FIESTAE 2011

Frontiers in InterfacE Science - Theory And Experiment

International symposium on the current status of surface and interface research in theory and experiment

June 29th - July 1st 2011

Fritz Haber Institute of the Max Planck Society, Berlin

FIESTAE 2011

Frontiers in InterfacE Science - Theory And Experiment

Fiestae,

a birthday present for Hajo Freund and Matthias Scheffler.

Gerard Meijer.

Hajo Freund turns 60…

From humble beginnings just a few decades ago, surface science, a field that spans chemistry, physics, and materials science, has emerged as one of the most fascinating interdisciplinary topics of research today. Studies of simple atomic and molecular adsorbates on low index surfaces of a small selection of elements have progressed to cover a multitude of complex surfaces and interfaces, and have a profound influence on fields such as heterogeneous catalysis, molecular beam epitaxy, low-dimensional ("nano") physics, and general solid state physics. Hajo Freund's professional career, ever since he earned his Diploma (in both chemistry and physics!) in 1975, has closely matched this development. His Ph.D. thesis (at the Universität zu Köln, 1978) dealt with spectroscopic studies of metal carbonyls and CO adsorbed on metal surfaces, which he analyzed in comparison to his own quantum chemical calculations. Realizing the enormous advantages of synchrotron radiation at an early stage, he spent two years as a postdoctoral fellow at the only dedicated synchrotron radiation light source then in existence, with Ward Plummer (University of Pennsylvania). His scientific achievements were quickly rewarded with the Habilitation and an associate professorship at the Universität Erlangen-Nürnberg (1983), where he expanded his scope of research beyond photo-emission and -absorption, for example to photo-induced desorption studies and electron energy loss spectroscopy.

The appointment to a Chair of Physical Chemistry at Ruhr-Universität Bochum (1987) gave him the chance to embark on an ambitious program of research into fundamental aspects of heterogeneous catalysis. Using epitaxial layers of oxides as substrates for small deposited metal clusters, he implemented a kind of model catalyst in which, under well-defined ultrahigh vacuum conditions, elementary steps of heterogeneous reactions could be studied with the methods of surface analysis. Notable examples of this concern hydrogenation, CO and CH_3OH oxidation reactions, work rewarded with the prestigious Leibniz Award of the German Science Foundation (DFG). These achievements led to his appointment, in 1995, to scientific member of the Max Planck Society and director of the Department of Chemical Physics at the Fritz Haber Institute. This transition marked an expansion of the experimental program, involving novel methods such as electron spin resonance on adsorbates in ultrahigh vacuum, a "photon-STM" for single particle luminescence experiments, sum-frequency and IR spectroscopy, to name a few.

This experimental basis expanded studies to materials of great interest in real-world catalysis, such as thin films of Al_2O_3, V_2O_3, SiO_2 and others, the preparation recipes of which were developed in his group. The reactivity of adsorbed metal nanoparticles was studied in novel triple molecular beam experiments, as well as their structure through AFM at ultralow temperatures with atomic resolution. The trend towards increasing complexity in surface science as a whole is thus mirrored in the intense research effort of Hajo Freund. This work, carried out with over 100 Ph.D. students and about 70 postdocs, has brought international recognition to him and his department, and numerous awards and honours, such as the Karl-Ziegler-Prize 2011 of the Gesellschaft Deutscher Chemiker. Beyond his intense research effort, Hajo Freund has found the time to serve in many important functions for the community, rendering important service to his colleagues, for example as founding member of the European Research Council.

We look forward to seeing many years of scientific activity from Hajo Freund, and to intense scientific and personal cooperation with him, in his inimitable "rheinisch" personal style. Hajo, "ad multos annos!"

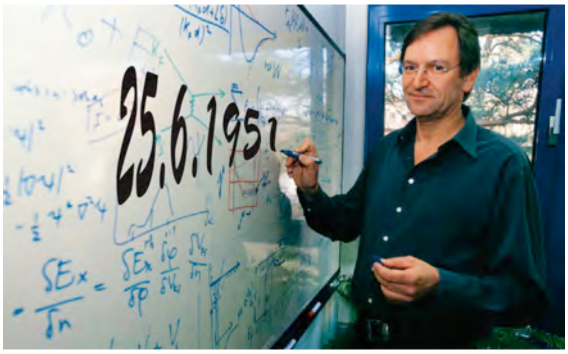
… and so does Matthias Scheffler!

The year is 1975. A young student of the Technische Universität Berlin is ready to leave his footprint on theoretical solid state physics. In talks with Frank Forstmann and Kyozaburo Kambe, he becomes aware of the potential of the newly introduced method of angle-resolved photoemission for electronic structure studies, which will eventually develop into one of the most important tools of solid state physics. Thus, he decides to put the analysis of such data on a sound theoretical foundation. The student, Matthias Scheffler, finds that the best place to do his Diploma thesis is the Fritz Haber Institute, where the first instrument of its kind in Germany is about to be installed. In his Ph.D. thesis (1978), he develops, among other things, a Green function approach for calculating photoemission spectra and thus sets the stage for the widespread application of this method in solid state physics. He probably does not anticipate that he will continue to make, beyond his many other endeavors, important contributions to this topic throughout his career.

Even earlier, at a summer school in Trieste, Matthias realizes the enormous potential of density functional theory (DFT), a method that would revolutionize our understanding of electronic structure, from simple 3D crystalline solids to molecules, surfaces, "nano" structures, and so on. Matthias and his collaborators would play a decisive role in this revolution, which has since led to a veritable "industry" of (even predictive) studies. Having moved to the Physikalisch-Technische Bundesanstalt in Braunschweig as staff scientist after his Ph.D., and eager to get better acquainted with the method, he spends a productive "sabbatical" period at IBM Thomas J. Watson Research Center in New York, shifting his focus to semiconductors and their (technologically important) defects. This expansion of his work would lead to several offers of high profile academic positions; fortunately the Max Planck Society is successful in appointing him as scientific member and founding director of the Department of Theory of the Fritz Haber Institute (1988), an important step in the evolution of the structure of the institute, strengthening the interaction between theory and experiment.

Expanding the development of DFT and pushing it forward, today Matthias Scheffler's department covers an ever-increasing number of topics, from the analysis of surface phases to complex molecular dynamics studies of adsorption and surface reactions. Such studies are accompanied by strong efforts in methods and code development, for example through his approaches of "*ab-initio* atomistic thermodynamics" and "first-principles statistical mechanics," or the inclusion of van der Waals bonding into DFT. The widespread use of DFT is documented in work on liquid and solid water and in biophysics, topics far apart from the original work of the department. The impact and importance of the method is demonstrated by the recent (2010) conference on DFT organized by Matthias Scheffler and his group, which attracted an audience of more than 1000 - setting a record for a theoretical physics conference. Beyond his active scientific work, he has formed a wide network of collaborations, organized summer schools to educate young scientists in the new methods of "computational materials science," and served the scientific community in many functions.

Given the ever-increasing depth and breadth of work of Matthias and his group, with advancements in the treatment of many-electron correlation and new numerical techniques, we can look forward to deep insights into systems that were too complex to deal with for theoretical treatment just a few years ago – let's hope for the experimentalists that predictive theoretical treatment does not render their work entirely redundant!



Program

Program

Tuesday June 28th, 2011

17:00-22:00 Registration
19:00-22:00 Reception

Wednesday June 29th, 2011

08:45 **Opening Address: Gerard Meijer**
09:00 **Joachim Sauer**, Berlin
Quantum chemistry of oxides: clusters, surfaces, catalysts
09:35 **Gianfranco Pacchioni**, Milano
Electron transfer at oxide surfaces: the MgO paradigm
10:10 **Marcus Bäumer**, Bremen
Rational design of catalysts: illusion or almost reality?

Coffee

11:15 **Horia Metiu**, Santa Barbara
Catalytic methane activation by modified oxides
11:50 **Hardy Gross**, Halle
Pushing the limits of electronic structure theory: from static to time-dependent probes

Lunch

14:00 **Jörg Libuda**, Erlangen
Model catalysis: from old ideas to new concepts
14:35 **Jörg Neugebauer**, Düsseldorf
Ab-initio thermodynamics: from catalytic surfaces to high strength steels
15:10 **Kristen Fichthorn**, University Park
Understanding the controlled growth of colloidal nanostructures

Coffee

16:15 **Günther Rupprechter**, Vienna
Surface science and technological catalysis on PdZn and PdOx
16:50 **Peter Stair**, Evanston
Atomic layer deposition for the synthesis of catalysts

Buffet Snacks

20:00 **POSTER SESSION**

Thursday June 30th, 2011

09:00 **Hans-Peter Steinrück**, Erlangen
Surface science of complex molecular systems
09:35 **Katharina Al-Shamery**, Oldenburg
Elementary processes in photocatalysis
10:10 **Chris van de Walle**, Santa Barbara
Point defects in titania

Coffee

11:15 **Peter Kratzer**, Duisburg
Atomic processes in GaAs nanowire growth
11:50 **Ward Plummer**, Baton Rouge
Broken symmetry and spatial confinement in correlated materials

Lunch

14:00 **Axel Groß**, Ulm
Dynamics simulations at surfaces: from hydrogen adsorption to electrochemical interfaces
14:35 **Ingrid Mertig**, Halle
Magnetoelectric coupling at interfaces and surfaces

15.10 CONFERENCE PHOTO

Coffee

15:40 **Angel Rubio**, San Sebastian
First-principles simulation of the spectroscopic properties of low dimensional systems
16:15 **Dietrich Menzel**, Munich
Photochemistry at nanoparticles

18:00 **CONFERENCE DINNER**

20:00 **AFTER-DINNER LECTURE**
Wolgang Eberhardt, Berlin
Surface and interface science: Research for the energy of tomorrow

Friday July 1st, 2011

09:00 **Eberhard Umbach**, Karlsruhe
Energy research: how can we meet the challenges?
09:35 **Sokrates Pantelides**, Nashville
From memories to frontiers in complex oxides

Coffee

10:40 **Roberto Car**, Princeton
Hydrogen bonds and quantum mechanics
11:15 **Cynthia Friend**, Cambridge MA
Heterogeneous catalysis for energy efficiency: the roles of dynamic defects

13:30 LAUDATIONES

Martin Stratmann, Düsseldorf

Ole Krogh Andersen, Stuttgart

John Hemminger, Irvine

followed by **RECEPTION**

from 17:00 **SUMMER PARTY OF THE FRITZ HABER INSTITUTE**

INVITED TALKS

Quantum chemistry of oxides: Clusters, surfaces, catalysts

Joachim Sauer
Institut für Chemie, Humboldt-Universität, Unter den Linden 6, 10000 Berlin, Germany

Combining quantum chemistry and experiment is a most successful strategy for solving problems in catalysis, surface science and cluster chemistry of oxides. Examples are presented for zeolites [1] "simple" metal oxides (MgO [2], Al_2O_3 [3], SiO_2 [4]), transition metal (vanadium) oxide [5] and rare earth (cerium) oxides (CeO_2) [6]. The challenges are connecting quantum chemical results with experiment, selecting proper quantum chemical tools, e.g. going beyond the generalized gradient approximation in density functional theory, treating long-range dispersion properly [7,8], and make use of wave-function based electron correlation methods for large systems [7,9].

[1] Svelle, S.; Tuma, C.; Rozanska, X.; Kerber, T.; Sauer, J. *J. Am. Chem. Soc.* 2009, **131**, 816-825.
[2] Kwapien, K.; Sierka, M.; Döbler, J.; Sauer, J.; Haertelt, M.; Fielicke, A.; Meijer, G. *Angew. Chem., Int. Ed.* 2011, **50**, 1716-1719.
[3] Nilius, N.; Ganduglia-Pirovano, M. V.; Brazdova, V.; Kulawik, M.; Sauer, J.; Freund, H. J. *Phys. Rev. Lett.* 2008, **100**, 096802.
[4] Löffler, D.; Uhlrich, J. J.; Baron, M.; Yang, B.; Yu, X.; Lichtenstein, L.; Heinke, L.; Büchner, C.; Heyde, M.; Shaikhutdinov, S.; Freund, H.-J.; Wlodarczyk, R.; Sierka, M.; Sauer, J. *Phys. Rev. Lett.* 2010, **105**, 146104.
[5] Rozanska, X.; Fortrie, R.; Sauer, J. *J. Phys. Chem. C* 2007, **111**, 6041-6050.
[6] Ganduglia-Pirovano, M. V.; Popa, C.; Sauer, J.; Abbott, H. L.; Uhl, A.; Baron, M.; Stacchiola, D.; Bondarchuk, O.; Shaikhutdinov, S.; Freund, H.-J. *J. Am. Chem. Soc.* 2010, **132**, 2345-2349.
[7] Tuma, C.; Sauer, J. *Phys. Chem. Chem. Phys.* 2006, **8**, 3955-3965.
[8] Kerber, T.; Sierka, M.; Sauer, J. *J. Comput. Chem.* 2008, **29**, 2088-2097.
[9] Tosoni, S.; Sauer, J. *Phys. Chem. Chem. Phys.* 2010, **12**, 14330-14340.

Electron transfers at oxide surfaces. The MgO paradigm: From F centers to tunneling effects

Gianfranco Pacchioni
Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,
via Cozzi, 53 - 20125 Milano, Italy

Electron transfer is a key aspect of the reactivity of oxide surfaces and interfaces. It has direct impact on the functionality of heterogeneous catalysts, sensors, oxides as passive layers in corrosion protection or as dielectric barriers in microelectronic devices. Understanding how molecules interact and exchange electrons with simple oxides (such as MgO) is a necessary prerequisite in order to be able to address and control phenomena occurring on more complex oxide surfaces. In this talk we will review 50 years of work aimed at understanding electron transfer processes at the surface of MgO. We will analyze the first experiments showing the activation by direct electron transfer of O_2 adsorbed on UV-irradiated MgO with formation of O_2^- radicals [1]. We will discuss the attempts to rationalize these results by extending to the surface concepts derived for the bulk material, and in particular the notion of oxygen vacancy, or F center [2,3]. We will critically review the successes and the failures of these models, and how using more sophisticated experimental and theoretical tools it has been possible in recent years to rationalize the formation of electron rich surfaces based on radically different models of electron traps [4-6]. We will discuss how F centers have been finally “seen” and how their properties have been measured thanks to sophisticated atomic probes and ultrathin films technology [7-10]. Finally, we will show how ultrathin MgO films can also give rise to spontaneous charge transfer with formation of superoxo O_2^- radicals even in absence of trapped electrons or other defects [11].
Thanks to 50 years of experimental and theoretical efforts, our present understanding of electron transfers at oxide surfaces can be considered quite detailed.

[1] J.H. Lunsford and J.P. Jayne, *J. Chem. Phys*. **44**, 1487 (1966).
[2] A. J. Tench, *Surf. Sci*. **25**, 625 (1971).
[3] R. R. Sharma and A. M. Stoneham *Chem. Soc. Faraday Trans*. II **72**, 913 (1976).
[4] E. Giamello, M. C. Paganini, D. Murphy, A. M. Ferrari, G. Pacchioni, *J. Phys. Chem*. B **101**, 97 (1997).
[5] D. Ricci, C. Di Valentin, G. Pacchioni, P. Sushko, A. Shluger, E. Giamello, *J. Am. Chem. Soc.* **125**, 738 (2003).
[6] M. Chiesa, M. C. Paganini, E. Giamello, D. M. Murphy, C. Di Valentin, G. Pacchioni, *Acc. Chem. Res*. **39**, 861 (2006).
[7] M. Sterrer, E. Fischbach, T. Risse, H. J. Freund, *Phys. Rev. Lett.* **94**, 186101 (2006).
[8] M. Sterrer, M. Heyde, M. Novicki, N. Nilius, T. Risse, H. P. Rust, G. Pacchioni, H. J. Freund, *J. Phys. Chem. B* **110**, 46 (2006).
[9] T. König, G. H. Simon, H. P. Rust, G. Pacchioni, M. Heyde, H. J. Freund, *J. Am. Chem. Soc.* **131**, 17544 (2009).
[10] T. König, G. H. Simon, U. Martinez, L. Giordano, G. Pacchioni, M. Heyde, H. J. Freund, *ACS Nano* **4**, 2510 (2010).
[11] A. Gonchar, T. Risse, H.-J. Freund, L. Giordano, C. Di Valentin, G. Pacchioni, *Angew. Chem*. **50**, 2635 (2011).

Rationally designed catalysts: (Still) illusion or (almost) reality?

Marcus Bäumer
Universität Bremen, Institut für Angewandte und Physikalische Chemie,
Leobener Str. NW2, 28357 Bremen, Germany

Control over the microscopic structure and composition is essential to develop active and selective catalytic systems. Whereas traditional techniques allow only very limited or no control in this respect, advanced techniques from nanotechnology and materials science offer new and fascinating manufacturing strategies for materials with defined structures down to the nanoscale. Is it possible to take advantage of this potential in view of rationally designed catalysts? My talk will deal with this question taking two illustrative examples: nanoporous metal foams and deposited colloidal nanoparticles.

A particularly interesting example with respect to the first class of systems is nanoporous gold (npAu), whose pore structure can be adjusted from nanometers to micrometers. In spite of the fact that structural features usually considered to be important ingredients for active gold catalysts (nanoparticles on selected oxide supports) are missing, it shows a surprising activity e.g. for the low temperature CO oxidation. Even more remarkable is the selectivity observed for oxidation reactions of alcohols. The product pattern for various alcohols is in full agreement with single crystal studies under UHV conditions showing that the catalytic properties are governed by Au and that the fundamental understanding of its surface chemistry allows far-reaching predictions regarding the catalytic performance of npAu. The activation of molecular oxygen, not being possible on pure gold however, is brought about by Ag atoms at the surface or TiO_2 deposits as predicted by DFT calculations.

The second part of my talk will focus on the structurally inverse situation, i.e. nanoparticles. Here, the potential of colloidal chemistry to precisely control the particle size and – in case of bimetallic particles – the composition will be highlighted. Likewise interesting is the possibility to take advantage of the organic ligand shell surrounding the particles from the synthesis as structural elements to bring in additional functionalities. A particular interesting example is the modification of metal-support interactions by such ligands. In the case of Pt/FeOx where a strong SMSI effect was predicted on the basis of UHV single crystal work, a strategy was found to induce such an enhancement of catalytic activity in a controlled fashion by applying ligand capped Pt nanoparticles. Other results comprising oxidation and hydrogenation reactions show that the ligands can also efficiently protect particles with respect to surface oxidation and prevent sintering while still allowing high catalytic activity.

