra-High Vacuum to Technically Relevant Conditions: The Example of Catalytic CO Oxidation*
Jul 2002	International Workshop on Towards Atomic Scale- and Time-Resolution at Interfaces, San Sebastian, Spain *Surface Knowledge from UHV to Technically Relevant Conditions: The Example of Catalytic CO Oxidation*

Sep 2002	WE-Heraeus Summer School on Computational Material Science, Halle (Saale), Germany *From Ab Initio to Thermodynamics: Numerical Concepts in the Modelling of Heterogeneous Catalysis*
Oct 2002	Asia-Pacific Surface & Interface Analysis Conference (APSIAC´02), Tokyo, Japan *Surface Knowledge from UHV to Technically Relevant Conditions: The Example of Catalytic CO Oxidation*
Nov 2002	Vrijdag-Fysisch Colloquium, Universiteit Leiden, The Netherlands *Surface Knowledge from UHV to Technologically Relevant Conditions: The Example of Catalytic CO Oxidation*
Nov 2002	ACC-NIOK Conference on The Molecular Basis of Catalysis, Amsterdam, The Netherlands *Surface Knowledge from UHV to Technologically Relevant Conditions: The Example of Catalytic CO Oxidation*
Dec 2002	Institutskolloquium, Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Germany *Oberflächenstrukturen vom Ultrahochvakuum bis zu realen Drücken: Das* Beispiel der CO-Oxidation
Jan 2003	XI. International Workshop on Computational Physics and Material Science: Total Energy and Force Methods, Trieste, Italy *First-Principles Atomistic Thermodynamics*
Mar 2003	DPG Frühjahrstagung, Dresden, Germany Surface Phase Diagrams, Oxide Formation and Catalysis – Insights from "Ab Initio Thermodynamics and Statistics"
May 2003	Technische Universität Hamburg-Harburg, Hamburg, Germany *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modelling in Heterogeneous Catalysis*
Jun 2003	International Max-Planck Research Summer School on Theoretical and Computational Materials Science, Stuttgart, Germany *An Introduction to Surface Physics*
Jun 2003	Workshop "Chemische Reaktivität von größenselektierten Clustern und Materie mit reduzierten Dimensionen", Berlin, Germany *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modeling in Heterogeneous Catalysis*
Jul 2003	Kolloquium des SFB 616, Universität Essen, Essen, Germany *Surface Phase Diagrams, Oxide Formation and Catalysis -- Insights from Ab Initio Thermodynamics and Statistics*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Ab Initio Atomistic Thermodynamics and its Applications in Heterogeneous Catalysis*

Aug 2003	Gordon Research Conference on Dynamics at Surfaces, Andover, U.S.A. *With Ab Initio to the Mescoscale? Challenges and Possibilities for the Modeling in Heterogeneous Catalysis*

Jutta Rogal

Jul 2003	Workshop on Oxide Formation on Metal Surfaces: Stability, Reactivity and High Pressure, Lund, Sweden *On the Thermodynamic Stability of PdO Surfaces*

Matthias Scheffler

Oct 2001	Seminar at Chemical Sciences Division, NIST, Gaithersburg, U.S.A. *Get Real! The Importance of Complexity for Understanding the Function of Surfaces*
Jan 2002	Seminar at Department of Chemical Engineering, Pennsylvania State University, University Park, U.S.A. *Surface Knowledge from Ultra-High Vacuum to Technically Relevant Conditions*
Jan 2002	Colloquium at Department of Physics, Pennsylvania State University, University Park, U.S.A. *Computational Sciences and Engineering from First Principles: From the Earth Core to Quantum Dots to Mad Cow Disease*
Jan 2002	Kolloquium der Gesellschaft Deutscher Chemiker (GDCh), Ortsverband Hannover, Germany *Status der ab initio Theorie in der modernen Festkörperphysik, Oberflächenchemie, Geologie, Ingenieurwissenschaften und Biologie*
Feb 2002	IVth - East West Surface Science Workshop (EWSSW´02) on Nanostructures on Surfaces, Pamporovo, Bulgaria *Surface Knowledge: Toward a Predictive Theory of Materials*
Apr 2002	Regional Workshop on Computational Condensed Matter Physics, Isfahan University of Technology (IUT), Isfahan, Iran *Computational Science and Engineering from First Principles I*
Apr 2002	Regional Workshop on Computational Condensed Matter Physics, Isfahan University of Technology (IUT), Isfahan, Iran *Computational Science and Engineering from First Principles II*
May 2002	Seminar at Department of Chemical Engineering, University of Wisconsin-Madison, Madison, U.S.A. *Get Real! The Importance of Complexity for Understanding the Function of Surfaces*
May 2002	Department of Physics, University of Maryland, College Park, U.S.A. *Computational Sciences and Engineering from First Principles – from the Earth Core to Quantum Dots to Mad Cow Disease*

May 2002	Fachbereichs-Kolloquium Physik, Metallurgie und Werkstoffwissenschaften, Technische Universität Clausthal, Germany *Status der ab initio Theorie in der modernen Festkörperphysik, Oberflächenchemie, Geologie, Ingenieurwesen und Biologie*
Jun 2002	Department of Applied Physics, Göteborg University and Chalmers University of Technology, Göteborg, Sweden *Surface Knowledge from Ultra-High Vacuum to Technically-Relevant Conditions*
Jun 2002	Search Conference on Development of Theoretical Methods for Complex Systems, VW-Stiftung, Schloss Reisensburg, Günzburg/Donau, Germany *Materials Design from First Principles*
Jul 2002	Workshop on Electronic Structure of Solids, IFW Dresden, Germany *Surface Knowledge from Ultra-High Vacuum to Technically Relevant Conditions*
Jul 2002	7th International Conference on the Structure of Surfaces (ICSOS-7), Newcastle, Australia *Can Surface Structures be Solved Directly by Theory?*
Oct 2002	Physical Chemistry Seminar, Department of Chemistry and Biochemistry, UCLA, Los Angeles, U.S.A. *Get Real! The Importance of Complexity for Understanding the Function of Surfaces*
Nov 2002	Conference on Realistic Theories of Correlated Electron Materials, KITP, UCSB, Santa Barbara, U.S.A. *Testing the Accuracy of the xc Energy of Electronic-Structure Theories for Real Materials*
Dec 2002	Colloquium at the Materials Research Laboratory, UCSB, Santa Barbara, U.S.A. *Present Status of Ab Initio Electronic Structure Calculations:* *From the Earth Core to Quantum Dots to Mad Cow Disease*
Jan 2003	DECHEMA, Frankfurt/Main, Germany *Modellierung von Materialien mittels ab initio Thermodynamik und ab initio Statistischer Mechanik*
Feb 2003	Gordon Conference on Chemical Reactions at Surfaces, Ventura, U.S.A. *From Ultra-High Vacuum to Technically Relevant Conditions: Surface Composition and Multi-Adsorbate Phases at Realistic T and p*
Feb 2003	43rd Sanibel Symposium, St. Augustine, Florida, U.S.A. *Atomic Thermodynamics and Statistical Mechanics from First Principles – Applications to Crystal Growth and Heterogeneous Catalysis*
Mar 2003	225th ACS National Meeting, New Orleans, U.S.A. *Surface Phase Diagrams and Surface Kinetics*

May 2003	2nd International Conference on Elementary Processes in Molecule-Metal Surface Interactions (ICEP-II), San Juan, U.S.A. *Adsorbate Surface Phase Diagrams, Surface Kinetics, and the Stability of Metal Oxides*
Jul 2003	Symposium on Computational Modelling of Catalysis, MPI für Kohlenforschung, Mülheim/Ruhr *Ab Initio Atomistic Thermodynamics and Statistical Mechanics: Application to Surface-Oxidation and Oxidation Catalysis*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Present Status of Ab Initio Electronic Structure Calculations*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Comparison of First-Principles Methods/Codes*
Sep 2003	10th International Conference on the Applications of Density-Functional Theory in Chemistry and Physics, Vrije Universiteit Brussels, Belgium *Materials Science from First Principles*
Nov 2003	AVS 50th International Symposium, Baltimore, U.S.A. *Get Real! – The Importance of Complexity for Understanding the Function of Surfaces*

Arno Schindlmayr

Feb 2002	13. Edgar-Lüscher-Seminar, Serneus, Switzerland *The GW Approach for Treating Excited States*
Feb 2002	Hands-on Course on KKR Band Structure and Spectroscopy Calculations, München, Germany *Electron Spectroscopy Within Density-Functional Theory*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Quasiparticle Band Structures and the GW Approximation*
Aug 2003	Euroconference on Ab initio Many-body Theory for Correlated Electron Systems, Trieste, Italy *The GW Approximation within a Density-Functional Context*

Catherine Stampfl

Oct 2001	Seminar “Selbstorganisation in komplexen nichtlinearen Systemen”, TU Berlin, Germany *Adsorption at, Desorption from, and Chemical Activity of Metal Surfaces*

Feb 2002	Workshop on Catalysis from First Principles, Vienna, Austria *The Role of the O-Ag Interaction in the Function of Silver as an Oxidation Catalyst*
Jun 2002	The European Materials Research Society (EMRS), Strasbourg, France *Why is a Noble Metal Catalytically Active? The Role of the O-Ag Interaction in the Function of Silver as an Oxidation Catalyst*

Krzysztof Tatarczyk

Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *When States Get Excited − or − a Short Guide to the Time-Dependent DFT*
Sep 2003	International Conference on Ab initio Electron-Excitations Theory: Towards Systems of Biological Interest, San Sebastian, Spain *Surface Plasmons in Surface Alloys, a Mystery?*

Mira Todorova

Jul 2003	Workshop on Oxide Formation on Metal Surfaces: Stability, Reactivity and High Pressure, Lund, Sweden *Oxide Formation on Pd Surfaces*

Independent Junior Research Group Head: J. Neugebauer

Scientists (temporary) paid from external funds:

Hazam O.A. Abu-Farsakh(ThD)	
Dr. Abdullah Al-Sharif(ThD)	
Prof. Dr. Randall Feenstra(ThD)	(AvH Award)
Prof. Dr. Abdallah Qteish(ThD)	
Dr. Chris Van de Walle(ThD)	(AvH Award)

Guest scientists, staying for at least six months:

Dr. Joel Ireta(ThD)

Graduate students: 8

(ThD) Together with the *Theory Department*

Recent Developments in the Independent Junior Research Group

Group leader: J. Neugebauer

1 General Remarks: Personnel

The head of the *Independent Junior Research Group* accepted an offer of the University of Paderborn for a C4-position as professor in Theoretical Physics starting in September 1, 2003. The Junior Research Group was therefore officially ended on August 31, 2003. In order to allow a smooth continuation of the projects and also to allow those Ph.D. students who are not moving to Paderborn to finish their work regularly, a joint agreement between the head of the group − Prof. J. Neugebauer − and the head of the Theory Department − Prof. M. Scheffler − has been made to provide the required resources (offices, computer resources).

Due to the fact that the group ended, the following report will not only focus on the issues and results achieved in the last two years but will also give a brief summary of the outcome of the group during its four years of existence (from August 1, 1999 to August 31, 2003).