[1] V. Zielasek, B. Jürgens, Ch. Schulz, J. Biener, M.M. Biener, A.V. Hamza, M. Bäumer, *Angew. Chem. Int. Ed.* **45**, 8241 (2006); *Angew. Chem.* **118**, 8421 (2006).
[2] B. Jürgens, Ch. Schulz, T. Nowitzky, V. Zielasek, J. Biener, M. M. Biener, A. V. Hamza, M. Bäumer, *Gold Bulletin* **40**, 142 (2007).
[3] A. Wittstock, V. Zielasek, J. Biener, C. Friend, M. Bäumer, *Science* **327**, 319 (2010).
[4] H. Borchert, D. Fenske, J. Kolny-Olesiak, J. Parisi, K. Al-Shamery, M. Bäumer, *Angew. Chem., Int. Ed.* **46** (2007) 2923, Angew. Chem. **119** (2007) 2981.
[5] B. Jürgens, H. Borchert, K. Ahrenstorf, P. Sonström, A. Pretorius, M. Schowalter, K. Gries, V. Zielasek, A. Rosenauer, H. Weller, M. Bäumer, *Angew. Chem. Int. Ed.* **47**, 8946 (2008), *Angew. Chem.* **120**, 9078 (2008).

Doped oxides as catalysts for methane activation

Eric McFarland[1] and Horia Metiu[2]
[1]Department of Chemical Engineering and [2]Department of Chemistry & Biochemistry,
University of California, Santa Barbara, California 93106, USA

We use density functional theory and experiments to study the chemical properties of the surfaces of substitutionally doped oxides (e.g. Pt-doped CeO_2 is CeO_2 with a fraction of the Ce atoms replaced with Pt atoms). Our goals are to use doping to improve the ability of oxides to catalyze methane or CO_2 activation and to find general rules that allow a classification of the behavior of various dopant-oxide pairs. Our calculations led us to classify the dopants into low-valence dopants (LVDs), high-valence dopants (HVDs), and flexible-valence dopants (FVDs). A low-valence dopant is one whose highest valence in its stable oxides is lower than the valence of the dopant it substitutes. For example a Cu dopant in La_2O_3 is a low-valence dopant because the highest valence in a stable Cu oxide is II and La in La_2O_3 is trivalent. We found the following rules for these dopants. 1. They lower substantially the energy of oxygen-vacancy formation. 2. The surface oxygen atoms in the doped oxide are more reactive than in the undoped oxide. 3. The LVDs affect oxygen atoms located at large distance from the dopant. 4. Surfaces doped with LVDs display a chemical compensation effect: the adsorption of an electron donor almost cancels the effect of the dopant. 5. Electron donors co-adsorbed on the surface of an oxide doped with LVDs interact very strongly. 6. The presence of LVDs in an oxide accelerates the oxidation reactions taking place through a Mars-van Krevelen mechanism, as compared to the same reaction on the undoped oxide. A high-valence dopant (HVD) is a dopant whose lowest valence in its stable oxides is higher than the valence of the cation it substitutes in the host oxide. An example is Ti-doped ZnO: the lowest valence of Ti in its stable oxides is III and it replaces Zn, whose valence is II. We have found the following rules for HVDs. 1. The presence of HVDs on the surface of an oxide increases the energy required for making oxygen vacancies in the neighbourhood of the dopant. 2. Gaseous oxygen adsorbs on an HVD dopant and is activated so that it reacts easily with CO to make a carbonate or with methane to make a methoxide and a hydroxyl. 3. The adsorption of an electron acceptor on a HVD tends to counteract the effect of the dopant on the doped oxide. Finally, there are dopants that do not fit in either of these categories. For example, consider Nb doping of CeO_2. Nb has three stable oxides, Nb_2O_5, NbO_2, and NbO; in the first oxide Nb's valence is higher than that of Ce, and in the other two it is lower. It is not clear *a priori* what valence the dopant will take when it is in the host oxide. We call such dopants flexible-valence dopants (FVDs). So far, we have found no common rules in the behavior of FVDs. We have also begun to study the effect of substitutional anion-doping and will report some of the preliminary results, if time permits.

Pushing the limits of electronic structure theory: From static to time-dependent probes

E.K.U. Gross
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06108 Halle, Germany

Traditional ab-initio calculations of materials are concerned either with ground-state properties or with photoemission and optical spectra. Recent years have seen the advent of a variety of time-resolved techniques, such a pump-probe spectroscopy, yielding a wealth of fascinating information complementary to the traditional techniques. In this lecture, time-dependent density functional theory (TDDFT) beyond the linear regime will be developed as a tool to analyse and control electronic motion in the time-domain. In particular:

(i) A novel approach to describe **electronic transport** through single molecules or atomic wires, sandwiched between semi-infinite leads, will be presented. The basic idea is to propagate the time-dependent Kohn Sham equations in time upon ramping up a bias between the metallic leads. In this way, genuinly time-dependent phenomena, not accessible in the standard Landauer approach, can be addressed. For example, employing an Anderson model, we demonstrate that Coulomb blockade corresponds, in the time-domain, to a periodic charging and discharging of the quantum dot [1].

(ii) With modern pulse-shaping facilities, the **control of electronic motion** is becoming more and more realistic. By combining quantum optimal control theory with TDDFT, we calculate shaped laser pulses suitable to control, e.g., the chirality of currents in quantum rings [2], the location of electrons in double quantum dots, as well as the enhancement of a single peak in the harmonic spectrum

(iii) A time-dependent generalization of the so-called **electron localization function** (TDELF) will be presented as a universally applicable tool to visualize and analyze electronic motion in a time-resolved fashion. As an example, a movie of the TDELF visualizing a laser-induced π-π* transition in acetylene will be shown.

(iv) In all practical calculations, approximate forms of the exchange-correlation potential of TDDFT need to be employed. One of the most popular approximations, the adiabatic local-density approximation (ALDA) will be analyzed as to whether the main error comes from the adiabaticity assumption, i.e. locality in time, or from the LDA, i.e. locality in space. For an exactly solvable model system where the **exact adiabatic approximation** can be extracted, we find the surprising fact, that the adiabaticity assumption can be an excellent approximation even in highly intense laser fields [3].

[1] S. Kurth, G. Stefanucci, E. Khosravi, C. Verdozzi, E.K.U. Gross, *Phys. Rev. Lett.* **104**, 236801 (2010).
[2] E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U. Gross, *Phys. Rev. Lett.* **98**, 157404 (2007).
[3] M. Thiele, E.K.U. Gross and S. Kümmel, *Phys. Rev. Lett.* **100**, 153004 (2008*).*

Model catalysis: Old ideas, new concepts

Jörg Libuda
Department of Chemistry and Pharmacy and Erlangen Catalysis Resource Center, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

Single-crystal based supported model catalysts have been a fascinating research topic for decades. [1] Consisting of nanometer-sized active metal or oxide particles supported on ordered oxide surfaces, such models expose complex yet well-defined reactive surfaces. New reaction mechanisms and kinetic effects can be identified on these systems and studied using a surface science approach.

Two examples are discussed from recent research. The first example is related to the phenomenon of metal oxide interaction and spillover in heterogeneous catalysis [2-4]. We have investigated the interaction of different reactants, e.g. O_2, CO, CO_2, CH_4, C_2H_4, H_2, H_2O, and SO_2, with noble metal nanoparticles on a reducible ceria surface. For the case of supported Pt nanoparticles it is shown that spillover, i.e. diffusion via the oxide-metal boundary, may occur for many different surface species including H, O, hydrocarbon fragments, or SO_x. Often, the spillover process is connected to a change of the charge or oxidation state of the surface species, thus giving rise to characteristic changes of the oxidation state of the reducible support. On ceria, these changes can be monitored with highest sensitivity using resonant photoelectron (RPES) spectroscopy and provide detailed insight into a rich surface chemistry.

The second example explores a novel field of research, which is supported model catalysts modified by ionic liquid (IL) layers [5-7]. Such IL-modified catalysts may show new and beneficial properties. It is noteworthy that the related ILs have an extremely low vapor pressure, so that thin films of these materials on model catalysts can be studied in ultrahigh vacuum (UHV) using surface science techniques. We prepare model systems using Pt and Pd nanoparticles supported on ordered alumina films on which thin IL films are deposited in UHV. These models are used to study the interaction of ILs with the oxide support, the metal particles, and the adsorbates. Interactions, which may be at the origin of the reactivity modifications observed for real catalysts, can be identified by infrared reflection absorption spectroscopy (IRAS).

[1] J. Libuda, M. Bäumer, H.-J. Freund, *J. Vac. Sci. Technol. A* 1994, **12**, 2259.
[2] G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman, J. Libuda, *Nature Materials* 2011, **10**, 310.
[3] Y. Lykhach, T. Staudt, N. Tsud, T. Skala, K. C. Prince, V. Matolin, J. Libuda, *Phys. Chem. Chem. Phys.* 2011, **13**, 253.
[4] F. Vines, Y. Lykhach, T. Staudt, M. P. A. Lorenz, C. Papp, H.-P. Steinrück, J. Libuda, K. M. Neyman, A. Görling, *Chem. - Eur. J.* 2010, **16**, 6530.
[5] H.-P. Steinrück, J. Libuda, P. Wasserscheid, T. Cremer, C. Kolbeck, M. Laurin, F. Maier, M. Sobota, P. S. Schulz, M. Stark, *Adv. Mat.* 2011, DOI: 10.1002/adma.201100211.
[6] M. Sobota, M. Happel, M. Amende, N. Paape, P. Wasserscheid, M. Laurin, J. Libuda, *Adv. Mat.* 2011, DOI: 10.1002/adma.201004064.
[7] M. Sobota, I. Nikiforidis, W. Hieringer, N. Paape, M. Happel, H.-P. Steinrück, A. Görling, P. Wasserscheid, M. Laurin, J. Libuda, *Langmuir* 2010, ***26,*** 7199.

Ab initio thermodynamics: From catalytic surfaces to high-strength steels

Jörg Neugebauer
Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Extending originally T=0K ab initio approaches to describe all relevant excitation mechanisms in solids such as configurational, electronic, vibronic and magnetic excitations provides a direct and fully parameter-free route to determine temperature, pressure and composition dependent free energies. This ability to compute accurate free energies opened completely new and highly successful routes to address materials science questions in areas as diverse as surface science/catalysis, opto- and microelectronics, or modern functional and structural alloys to name only a few. In the talk a brief overview about the beginnings, the present status but also the future tasks of this exciting research field will be given.

Understanding the controlled growth of colloidal nanostructures

Kristen A. Fichthorn
Penn State University, USA

We employ first-principles, density-functional theory (DFT) calculations to resolve the role of polyvinylpyrrolidone (PVP) in the controlled synthesis of colloidal Ag nanostructures. This polymer plays a central but poorly understood role in the selective formation of a large variety of metal nanostructures. One hypothesis is that PVP is an effective structure-directing agent because of its surface-sensitive binding. Examining the case of Ag, it has been proposed that PVP binds more strongly to Ag(100) than to Ag(111). Interestingly, this binding involves both direct chemical bonds and van der Waals (vdW) interactions. We compare two methods for including vdW interactions in DFT: Grimme's method and the Tkatchenko-Scheffler method and find the latter method to be the most suitable. We find that the binding of 2-pyrrolidone is stronger on Ag(100) than on Ag(111), consistent with experimental observations. Our studies indicate that an interplay between direct bonding, vdW attraction, and Pauli repulsion is responsible for this surface sensitivity and that a delicate balance between these interactions may be a requirement for a successful structure-directing agent.

Surface science and technological catalysis on PdZn and PdO_x

Günther Rupprechter
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria

Model catalysis has come a long way and an increasing number of technical catalysts can be mimicked by planar model systems prepared under ultrahigh vacuum [1]. Surface Science studies can also be carried out at near atmospheric pressure, e.g. by using polarization-modulated infrared reflection absorption spectroscopy (PM-IRAS) or high-pressure X-ray photoelectron spectroscopy (HP-XPS) [2,3]. Nevertheless, despite the arsenal of characterization methods, sometimes very basic questions about catalytic selectivity or specific activity of different phases (such as metal vs. oxide) remain unanswered or even prompt very "vivid" discussions between research groups. In this contribution we discuss two examples: (i) methanol steam reforming and (ii) good ol´ CO oxidation and hope to shed some light on them, also by comparison with technological catalysts.

(i) Methanol can be used for H_2 generation via catalytic methanol steam reforming ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) on Pd-ZnO catalysts, provided the reaction runs with high selectivity, avoiding undesired CO. PdZn alloys have been identified as active phase and we have utilized both model (PdZn/Pd(111)) and technological (PdZn-ZnO) catalysts, examined by *in situ* PM-IRAS, FTIR, EXAFS and XPS [3,4]. Although a multilayer and a monolayer PdZn surface alloy both exhibited an identical Pd:Zn 1:1 surface composition, their geometric and electronic structures were different. The CO_2-selective multilayer alloy featured a lowered density of states close to the Fermi edge and surface ensembles of PdZn exhibiting a "Zn-up/Pd-down" corrugation, representing "bifunctional" sites for water and methanol activation.

(ii) Despite molecular beam studies of reaction probabilities of CO oxidation on metallic and oxidic palladium [5], the active species present under technical conditions is still controversially discussed. This study aimed at a fundamental investigation of the reaction mechanism of CO oxidation on industrial-grade Pd catalysts, using *in situ* FTIR, EXAFS and *ex situ* HRTEM, by evaluating the activity of different PdO_x (x=0-1) species [6]. The highly dynamic behaviour of partial PdO_x formation, that can be easily decomposed/reduced (at low temperature) to metallic palladium in the presence of CO, led under very specific conditions to oscillatory behaviour, which provides a direct route to identify the (more) active phase.

[1] H.-J. Freund, *Chem., A Eur. J.* **16** (2010) 9384.
[2] G. Rupprechter, *Advances in Catalysis* **51** (2007) 133.
[3] Ch. Rameshan et al., *Angew. Chemie Int. Ed.* **49** (2010) 3224.
[4] K. Föttinger, J.A. van Bokhoven, M. Nachtegaal, G. Rupprechter, *J. Phys. Chem. C Lett.* **2** (2011) 428.
[5] H. Gabasch, A. Knop-Gericke, R. Schlögl, M. Borasio, C. Weilach, G. Rupprechter, S. Penner, B. Jenewein, K. Hayek, and B. Klötzer, *PCCP* **9** (2007) 533 (and references therein).
[6] K. Zorn, S. Giorgio, C.R. Henry, H. Grönbeck, G. Rupprechter, *J. Phys. Chem. C* **115** (2011) 1103.

Atomic layer deposition for the synthesis of catalysts

Peter C. Stair
Professor of Chemistry, Department of Chemistry, Northwestern University
Director, Northwestern University Center for Catalysis and Surface Science
Director, Institute for Catalysis in Energy Processes
Deputy Director, Institute for Atom-efficient Chemical Transformations.
Senior Scientist, Chemical Sciences and Engineering Division, Argonne National Laboratory, USA

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane.

More recently we have studied the synthesis of supported metal particles and developed what we call “ABC-type” ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible the synthesis exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles can be stabilized against sintering while still remaining active at high temperatures and reaction conditions.

Surface science of complex molecular systems

Hans-Peter Steinrück
Physikalische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 3,
D-91058 Erlangen, Germany

Chemical reactions on surfaces can be followed in detail using X-ray photoelectron spectroscopy (XPS or ESCA). From the binding energies of the adsorbate and substrate core levels, detailed information on the chemical composition, chemical state (e.g. oxidation state), adsorption sites, but also on the photoemission process itself can be derived. Based on the understanding obtained for simple adsorbate systems, now complex molecular systems can be studied in great detail. In this presentation two examples will be addressed. The first deals with the adsorption of **metalloporphyrins on metal surfaces** and their interaction with small molecules. In particular we focus on the synthesis of metalloporphyrin monolayers by direct metalation of porphyrin monolayers, the chemical interaction with the metal surface and attachment of axial ligands on the central metal ion of the metalloporphyrin. The second example is the characterization and modification of the **surface properties of ionic liquids.** Due to their low vapor pressure the full arsenal of UHV-based surface science methods can be applied to investigate this material class and detailed information can be derived.

[1] J. M. Gottfried, K. Flechtner, A. Kretschmann, T. Lukasczyk, and H.-P. Steinrück, *J. Am. Chem. Soc.* **128** (2006) 5644-5645.
[2] K. Flechtner, A. Kretschmann, L. R. Bradshaw, M.-M. Walz, F. Maier, H.-P. Steinrück and J. M. Gottfried, *J. Phys. Chem.* **111** (2007) 5821-5824.
[3] T. E. Shubina, H. Marbach, K. Flechtner, A. Kretschmann, N. Jux, F. Buchner, H.-P. Steinrück, T. Clark, and J. M. Gottfried, *J. Am. Chem. Soc.* **129** (2007) 9476-9483.
[4] K. Flechtner, A. Kretschmann, H.-P. Steinrück, and J. M. Gottfried, *J. Am. Chem. Soc.* **129** (2007) 12110-12111.
[5] F. Buchner, I. Kellner, W. Hieringer, A. Görling, H.-P. Steinrück, H. Marbach, *Phys. Chem. Chem. Phys.* **12** (2010) 13082-13290.
[6] W. Hieringer, K. Flechtner, A. Kretschmann, K. Seufert, W. Auwärter, J.V. Barth, A. Görling, H.-P. Steinrück, J. M. Gottfried, *J. Am. Chem. Soc.* **133** (2011) 6206-6222.
[7] F. Maier, J. M. Gottfried, J. Rossa, D. Gerhard, P. S. Schulz, W. Schwieger, P. Wasserscheid, H.-P. Steinrück, *Angew. Chem. Int. Ed.* **45** (2006) 7778-7780 and *Angew. Chem.* **118** (2006) 7942-7944.
[8] H.-P. Steinrück, *Surf. Sci.* **604** (2010) 481-484 (Invited Prospective Article).
[9] K. R. J. Lovelock, I. J. Villar-Garcia, F. Maier, H.-P. Steinrück, P. Licence, *Chem. Rev.* **110** (2010) 5158-5190.
[10] H.-P. Steinrück, J. Libuda, P. Wasserscheid, T. Cremer, C. Kolbeck, M. Laurin, F. Maier, M. Sobota, P. S. Schulz, M. Stark, *Adv. Mater.* (2011).