In the last two years a number of members of the group finished their diploma or Ph.D. thesis. Lars Ismer (working on biomolecules) and Matthias Wahn (developing an alternative exact-exchange formalism) received in 2002 their diploma. Both decided to stay in the group and to start a Ph.D. project. Günther Schwarz (studying point defects on semiconductor surfaces) and Andréia Luísa da Rosa (identifying the microscopic mechanisms of antisurfactants on nitride surfaces) received their Ph.D. in 2002 (G. Schwarz) and 2003 (A. da Rosa). Both accepted researcher positions: Dr. G. Schwarz is now working at the University of Erlangen in the group of Prof. O. Pankratov, Dr. da Rosa is working at the University of Brighton in the group of Prof. M. Heggi. In addition to the above mentioned members the group consisted of five Ph.D. students (one within a joint project with the group of Prof. A. Waag, Universität Braunschweig) and one postdoc.

Most of the positions had been externally funded by the German Research Society (DFG), European community network activities, the Alexander von Humboldt or the Volkswagen Foundation:

- DFG, Priority Program “Gruppe III-Nitride”: J. Neugebauer (*Surfactant induziertes Wachstum von GaN-Oberflächen*)
- Sfb 296$^{(ThD)}$: J. Neugebauer and M. Scheffler (*Wachstumskorrelierte Eigenschaften niederdimensionaler Halbleiterstrukturen − Ab initio Rechnungen zur Wachstumskinetik von niederdimensionalen Strukturen auf Gruppe III-Nitridhalbleitern*)
- DFG research group at Universität Bremen: J. Neugebauer (*Physics of wide-bandgap, nano-structured, light-emitting devices*)
- European Commission, Research Training Network: J. Neugebauer (*Interface analysis at atomic level and Properties of Advanced Materials (IPAM)*)
- VolkswagenStiftung$^{(ThD)}$: M. Scheffler, J. Neugebauer, and A. Qteish (*Structural and electronic structure properties of solid: Implementation and ana-lysis of the exact-exchange functional in density-functional theory*)

The superscript $^{(ThD)}$ indicates joint activities with the Theory Department.

The group was also host to a number of scientific guests: Dr. Chris Van de Walle (Palo Alto Research Center, CA, U.S.A.) regularly visited the group for one month every year (since 1999). Prof. R. Feenstra (Carnegie-Mellon University, Pittsburgh, U.S.A.) also visited the group on a regular basis and stayed here for a total of 6 months. Prof. A. Qteish (Yarmouk University, Jordan) and members of his group visited the FHI for three months every year (since 2001) to work on a joint project funded by the VolkswagenStiftung. A particularly close collaboration was with the Theory Department of the Fritz-Haber-Institut.

The group had also strong collaborations with several outside groups: Infineon, CEA Grenoble/France, Xerox PARC (Palo Alto/U.S.A.), Carnegie Mellon University (Pittsburgh/U.S.A.), University of Mexico City/Mexico. In September 2001 a joint experimental and theoretical study with the Univsität Ulm (group of Prof. A. Waag) started under the subject area “GaMnAs alloys for spin electronics”. The group was actively involved in organizing the Symposium “GaN and related materials” at the MRS 2000 Fall Meeting, the International Workshop on “III-Nitride Based Materials and Devices” at the Harnack-Haus in Berlin (January 2001) and in organizing and preparing the “hands-on” workshop in Berlin: “Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering and Biology”.

2 General Remarks: Scientific Aspects

One of the key objectives of the group was to understand/identify how microscopic processes on the surface affect mesoscopic/macroscopic materials properties and how by modifying the microscopic processes mesoscopic/macroscopic properties may be controlled. Examples, in which the group was interested, concerned the identification of surfactants (to realize atomically smooth interfaces and/or surfaces), antisurfactants (to create quantum dots or nano-structures), or to identify surface phenomena which would allow to kinetically stabilize bulk structures such as chemically ordered alloys (which are thermodynamically unstable) or to achieve doping concentrations well above the solubility limit.

A challenge in studying and identifying such phenomena is the large range of length and time scales needed to describe the effect atomic processes have on meso-/macroscale properties. A main activity of the group was therefore to develop and apply methods to bridge the gap between atomistic growth processes and mesoscopic growth phenomena. The approach taken was to start from density-functional theory (which is a well established tool to describe structure and energetics on an atomic scale) and to combine it with “classical” mesoscopic/macroscopic concepts such as thermodynamics, statistical mechanics, or continuum elastic theory.

The investigations had been mainly focussed on group-III nitrides for two reasons: *(i)* as shown by the group this system exhibits properties and growth phenomena not observed for any other semiconductor system and *(ii)* a deeper knowledge of these phenomena is crucial to overcome materials limitations and improve materials quality. Since the theoretical approaches developed are based on density-functional theory it was straightforward to apply them also to other materials systems. For example, triggered by cooperations with experimental groups also surface phenomena on “traditional” III-V semiconductors, metals, and magnetic materials had been studied.

While most of the actual calculations were based on standard density-functional theory using the local density or the generalized gradient correction (LDA/GGA) we were also interested in alternative schemes to overcome well known deficiencies of this approach. A particular issue was the realistic description of the bandgap. We therefore studied, implemented, and tested alternative exchange-correlation functionals (such as the exact exchange formalism within the Kohn-Sham formalism).

A further topic studied in the group is the description and calculation of hydrogen-bonded systems. This work was initiated by an Alexander von Humboldt fellowship

(Dr. J. Ireta). While this topic initially had no connection to our main topic of semiconductor growth we soon realized that the methods and concepts which have been originally developed to describe periodic structures such as bulk crystals or surfaces are also a powerful tools to study quasi-one-dimensional structures in proteins such as the α-helix.

In the following a more detailed description of the above described activities will be given.

3 Methodological Developments

3.1 Simulations on an atomic scale

As mentioned above the method of choice to study structure, energetics and processes on an atomic scale had been density functional theory. Specifically, a plane-wave basis set and pseudopotentials had been used. Initially, most of the calculations had been performed using the program package “fhi98md” which had been developed in the Theory Department. For many projects, however, additional features and new algorithms were needed. We have therefore developed in our group a new, fully modular and object oriented C++ library (SFHIngX) which allowed a fast and efficient implementation of all required features and algorithms (see below). The C++ library has become fully operational in 2002 and has been used for all new projects.

3.1.1 Optimizing the *ab initio* calculations: An object-oriented approach to density-functional calculations

A challenge in identifying microscopic mechanisms is the large number of possible systems to be studied (to find the structure/barrier with the lowest energy) and the large system size required to describe structure and kinetics on realistic surfaces (e.g. diffusion along or over a surface step). Therefore, there is a constant need to improve the plane-wave code with respect to efficiency (the algorithms efficient for small system are often not the most efficient ones for large systems and vice versa) and accuracy (implementation and testing of new exchange-correlation functionals, e.g., exact exchange). To do this, an effective code/formalism is needed which allows the rapid implementation and exploration of new algorithms and methods in *ab initio* methods.

We have developed a framework which strongly simplifies development and testing of new methods in the field of DFT. It is based on generic template programming techniques of C++ to access automatically efficient BLAS and LAPACK routines. This together with a matrix-based notation provides an efficient tool to describe new algorithms at FORTRAN77 speed. Such a high abstraction level and modularity make it easy for beginners to understand and modify parts of the new DFT library. Using this library the new *ab initio* code SFHIngX was created. The present version employs a plane-wave basis set and a broad variety of electronic minimization methods. Its Hamiltonian supports various exchange-correlation functionals. Beside conventional L(S)DA and PBE the Exact-Exchange formalism (EXX) is implemented. On top of the class hierarchy are modules like damped and quasi Newton to relax structures, modules to perform automatic transition state search, to calculate the phonon spectra and thermodynamic potentials, and to run molecular dynamics. Furthermore, many small add-ons are available to analyze the electronic structures, the chemical bonds as well as the vibrational behavior. (S. Boeck, A. Dick, L. Ismer)

3.1.2 Beyond local-density functionals

A very promising scheme to overcome the well known bandgap problem of local- or nearly local-density functionals such as LDA and GGA is the exact exchange (EEX) method. In this approach the partial self-interaction of an electron with itself, which occurs when using the local density or generalized gradient approximations is completely eliminated. We have implemented the approach in our new plane-wave code and applied it to calculate the bandstructure for a wide variety of semiconductors. Generally, we find good agreement with experimental data. For group-III nitride and II-VI compound semiconductors we could for the first time include the cation semicore *d* states within the EXX formalism. These calculations revealed a number of partly unexpected results: *(i)* The EXX results agree nicely with previous GW calculations, *(ii)* the *pd* repulsion is almost identical to that in LDA/GGA leading to too small bandgaps, and *(iii)* in contrast to common belief the removal of the self-interaction does not significantly lower the energetic position of the semicore states. The new approach allowed also to study the bandgap of InN, a semiconductor where the determination (both theoretical and experimental) of the bandgap had been notoriously difficult. (A. Qteish, A. Al-Sharif, H. Abu-Farsakh, S. Boeck)

3.1.3 Alternative formulation of the exact exchange formalism

A major obstacle of the EXX formalism is that it is computationally rather expensive with respect to both memory and CPU-time – in comparison with corresponding

LDA/GGA calculations by about 2 to 3 orders of magnitude. We have therefore developed an alternative formulation of the EXX-method that is based on a variational principle and only requires as input ground state properties. In this formulation the calculation of unoccupied states is no longer required and the problem reduces to the minimization of a simple energy functional. To test the method calculations for closed-shell atoms (beryllium and neon) have been performed which showed excellent agreement with previous studies. (M. Wahn)

3.1.4 Efficient description of zero dimensional defects/impuritieswithin a supercell formalism

A common problem encountered when describing point defects in bulk or on the surface is the slow convergence with respect to the system size. We have therefore performed a systematic study of the dependence of properties on cell size for neutral and charged defects in bulk and at the surface. Based on these studies we have developed a schema which allows to eliminate the k-dispersion of defects in a supercell. Applying this scheme we found that it is possible to reduce the CPU time for defect/impurity calculations by two orders of magnitude without loosing accuracy. We further developed an approach which allows to get converged results for charged systems even in modestly sized supercells. (G. Schwarz)

3.1.5 Approximate total energy formalisms

Many systems in which we were interested allowed a partition into strongly perturbed regions (e.g. regions within the vicinity of a defect, dislocation core, etc. where broken bonds exist) and weakly perturbed regions where only strain induced small perturbations from the bulk structure exists. While for the strongly perturbed regions the application of *ab initio* methods turned out to be important for the weakly perturbed regions simplified energy functionals were often found to be sufficient. We have therefore compared various valence force field models with a large number of *ab initio* calculated structures and energies. Based on these results and using simulated annealing to globally minimize the least square fit optimum parameters for these models have been identified. (L. Lymperakis)

We have further proposed a new model that correctly takes into account the long-range electrostatic interactions, correctly describes (unlike the original approaches) the differences between the zinc-blende and wurtzite structure, and can be applied to binary and ternary compound semiconductors. (F. Grosse)

3.2 Simulations on a mesoscopic scale

In order to bridge the very different time and length scales between atomistic DFT calculations (time: $10^{-15\ldots-12}$ s, length: $\approx 10^{-9}$ m) and the growth morphology (time: $10^{0\ldots3}$ s, length: $10^{-8\ldots-6}$ m) we were exploring and developing various approaches.