Elementary processes in photocatalysis

Katharina Al-Shamery
Carl v. Ossietzky University Oldenburg, Faculty V, D-26111 Oldenburg, Germany

The need for renewable energies is of growing demand world wide. One of the most promising approaches which circumvents problems with the fluctuations of the renewable energy sources is the chemical storage of solar energy. However, in order to be able to tailor the best photocatalysts for achieving high efficiencies of photoinduced processes it is crucial to gain a principal understanding of the underlying elementary processes. Some of the key features are long life times of electronically excited states and the concomitant dissipation into the desired molecular motions prior to bond breaking and bond making. A promising approach is to reduce the photoactive material to nanometer dimensions to enhance cross sections of photochemical reactions [1,2]. Real time femtosecond measurements using time resolved second harmonic generation at metal-semiconductor interfaces will be presented. They exhibit the intriguing influence of interfacial trapping of hot electrons on electron phonon coupling processes. Fundamental investigations using femto- and nanosecond laser pulses combined with quantum state resolved detection methods give insight into the energy partitioning processes in photo desorption and photo reaction. Results on laser induced desorption of CO and NO adsorbed on Pt and Pd-nanoaggregates on an oxidic support will be compared with each other. Phenomena such as energy pooling processes in adsorbates at nanoparticulate surfaces on ultrafast time scales, adsorbate induced nanoparticle reshaping in the course of photochemical reactions, spill over in photochemistry or the role of the particle perimeters will be presented. As an example of a photo reaction results on the photodissociation of methane will be shown. New perspectives for future designs of more efficient photochemical materials will be outlined.

[1] K. Al-Shamery, J. *Phys. Cond. Matt*. **18** (2006) 1581-1601.
[2] K. Al-Shamery, A. Al-Shemmary, R. Buchwald, D. Hoogestraat, M. Kampling, P. Nickut, A. Wille, *European Physical Journal B (Condensed Matter and Complex Systems)* **75** (2010) 107-114.

I13

Point defects in titania

Chris G. Van de Walle
Materials Department, University of California, Santa Barbara, USA

TiO_2 is a material of increasing interest in electronics and optoelectronics, with applications in high-k dielectrics, solar cells, and photocatalysis. Rutile TiO_2 has a wide band gap of 3.1 eV and exhibits a tendency for unintentional *n*-type conductivity. Understanding and controlling this conductivity is a key step toward the wider application of TiO_2 as a semiconductor. Here we use density functional theory to address the structural and electronic properties of point defects and impurities in TiO_2. The use of a hybrid functional allows us to overcome the “band-gap problem”. Unintentional *n*-type conductivity in TiO_2 has often been attributed to oxygen vacancies. We find that oxygen vacancies are indeed shallow donors, but they have high formation energies and hence their equilibrium concentration will be low. Consequences for electronic transport and for the behavior of oxygen vacancies on the TiO_2 surface will be discussed.

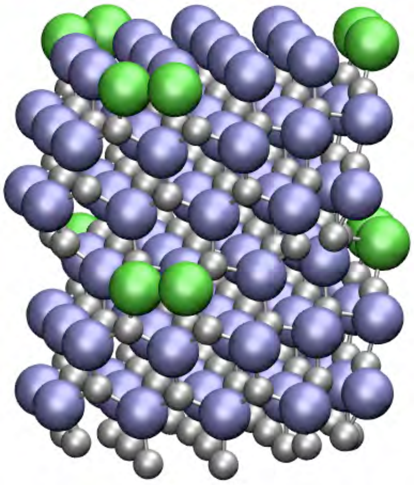
Work performed in collaboration with Anderson Janotti, Joel Varley, Patrick Rinke, and Georg Kresse.

I 14

Atomic processes in GaAs nanowire growth

Peter Kratzer, Volker Pankoke, and Sung Sakong*
Faculty of Physics, University Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany

The spontaneous growth of solid nanoscale wires from a semiconducting material on a substrate by vapor-phase epitaxy has raised expectations for wide-spread application of these cheaply available quasi-one-dimensional structures, e.g. in solar cells or thermoelectric converters. Using nanoparticles of Au (or other metals) as catalyst allows one to achieve high growth speed of GaAs wires along the (−1−1−1) direction. Moreover, apart from GaAs wires with the usual zincblende (ZB) crystal structure, it is also possible to grow wires with wurtzite (WZ) structure, i.e., to synthesize a hitherto unknown metastable GaAs polytype. Here, we present results of density functional theory (DFT) calculations addressing various atomistic aspects of GaAs wire growth.



The relative stability of WZ wires is related to the lower surface energy of WZ as compared to ZB GaAs. By comparing experimental and simulated STM images, we could identify {1−100} and {11−20} facets forming the sidewalls of the WZ wires [1]. While WZ wires are thermodynamically stable only below a certain diameter, larger ones may be obtained via kinetically controlled growth. By employing a motif expansion parameterized to reproduce the DFT formation energy of a large variety of thin wires, we are able to extrapolate reliably up to the WZ-ZB transition, where DFT calculations are not feasible. We find that the WZ wires become thermo–dynamically metastable beyond a diameter of 65Å, if the extra stabilization of ZB wires by edge reconstruction (see Figure) is taken into account. [2]

In order to elucidate the role of the Au particle as catalyst, we perform DFT calculations for adsorption of Ga and As atoms and As_2 molecules on the Au(111) surface. Apart from the known bulk alloying of Au and Ga, we find at low Ga coverage evidence for a **surface alloy**. Both the clean Au surface and the surface alloy are able to bind and to dissociate As_2 molecules. The calculated adsorption energy of an As_2 molecule of 2.1 eV on Au(111) and 2.3 eV on the surface alloy are larger than on pure GaAs surfaces. Thus, in addition to the Au particle's function as reservoir for Ga, its surface may also act as a short-time buffer for As species before wire growth proceeds by nucleation of a new GaAs layer. These findings suggest that the sticking and dissociation probability of As_2 molecules hitting the Au particle directly from the gas phase are important factors determining the growth speed of MBE-grown GaAs nanowires.

[1] E. Hilner, U. Håkanson, E. Fröberg, M. Karlsson, P. Kratzer, E. Lundgren, L. Samuelson, and A. Mikkelsen, *Nano Lett.* **8**, 3978 (2008).
[2] V. Pankoke, P. Kratzer, and S. Sung, *Phys. Rev. B*, submitted.

I 15

Emerging functionality driven by broken symmetry and spatial confinement

*Ward Plummer**
Louisiana State University, Baton Rouge, USA

The exotic behavior exhibited by many of the transition metal compounds, like superconductivity, colossal magnetoresistance, magnetoelasticity, ferroelectric and multiferroic behavior, are due to the close coupling between the many degrees of freedom in these materials. Spin, charge, orbital and lattice parameters are coupled in an interesting nonlinear fashion. Breaking the symmetry by creating a surface is an opportunity to probe the details of the coupling in a well-controlled fashion and is of immense technological importance, since any device will be created from thin film interfaces with broken symmetry. Spatially confining these materials via lithographic techniques also produces emergent behavior, which may also be technologically relevant. I will present three to four examples as illustrations: (1) A purely electronic Mott metal-to-insulator transition at the surface of $Ca_{1.9}Sr_{0.1}RuO_4$; (2) Surface-stabilized nonferromagnetic ordering of the double layered ferromagnetic manganite $La_{2-2x}Sr_{1-2x}Mn_2O_7$, and; (3) Time-resolved electronic phase transitions in thin manganite wires. Time permitting the surface enhanced orthorhombicity and magnetic ordering of the superconductor $Ba(Fe_{1-x}Co_xAs)_2$ will be presented.

* Funded by NSF and DOE.

Dynamics simulations at surfaces: From the quantum dynamics of hydrogen adsorption to the ab initio molecular dynamics at electrochemical interfaces

Axel Groß
Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Two decades ago, the improvement of the computer power and the development of more efficient electronic structure codes based on density functional theory (DFT) allowed the mapping out of the potential energy surfaces (PESs) of simple diatomic molecules interacting with low-index metal surfaces. This motivated the study of the gas-surface interaction dynamics performed on interpolations of the first-principles PESs. Quantum dynamical calculations taking into account all molecular degrees of freedom demonstrated the importance of the high-dimensionality of these simulations. These simulations performed at the FHI elucidated processes such as dynamical steering in the adsorption [1].
However, the computional effort of both the interpolation of a first-principles PES as well as of quantum dynamical simulations increases substantially with the number of considered degrees of freedom. This problem does not arise in ab initio molecular dynamics (AIMD) simulations in which the forces necessary to integrate the classical equations of motion are determined "on the fly". And nowadays it has become possible to run a sufficient number of AIMD trajectories in order to obtain statistically meaningful results for reaction probabilities at surfaces. Thus much more complex dynamical processes rather than the adsorption on clean close-packed surfaces can be addressed. This will be demonstrated using the adsorption dynamics on precovered surfaces as an example [2]. Even processes at solid-liquid interfaces are accessible by AIMD simulations, as illustrated in Fig. 1, giving insights into the microscopic structure and dynamics at these interfaces [3] which would have been impossible to obtain just a few years ago.

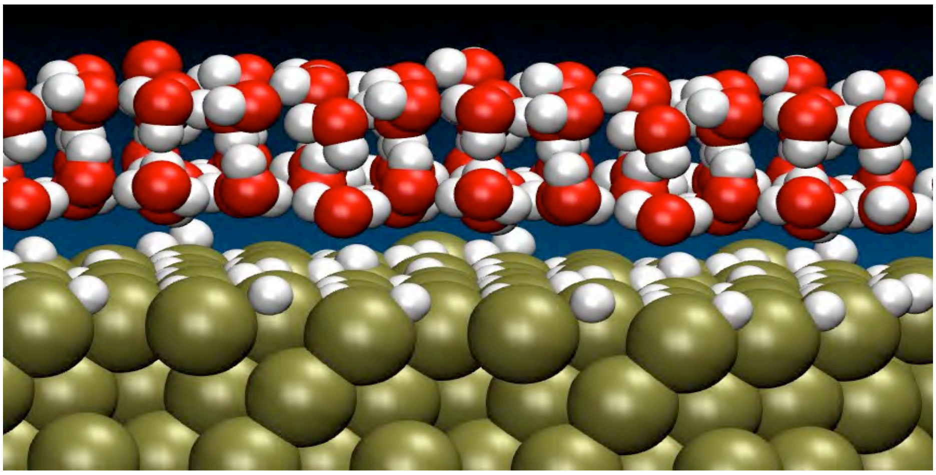


Fig. 1 Snapshot of an ab initio molecular dynamics simulations of water layers above a hydrogen covered Pt(111) surface.

[1] A. Groß, S. Wilke, and M. Scheffler, *Phys. Rev. Lett.* **75**, 2718 (1995).
[2] A. Groß and A. Dianat, *Phys. Rev. Lett.* **98**, 206107 (2007).
[3] S. Schnur and A. Groß, *New J. Phys.* **11**, 125003 (2009).

I 17

Magnetoelectric coupling at multiferroic interfaces

M. Fechner[1], I. V. Maznichenko[2], M. Hölzer[2] S. Ostanin[1], A. Ernst[1], J. Henk[1],
and I. Mertig[1,2]
[1]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
[2]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

When magnetism and ferroelectricity coexist in the same crystalline phase of a material it is called multiferroic. Furthermore, the crystal symmetry of a multiferroic material allows for magnetoelectric coupling which is quite useful since the coupling offers magnetization switching by an external electric field or electric polarization switching by an external magnetic field. Considering this mechanism data storage would be revolutionized since it would allow writing magnetic information by an electric field. Nowadays there exist different pathways to grow multiferroic materials. One class are single-phase multiferroics, where ferroelectricity and magnetism appear in the same phase of the compound (e.g. $BiFeO_3$). However, in most of these materials the electric polarization and magnetization interact only weakly with each other and ferromagnetism usually disappears far below room temperature. A more promising approach to create multiferroic materials is to combine two single-phase ferroic materials via an interface, i.e. by growing a thin ferromagnetic film epitaxially on a ferroelectric substrate or vice versa. Magnetoelectric coupling is expected to occur. Ab-initio calculations have shown extremely promising results regarding composite multiferroics. Although these calculations go ahead of experiment they explore the trends and basic physics of magnetoelectric coupling.

In the first part we want to discuss a model system for ferroelectric/ferromagnetic interfaces. Using first principle methods, we investigate different ultrathin ferromagnetic films (Co and Fe) on top of ferroelectric $ATiO_3$ (A=Pb,Ba) perovskites concerning the occurrence of magnetoelectric coupling. The calculations show that at the interface a moderate change of the size of the total magnetization occurs. Furthermore, the magnetic order of the Fe film is sensitive to its thickness, so an unexpected antiferrimagnetic ordering appears for 2ML Fe whereas for all other thicknesses ferromagnetic ordering is preferred. Hybridization and strain effects at the interface can explain the observations.

The second part of the talk will focus on changes of the magnetoelectric coupling by interface alloying. The effect of Fe-Co alloying on magnetoelectricity of thin-film Fe_{2-x} $Co_x/BaTiO_3(001)$ will be discussed. The results based on the coherent-potential approximation to density-functional theory show that the presence of >0.25 Co at.% per Fe atom stabilizes the ferromagnetic order in the two-ML thick and magnetically soft Fe films. Another possibility is to use a CrO_2-terminated interface instead of TiO_2 .This enhances magnetoelectricity in the system significantly, showing an unexpected change in magnetization induced by polarization reversal. In the case of two layers, for instance, the magnetic order of the $Fe_{2-x}Co_x$ bilayer can be switched from nearly zero ferrimagnetic to strongly ferromagnetic upon the polarization reversal.

New developments in the first principles simulation of the spectroscopic properties of low-dimensional systems

Angel Rubio
Nano Bio Spectroscopy Group, Departamento de Física de Materiales,
Universidad del País Vasco. European Theoretical Spectroscopy Facility (ETSF),
Edificio Korta, Avda. Tolosa 72, 20018 San Sebastián, Spain

There has been much progress in the synthesis and characterization of nanostructures however, there remain immense challenges in understanding their properties and interactions with external probes in order to realize their tremendous potential for applications (molecular electronics, nanoscale opto-electronic devices, light harvesting and emitting nanostructures). In this talk we will review the recent advances within density-functional based schemes to describe spectroscopic properties of those complex systems. Special emphasis will be made in modeling new materials and simulate new time and spatially resolved spectroscopies. We will address both linear and non-linear response regimes to study the optical absorption and luminescence of bio-chromophores, one-dimensional polymers and nanotubes and layered materials. Moreover, we will illustrate how an optimal control theory can be implemented such that we could have control of the quantum state of a molecular structure. The technique will address control of high-harmonic generation and successful control of the chirality of currents in nano-rings and in general qbits for quantum information. We will highlight the impact of the enviroment and discuss how to extend the theory to be able to describe dissipation and open-quantum systems.

I 19

Photochemistry at nanoparticles

Dietrich Menzel
Fritz-Haber-Institut, Berlin, and
Physik-Department E20, TU München, Garching, Germany

On the basis of an outline of existing knowledge about photochemical reactions on surfaces of bulk crystals I will discuss the special additional effects which are induced by the use of metallic nanoparticles (MNPs) as substrates. These are in particular plasmon enhancement, and confinement of excitations in the MNPs. A summary of research done in the Fritz-Haber-Institut in the past 6 years on a specific system (Photoinduced reactions of NO dimers on Ag NPs, in particular NO photodesorption) shows that the NPs induce strong, size-dependent effects on the efficiency of photoreactions as expressed by the desorption cross sections. The intrinsic mechanism, however, stays the same under most conditions, as shown by detailed state-resolved and size-dependent detection of desorbing molecules. This is even so for femtosecond excitation where a new mechanism of ultrafast re-excitation of hot electrons in the NPs is postulated which leads to nonlinear enhancement of the desorption probability at very low fluences.

After-Dinner Talk

Surface and interface science: Research for the energy of tomorrow

Wolfgang Eberhardt
Technische Universität Berlin, Germany

Energy research: how can we meet the challenges?

Eberhard Umbach
Karlsruhe Institute of Technology, Germany

The recent reconsideration of global challenges like climate development, security of energy supply, limited resources, waste disposal, and energy costs has put energy research at the top of the priority list. This is particularly true for Germany whose government has announced an extremely ambitious energy concept. A reduction of the primary energy use by 50 % and of the CO_2 emissions by 80 % until 2050 as well as a nuclear phase out within 10 years and 80 % contribution of Renewables to the total electricity consumption until 2050 are hard to meet if at the same time the energy supply should be sustainable, secure and affordable. It is apparent, that very much research is required to develop new concepts for, e.g., energy conservation and mobility and to make the Renewables competitive such that they can indeed play the major role assigned to them in the future. This can only be achieved if we succeed in coping with fluctuating energy sources requiring, e.g., effective energy storage and with supply shortfalls of primary energy sources or of material resources. Although nobody really knows the frame conditions in 20 or 50 years, and hence nobody knows which energy mix will then be the optimum, it is easy to predict that chemical processes will play an increasingly important role in this energy mix of the future. And it is obvious that interface science and heterogeneous catalysis have to make decisive contributions if the complete reorganization of our energy system should be successful.

From memories to frontiers in complex oxides

Sokrates T. Pantelides
Department of Physics and Astronomy, Vanderbilt University, Nashville, TN37235 USA
and Materials Science and Technology Division, Oak Ridge National Laboratory,
Oak Ridge, TN 37831 USA

After reminiscing over the early years when Matthias spent two years as my post-doc at the IBM Research Division, the talk will cover recent work on energy-related transition-metal oxides (TMOs): using density-functional calculations and scanning transmission electron microscopy to unravel the mechanism of recently observed room-temperature colossal ionic conductivity in multilayer TMO structures for fuel-cell applications and to identify a mechanism that helps unblock one-dimensional diffusion channels for Li ions in $LiFePO_4$ for battery applications.

I 23

Quantum mechanics and hydrogen bonds

Roberto Car
Princeton University, USA

The momentum distribution of the protons participating in hydrogen bonds in water and ice deviates considerably from the classical equilibrium distribution. As a consequence the molecular structure of water and ice is directly affected by quantum mechanics. Yet the effect is essentially quasi-harmonic and quasi-classical in nature. New physics arises in presence of proton tunneling, which is collective and dominated by strong local correlations.

Heterogeneous catalysis for energy efficiency: The roles of dynamic defects

Cynthia M. Friend
Harvard University, Department of Chemistry, 12 Oxford St.;
Cambridge, MA 02138 USA

The roles of dynamic defects in determining the reactivity and selectivity of surface reactions important in heterogeneous catalysis will be illustrated for coupling reactions on gold and titania. On gold, oxidation of the surface leads to the formation of metallic nanoparticles that induce a variety of selective oxidative coupling reactions. Coupling of alcohols with various other reactants will be used to illustrate how experiment and theory provide insight into these important reactions and indicated the possible utility of gold as a “green” chemical agent that operates at low temperature. On titania, coupling reactions are induced by reduced Ti cations, including interstitials that migrate to the surface and induced C=O bond breaking in aldehydes. A combination of reactivity measurements, imaging and density functional theory was used in these studies. In both cases, the dynamic nature of surfaces under reaction conditions plays a role in determining activity and selectivity.