3.2.1 Thermodynamic concepts

For high-temperature growth techniques such as MOCVD (metal-organic vapor phase epitaxy) or HVPE (hydride vapor-phase epitaxy) the surface is close to thermodynamic equilibrium. We have therefore developed a first-principles approach to derive generalized surface phase diagrams for systems consisting of adsorbate/impurity covered surfaces in thermodynamic contact with a gaseous environment. Using this approach gives immediate access to the atomic structure and phase transitions under realistic growth conditions. We were also able to show that for realistic systems the number of degrees of freedom can be reduced by two. For example, for a surface alloy consisting of three chemical species (such as H on GaN) the Gibbs' Phase Rule produces four degrees of freedom, resulting in a four-dimensional phase space that is difficult to analyze or interpret. With the new approach it is possible to express the surface energy in terms of two degrees of freedom which can be directly related to the experimental growth parameters. The method has been applied to describe the effect hydrogen has on GaN surfaces and to analyze the formation of extended defects. (C. Van de Walle)

3.2.2 Combination of DFT, empirical potentials, and continuum elastic theory

A major challenge in describing extended defects such as dislocations is the large range of relevant length scales: While the core structure itself is rather localized the strain field is long range. Previous studies on dislocations in semiconductors therefore focused on isolated aspects: Density-functional theory (DFT) calculations give an accurate description of the core structure but are restricted to rather small system sizes thus excluding part of the strain field. Empirical potentials permit large scale calculations thus allowing to accurately describe strain effects but the accuracy near/in the core region is rather limited. To overcome these deficiencies we have developed a multiscale approach which combines elements of DFT, empirical potentials, and continuum elas-tic theory and which allows to treat systems containing more than 10^5 atoms. (L. Lymperakis)

3.2.3 Adatom density kinetic Monte Carlo

Kinetic Monte Carlo (kMC) simulations are one of the key methods to perform growth simulations on realistic length and time scales. A major problem in applying conventional kMC techniques is that the number of microscopic events and thus the computation effort scale exponentially with temperature. An analysis of typical kMC runs showed that this effect is mainly related to calculating the full trajectory of each surface adatom. We have therefore developed a method which allows (similar as in density-functional theory for the electrons) to replace the individual adatom trajectories by an adatom density. Applying this approach the number of time steps could be reduced by two up to four orders for typical systems. (L. Mandreoli)

4 Applications

4.1 Surface structure, morphology, and growth

A first step towards understanding/controlling the surface morphology is the knowledge of the relevant surface structures and of the various microscopic processes. For group-III nitrides many of these calculations had been done by our group. In the last two years we focused on specific problems to help interpreting recent experiments and to identify mechanisms which can be used to affect and control the surface morphology and/or the bulk properties.

4.1.1 Bare nitride surfaces

Non-polar surfaces: Non-polar nitride surfaces are technologically very attractive since they promise devices without built-in polarization fields. We have therefore studied the energetics of a wide variety of surface structures. Our results show that in contrast to non-polar surfaces for “traditional” III-V semiconductor surfaces such as the (110) surface a highly non-stoichiometric structure is energetically most stable. The structure consists of two compressed metallic Ga bilayers. Since similar structures had been identified also for various polar surface orientations this implies that polar and non-polar surfaces exhibit very similar properties. (L. Lymperakis in collaboration with R. Feenstra and J. Northrup)

Nucleation and desorption: The quality of MBE grown epitaxial GaN films is typically best under extreme Ga-rich conditions. A major technological problem is that under such conditions Ga-droplets may be formed. Therefore, experimentally detailed investigations regarding adsorption and desorption behavior had been performed by various groups. Surprisingly, different groups observed largely different activation energies for Ga-droplet formation (ranging from 2.5 eV up to almost 5 eV) and prefactors (ranging from 10^{13} s^{-1} up to 10^{25} s^{-1}). In order to shed some light onto this puzzling behavior we have derived an *ab initio* based growth model which takes into account the nucleation of Ga clusters. This model was able to consistently explain the contradictory results of the activation energy and allowed an unambiguous determination of the onset of Ga droplet formation during Ga-rich GaN growth. (L. Lymperakis in collaboration with B. Daudin (Grenoble))

4.1.2 Adsorbate covered surfaces

In order to grow semiconductor devices it is crucial to have a high control over the surface morphology. Experimentally, it is well known that the surface morphology sensitively depends on the specific growth conditions such as the ratio between III/V elements (stoichiometry), the growth method (e.g. MBE, MOCVD, or HVPE), temperature, or the presence of impurities. While the first parameters are intrinsic to the materials system and thus allow only a rather limited control over the surface morphology the use of impurities promises to give a much wider flexibility. In order to understand the effect impurities have on surface properties such as structure, stability, adatom kinetics we have derived surface phase diagrams for a number of impurities (e.g. H, In, Si) on GaN surfaces. Depending on impurity concentration, growth conditions (presence of hydrogen), and Ga/N stoichiometry a rich behavior of effects has been found. In particular, our studies allowed to predict which impurities under what conditions behave e.g. as surfactant, anti-surfactant, etc. Some prominent examples are discussed below.

Surfactants: For the technologically relevant wurtzite (0001) surfaces our results show that indium adatoms reduce the surface energy and form a liquid-like metallic film consisting of two and more layers. Calculations further show that this film strongly influences the migration paths and the diffusion barriers: The presence of the metallic film opens an unexpected but very efficient diffusion channel *below the surface* which was found to strongly enhance the lateral mobility for N adatoms. The activation barrier for this channel is much lower than for on-surface diffusion and is operative already at MBE conditions. Our predictions have triggered a number of experimental studies (Universität Bremen, CEA Grenoble) which nicely confirm the theoretical studies. Based on these results we could further show that In acts as surfactant only in a limited growth window. Going to higher In concentrations our results showed that InGaN formation occurs which leads at medium concentrations to the formation of In-rich nanoclusters and at high concentrations to the formation of extended defects. (T. Zywietz in collaboration with M. Scheffler, J. Northrup, R. Feenstra)

Antisurfactants and kinetically enhanced doping: An *ab initio* derived phase diagram of Si on the GaN(0001) surface showed that Si has a dramatically different effect on surfaces under MBE and MOCVD conditions. Surfaces under MOCVD conditions are found to stabilize Si in the top surface layers – under these conditions surface segregation is an important issue. Furthermore, under these conditions the Si-terminated surface structures are unstable against the formation of Si_3N_4. The formation of Si_3N_4 clusters on the surface blocks locally further growth and leads to three-dimensional growth and rough surfaces. Under these conditions Si acts thus as antisurfactant. For MBE conditions, however, a complete different behavior is found. Under these conditions Si is actually highly unstable in the top-surface layers leading to an efficient incorporation of Si in bulk GaN. This mechanism has been found to kinetically stabilize the incorporation of Si donors in bulk GaN and allows to achieve doping concentrations well above the equilibrium doping limit. (A. da Rosa in collaboration with R. Feenstra and J. Northrup)

Kinetically stabilized alloys: Investigations on stepped nitride surfaces showed that at surface steps atoms prefer unusually low coordinated sites (the step atoms are attached by only one or two chemical bonds). Further studies showed that these sites are chemically very selective and allow to grow novel bulk alloys which thermodynamically are not stable. The existence of such theoretically predicted structures has been recently confirmed by experimental electron microscopy and optical studies at the University of Erlangen in a joint project. (L. Lymperakis in collaboration with J. Northrup, M. Albrecht, H. Strunk)

4.2 Magnetic surfaces

Transition-metal nitrides such as e.g. MnN are promising magnetic materials for applications in magnetic recording and sensing and for spintronic applications. Using novel spin-polarized scanning-tunneling microscopy (STM) techniques these surfaces had been recently studied by A. Smith (Ohio State University) and a rich set of magnetic and non-magnetic structures had been identified. While these studies gave important insight into the existence of these reconstructions a theoretical study of the surface structure which could explain the driving forces, i.e., whether the structure is driven by magnetic and/or atomic reconstruction, was lacking. Therefore, employing density-functional theory calculations in the local spin density approximation (LSDA) we have studied atomic geometry, electronic and magnetic structures, as well as the thermodynamic stability of such surfaces. (A. Dick in collaboration with A. Smith)

4.3 Alkali atoms on metal surfaces

The atomic structure and energetics of the on-top and substitutional phase of the Al(111)-($\sqrt{3}\times\sqrt{3}$)R30:Rb adsorbate system have been studied. Since the energy difference between the two phases is extremely small ($\approx$ 20 meV) extensive checks with respect to the choice of the exchange-correlation functional and the construction of the Rb pseudopotential had been performed. All tests clearly showed the substitutional adsorption site to be energetically favorable. Equivalent calculations performed for K revealed a clear chemical trend in the adsorption energetics for Na, K, and Rb: The energy gain between the substitutional and the on-top configuration decreases with increasing atomic radius of an alkali atom. (P. Scharoch in collaboration with M. Scheffler)

4.4 Extended defects in group-III nitrides

Using the multiscale technique described in Sec. 3.2.2 edge dislocations in GaN have been investigated. Since epitaxially grown GaN films are often highly strained the calculations have been performed for strained and unstrained GaN. Under tensile strain, as characteristic e.g. for hydrogen vapor phase epitaxy (HVPE) grown GaN, our calculations reveal a novel and hitherto not reported dislocation type. Based on the calculated atomic geometry high-resolution transmission electron microscopy (HR-TEM) image simulations have been performed. A comparison with experimental HR-TEM images of dislocations in HVPE-grown GaN gave an excellent agreement.

Interestingly, in contrast to all previously identified dislocation structures in GaN the new structure is fully reconstructed implying that the dislocation should be electrically inactive, i.e., deep defect states should be absent. However, an analysis of the electronic structure clearly revealed the existence of deep defect states. The origin of these states is a giant local strain field which causes a metallization of bulk GaN in the vicinity of the core. An important implication of this result is that dislocations in GaN are intrinsically (i.e., independent on the specific core structure) electrically active. (L. Lymperakis in collaboration with M. Albrecht, H. Strunk)

4.5 Doping related issues

Hydrogen is an omnipresent impurity which is well known to affect the doping efficiency of many materials. However, so far it had been not possible to predict the electrical activity of hydrogen in a specific material without extensive experiments or calculations. We have therefore performed a systematic DFT-study covering a wide range of materials. A surprising result of this study was the existence of a universal alignment for the electronic transition level of hydrogen in semiconductors, insulators and even aqueous solutions. It could be further shown that the alignment is closely related to the line-up of electronic band structures at heterojunctions. The discovery of the universal alignment allows the prediction of the electrical activity of hydrogen in any host material once some basic information about the band structure of that host is known. These studies had been published in Nature and received a lot of attention not only in the semiconductor community but also from researchers working on hydrogen-storage systems, fuel cells, or in electrochemistry. (C. Van de Walle)