POSTER CONTRIBUTIONS

Electron stimulated chemistry in organic-water ices

Heather Abbott[1,2]*, Gregory Grieves*[2] *and Thomas Orlando*[2]
[1]*Kennesaw State University, Department of Chemistry & Biochemistry,*
Atlanta, GA, USA
[2]*Georgia Institute of Technology, School of Chemistry & Biochemistry,*
Atlanta, GA, USA

From the surfaces of moons in the outer solar system to tiny dust grains in the interstellar medium, icy surfaces are prevalent throughout our universe. Understanding the radiation processing of these organic-water ices may be the key to unraveling the prebiotic chemistry that led to life. Our laboratory measurements of model organic-water ices (i.e., mixtures of H_2O, C_2H_6, CH_3NH_2 and CH_3CN) have been performed under ultrahigh vacuum conditions. Low-energy electrons (< 200 eV) are used to simulate the secondary electrons produced by cosmic rays and are shown to induce proton transfer plus product desorption in a single event at cryogenic temperatures (~55 K). This abiogenic pathway is likely to be important in the production of gas-phase ions that react to form more complex molecules (e.g., in the interstellar medium). Furthermore, threshold energies for the electron stimulated desorption of cationic clusters suggest that Intermolecular Coulombic Decay (ICD) contributes to the production of certain cations.

Investigation of the dynamical and thermodynamic stability of a single monolayer SiN_x interfaced with TiN

Tobias Marten, Eyvaz Isaev, Björn Alling, Lars Hultman, and Igor A. Abrikosov
Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

Superhard nanocomposites attract large scientific and industrial interest for their possible usage in protective coatings on cutting tools and mechanical components as well as for their fundamentally intriguing physical properties. In particular, the TiN-SiN_x nanocomposites have become a model system for this class of materials with established superhardness (H~40 GPa), high thermal stability, and oxidation resistance. We investigate the dynamical and thermodynamic stability of a single monolayer of SiN_x sandwiched isostructurally between B1-TiN (001) and (111) oriented slabs. We show that the distortion of the Si-N bond almost, but not completely, stabilizes the (001) interface dynamically while the (111) interface is dynamically stable. However, both interfaces are unstable with respect to formation of Si vacancies. This means that unlike the conclusions in some previous studies, the interesting physical properties of real existing TiN-SiN_x nanocomposites cannot be understood from the calculated properties of isostructural SiN/TiN interfaces with a Si_1N_1 stoichiometry [1,2].

[1] B. Alling, E. I. Isaev, A. Flink, L. Hultman, and I. A. Abrikosov, *Phys. Rev. B* **78**, 132103 (2008).
[2] T. Marten, E. I. Isaev, B. Alling, L. Hultman, and I. A. Abrikosov, *Phys. Rev. B* **81**, 212102 (2010).

Surface study of ferromagnetic shape memory alloys

S.R. Barman[1]*, S.W.D'Souza*[1]*, Abhishek Rai*[1]*, J. Nayak*[1]*, M. Maniraj*[1]*, D.L. Schlagel*[2]*,*
T.A. Lograsso[2]*, Aparna Chakrabarti*[3]
[1]*UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore, 452001, Madhya Pradesh, India*
[2]*Ames Laboratory U. S. DOE, Iowa State University, Ames, Iowa 50011-3020, USA*
[3]*Raja Ramanna Centre for Advanced Technology, Indore, 452013, Madhya Pradesh, India*

Ni_2MnGa(100) single crystal surfaces studied using low energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS) exhibit intrinsic surface properties dissimilar to the bulk. Moreover, they exhibit influence of compositional variation at the surface depending on annealing conditions. The Ni_2MnGa surface becomes Ni-rich and Mn deficient after sputtering. However, as the annealing temperature is increased Mn segregates to the surface and at sufficiently high annealing temperatures (700 K) the Mn deficiency caused by sputtering is compensated and a stoichiometric surface is obtained. In the martensitic phase, the LEED spot profiles show the presence of an incommensurate modulation for the stoichiometric surface. At higher annealing temperatures (950 K) the surface becomes Mn rich. LEED has been observed for the Mn rich surface too, but in contrast to the stoichiometric surface, a commensurate modulation is observed. The surface martensite transition exhibits a hysteresis whose width is five times larger than in bulk. A pre-martensite phase is observed from temperature dependent LEED. Both the surface martensitic and pre-martensitic transition temperatures decrease as the Mn/Ni ratio at the surface increases. For the stoichiometric surface, a detailed analysis of the temperature dependent photoemission spectra show the existence of a pseudogap near the Fermi level in the pre-martensite phase that persists in the martensite phase. This demonstrates that the modulation has an electronic origin possibly related to charge density waves.

Neural network potential-energy surfaces for materials science

N. Artrith, T. Morawietz, and J. Behler
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum,
D-44780 Bochum, Germany

The reliability of the results obtained in theoretical simulations strongly depends on the quality of the employed interatomic potentials. While electronic structure methods like density-functional theory (DFT), as implemented e.g. in the FHI-aims package [1], provide an accurate description of many systems, the high computational costs limit the system size that can be studied. Therefore, the development of more efficient, approximate potentials is an active field of research.

In recent years artificial Neural Networks (NN) have become a valuable tool to represent ab initio potential-energy surfaces (PES) very accurately [2-5]. They are constructed using a set of reference points and then allow to evaluate the energy and forces several orders of magnitude faster with almost the accuracy of the underlying electronic structure data. Recently, the NN method has been extended to high-dimensional potential-energy surfaces thus now enabling molecular dynamics studies of very large condensed systems [6-8]. Several examples are presented showing how total energies obtained from FHI-aims calculations can be used to set up NN PESs, which can then be applied to simulations of extended systems.

[1] V. Blum et al., *Comp. Phys. Comm.* **180**, 2175 (2009).
[2] T.B. Blank, S.D. Brown, A.W. Calhoun, and D.J. Doren, *J. Chem. Phys.* **103**, 4129 (1995).
[3] S. Lorenz, A. Groß, and M. Scheffler, *Chem. Phys. Lett.* **395**, 210 (2004).
[4] S. Lorenz, M. Scheffler, and A. Groß, *Phys. Rev. B* **73**, 115431 (2006).
[5] J. Behler, S. Lorenz, and K. Reuter, *J. Chem. Phys.* **127**, 014705 (2007).
[6] J. Behler, and M. Parrinello, *Phys. Rev. Lett.* **98**, 146401 (2007).
[7] J. Behler, *J. Chem. Phys.* **134**, 074106 (2011).
[8] N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* **83**, 153101 (2011).

Reactive chemical doping of the Bi_2Se_3 topological insulator

H. M. Benia*[1], C. Lin[1], K. Kern[1, 2] and C. R. Ast[1]
[1]Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany.
[2]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Topological insulators are a recently discovered new class of materials with a strong spin-orbit coupling which distinguish themselves from other materials through fundamental symmetry considerations [1–2]. Decorating their surface with adatoms or molecules leaves the topological surface state protected [3–4]. Here, we studied using angle resolved photoemission spectroscopy (ARPES) the evolution of the surface electronic structure of the topological insulator Bi_2Se_3 as a function of water vapor exposure. We find that a surface reaction with water induces a band bending shifting the Dirac point deep into the occupied states and creating quantum well states with a strong Rashba-type splitting. The surface is thus not chemically inert, but the topological state remains protected. The band bending is traced back to Se-abstraction leaving positively charged vacancies at the surface. Due to the presence of water vapor, a similar effect takes place when Bi_2Se_3 crystals are left in vacuum or cleaved in air, which likely explains the aging effect observed in the Bi_2Se_3 band structure [5].

[1] Fu, L. & Kane, C. L., *Phys. Rev. B* **76**, 045302 (2007).
[2] Hasan, M. Z. & Kane, C. L., *Rev. Mod. Phys.* **82**, 3045 (2010).
[3] Hor, Y. S. *et al.*, *Phys. Rev.* B **79**, 195208 (2009).
[4] Chen, Y. L., *Science* **329**, 659 (2010).
[5] Fiete, G. A., *Science* **332**, 546 (2011).

Towards catalysis by free gold clusters in CO and O_2 atmosphere: An ab initio study

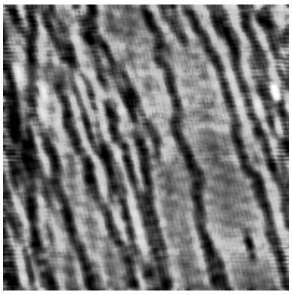
Elizabeth C. Beret, Merel M. van Wijk, Luca M. Ghiringhelli, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

The marked catalytic activity of gold clusters has inspired a large number of scientific contributions in the recent years. However, many questions still lack a satisfying answer, for example what are the structures and stoichiometries of the gold particles in the presence of the reactive gases at finite temperature, and how do they change with particle size [1]. By focusing on the CO oxidation reaction, we answer to the above-mentioned questions for small neutral and anionic gold clusters modeled in a gas phase atmosphere containing CO and O_2 at variable partial pressures, and in a temperature range between 100 and 600 K. To this aim, DFT (PBE)–based ab initio atomistic thermodynamics [2] is applied, including full account of the vibrational contribution to the free energy. The candidate structures at a given stoichiometry are produced by means of an unbiased efficient sampling of the conformational space. As a result, the preferred cluster+adsorbate structures for different environmental conditions are obtained and interpreted as candidate intermediates in the catalytic CO oxidation reaction. Our structurally unbiased search finds also some cluster+adsorbate isomers that contain CO_2 moieties. The stability of such structures with respect to the dissociation of the CO_2 species is estimated. In this way, we aim to capture the different behavior of the system in two different kinds of realistic conditions: a) an experiment where the product CO_2 is constantly removed from the system (like in a flow tube reactor) and b) one where an equilibrium with the product CO_2 is reached. On the basis of these considerations, we single out likely reaction paths for CO oxidation catalyzed by gold clusters.

[1] R. Meyer, C. Lemire, S. K. Shaikhutdinov and H. J. Freund, *Gold Bull.* **37** (2004) 72–124.
[2] K. Reuter and M. Scheffler, *Phys. Rev. B* **65** (2001) 035406; K. Reuter and M. Scheffler, *Phys. Rev.* B **68** (2003) 045407.

Monitoring adsorbate phases: A means to detect hidden order parameters

E. Bertel[1], M.Cordin[1], N. Oberkalmsteiner[1], J. Redinger[2], M. Baranov[3], S. Diehl[3]
[1]Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria
[2]Department of Applied Physics, Vienna University of Technology, Vienna, Austria
[3]Institute for Quantum Optics and Quantum Information, Austrian Academy of Sciences, Innsbruck, Austria



Low-dimensional systems tend to be unstable towards various types of ordering, for instance charge-, spin-, or orbital ordering. Low-dimensionality and the competition between order parameters conspire to drive fluctuations throughout an extended parameter range. Consequently, the relevant order parameters are difficult to identify. Suitable adsorbates may tilt the balance towards a stable symmetry-broken state, which is then accessible to detailed analysis. The method is demonstrated using Br/Pt(110) as a quasi-1D model system. The observed phase transition is described within the framework of an extended Landau theory including the coupling of the order parameter to the adsorbate.

Similar results were recently found for iron-pnictide superconductors [1]. Application of the present ideas suggests an imminent charge-ordering instability in at least some members of this family.

[1] M. Golden et al., *Phys. Rev. B* **80** (2009) 140507(R).

Monte Carlo simulations of Au-Pd planar surface alloys

J.A. Boscoboinik, Z. Li, F.C. Calaza, M.T. Garvey, W.T. Tysoe
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany

The formation of bimetallic surface alloys was simulated using Monte Carlo methods. The study was focused on the distribution of gold and palladium atom ensembles on the surface, since such ensembles have shown to have an influence in the catalytic activity of bimetallic alloys. In particular, the simulations were compared with experimentally obtained gold-palladium surface alloys and the ensemble distributions were related to the presence of adsorption sites for catalytically relevant species, such as hydrogen, oxygen, carbon monoxide, and the formation of ethylidyne from ethylene.

P 9

Surface modification of ZnO surfaces with organic molecules

Ney Henrique Moreira, Adriel D. Garcia, Andreia L. da Rosa and Thomas Frauenheim
Bremen Center for Computational Materials Science, University of Bremen
Am Fallturm 1, 28359, Bremen, Germany

The understanding of the interaction of organic species with inorganic surfaces and nanostructures constitutes a step forward in the development of semiconductor based biosensors. ZnO is a well-known bio-friendly semiconductor with potential applications in electronics and optoelectronics including sensors, field effect transistors, and lasers. Density functional theory has been employed to investigate ZnO(10$\underline{1}$0) surfaces modified with substituted methane molecules (Me–X, with X= OH, NH_2, SH, COOH, and CN). We have found three relevant stabilization mechanisms acting on the surface stabilization: the passivation of surface oxygen lone-pairs happens via dissociative chemisorption processes, the electrostatic adsorbate interations involving Zn surface sites and hydrogen interactions involving oxygen surface sites. Covalent ligand-substrate interactions have been found to play only a marginal role on the surface stabilization. Contradicting the usual chemical intuition, we have found no significant evidence for the formation of classical Lewis acid-base adducts on Zn surface sites. In all cases, the formation of one monolayer coverage has been found under ligand-rich conditions.

[1] N. H. Moreira, G. Dolgonos, B. Aradi, A. L. da Rosa and Th. Frauenheim, *J. Chem. Theory Comput.* **5**, 605 (2009).
[2] N. H. Moreira and A. L. Rosa and Th. Frauenheim, *Appl. Phys. Lett.* **94**, 193109 (2009).
[3] A. D. Garcia, N. Moreira, G. Dolgonos, A. L. da Rosa and T. Frauenheim, *J. Phys. Chem. C* (2010), accepted.

The role of localization in the atomic structure of transition-metal nanoclusters: A hybrid-DFT investigation

Mauricio J. Piotrowski[1]*, Paulo Piquini*[1] *and Juarez L. F. Da Silva*[2]
[1]*Federal University of Santa Maria, Department of Physics, Santa Maria, Brazil*
[2]*University of São Paulo, Institute of Physics of São Carlos, São Carlos, SP, Brazil*

Density functional theory (DFT) within local (local density approximation - LDA) and semilocal (generalized gradient approximation - GGA) approximations for the exchange-correlation energy functional has difficulties to describe particular systems and properties due to the incorrect description of the self-interaction problem. In this work, we will report a hybrid-DFT (HSE functional) study of the structural and electronic properties of the Co_{13}, Rh_{13}, and Hf_{13} clusters. We found that a partial correction of the self-interaction problem decreases the stability of open structures such as the double simple cubic (DSC), and hence, compact structures such as the icosahedron (ICO) can become the lowest energy structure for Rh_{13}. For Co_{13}, the planar structure (hexagonal bilayer -HBL) became almost degenerated with ICO, while there is no change in the relative stability for the Hf_{13} cluster. Therefore, our results suggest that DSC-like structures found for several TM_{13} clusters might be a result of the self-interaction problem, and not a real physical result. Using the sd-hybridization analysis, we found that the sd-hybridization decreases for DSC and increases for ICO for Co_{13} and Rh_{13}. For Hf_{13}, the sd-hybridization decreases for all configurations, and hence, it does not change the relative stability.

Hydrogenation of unsaturated hydrocarbons over Pd: Activation and reactivity of the pro-chiral molecule isophorone

K.-H. Dostert, A. Savara, W. Ludwig, S. Schauermann and H.-J. Freund
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany

Recent progress in understanding the micro-kinetics and the reaction mechanism of the hydrogenation of simple unsaturated compounds on Pd [1,2] opened up opportunities to investigate more complex systems. The aim of the long term project is to study the mechanism and the kinetics of heterogeneous enantioselective hydrogenation over Palladium on a prototypical compound.

Currently we focus on the selective hydrogenation of the pro-chiral molecule Isophorone, which contains conjugated C=O and C=C bonds. In the first step we studied the adsorption properties of Isophorone on Pd(111) by different techniques: IRAS measurement and Temperature Programmed Desorption (TPD) in a UHV molecular beam setup was combined with Synchrotron NEXAFS experiments. The experimental results reveal a partial dehydrogenation of Isophorone on Pd at low temperature and a mostly flat adsorption geometry. These results get strongly supported by theoretical calculations [3].

Additionally, we present first results on the selective hydrogenation of Isophorone over Pd(111). We show that predominant hydrogenation of the C=C entity occurs and nearly no hydrogenation of the C=O functional group is detected.

[1] Neyman, K.M. and S. Schauermann, Hydrogen Diffusion into Palladium Nanoparticles: Pivotal Promotion by Carbon. *Angewandte Chemie-International Edition*, 2010. **49**(28): p. 4743-4746.
[2] Wilde, M., et al., Influence of Carbon Deposition on the Hydrogen Distribution in Pd Nanoparticles and Their Reactivity in Olefin Hydrogenation. *Angewandte Chemie-International Edition*, 2008. **47**(48): p. 9289-9293.
[3] Liu, W., et al., Towards Low-temperature Dehydrogenation Catalysis: Isophorone on Pd(111), *in preparation*.

P 12

Electronic properties of non-polar III-N surfaces

H. Eisele[1], S. Schaafhausen[2], A. Lenz[1], A. Sabitova[2], L. Ivanova[1], M. Daehne[1],
Y.-L. Hong[3], S. Gwo[3], Ph. Ebert[2]
[1]Technische Universität Berlin, Germany
[2]Forschungszentrum Jülich, Germany
[3]National Tsing-Hua University, Taiwan

InN and GaN, and their alloys, together as active materials in light emitting devices enable to cover the whole visible spectral range. Beside this principle possibility, there are a couple of open fundamental questions to realize and improve such light emitter. For InN, e.g., the fundamental bulk band gap is still under discussion, as well as the energetic position of the Fermi level. Furthermore, the internal piezo-electric fields along the wurtzite material c-axis typically cause a charge separation due to the quantum-confined Stark effect. To overcome this, the growth of devices along the non-polar crystal directions is considered. Thus, we addressed these fundamental material properties at the non-polar III-N surfaces using scanning tunneling microscopy (STM) and spectroscopy (STS) in ultra-high vacuum.

For the GaN($10\underline{1}0$) surface we observed a direct surface band gap with electronic surface states being energetically located outside of the fundamental bulk band gap. The energetic minimum of the intrinsic, empty Ga-related surface state is located at the Gamma-point of the surface Brillouin zone 0.1-0.2 eV above the bulk conduction band minimum (CBM), and shows a strong contribution from the M-bar point at higher energies. Furthermore, an extrinsic contribution from surface defects and steps is observed in the tunneling current, being energetically located around the Fermi level at about 1.0 eV below the CBM.