4.6 Biomolecules (proteins)

4.6.1 Mechanical response

Proteins undergo constant motions and structural changes in cells under normal physiological conditions. These processes might compress or tense its tertiary and secondary structure. Therefore, the knowledge of protein mechanical properties is necessary to understand its biological function. We have therefore studied the mechanical response of a protein under tensile and compressive strain. Specifically, we investigated the response of an infinite polyalanine chain in α-helical conformation since this protein has been experimentally extensively studied and is regarded as one of the key structures to understand helix formation. Our results showed the existence of a first order phase transition, a feature which had been also observed in recent experiments. Based on our studies the microscopic mechanism causing this transition could be explained. (J. Ireta in collaboration with M. Scheffler, A. Rojo, and M. Galván)

4.6.2 Thermodynamic properties

Entropy is believed to strongly affect the stability of proteins. In order to analyze the effect entropy has on the stability of the secondary structure we have calculated the full phonon-dispersion relation of poly-alanine in an infinite alpha-helical conformation using DFT-PBE and within the harmonic regime. A comparison with recent experimental results showed an excellent agreement for all branches below 2000 cm^{-1}. For the high-frequency hydrogen-stretch modes, however, the calculated modes were systematically lower (by 50 – 100 cm^{-1}) than the experimental values. An analysis of this effect showed that it is related to the small atomic mass of hydrogen which gives rise to sizeable anharmonic contributions. Using the vibrational spectra for the first time a full *ab initio* based thermodynamic analysis of the helix could be performed. (L. Ismer, J. Ireta)

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Scharoch, P., J. Neugebauer and M. Scheffler: Al(111)-($\sqrt{3} \mathrm{x} \sqrt{3}$)R30: On-top versus substitutional adsorption for Rb and K (5 pages). Phys. Rev. B **68**, 035403 (2003).

Van de Walle, C.G. and J. Neugebauer: Structure and energetics of nitride surfaces under MOCVD growth conditions. J. Cryst. Growth **248**, 8-13 (2003).

Van de Walle, C.G. & J. Neugebauer: Universal alignment of hydrogen levels in semiconductors, insulators and solutions. Nature **423**, 626-628 (2003).

Dissertation (Doctoral Thesis)

da Rosa, A.L.: Dichtefunktionaltheoretische Untersuchungen zu *Anti-Surfactants* auf Galliumnitridoberflächen. TU Berlin 2003.

Invited Talks of the Members of the Independent Junior Research Group

Sixten Boeck

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
Introduction to the SFHIngX Code

Joel Ireta

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
Structural Analysis of Biological Systems

Lars Ismer

Jul 2003 Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany
First-Principles Molecular Dynamics

Jörg Neugebauer

Jan 2002 Gemeinsames Kolloquium des Instituts für Kristallzüchtung (IKZ) Berlin und der Brandenburgischen Technischen Universität (BTU) Cottbus, Berlin, Germany
Kristallwachstum im Computer: Von der atomaren Skala zum Bauelement

Jan 2002 Kolloquium an der Universität Paderborn, Germany
Von der Schrödingergleichung zum Bauelementedesign: Multiskalenmethoden in der Materialwissenschaft

Feb 2002 3. Kinetik-Seminar der DGKK, Dresden, Germany
Parameterfreie Beschreibung des Kristallwachstums auf mikroskopischer und mesoskopischer Skala

Mar 2002 Workshop on Hydrogen: Ionic, Atomic and Molecular Motion,
Schloss Ringberg, Rottach-Egern, Germany
Cooperativity of Hydrogen Bonds and Charge Transfer in Alpha Helices

May 2002 Kolloquium an der Universität Regensburg, Germany
Multiskalenmethoden in der Materialwissenschaft: Von der Schrödingergleichung zum Bauelementedesign