For the InN($11\underline{2}0$) surface a similar behavior was observed: The measured, 0.7 +/- 0.1 eV wide band gap is free of intrinsic surface states and hence can be assigned to the bulk. Again, surface steps contribute to the tunneling current below the Fermi energy. A previously predicted intrinsic electron accumulation can be excluded for this InN($11\underline{2}0$) surface, since the Fermi level is located energetically within this band gap, but it might be extrinsic due to chemical reactions at such surfaces.

Glycerol oxidation over gold at different electrochemical environments

Janaina Fernandes Gomes, Fernanda Batista Castelo de Paula and
Germano Tremiliosi-Filho
Instituto de Química de São Carlos, Universidade de São Paulo,
C.P. 780 – 13560.970 - São Carlos, SP, Brazil

Glycerol is usually used in pharmaceuticals and cosmetics industries. At present, glycerol is produced in large quantities as a co-product of the biodiesel fabrication. As a result, in a short timescale, the glycerol production will surpass its current demand. For this reason, alternative applications for the exceeding glycerol will be necessary. One of the possibilities is the use of glycerol in Direct Glycerol Fuel Cells (DGFC) for both electricity generation and chemicals electrosynthesis. Glycerol oxidizes by different reaction pathways leading to the formation of many partially oxidized products, in addition to the final product, CO_2. In the present work, the electrochemical oxidation of glycerol on gold in acid and alkaline media was investigated by cyclic voltammetry and *in situ* FTIR spectroscopy with the aim to explore the pH effect on the catalyst activity towards the glycerol oxidation and on the selectivity of this reaction.

Dynamical detuning of Rabi oscillations in time-dependent density functional theory

J.I. Fuks[1], N. Helbig[1], I.V. Tokatly[1,2] and A. Rubio[1,3]
[1]Nano-Bio Spectroscopy group and ETSF Scientific Development Center, Dpto. Física de Materiales, Universidad del País Vasco,
Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastían, Spain
[2]IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain
[3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Through the exact solution of a two-electron singlet system interacting with a monochromatic laser we prove that all adiabatic density functionals within time-dependent density-functional theory are not able to discern between resonant and non-resonant (detuned) Rabi oscillations. This is rationalized in terms of a fictitious dynamical exchange-correlation (xc) detuning of the resonance while the laser is acting. The non-linear dynamics of the Kohn-Sham system shows the characteristic features of detuned Rabi oscillations even if the exact resonant frequency is used. We identify the source of this error in a contribution from the xc-functional to the non-linear equations describing the electron dynamics in an effective two-level system. The constraint of preventing the detuning introduces a new strong condition to be satisfied by approximate xc-functionals.

In the present work we use the example of Rabi oscillations to identify the physics behind the failure of adiabatic constructions to describe resonant non-linear dynamics. Our results show that the problems are not limited to adiabatic TDDFT but affect any mean-field theory.

Vibrational spectroscopy of platinum cluster model catalysts

Dan J. Harding, Christian Kerpal, David M. Rayner, André Fielicke and Gerard Meijer
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Isolated transition metal clusters in the gas phase and their complexes with small molecules are frequently suggested as model systems for the study of active sites of heterogeneous catalysts. In our experiments we combine resonant IR excitation with mass spectrometric detection to obtain detailed size-specific insights into the structure of the clusters and their gas-phase chemistry. The coverage of a wide frequency range from the mid-IR to below 100 cm^{-1} becomes possible by using the Free Electron Laser for Infrared eXperiments (FELIX) as an intense and tunable light source. Here we present vibrational spectra of small platinum clusters and their complexes with methane and hydrogen in the range from 100 to 2200 cm^{-1}. Comparison with spectra calculated using density functional theory allows the determination of the cluster structures and investigation of the effects of the cluster's structures on reactivity.

The observation of electronic energy bands in argon and krypton clusters

Marko Förstel[1,2]*, Melanie Mucke*[1]*, Tiberiu Arion*[1]*, Toralf Lischke*[1]*, Silko Barth*[1]*, Volker Ulrich*[1]*, Gunnar Öhrwall*[3]*, Olle Björneholm*[3]*, Uwe Hergenhahn*[1] *and*
Alex M. Bradshaw[1,4]
[1]*Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching, Germany*
[2]*Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany*
[3]*Division of Molecular and Condensed Matter Physics, Department of Physics and Astronomy, Box 516, SE-75120 Uppsala, Sweden*
[4]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4- 6, 14195 Berlin, Germany*

One of the main motivations for the study of clusters is the search for the onset of bulk properties: How many atoms or molecules do we need to combine in order to make a small piece of condensed matter?

In recent experiments within our collaboration for the first time evidence not only for the appearance of electronic bands in a cluster, but also for their dispersion was seen. Firstly, this result was obtained on large Ar clusters ($\langle N \rangle = 1670$), for which the valence band photoemission immediately at threshold was recorded. Some two-three eV above threshold the spectrum is dominated by a prominent feature, which undergoes strong changes in apparent binding energy and which can only be observed over a narrow range of photon energies. Here, we will present a series of experiments in which we follow the appearance of this feature vs. cluster mean size $\langle N \rangle$. A similar behavior is seen in photoemission from Kr clusters.

P 17

Role of hybridization in the Rashba effect of a metallic layer on a W(110) surface

M. Hortamani[1], R. Wiesendanger[1], P.Ferriani[2], S. Heinze[2]
[1]Institute of Applied Physics, University of Hamburg, Germany
[2]Institute of Theoretical Physics and Astrophysics, University of Kiel, Germany

The generation of a dissipationless spin current, important for spintronics and quantum computer, in a two-dimensional electron gas without the application of an external magnetic field can be achieved by exploiting the spin-orbit coupling (SOC) at metal surfaces. Due to the breaking of the spatial inversion symmetry, surface electrons are subject to an electric field perpendicular to the surface and experience an effective magnetic field. The coupling of such a magnetic field to the electron spin causes a k-dependent spin splitting of the surface state known as the Rashba effect. Since the Rashba splitting in a free electron gas depends on the nuclear number and the potential gradient, a modification of the size of the splitting can be obtained by terminating the substrate with heavy elements. For example, it has been observed that the Rashba splitting of the W(110) surface is enhanced when the surface is covered by gold. Surprisingly, this effect increases even more when the adlayer is replaced by lighter elements, such as silver and even aluminium [1,2].

In order to understand the mechanism that determines the size of the spin-orbit splitting for a monolayer of gold, silver, and aluminium on the W(110) surface, we carried out a systematic calculation based on density functional theory using the full-potential linearized augmented plane-wave (FLAPW) method as implemented in the FLEUR code. We found a trend of the surface state spin-splitting in agreement with experiments [1,2]. We show the effect of the overlayer-substrate hybridization on the atomic wave function and the potential gradient at surface and interface, and discuss the role of the nuclear number on Rashba splitting.

[1] A. Shikin, et al., *PRL* **100**, 57601 (2008).
[2] A. Rybkin, et al., *PRB* **82**, 233403 (2010).

First-principles determination of the α-α' interfacial energy in Fe-Cr alloys

Song Lu[1], *Qing-Miao Hu*[2], *Rui Yang*[2], *Börje Johansson*[1,3], *and Levente Vitos*[1,3,4]
[1] *Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm SE-100 44, Sweden*
[2] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China*
[3] *Department of Physics and Materials Science, Uppsala University, Uppsala SE-75121, Sweden*
[4] *Research Institute for Solid State Physics and Optics, P.O. Box 49, Budapest H-1525, Hungary*

The Fe-Cr alloys form the basis of stainless steels, which are extensively used in domestic and industrial areas due to their excellent properties. Owing to the large miscibility gap below about 500 °C, Fe-Cr is a typical binary system showing phase decomposition. When aged at the temperature range of 300 to 500 °C, alloys with compositions within the miscibility gap separate into α (Fe-rich) and α' (Cr-rich) phases, both having the body-centered-cubic (bcc) structure. The phenomenon is commonly known as the "475 °C embrittlement" and it degrades seriously the alloy properties. The interfacial energy γ between the decomposed phases plays an important role to the morphology and thermodynamics of phase decomposition. However, due to the complexity of the interface the accurate determination of the composition-dependent interfacial energy, either experimentally or theoretically, has been very limited.

In this presentation, we show that the interfacial energies γ between the Cr-rich α'-Fe_xCr_{1-x} and Fe-rich α-$Fe_{1-y}Cr_y$ phases ($0 < x, y < 0.35$) are between ~0.02 and ~0.33 Jm^{-2} for the ferromagnetic state and between ~0.02 and ~0.27 Jm^{-2} for the paramagnetic state. Although for both magnetic states, the interfacial energy follows a general decreasing trend with increasing x and y, the fine structures of the $\gamma(x, y)$ maps exhibit a marked magnetic state dependence. The subtleties are shown to be ascribed to the magnetic interaction between the Fe and Cr atoms near the interface. The theoretical results are applied to estimate the critical grain size for nucleation and growth in Fe-Cr stainless steel alloys.

[1] Song Lu, *et al.*, *Phys. Rev. B* **82**, 195103 (2010).

P 19

Polyalanine microsolvation

Joel Ireta
Chemistry Department, Autonomous Metropolitan University at Iztapalapa
Mexico City, Mexico

Water is fundamental for the folding mechanism, dynamics and function of proteins. Yet, its precise role at the molecular level is not fully understood, especially that of water molecules in the protein-solvent interface. In this poster it is presented a density functional theory study of the microsolvation of polyalanine. Full geometry optimizations of finite and infinite polyalanine chains microsolvated with up to twenty water molecules were carried out using the Perdew-Burke-Ernzerhof approximation to the exchange correlation functional. Particularly, it is investigated the effect of the water-water hydrogen bonding network on the structure and stability of the helical and beta-sheet conformations. It is found that the water-water hydrogen bonding network exerts a compression along the alanine backbone promoting the stabilization of the polyproline like conformation in isolated strands and the twisting in beta sheet structures. Moreover the energetic analysis of the microsolvation process indicates that the transformation from extended to helix conformation is favored by the desolvation process of the backbone, which is in concordance with some experimental results.

P 20

Density functional calculation for adatoms on graphene

Akira Ishii and Kengo Nakata
Department of Applied Mathematics and Physics, Tottori University Koyama, Tottori 680-8552, Japan, JST-CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

The graphene itself is a very interesting material to be investigated both experimentally and theoretically. Nowadays, excellent experiments for graphene sheets become possible. However, the graphene is very interesting also for substrates of nanostructure because of its two dimensionality. In order to promote such investigations, the adsorption of atoms and molecules on graphene should be studied, but such studies have not been done so much.

In recent theoretical study [1,2,3,4], the adsorption sites and adsorption energies for some atomic species have been reported. The aim of this investigation is to understand the general mechanism of adatom adsorption on a graphene sheet. In this work, we investigate computationally adsorption energies, adsorption sites and migration barrier energies on graphene sheet for a lot of atomic species including transition metals, noble metals, nitrogen and oxygen, from atomic number 1 to 83, using the DFT calculation. We used VASP [5,6,7,8] which was the first-principle calculation code of the high precision using the PAW method. The calculations are done for adatoms at three sites having symmetry, H6 (hexagonal), B (bridge) and T (on-top) on a 3 x 3 super cell. The spin-polarization is included in the calculation. The calculated results show us that the adsorption at the H6-site mainly for simple and transition metal elements. The non-metallic elements showed the tendency to be adsorbed at the B-site. Many metallic adatoms show ferromagnetic behavior at least for single atom adsorption on graphene. The result of this work will be helpful for the choice of material for electrode on graphene or growth of graphene on substrates.

This work is supported by JST-CREST project.

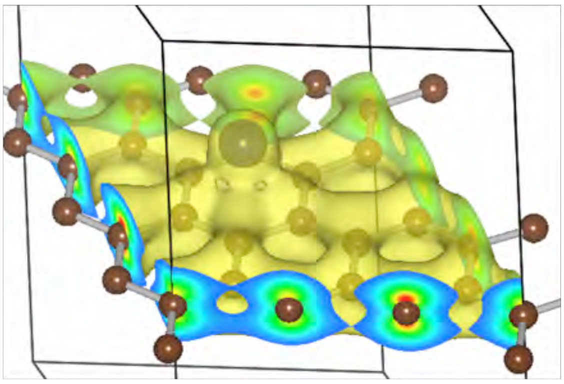


Figure: Calculated wave function image of a typical orbital for the adsorption of chromium adatom on graphene. The picture shows us the strong hybridization of oxygen orbital and carbon orbitals of graphene.

[1] A. Ishii, M. Yamamoto, H. Asano and K. Fujiwara, *Journal of Physics: Conference Series* **100** (2008) 052087.
[2] A. Ishii, T. Tatani, H. Asano and K. Nakada, *phys. stat. sol. (c)* **7** 347-350 (2010).
[3] T. Nakada and A. Ishii, *Solid State Commun.* **151** (2011) 13.
[4] T. Nakada and A. Ishii, in *Graphene / Book 1 (ISBN 978-953-308-60-2) INTECH*, 2011, in press.
[5] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, RC558 (1993).
[6] G. Kresse, *Thesis*, Technische Universitaet Wien 1993.
[7] G. Kresse and J. Furthmuller, *Comput. Mat. Sci.* **6**, 15-50 (1996).
[8] G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).

Electronic band structures of solar energy conversion materials from the *GW* perspective

Huihui Wang, Feng Wu, Hong Jiang
College of Chemistry, Peking University, 100871 Beijing, China

Direct utilization of solar energy in the form of solar fuels is currently one of the most actively pursued frontiers in basic energy sciences. In particular, the direct photo-splitting of water to H_2 and O_2 is regarded as the "holy grail" for solar energy conversion. The most grand challenge for direct solar energy conversion is to find a semiconductor material that meets several crucial requirements simultaneously, including, in particular, 1) a suitable band gap that allows efficient absorption of solar energy, and 2) appropriate valence and conduction band positions that match the redox potentials of H^+/H_2 and H_2O/O_2. Electronic band structures of photo-catalytic semiconductors therefore play a crucial role in solar-energy conversion. From a theoretical point of view, Kohn-Sham density functional theory (KS-DFT) in the standard local density or generalized gradient approximation (LDA/GGA) has serious difficulty in describing electronic properties of extended systems. In this work, many-body perturbation theory in the GW approximation, currently the most accurate first-principles approach for electronic band structure of extended systems, is applied to investigate electronic properties of several prototypical solar energy conversion materials. In particular several early transition metal dichalcogenides MX_2 (M=Zr, Hf, Mo, W, and X=S and Se) and alkali tantalates ($ATaO_3$, A=Li, Na and K) are considered. By combining first-principles calculations with phenomenological analysis, key factors that determine the electronic band structures of these materials are discerned. Absolute band positions with respect to the vacuum level are also calculated by combining KS-DFT calculations in the slab model and GW quasi-particle corrections. Results from these theoretical calculations can provide useful information for the rational design of photo-catalysts for visible light water splitting.

Theoretical study of Au and Pd adsorption on a hematite surface

Adam Kiejna and Tomasz Pabisiak
Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, PL-50-204
Wrocław, Poland

Structure, composition, magnetism, and stability of different terminations of the hematite (0001) surface were studied both within DFT GGA and GGA+U approach. Most of the considered terminations exhibit very large (up to 90%) relaxation of the first and/or second interlayer distance. For all terminations the surface preserves the antiferromagnetic character of the bulk crystal. On-site Coulomb correlations accounted for in the GGA+U approach have relatively small effects on the atomic geometry of the oxide surface but significantly improve the electronic structure and magnetic moments. The adsorption of Au and Pd atoms was considered at the two most stable terminations (either of oxygen or iron layer). Changes in atomic configuration, energetics, electronic and magnetic properties caused by Au and Pd adsorption in different sites and for different Au and Pd coverages were investigated. Both Au and Pd atoms bind strongly to the oxide surface and induce large changes in its geometry. In the most stable Au and Pd adsorption sites the adsorbate atoms form threefold bonds with surface oxygen atoms. The binding is stronger for Pd than Au and for both adsorbates is distinctly stronger at the oxygen than at the iron terminated surface. The account for on-site Coulomb correlation in the GGA+U enhances the calculated adsorption energies by about 1-2 eV. The adsorbate interactions and bonding with oxide atoms are discussed based on the calculated electronic structure and the electron charge transfer in the system.

Distinction of enantiomers by ultra-short laser pulses

Dominik Kröner
Universität Potsdam, Theoretische Chemie, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany

The qualitative and quantitative distinction of enantiomers is a typical task in modern chemical analysis. In previous years circular dichroism (CD) has been combined with laser ionization mass spectrometry (LIMS), using resonance enhanced multi-photon ionization (REMPI) by ns- [1] or fs- [2] laser pulses. This technique allows not only to identify unknown substances, but in addition to simultaneously measure the CD in ion yield. This makes the determination of enantiomeric excess possible [1], even the outcome of enantioselective laser control could be detected [3].
Recently the effect of the pulse duration on the CD in ion yield has been investigated by fs-LIMS for 3-methyl-cyclopentanone (3-MCP) resulting in a clear interdependency. Inspired by these findings, we investigated the CD in the populations of the first excited state of the REMPI process, caused by the interaction of (R)-3-MCP with either left or right circularly polarized laser pulses, as a function of the pulse duration.
We present laser driven quantum electron dynamics based on ab initio electronic structure calculations, namely TD-CIS(D)/6-311++(2d,2p). The theoretical description of the experiments requires a complete description of the field-dipole coupling, including both electric field-electric dipole and magnetic field-magnetic dipole interactions. Our calculations not only reproduce experimental observations but also offer possible explanations of the measured effects [4].

Acknowledgments: Financial support by the German Research Foundation (KR 2942).

[1] U. Boesl, A. Bornschlegl, *Chem. Phys. Chem.* **7**, 2085 (2006).
[2] H. G. Breunig, G. Urbasch, P. Horsch, J. Cordes, U. Koert, K. M. Weitzel, *Chem. Phys. Chem.* **10**, 1199 (2009).
[3] D. Kröner, M. F. Shibl, L. González, *Chem. Phys. Lett.* **372**, 242 (2003).
[4] P. Horsch, G. Urbasch, K. M. Weitzel, D. Kröner, *Phys. Chem. Chem. Phys.* **13**, 2378 (2011).

P 24

Adsorption of carbon on Pt clusters

Vasudeo Pandurang Babar[1,2] *and Vijay Kumar*[1]
[1]*Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122001, Haryana, India*
[2]*Centre for Modeling and Simulation, University of Pune, Pune – 411007, India*

Pt clusters are used as catalyst in many technological applications such as fuel cells. Often in these reactions some organic molecules are involved and/or carbon is used as support. Moreover for the growth of graphene, it is of considerable interest to know how carbon interacts with metals. Recently clusters of elemental Pt have been studied from first principles calculations and it has been shown [1] that the atomic structures of small clusters are quite different from bulk and that clusters with up to 22 atoms have all the atoms on the surface. Further at around the size of 40 atoms, there is an early transition to bulk fcc structure in the form of octahedral clusters. While in a real catalyst, there is a distribution of atomic sizes, it is believed that small clusters may be playing the dominant role in catalysis. We have studied [2] interaction of one carbon atom on such clusters with up to 44 atoms as well as an infinite Pt(111) surface using projector augmented wave pseudopotential method and generalized gradient approximation for exchange-correlation energy. We obtain strong bonding of carbon and an oscillatory behavior of the adsorption energy as the size is increased with a tendency to decrease towards the value of an infinite Pt(111) surface. The large binding energy reduces the magnetic moments of Pt clusters.

[1] V. Kumar and Y. Kawazoe, *Phys. Rev. B* **77**, 205418 (2008).
[2] V.P. Babar and V. Kumar, *to be published*.

Active sites for methane activation in MgO and Li doped MgO

Karolina Kwapien and Joachim Sauer
Humboldt-Universität zu Berlin, Institut für Chemie, Unter den Linden 6,
10099 Berlin, Germany

C-H bond activation is a subject of immense practical and fundamental interest. Particularly conversion of methane into more valuable chemicals and fuels represents a challenge for the future. A chemical of particular importance is ethene, which can be obtained by oxidative coupling of methane (OCM).

A prototype catalyst for the OCM reaction is lithium doped magnesium oxide [1]. It is believed that the $O^{\bullet-}$ oxygen radical anion, which is formed after substitution of a magnesium ion by a lithium ion, is the oxidizing species responsible for hydrogen abstraction from CH_4 and the formation of methyl radicals.

Based on the hypothesis that $Li^{+}O^{\bullet-}$/MgO is the active site for OCM surface reactions we first studied methane activation by $(MgO)_n^{+}$ and $LiO(MgO)_{n-1}$ gas phase clusters. However recent studies could not find evidence for $Li^{+}O^{\bullet-}$ species under OCM relevant conditions. Moreover, it was shown that Li is not necessary for C-H activation, but addition of Li enhances the OCM activity most likely by restructuring the material accompanied by creating more defects such as edges, corners and kinks. [2] Therefore, in addition to models of $Li^{+}O^{\bullet-}$ sites we considered different types of defect sites on MgO, and studied their reactivity towards methane.

Our results show that the H abstraction energy barriers for Li doped MgO clusters are smaller than 30 kJ/mol, while for the Li doped slab model the barrier increases till 61 kJ/mol. A similar apparent energy barrier was also calculated for a solid OCM catalyst by Catlow et al. (74 kJ/mol) [3], whereas the observed one is almost twice as high (147 kJ/mol) [4]. This indicates that the $Li^{+}O^{\bullet-}$ species is too reactive and it is not responsible for the rate-determining step in OCM.

[1] J. H. Lunsford, *Angew. Chem. Int. Ed.*, **34**, 970 (1995).
[2] M. Myrach, N. Nilius, S. V. Levchenko, A. Gonchar, T. Risse, K.-P. Dinse, L. A. Boatner, W. Frandsen, R. Horn, H.-J. Freund, R. Schlögl, M. Scheffler, *Chem. Cat. Chem.*, **2**, 854 (2010).
[3] C. R. A. Catlow, S. A. French, A. A. Sokol, J. M. Thomas, *Phil. Trans. R. Soc. A*, **363**, 913 (2005).
[4] J. Sun, J. W. Thybaut and G. B. Marin, *Catal. Today*, **137**, 90 (2008).

Surfaces of doped MgO at realistic temperatures and pressures: Defect concentration, distribution, and charge states

Norina Richter, Sergey Levchenko, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany

Native defects can dramatically modify the chemical properties of oxide surfaces. Even for a clean and flat surface of a binary oxide, we expect formation of anion and cation vacancies, interstitials, and their combinations. Moreover, the defects can be present in different charge states. However, experimental determination of the defect concentration at realistic temperatures and pressures is a challenging task, if at all possible. In this work, we calculate the electronic structure and formation energies of neutral and charged oxygen vacancies in the bulk and at the MgO (100) and (111) surfaces, and estimate their concentration and distribution at realistic temperatures and pressures using density-functional theory (DFT) and the *ab initio* atomistic thermodynamics approach [1]. It is demonstrated that a significant concentration of doubly charged O vacancies can be present at the (100) surface at realistic conditions, but not at the thermodynamically stable octopolar reconstruction of the polar (111) surface. While there are numerous studies of neutral oxygen vacancies in bulk MgO and at the MgO surface, calculations of formation energies of charged F centers at the MgO surface are scarce. The reason is that the traditional way of dealing with charged defects in a supercell approach, the neutralizing background method, is not directly applicable to surfaces, while cluster models are increasingly more difficult to use when it comes to higher charge states, since embedding is problematic. In our slab approach we simulate distributed doping by the virtual crystal approximation [2]. We also analyze how the proximity of a dopant providing localized acceptor states (local effect of doping), as well as localization of the acceptor states, affect the vacancy formation energies. The Li substitutional defect is used as a prototype of such a dopant. The effects of electron exchange and correlation on our results, in particular the self-interaction error and the band-gap problem, are discussed in detail. These problems are addressed by employing the hybrid range-separated exchange-correlation functional HSE06 with different values of the screening parameter, with PBE and PBE0 functionals as limiting cases.

[1] K. Reuter and M. Scheffler, *Phys. Rev. B* **65**, 035406 (2001); C. M. Weinert and M. Scheffler, *Mat. Sci. Forum* **10-12**, 25 (1986); M. Scheffler and J. Dabrowski, *Phil. Mag. A* **58**, 107 (1988).
[2] L. Vegard, Z. Phys. **5**, 17 (1921); M. Scheffler, *Physica* **146B**, 176 (1987).

Formation of coinage metal-carbonyl complexes on oxide surfaces

Runhai Ouyang and Wei-Xue Li
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS, Dalian 116023, China

Understanding the structure-reactivity relationships of the reactions catalyzed by the metal aggregates such as clusters and/or nanoparticles (NPs) supported on oxides at ambient pressures is important for rationalizing the design of catalysis. This is however difficult due to the ability of the reactants to alter the size, shape and charge state of the supported aggregates. A special case of the reactant induced alteration is oxidative disruption and reductive agglomeration of the supported noble metal NPs observed in CO ambient. To reveal the factors affecting the stability of the supported metal aggregates under the presence of CO, the insights into the metal adsorption and its interaction with CO, dependence on the oxide supports and effect on the dispersion of the metal aggregates are essential, and studied by density functional theory calculations. We find that for the coinage metals (CM) Cu, Ag and Au adsorbed on an oxide surface, the presence of CO would lead to the formations of the CM-carbonyl complexes. On polar and/or high work function oxide surfaces, the formations of metal cations are preferential and bound strongly with CO in form of the metal-carbonyl complexes. Further calculations show that for CM aggregates supported on polar and/or high work function oxides, the presence of CO would disintegrate the CM aggregates to the metal-carbonyl complexes. Whereas on low work function oxides, the CM aggregates would be resistant to the dispersion and the carbonyl formation. The importance of the oxide supports on the charge transfer and the effect on the stability of the metal aggregates supported are highlighted.

Towards low-temperature dehydrogenation catalysis: Isophorone on Pd(111)

Wei Liu, Aditya Savara, Xinguo Ren, Wiebke Ludwig, Karl-Heinz Dostert,
Swetlana Schauermann, Alexandre Tkatchenko, Hans-Joachim Freund,
Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-14195 Berlin, Germany

Heterogeneous catalysis plays an essential role in chemical processing industry, pharmaceuticals, and clean energy technologies. A microscopic understanding of the structure of the catalyst surface is essential for efficient catalyst design. Here we present a joint theoretical and experimental study on the structure of a model organic/metal catalyst: isophorone ($C_9H_{14}O$) on the Pd(111) surface. Both static density-functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulations are carried out to elucidate the underlying adsorption and dehydrogenation processes. A combination of the hydrogen-deuterium exchange experiments with the energetic and vibrational calculations are able to reveal the reaction pathway from the weakly chemisorbed $C_9H_{14}O$ reactant to the strongly chemisorbed $C_9H_{10}O$ products with four C-H bond cleavages. Both the temperature-programmed desorption (TPD) data and the relatively small magnitude of the activation barrier derived from the climbing image nudged elastic band (CI-NEB) method confirm the feasibility of the low-temperature dehydrogenation in the isophorone/Pd(111) system. The coexistence of different isophorone moieties on the Pd(111) surface is attributed to an interplay of covalent and van der Waals bonding, along with zero-point motion, and kinetic effects.

Stacking faults in (Ga,Mn)As and uniaxial magnetocrystalline anisotropy

F. Maca, J. Masek, M. Kopecky, J. Kub and T. Jungwirth
Institute of Physics ASCR, Condensed Matter Theory, Na Slovance 2
Praha, Czech Republic

High resolution X-ray diffraction measurements of (Ga,Mn)As and (Ga,Mn)(As,P) epilayers showed a structural anisotropy in the form of stacking faults which are present in the (-1-11) and (111) planes and absent in the (-111) and (1-11) planes. Our full-potential density functional calculations explain the energetic preference of substitutional Mn to decorate the stacking faults. This preference energy is comparable with the formation energy of the faults in pure GaAs. We surmise that the enhanced Mn density along the common [1-10] direction of the stacking fault planes represents the micro-structural origin of the in-plane uniaxial magnetocrystalline anisotropy of these semiconductors.

First-principles kinetic Monte Carlo simulations of ammonia oxidation at $RuO_2(110)$: Selectivity vs. semi-local DFT

Claudia Mangold[1] *and Karsten Reuter*[1, 2]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,*
14195 Berlin, Germany
[2]*Technische Universität München, Lichtenbergstr. 4*
85747 Garching, Germany

Reaching a detailed mechanistic understanding of high selectivity in surface catalytic processes is one of the central goals in present-day catalysis research. The Surface Science approach to this problem focuses on the investigation of well-defined model systems that reduce the complexity but still capture the relevant aspects. In this respect, the almost 100% selectivity reported in detailed experiments for the oxidation of NH_3 to NO at $RuO_2(110)$ [1] presents an ideal benchmark for a quantitative theoretical analysis. To this end we performed detailed kinetic Monte Carlo (kMC) simulations based on kinetic parameters derived from density-functional theory (DFT).

The obtained turnover frequency for molecular nitrogen is in rather good agreement with the experimental data. However, even with an extended set of elementary processes we are not able to reproduce the experimental findings for the production of NO and therewith the selectivity. The central quantities that decisively determine the latter are the binding energy of NO and the N diffusion barrier. Suspecting the approximate energetics obtained with the employed semi-local DFT functional as reason for the discrepancy, we recalculate the kinetic parameters with different functionals and discuss the resulting effects in the kMC simulations.

[1] Y. Wang *et. al.*, *J. Phys. Chem. B* **109** (2005) 7883.

The mechanisms underlying the enhanced resolution of atomic force microscopy with functionalized tips

Nikolaj Moll, Leo Gross, Fabian Mohn, Alessandro Curioni, and Gerhard Meyer
IBM Research - Zurich, 8803 Rüschlikon, Switzerland

By functionalizing the tip of an atomic force microscope (AFM) with a molecule or an atom that significantly contributes to the tip–sample interaction, the resolution can be dramatically enhanced. The interaction and therefore the resolution crucially depend on the chemical nature of the tip termination. Employing a tip functionalized with a CO molecule, atomic resolution of a pentacene molecule was recently demonstrated. In this work, the interaction between the CO tip and the pentacene imaged are studied with first principles calculations. The calculated frequency shifts compare very well with the experiment. The different energy contributions are analyzed and the Pauli energy is computed. We demonstrate that the source of the high resolution is Pauli repulsion, whereas van der Waals and electrostatic interactions only add a diffuse attractive background.

P 32

Towards more realistic models of nanostructures in catalysis described from first principles

Konstantin M. Neyman
Institució Catalana de Recerca i Estudis Avancats (ICREA) and Departament de Química Física & Institut de Química Teòrica i Computacional (Universitat de Barcelona), Barcelona, Spain

Differences in the complexity of single crystal surfaces and “real” catalysts cause a problem known as material gap in catalysis. This major obstacle hinders the extension of profoundly understood processes on crystal surfaces to equally good understanding of heterogeneous catalysis. Indeed, active components of most working catalysts are nanoparticles exposing defects and irregularities that often control the reactivity. To understand the reactivity of such systems it is crucial to go beyond the still common single-crystal description. For that, model metal catalysts formed of well-characterized supported nanoparticles have been proven very fruitful experimentally [1].

Computational strategy to model experimentally studied catalysis-relevant nanoparticles will be outlined. Applications to metal [2-6], oxide [7] and metal/oxide [8] nano-structures will be discussed.

[1] Metal deposits on well-ordered oxide films. M. Bäumer, H.-J. Freund, *Progr. Surf. Sci.* **61** (1999) 127.
[2] On the mechanism of formation of metal nanowires by self-assembly. F. Viñes, F. Illas, K.M. Neyman, *Angew. Chemie Int. Ed.* **46** (2007) 7094
[3] Methane activation by platinum: Critical role of edge and corner sites of metal nanoparticles. F. Viñes, Y. Lykhach, T. Staudt, M.P.A. Lorenz, C. Papp, H.-P. Steinrück, J. Libuda, K.M. Neyman, A. Görling, Chemistry - *Eur. J.* **16** (2010) 6530.
[4] How the C-O bond breaks during methanol decomposition on nanocrystallites of palladium catalysts.I.V. Yudanov, A.V. Matveev, K.M. Neyman, N. Rösch, *J. Am. Chem. Soc.* **130** (2008) 9342.
[5] Edge sites as a gate for subsurface carbon in palladium nanoparticles. F. Viñes, C. Loschen, F. Illas, K.M. Neyman, *J. Catal.* **266** (2009) 59.
[6] Hydrogen diffusion into Pd nanoparticles: Pivotal promotion by carbon. K.M. Neyman, S. Schauermann, *Angew. Chemie Int. Ed.* **49** (2010) 4743
[7] Greatly facilitated oxygen vacancy formation in ceria nanocrystallites. A. Migani, G.N. Vayssilov, S.T. Bromley, F. Illas, K.M. Neyman, *Chem. Commun.* **46** (2010) 5936.
[8] Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles. G.N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G.P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K.C. Prince, V. Matolin, K.M. Neyman, J. Libuda, *Nature Materials* **10** (2011) 310.

Structural study of Cu/Ru(10-10) and O/Ru(10-10) by means of directional elastic peak electron spectroscopy

Michal Jurczyszyn, Ireneusz Morawski, Jacek Brona, Marek Nowicki
Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9,
50-204 Wrocław, Poland

The structure of the first few atomic layers of the Cu/Ru(10-10) and O/Ru(10-10) adsorption systems was investigated by means of directional elastic peak electron spectroscopy (DEPES) [1]. All experiments were performed by using a retarding field analyzer (RFA). In DEPES the intensity of elastically backscattered electrons was measured as a function of the incidence angle of the primary electron beam at different energies. The characteristic intensity maxima, which originate from the forward focusing of primaries, are observed at incidence angles parallel to the close packed rows of atoms. Previous scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) investigations indicate the formation of a Cu(111) overlayer at large coverages [2]. The DEPES data for 6 ML of Cu on Ru(10-10) presented as stereographic distributions indicate the six-fold symmetry pattern characteristic for two mutually rotated Cu(111) domains [3]. Theoretical DEPES distributions were obtained for Cu and Ru by using the multiple scattering (MS) theory [4]. An R-factor analysis indicates nonequivalent concentrations of Cu domains.

Experimental DEPES distributions show that the formation of oxygen monolayer significantly influences the recorded DEPES intensities. The anisotropy maps, which show the relative signal change from the adsorbate with respect to the clean substrate, reveal very well visible intensity maxima characteristic for the (2x1)p2mg structure of oxygen. The experimental data are confirmed by theoretical DEPES distributions.

[1] S. Mroz, M. Nowicki, *Surf. Sci.* **297** (1993) 66.
[2] J. Brona, R. Wasielewski, A. Ciszewski, *in preparation*.
[3] M. Jurczyszyn, J. Brona, I. Morawski, M. Nowicki, *in preparation*.
[4] I. Morawski, M. Nowicki, *Phys. Rev. B* **75** (2007) 155412.

P 34

Screened hybrid density functional theory for thermodynamic properties of complex transition metal and rare earth oxides

Joachim Paier, *Matthias Haasler, Christopher Penschke, and Joachim Sauer*
Humboldt Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany

Transition metal (TMOs) and rare-earth oxides (REOs) are important players in catalysis. However, very often structure as well as the actual "active chemical species" (e.g. valency, oxidation state etc.) of the catalyst are not known [1]. Density-functional theory certainly helps answering the aforementioned questions, but conventional semilocal functionals are known to suffer from self-interaction error (SIE) challenging the validity of computed results. Specifically for TMOs and REOs, the SIE leads to an erroneous description of their electronic structure causing artefactual metalization of d and f electrons. Hybrid functionals, which mix a small fraction of exact, Hartree-Fock-type exchange to the remainder of semilocal exchange, are known to perform favorably for molecular systems and have recently been shown to improve on the electronic structure of so-called correlated systems [2,3].

This work puts particular emphasis on the oxidation and reduction reactions involving vanadium and (mixed valence) cerium oxides. We assess the screened hybrid functional after Heyd, Scuseria, and Ernzerhof (HSE) [4] and compare results to the conventional semilocal functional named after Perdew, Burke, and Ernzerhof (PBE) [5]. Heats of formation as well as reduction/oxidation energies of the aforementioned systems will help us calibrating the different density functionals by determining the methods' error margins.

[1] M. V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, *Surf. Sci. Reports 62* (2007) 219
[2] J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, G. Kresse, *Phys. Rev. B* **75** (2007) 045121.
[3] M. V. Ganduglia-Pirovano, J. L. F. Da Silva, J. Sauer, *Phys. Rev. Lett.* ***102*** (2009) 026101.
[4] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys. 118* (2003) 8207; *124* (2006) 219906(E).
[5] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett. 77* (1996) 3865.

Heats of adsorption and surface reaction for carbon monoxide and oxygen on Pd nanoparticles as determined by UHV single crystal adsorption microcalorimetry

M. Peter, S. Adamovsky, J.M. Flores-Camacho, J.-H. Fischer-Wolfarth,
S. Schauermann, H.-J. Freund
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany

Understanding the energetics of gas-surface interactions and establishing the correlation with the structural properties of the surface is an essential issue in heterogeneous catalysis. Such interactions can be quantified by measuring the amount of heat released upon adsorption of the gas phase molecules. This can be realized by a method of single crystal adsorption calorimetry (SCAC) that relies on measuring the temperature rise on ultrathin (1-10 μm) single crystals with a pyroelectric detector [1,2].