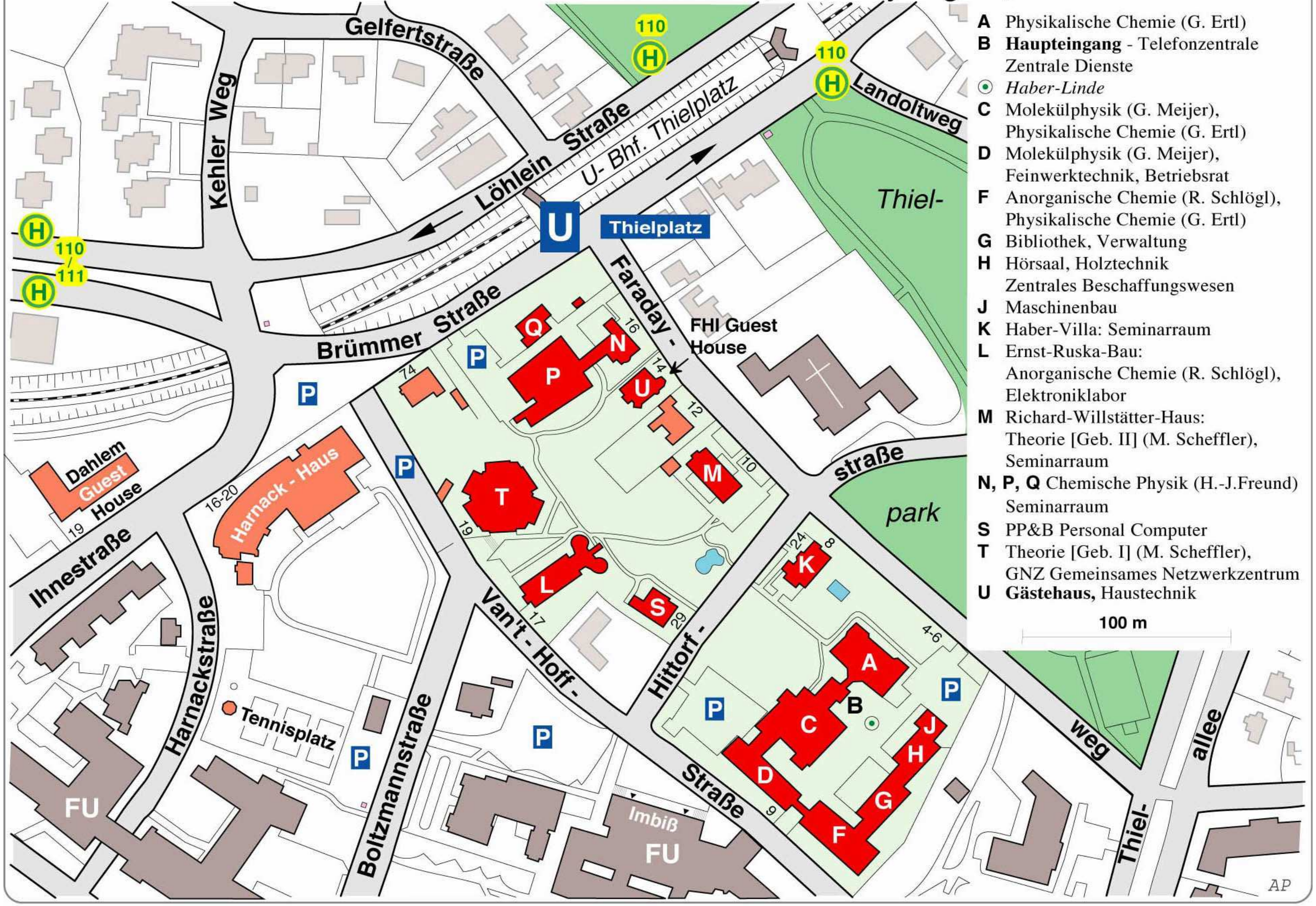
Jun 2002	DFT-Kolloquium am MPI für Mathematik, Leipzig, Germany *Multiskalenmethoden in der Materialwissenschaft*
Jul 2002	Kolloquium “Moleküle im Rechner”, FU Berlin, Germany *Kooperativität von Wasserstoffbrückenbindungen in Proteinen*
Sep 2002	3rd International Meeting on Challenges in Predictive Process Simulation (CHIPPS 2002), Prague, Czech. Rep. *Ab Initio Materials Design: From a Microscopic to a Mesoscopic Scale*
Feb 2003	DFG-Workshop “Substitutionseffekte in ionischen Halbleitern”, Schloss Rauischholzhausen, Marburg, Germany *Ab Initio (Parameter-Free) Analysis of Ionic Solids*
Mar 2003	APS-March Meeting, Austin, U.S.A. *Adatom Kinetics On and Below the Surface: The Existence of a New Diffusion Channel*
Mar 2003	2nd Crystal French-German Growth Meeting, Nancy, France *Crystal Growth Simulations Across Length and Time Scales*
Mar 2003	ONR Workshop on Defect Characterization Techniques in Wide Gap Semiconductors, Maui, Hawaii, U.S.A. *Analysis of Nitride Defects and Growth by Ab Initio Multiscale Modeling*
Mar 2003	DPG-Frühjahrstagung, Dresden, Germany *Tailoring Materials Properties by Surface Engineering*
May 2003	6th German-Vietnamese Seminar on Physics and Engineering, Chemnitz, Germany *Ab Initio Multiscale Simulations of Semiconductor Doping and Growth*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Algorithms for Total Energy Minimization*
Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Multi-Scale Approaches to Bridge Length and Time Scales*
Jul 2003	International Conference on Defects in Semiconductors, Aarhus, Denmark *Surface Controlled Doping and Defect Formation in Group-III Nitrides*

Sep 2003	WE-Heraeus-Ferienkurs “Nitridische und oxidische Wide-Gap-Halbleiter”, Magdeburg, Germany *Einführung in die Dichtefunktionaltheorie am Beispiel der GaN-Oberfläche*
Sep 2003	WE-Heraeus-Ferienkurs “Nitridische und oxidische Wide-Gap-Halbleiter”, Magdeburg, Germany *Elektronische Oberflächen- und Grenzflächeneigenschaften von Nitriden*
Sep 2003	E-MRS Fall Meeting, Symposium C, Warsaw, Poland *Multiscale Modelling of Group-III Nitride Growth*
Oct 2003	Bunsen Kolloquium “Bestimmung von Materialeigenschaften mit Dichte-Funktional-Methoden: Stand der Forschung”, Darmstadt, Germany *Von der Energie zum chemischen Potential*
Oct 2003	Bunsen Kolloquium “Bestimmung von Materialeigenschaften mit Dichte-Funktional-Methoden: Stand der Forschung”, Darmstadt, Germany *Ab initio basierte Multiskalenmethoden*

Abdallah Qteish

Jul 2003	Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering, and Biology, Berlin, Germany *Exact-Exchange Approach of the Kohn-Sham Formalism*

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



A	Physikalische Chemie (G. Ertl)
B	**Haupteingang** - Telefonzentrale Zentrale Dienste
⊙	*Haber-Linde*
C	Molekülphysik (G. Meijer), Physikalische Chemie (G. Ertl)
D	Molekülphysik (G. Meijer), Feinwerktechnik, Betriebsrat
F	Anorganische Chemie (R. Schlögl), Physikalische Chemie (G. Ertl)
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
T	Theorie [Geb. I] (M. Scheffler), GNZ Gemeinsames Netzwerkzentrum
U	**Gästehaus,** Haustechnik