We apply a newly developed SCAC set up [2] to determine the adsorption heats of carbon monoxide and oxygen on Pd nanoparticles, supported on a well-defined Fe_3O_4/Pt(111) film [3]. To address the size dependent properties of the adsorbate-particle system, the nanoparticle size was varied in the range of ~ 100 to 5000 Pd atoms per cluster. We observe different trends for the particle size dependence of the CO and O adsorption energies and provide the first direct experimental observation that the CO adsorption energy decreases with decreasing particle size. This result is in line with the theoretical studies [4]. By measuring the CO adsorption energies on the oxygen precovered Pd nanoparticles and Pd(111) at different temperatures, the energetics of the CO-O interaction and the heats of the CO oxidation reaction on the surface were determined.

[1] Campbell C. T., et al., *Rev. Sci. Instr.* 2004, **75** 11.
[2] Fischer-Wolfarth J.-H., et al., *Rev. Sci. Instrum.*, in print.
[3] Fischer-Wolfarth J.-H., et al., *Phys. Rev. B.* 2010, **81,** 241416-(R)
[4] Yudanov I. V., et al., *J. Phys. Chem. C* 2008, **112**, 20269.

Chemical bonding of water to metal surfaces studied with core-level spectroscopies and DFT

T. Schiros[1,2,†], K.J. Andersson[2,3], L.G.M. Pettersson[2], A. Nilsson[1,2], and H. Ogasawara[1]
[1]Stanford Synchrotron Radiation Lightsource, 2575 Sand Hill Road, Menlo Park, CA 94025, USA
[2]FYSIKUM, Stockholm University, AlbaNova University Center, S-10691 Stockholm, Sweden
[3]Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark, Fysikvej 312, DK-2800 Kgs. Lyngby, Denmark
†Current Address: Columbia University Nanoscience and Engineering Center (NSEC) 538 W. 120th St. Schapiro CEPSR, NY, NY 10027, USA

The nature of the contact layer of water on surfaces is of relevance for many practical fields, including corrosion, electrochemistry, environmental science and heterogeneous catalysis. Here we focus on the geometric and electronic structure of the water contact layer on transition metal surfaces and the interaction between the water monolayer and the surface. By combining synchrotron radiation-based x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) techniques with density functional theory (DFT) computational methods we obtain element-specific information on the partial local density of states, local atomic structure, geometrical parameters and molecular orientation, allowing general principles for water-metal interaction to be derived.

Motion of adatoms on a curved fullerene C_{60} surface: An *ab initio* MD study

Lavanya M Ramaniah[1] and Mauro Boero[2]
[1]High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400085, India
[2]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, CNRS-UdS, 23 Rue de Loess, F-67037 Strasbourg, France; JAIST, 1-1 Asahidai, Nomi-shi, Ishikawa 923-1292, Japan; CREST, Japan Science and Technology Agency, Sanban-cho, 102-0075 Tokyo, Japan

Adatom behavior on surfaces is of vital importance to processes such as adsorption, desorption, surface chemical reactions and crystal growth. While most studies have focused on planar surfaces, the curved surfaces offered by fullerene molecules present a novel arena for testing the fascinating problem of the behavior and motion of atoms.

In this work, we present first-principles finite-temperature Car Parrinello dynamical simulations [1] of the motion of between one and three hetero-atoms on the surface of a fullerene C_{60} molecule and seek to characterize their behavior.

Our simulations of a single K or Na alkali metal atom on the surface of a C_{60} molecule in a temperature range up to 300 K [2] provide the first *direct* evidence for the heteroatom motion, postulated earlier in experiments involving dipole moment and polarizability measurements [3], and show that an alkali metal atom can move both on the surface and radially outward from the surface, resulting in a dynamics ranging from *diffusive* to *free* orbital motion, on time-scales of up to a few picoseconds. This motion is contrasted with that of a lone Ta metal atom on the C_{60} surface [4].

Dynamical simulations of the $C_{60}Ta_3$ system [5], on which photo-fragmentation studies had earlier revealed a fragmentation channel of C_3 units [6], show that the Ta atoms on the surface of the fullerene are affected by a rather high mobility, similar to the surface diffusion of a physisorbed species. Though a Ta dimer is formed at relatively low temperatures, the $C_{60}Ta_3$ cluster is dynamically stable up to a temperature of ~1000 K, ruling out purely thermal heating as a major factor responsible for any fragmentation process at least on time scales of a few picoseconds. The results have been sought to be understood *via* a detailed analysis of the electronic structure and bonding, using electron localization functions and maximally localized Wannier orbitals [7].

[1] CPMD, Copyright IBM Corp (1990–2008) and MPI für Festkörperforschung, Stuttgart (1997–2001)(1990–2008), http://www.cpmd.org/.
[2] L M Ramaniah and M Boero, *Journal of Chemical Physics* **133**, 134701 (2010).
[3] D Rayane, R Antoine, Ph Dugourd, E Benichou, A R Allouche, M Aubert-Frecon and M Broyer, *Phys. Rev. Lett.* **84**, 1962(2000); P Dugourd, R Antoine, D Rayane, E Benichou and M Broyer, *Phys.Rev. A* **62**, 011201 R(2000).
[4] F Tast, N Malinowski, S Frank, M Heinebrodt, I M L Billas, and T P Martin, *Phys. Rev. Lett.* **77**, 3529 (1996).
[5] L M Ramaniah and M Boero, *European Journal of Physics D* **51**, 369 (2009).
[6] L M Ramaniah, M Boero and M Laghate, *Physical Review B* **70**, 35411 (2004).
[7] M Matsubara, C Massobrio, L M Ramaniah and M Boero, *Physical Review B* **81**, 195433 (2010).

Towards a general-purpose first principles method: A critical assessment of the random phase approximation and beyond

Xinguo Ren[1]*, Joachim Paier*[2]*, Patrick Rinke*[3]*, and Matthias Scheffler*[1]
[1]*Fritz Haber Institute of the Max Planck Society, Berlin, Germany*
[2]*Institute for Chemistry, Humboldt University, Berlin, Germany*

Owing to its broad applicability and promise to overcome several intrinsic deficiencies of local/semilocal approximations to density functional theory (DFT), the random phase approximation for the ground-state correlation energy (cRPA) in combination with exact exchange (EX) has brought DFT one step further towards a "general-purpose first principles method". This is largely due to three attractive features: The exact-exchange energy (EX) cancels the spurious self-interaction error present in the Hartree energy exactly. The RPA correlation (cRPA) energy is fully non-local and includes long-range van der Waals (vdW) interactions automatically and highly accurately. Moreover, dynamic electronic screening is taken into account by summing up a sequence of "ring diagrams" to infinite order, which makes EX+cRPA applicable to small-gap or metallic systems.

However, the standard RPA practice, i.e., evaluating both the EX and cRPA terms using Kohn-Sham orbitals from local/semi-local functionals, systematically underestimates bond strengths across a variety of systems. Two recent additions to cRPA have successfully ameliorated the underbinding problem: second-order screened exchange (SOSEX) [1,2] and renormalized single excitation corrections (RSE) [3]. From a diagrammatic point of view, SOSEX and RSE correspond to different types of many-body correlation terms that are, however, compatible with each other. In this work, we systematically benchmark the influence of SOSEX, RSE, and their combination on the atomization energies of the covalently bound G2 molecular set, the binding energies of the weakly bound S22 molecular set, and hydrogen-transfer and non-hydrogen-transfer reaction barrier heights (HTBH38/04 and NHTBH38/04 sets). We found that both SOSEX and RSE corrections to cRPA improve upon the notorious tendency of EX+cRPA to underbind. Surprisingly, reaction barrier heights obtained using EX+cRPA based on a KS reference alone are already remarkably accurate. EX+cRPA+SOSEX+RSE lives up to the challenge of providing a comparable level of accuracy for reaction barrier heights and overall gives the most balanced performance, which holds great promise for widespread application in the future.

[1] A. Grüneis *et al.*, *J. Chem. Phys.* **131**, 154115 (2009).
[2] J. Paier *et al.*, *J. Chem. Phys.* **132**, 094103 (2010).
[3] X. Ren *et al.*, *Phys. Rev. Lett.* **106**, 153003 (2011).

Surface defects activate new reaction paths: Formation of formate during methanol oxidation on defective Ru(0001)

Irene Palacio Rodríguez, Oscar Rodríguez de la Fuente
Departamento de Física de Materiales,Universidad Complutense, Madrid-28040, Spain

An optimum understanding of the existing molecular mechanisms taking place while reactions occur on surfaces, should preferably be based on a correct identification of the intermediate species and the reaction paths, so to avoid trial-and-error approaches. We have co-adsorbed methanol and oxygen on Ru(0001), with surfaces having a variable density of defects. In this way, with Infrared Reflection-Absorption Spectroscopy (IRAS), we have identified reaction paths, intermediates and products in the methanol/Ru(0001) system at room temperature. We show that oxygen coadsorption on the flat surface stabilizes intermediate species, namely formaldehyde and formyl. Surface defects, on the other hand, promote the stabilization of methoxy, and not the stabilization of the former intermediates. We show the opening of a new reaction channel, which appears just on the defective surface: the formation of formate (HCOO), catalyzed by surface steps. This particular case shows how surface defects profoundly affect the catalytic activity, activating new reaction paths, which are not available when the density of defects is low.

Unraveling the stability of polypeptide helices: Critical role of van der Waals interactions

V. Blum, M. Rossi, A. Tkatchenko, J. Ireta[1]*, and M. Scheffler*
Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6,
D-14195, Berlin, Germany
[1]*Universidad Autónoma Metropolitana, Iztapalapa, Mexico*

The rules of structure formation in molecules and materials are in principle exactly known through quantum mechanics, but fully ab initio predictions are still a considerable challenge when more than just a few atoms are involved. Our focus is the prediction of secondary structure and dynamics in polypeptides, i.e., the building blocks of proteins. In particular, we here target from first principles the structure, stability and dynamics of helical secondary structure and the underlying interactions: hydrogen (H-) bonding, van der Waals (vdW) interactions and, in the present case, a specific ionic termination. We employ density functional theory based on the PBE exchange-correlation functional, with a correction to include vdW interactions that is derived from the self-consistent electron density [1] (PBE+vdW). This method describes the stability of small peptides (32 conformers) with an accuracy of 0.4 kcal/mol in comparison to "gold standard" CCSD(T) calculations. When applied to infinite periodic helices, the vdW interactions stabilize the helical structures by more than a factor of two compared to pure PBE functional and (for finite helices) significantly modifies the potential energy landscape [2]. To illustrate the significance of our findings for peptide secondary structure, we address the remarkable thermal stability of the Ac-Ala_{15} –LysH^+ peptide in vacuo (up to T ~700K [3]). Direct ab initio molecular dynamics simulations of up to 70 ps with PBE+vdW demonstrate that Ac-Ala_{15}–LysH^+ maintains a helical structure at 500 and 700K, unfolding only at 800K, in agreement with experiment. Plain PBE renders the molecule too unstable, unfolding already at 700K. At 500K, PBE+vdW still favors a mostly α-helical conformation, while plain PBE favors a floppy 3_{10} helical structure. An interplay between vdW, connecting H-bonds from the Lys termination, and the charge are fundamental to capture the observed stability of this helix. What is remarkable is the degree of specificity with which vdW interactions appear to assist in the stabilization of peptide helices, together with the other, qualitatively different non-covalent interactions (H-bonds, electrostatic) that govern the secondary structure of peptides.

[1] A. Tkatchenko and M. Scheer, *Phys. Rev. Lett.* **102**, 073005 (2009).
[2] A. Tkatchenko, M. Rossi, V. Blum, J. Ireta, and M. Scheffler, *Phys. Rev. Lett.* **106**, 118102 (2011).
[3] M. Kohtani, T. C. Jones, J. E. Schneider and M. F. Jarrold, *J. Am. Chem. Soc.* **126**, 7420 (2004).

On the importance of van der Waals forces in ice

Biswajit Santra[1], Jiří Klimeš[2], Dario Alfè[2], Alexandre Tkatchenko[1], Ben Slater[2], Angelos Michaelides[2], Roberto Car[3], and Matthias Scheffler[1]
[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
[2] University College London, London, UK
[3] Princeton University, Princeton, USA

A detailed understanding of how water molecules interact with each other is critically important to a wide variety of physical, chemical, and biological processes. It has long been recognized that water molecules interact with each other through a combination of hydrogen bonding and van der Waals (vdW) forces. However, the role of vdW interactions on many parts of the phase diagram of water are largely unexplored. Here we report a systematic series of *ab initio* studies aimed at understanding the role of vdW forces on the cohesive properties of various ambient and high pressure phases of crystalline ice. Using diffusion quantum Monte Carlo (DMC), accurate lattice energies -- which agree well with experimental values -- of several ice phases have been obtained. Then employing density-functional theory with various conventional exchange-correlation functionals and vdW corrected functionals [1,2,3] we show that the vdW contribution to the lattice energy increases monotonously from the ambient to the high pressure phases of ice. Conversely, the strength of the hydrogen bonds between the water molecules decreases as the pressure increases, with the result that in the highest pressure phase one quarter of the entire lattice energy comes from vdW forces. The strong sensitivity of vdW forces to density means that vdW must be accounted for if transition pressures between the various phases within even an order of magnitude of experiment are to be obtained. This study shows that vdW forces play a greater role than previously expected in ice at high pressures and moves us a step closer to the first accurate phase diagram of ice and water obtained exclusively from *ab initio* methods.

[1] M. Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004).
[2] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).
[3] J. Klimeš, D. R. Bowler, and A. Michaelides, *J. Phys.: Cond. Matt.* **22**, 022201 (2010).

Patterning nanoroads and quantum dots on fluorinated graphene

Morgana Ribas[1], *Abhishek Singh*[2], *Pavel Sorokin*[1], *Boris Yakobson*[1]
[1]*Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, USA*
[2]*Materials Research Centre, Indian Institute of Science and Rice University, Bangalore, 560012 India*

Graphene nanoroads [1] and quantum dots [2] patterned on functionalized graphene combine metallic and semiconducting properties on a same mechanically intact sheet. Using density functional methods we investigate different stoichiometric phases of fluorinated graphene and find that the complete '2D-teflon' CF phase is thermodynamically more stable. The formation of fluorinated graphene favors the nucleation of aromatic 'magic' clusters, but unlike hydrogenated graphene [3] it does not have a nucleation barrier. The CF is an insulator and turns out to be a perfect matrix-host for patterning nanoroads and quantum dots of pristine graphene. Depending upon the edge orientation and width the electronic and magnetic properties of the nanoroads can be tuned. The HOMO-LUMO energy gaps are size dependent and show a typical confinement of Dirac fermions. Furthermore, we study the effect of different coverages of F on graphene (CF and C_4F) on the band gaps, and show their suitability to host quantum dots of graphene with unique electronic properties [4].

[1] Singh, A. K.; Yakobson, B. I., *Nano Lett.* 2009, **9** (4), 1540.
[2] Singh, A. K.; Penev, E. S.; Yakobson, B. I., *ACS Nano* 2010, **4** (6), 3510.
[3] Lin, Y.; Ding, F.; Yakobson, B. I., *Phys. Rev. B* 2008, **78** (4), 041402.
[4] Ribas, M. A.; Singh, A. K.; Sorokin, P; Yakobson, B. I., *Nano Res.*, 2011, **4**, 143.

The effect of non-magnetic impurities on magnetic and cohesive properties of grain boundaries in nickel

Monika Všianskà[1,2,3] and Mojmír Šob[1,2,3]
[1] Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic
[2] Central European Institute of Technology, CEITEC MU, Masaryk University, Brno, Czech Republic
[3] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic

The macroscopic mechanical behaviour of polycrystalline metallic materials is largely determined by cohesion of the grain boundaries (GB) which is strongly affected by segregated impurities. Here we present an ab initio study of segregation of 12 non-magnetic *sp*-impurities (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at $\Sigma5(210)$ GB and (210) free surface (FS) in *fcc* ferromagnetic nickel and analyze their effect on structure, magnetic and mechanical properties. We determine the preferred segregation sites of the impurity atoms at the Σ 5(210) GB, their segregation enthalpies and strengthening/embrittling energies with their decomposition into the chemical and mechanical components. We find interstitially segregated Si as a GB cohesion enhancer, substitutionally segregated Al and interstitially segregated P with none or minimum strengthening effect and interstitially segregated S, Ge, As, Se and substitutionally segregated Ga, In, Sn, Sb and Te as GB embrittlers in nickel. Interstitial impurities modify the magnetic moments at the GB and in its immediate neighborhood stronger than substitutional ones. Whereas there is a slight enhancement of magnetization at the clean GB and FS with respect to bulk nickel (3–7 % and 24 %, respectively), most of the above impurities nearly kill or substantially reduce the magnetic moments at the FS and, when segregating interstitially at the GB (i.e. Si, P, S, Ge, As, and Se), they produce magnetically dead layers at the boundary, which are caused by a strong hybridization of *sp*-states of the impurities with the *d*-states of nickel and a redistribution of electron states in both majority and minority bands.

This research was supported by the Grant Agency of the Czech Republic (Projects No. 202/09/1786 and 106/09/H035), the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. IAA100100920), by the Research Projects AV0Z20410507 and MSM0021622410 and by the Project CEITEC–Central European Institute of Technology (CZ.1.05/1.1.00/02.0068) from the European Regional Development Fund.

P 44

Singlet and triplet states of azobenzene: Quantum Monte Carlo study

M. Dubecký, R. Derian, L. Horváthová, I. Štich
Center for Computational Materials Science, Institute of Physics,
Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic

A combination of Quantum Monte Carlo techniques (QMC) and medium accuracy quantum chemistry methods (CAS-SCF) are used to calculate energies of ground and excited singlet [1] and triplet states [2] of *trans*-azobenzene. The accuracy of our approach is demonstrated by excellent agreement of calculated excitation energies with experiments. However, such an agreement is only achieved after finite-temperature corrections. To this end we use a model reducing the molecular degrees-of-freedom to the CNNC dihedral, which is sampled by DFT Car-Parrinello-type of molecular dynamics. Our data based on a combination of different techniques (DFT, CAS-SCF, QMC, and Car-Parrinello dynamics) provide novel insights which allow for disentanglement of singlet and triplet signals in gas-phase electron energy loss spectrum with overlapping singlet and triplet contributions.

[1] M. Dubecký, R. Derian, L. Mitas, and I. Štich, *J.Chem.Phys.* **133**, 244301 (2010).
[2] M. Dubecký, R. Derian, L. Horváthová, M. Allan, and I. Štich, *submitted* (2011).

Charge sensitive x-ray photoelectron spectroscopy for probing molecular nature of electret formation

Sefik Suzer
Department of Chemistry, Bilkent University, 06800, Ankara, Turkey

Electrification or electret formation is well-known to men for more than 2500 years, and has also been intelligently utilized for that long. Semiconducting materials are best described by filled conduction and empty valence bands with an energy separation or band gap E_g. However, additional electronic states due to doping or defects, imperfections at their surfaces and/or grain boundaries contribute significantly to their electrical properties. In the other end, we have insulating materials like polymers, metal oxides, nitrides, and sulphides, etc., which are described with the same language but having larger E_g values, where electrons are localized, leading to extremely low conductivities. Similarly, other electronic states, like interface and impurity states, defect sites, etc. dominate the electrical properties of these. In addition, electrical properties are strongly influenced by external stresses, like exposure to light, energetic particles, as a result of friction, mechanical distortions, etc., which are attributed to insertion of localized electrons and/or ions at interfaces, grain boundaries, or in bulk sites like cavities. In stark contrast to metallic and semiconducting systems, the atomic/molecular-level nature of electrets is poorly understood in most cases. Kelvin Probe Atomic Force Microscopy (KP-AFM) has been the most advanced analytical tool for probing the charge developed and mapping in the submicron dimensions. However, as in most electrical based measurements it lacks chemical specificity. On the other hand, spectroscopic techniques like IR, Raman, NMR or variants of them coupled with scanning probe techniques like NSOM, etc. have excellent chemical specificity, but they are not sensitive to charge and/or electrostatic potentials developed. In this respect, ESR and EPR techniques have been quite successful for analysis of trapped charges on polymer and/or oxide surfaces, especially in combination with other surface specific techniques, but use of these techniques is also limited since they can only probe radicals and paramagnetic species. This is where the method we have developed and successfully applied to probing charging/discharging phenomena in various materials, called: **"Surface and Charge Sensitive Chemical Analysis using X-ray Photoelectron Spectroscopy"** comes very handy [1-7]. The methodology, as well as its applications for characterizing various organic/inorganic materials will be presented.

[1] U. K. Demirok, G. Ertas, S. Suzer, *J. Phys.Chem. B* **108,** 5179 (2004).
[2] G. Ertas, U.K. Demirok, A. Atalar, S. Suzer, *Appl. Phys. Lett.* **86** 183110 (2005).
[3] H. Sezen, G. Ertas, A. Dana, S. Suzer, *Macromolecules* **40** 4109 (2007).
[4] S. Suzer, H. Sezen, A. Dana, *Anal. Chem.* **80** 3931 (2008).
[5] H. Sezen, G. Ertas, S. Suzer, *J. Electr. Spectros. Rel. Phen.* **178-179** 373 (2010)
[6] H. Sezen, S. Suzer, *Surf. Sci. Lett.* **604** L159 (2010).
[7] H. Sezen, E. Ozbay, O. Aktas, S. Suzer, *Appl. Phys. Lett.* **98**, 111901 (2011).

Stabilisation of polar ZnO(0001) surfaces in dry and humid environment

Mira Todorova, Markus Valtiner, Jörg Neugebauer
Max-Planck-Insitut für Eisenforschung GmbH, Max-Planck-Straße 1,
40237 Düsseldorf, Germany

Combining density-functional theory calculations with thermodynamic considerations we study the atomic structure of the polar ZnO(0001) surfaces in dry and humid environment. We show that vibrational contributions significantly affect the stabilization of the surface structures, due to an energetic near degeneracy of a large number of very different reconstructions with similar stoichiometry. The large impact of the vibrational entropy on the surface structure gives rise to temperature dependent surface phase diagrams. By going beyond the thermodynamic limit we extend the concept of equilibrium surface phase diagrams to include kinetically stabilized surface reconstructions and construct meta-stable phase diagrams. This enables us to consistently describe and explain all experimentally observed surface structures on polar ZnO(0001) surfaces.

[1] M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, *Phys. Rev. Lett.* **103**, 065502 (2009).
[2] M. Valtiner, M. Todorova, and J. Neugebauer, *Phys. Rev. B* **82**, 165418 (2010).

Unveiling the phonon-selected electron-phonon coupling constants in nanometer superconducting lead films by helium atom scattering

I. Yu. Sklyadneva[1], *Giorgio Benedek*[2,4], *E. V. Chulkov*[1], *P. M. Echenique*[1],
R. Heid[3], *K.-P. Bohnen*[3], *J. Peter Toennies*[4]
[1]*Donostia International Physics Centre, San Sebastian, Spain.*
[2]*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Italy.*
[3]*Karlsruher Institut für Technologie, Institut für Festkörperphysik, Karlsruhe, Germany.*
[4]*Max Planck Institut für Dynamik und Selbstorganisation, Göttingen, Germany.*

The recent discovery of superconductivity in single monolayer lead films raises intriguing questions about the electron-phonon coupling in quasi-two-dimensional systems. Recent calculations carried out at the Donostia International Physics Center and at Karlsruhe show that the electron-phonon coupling strength for *each phonon mode* in a superconducting film can be measured by inelastic helium atom scattering (HAS) [1]. This surprising ability of HAS relies on two circumstances. First, in ultra-thin metal films the e-p coupling range exceeds the film thickness, enabling HAS to detect all the film phonons, even those one nanometer below the surface (*quantum sonar*). This result explains recent HAS experiments in which many more than the usual one or two phonon dispersion curves were detected by HAS [2]. More important, the ab-initio theoretical analysis shows that HAS scattering amplitudes are proportional to the phonon-induced surface charge density oscillations, and therefore to the e-p coupling for that particular phonon (*mode-lambda*). Thus He-atom scattering is the first experiment providing mode-selected e-p coupling strengths (*mode-lambda spectroscopy*). Besides superconductivity in ultra-thin films, the mode-lambdas are relevant for inelastic photoemission, phonon-induced surface reactions, scanning tunnel spectroscopy (STS) and other thin-film properties.

[1] Yu. Sklyadneva, G. Benedek, E. V. Chulkov, P. M. Echenique, R. Heid, K.-P. Bohnen, J. P. Toennies, *submitted for publication*.
[2] J.Braun, P. Ruggerone, G. Zhang, J.P. Toennies, and G. Benedek, Surface Phonon Dispersion Curves of Thin Pb Films on Cu(111). *Physical Review B* **79**, 205423 (2009).

Hydrogen interaction with 4H-SiC surfaces

E. Wachowicz and A. Kiejna
Institute of Experimental Physics, University of Wrocław, Wrocław, Poland

Silicon carbide is a promising material for the fabrication of microelectronic devices. Due to its wide band gap, it is suitable for applications related to high power, high frequencies, and high temperatures. Hydrogen is one of the most common impurities in electronic technology strongly influencing the electronic characteristics of the semiconductor material. Interaction of hydrogen with SiC surfaces often occurs in technological processes, such as chemical vapour deposition or dry etching. It can also play an important role in growing of quasi-free-standing epitaxial graphene on SiC. In order to understand the interaction of H with SiC surfaces, the ab initio study of hydrogen adsorption on Si- and C-terminated surfaces is performed. The most favorable adsorption sites depending on the hydrogen coverage are identified. The changes in the electronic structure resulting from H adsorption are analyzed. The Mulliken population analysis is performed in order to have insight into the bond formation process. Moreover, the surface phase diagrams are obtained with the help of the ab initio thermodynamics method.

Mechanism of Ni-Al_2O_3 poisoning: Theoretical and experimental studies

I. Czekaj , J. Wambach, R. Struis, T. Schildhauer, S. Biollaz
Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Recently, surface modifications as well as carbon deposition on a commercial Ni/Al_2O_3 catalyst during the production of methane from synthesis gas were investigated by *quasi in-situ* X-ray photoelectron spectroscopy (XPS) [1, 2]. Further, we studied the sulphur poisoning processes on the Ni/Al_2O_3 catalyst used for the methanation process [3].
In the present work we extended our investigations by theoretical studies on the adsorption of sulphur-containing compounds on the Ni/Al_2O_3 catalyst for a better understanding of chemical processes appearing during regeneration of the catalyst by steam. The focus was to study possible catalyst changes and the thus modified catalytic behavior of the nickel particles (e.g. pure metal or Ni_3C), as well as to see differences in the poisoning behavior, when sulphur adsorbs either on Ni particles or on the support. In experimental studies we developed a Temperature Programmed Steaming method allowing the differentiation of carbon deposition on spent catalysts like Ni_3C, amorphous and graphitic carbon. The theoretical studies were done using Density Functional Theory calculations (StoBe) with cluster model and non-local functional (RPBE) approach. For modeling the catalyst, an $Al_{15}O_{40}H_{35}$ cluster has been selected representing the γ-Al_2O_3(100) surface, and Ni metal particles of different sizes were cut from a Ni(100) surface and deposited on the $Al_{15}O_{40}H_{35}$ cluster. Several poisoning agents have been found to be stable on both Ni clusters and alumina support such as COS, H_2S, or hydrogen thiocarbonates. Our results clearly demonstrate that these sulphur species are not only stabilized on the nickel, but also on the support surface with compatible strengths. The most stable species are carbonyl sulphides and hydrogen sulphide and both species are suspected to be present at the catalyst surface under SNG production conditions.

[1] I. Czekaj, F. Loviat, F. Raimondi, J. Wambach, S. Biollaz, A. Wokaun; *Appl. Catalysis A: General* 2007, ***329***, 68.
[2] F. Loviat, I. Czekaj, J. Wambach, A. Wokaun; *Surf. Sci.* 2009, ***603****,* 2210.
[3] R. Struis, T. Schildhauer, I. Czekaj, M. Janousch, C. Ludwig, and S. Biollaz, *Appl. Catal. A* 2009, ***362****,* 121.

Model studies of supported catalyst preparation: Pd deposition on iron oxide films from the liquid phase

Huifeng Wang, Rhys Dowler, William Kaden, Martin Sterrer,
and Hans-Joachim Freund,
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics,
Faradayweg 4-6, D-14195 Berlin, Germany.

In this contribution we present results of surface science studies related to the preparation of supported metal catalysts on well-defined oxide surfaces applying procedures used in real catalysis. While in most UHV model studies of supported metal catalysts the metal is deposited onto a clean surface by physical vapor deposition, the standard methods in real catalyst preparation, e.g. impregnation or deposition-precipitation, are wet chemical routes with the important processes occurring at the solid-liquid interface, followed by calcination and reduction to transform the catalyst precursor into the active compound. The aim of the present work is to apply those preparation procedures to well-defined oxide surfaces using thin oxide films as substrates that allow standard surface science characterization techniques to be applied. We present experimental results for Pd deposition from $PdCl_2$ containing solutions with different pH onto $Fe_3O_4(111)$ films.

STM showed that uniformly distributed Pd nanoparticles can be prepared by using the deposition-precipitation method. XPS was used to follow the evolution of Pd species at each preparation stage and to study the influence of Pd precursor solution pH on the speciation of Pd complexes on the surface. The Pd particles were further characterized by CO chemisorption with TPD and IRAS. Interestingly, different chemisorption properties of Pd/Fe_3O_4 were found after CO or H_2 reduction at 500 K. CO-reduced Pd samples showed normal CO adsorption behavior, while a striking suppression of CO adsorption was brought about by H_2 reduction. XPS results indicated a change in the electronic structure of Pd after H_2 reduction which can be recovered by reoxidation and CO reduction. The results of these experiments will be compared with the respective results for Pd clusters prepared by physical vapor deposition on $Fe_3O_4(111)$.

Photochemistry of N_2O on Ag(111)

Ki Hyun Kim[1,2], *Kazuo Watanabe*[1,3], *Dietrich Menzel*[1,4], *Hans-Joachim Freund*[1]
[1]*Fritz Haber Institute of Max Planck Society,* [2]*Michigan State University,* [3]*Tokyo, Japan University of Science,* [4]*Technische Universität München, Germany*

Photoreactions of N_2O adsorbed on Ag(111) induced by nanosecond UV laser pulses have been studied by temperature programmed desorption (TPD) and angle-resolved mass-selected time-of-flight (MS-TOF) measurements.

N_2O molecules in the first monolayer desorb molecularly by heating but photodissociate into N_2 + O or photodesorb molecularly or dissociatively at photon energies above 3.5 eV. TOF spectra of photodesorbed N_2 as well as N_2O measured at $h\nu = 4.7$ eV consist of two velocity components (T_{tr}= 2200 and 600 K for N_2, and 3100 and 1100 K for N_2O). The desorption flux of the fastest component of N_2O is peaked ~25° off the surface normal, whereas the others are directed in the surface normal. Origins and photoexcitation as well as photodesorption mechanisms of the N_2O and N_2 signals will be discussed.

Role of defects in surface chemistry on $Cu_2O(111)$

A. Önsten, J. Weissenrieder, D. Stoltz, S. Yu, M. Göthelid, and U.O. Karlsson
Materials Physics, KTH Royal Institute of Technology, S-164 40 Kista, Sweden

Scanning tunneling microscopy and high resolution photoemission spectroscopy have been used to investigate defects on $Cu_2O(111)$ and their interaction with water and SO_2. Two types of point defects are identified, namely oxygen and copper vacancies. Oxygen vacancies can form a $(\sqrt{3}x\sqrt{3})R30°$ reconstruction but are also present to a varying extent on (1x1)-terminated surfaces, as shown by STM. Multiply under-coordinated oxygen atoms (O*MCUS*) such as oxygen atoms adjacent to copper vacancies are believed to play a pivotal role in the stabilization of both SO_2 and water reaction products. Water adsorption at 150 K results in both molecular and a small amount of dissociated water. Dissociation is suggested to occur through bonding of oxygen in the molecule to a copper site adjacent to an oxygen vacancy in the substrate and hydrogen bonding to a neighboring O*MCUS* atom. All water adsorption products have left the surface at 210 K. SO_2 interacts with oxygen atoms in the surface giving SO_3-like species both at 150 K and at room temperature. At room temperature, SO_3 is believed to form upon interaction with O*MCUS* atoms only. When adsorbing SO_2 at 150 K and slowly heating to 280 K, SO_3 species are continuously replaced with SO_4 and at 280 K, only a small amount SO_4 remains on the surface. SO_4 formation appears to be coverage dependent.

Two-photon photoemission versus scanning tunneling spectroscopy at ultrathin NiO(100) films

Mario Kiel, Stephan Großer, Anke Höfer, Klaus Duncker, and Wolf Widdra
Institute of Physics, Martin-Luther Universität Halle, 06120 Halle, Germany

By combining scanning tunneling microscopy and spectroscopy (STM, STS) with two-photon photoemission (2PPE) the electronic structure of ultrathin NiO(001) films has been investigated in the region of unoccupied states. The NiO monolayer which has been grown by reactive metal deposition in an O_2 atmosphere on a Ag(001) substrate forms an uniaxially compressed (2×1) structure and is characterized by two well-developed unoccupied Ni 3d states as determined by STS. For NiO films from 2 ML to 9 ML, STM and LEED show an unreconstructed (1x1) structure as is expected for the NiO(001) rocksalt structure. With increasing layer thickness the STS spectra develop distinct variations. Additionally for thicker layers a Ni3d-derived surface state develops within the band gap on NiO as based on STS. Using two-color 2PPE the unoccupied electronic states are addressed in an alternative way as compared to STS. For the NiO monolayer the 2PPE spectra reveal Ni 3d states at 2.4 and 3.7 eV above the Fermi energy which compare well with the STS spectra for defect-free NiO monolayer islands. For the NiO(001) bilayer 2PPE can identify the unoccupied Ni 3d state seen by STS as well as the first three image potential states. The lifetime of these states will be discussed.

Support by the German joint research network Sonderforschungsbereich 762 “Functionality of oxidic interfaces” of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Elucidating hydrogen absorption in alumina-supported platinum group metal nanocrystals

Markus Wilde
Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, 153-8505 Tokyo, Japan

The possibility of hydrogen (H) absorption by finely dispersed nanoparticles of platinum group metals (Pd, Pt) is an issue of debate in olefin hydrogenation and fuel cell catalysis, where particle-absorbed hydrogen is considered a potentially reactive species. Nanocrystals exhibit peculiar H-absorption properties that may differ drastically from those of the respective bulk metals. Owing to the large surface area of nanoparticles, this behavior has frequently been attributed to H stabilization in subsurface-sites.

By perfecting the depth resolution in H profiling via resonant $^{1}H(^{15}N,ag)^{12}C$ nuclear reaction analysis (NRA) we achieved the distinction of *surface-adsorbed* from *volume-absorbed* H on/inside only 1-2 nm high and 5-10 nm wide nanocrystals of Pd and Pt, supported on a H-free thin film Al_2O_3/NiAl(110) substrate. The nanocrystals show substantial hydrogenation in low pressure ($\leq 6\times10^{-3}$ Pa) H_2 gas at 100-300 K, even in the case of Pt, for which H absorption is strongly endothermic in the bulk metal. In stark contrast to the common subsurface site stabilization model, we observe that the entire interior of the nanocrystals is subject to H incorporation [1]. We further demonstrate that the Pd-NC-absorbed H is essential for the olefin hydrogenation reactivity of the NCs, confirming the crucial importance of cluster-absorbed H in catalysis [2]. Elucidating the particular reactivity of subsurface-absorbed H in olefin hydrogenation is work in progress.

[1] M. Wilde et. al., *Phys. Rev. B* **77**, 113412 (2008).
[2] M. Wilde, S. Schauermann, et al., *Angew. Chem. Int. Ed.* **47**, 9289 (2008).

Impurity pairs as possible origin of d^0 magnetism in doped oxides

Hua Wu[1,2], Alessandro Stroppa[3], Sung Sakong[4], Silvia Picozzi[3], Matthias Scheffler[5], and Peter Kratzer[4]
[1]University of Cologne, Germany, [2]Fudan University, Shanghai, China, [3]CNR-SPIN, L'Aquila, Italy, [4]University of Duisburg-Essen, Germany, [5]Fritz-Haber Institute, Berlin, Germany

Ferromagnetism observed in some defective but originally nonmagnetic materials, which are free of magnetic *d* or *f* electrons, has been referred to as d^0 magnetism. In this respect, 2*p* hole doped oxides have recently been envisaged as an important subgroup of magnetic semiconductors for potential spintronic applications. The origin of the d^0 magnetism in these hole doped oxide semiconductors remains, however, puzzling, in spite of a widespread view that the dual character of the 2*p* holes— quite strong Hund exchange and considerable delocalization—gives rise to the d^0 magnetism.

Here we studied, using DFT calculations, the nature and origin of the d^0 magnetism in hole doped oxides by focusing on model systems—substitutional C or N doped MgO and ZnO. Our LDA or GGA calculations demonstrate that single C or N impurities are not stable as widely assumed in the literature, which may simply be due to their strong electronegativity. The impurities prefer pairing, and the resultant C_2 (or charged N_2^{2+}) dimers have a molecular spin=1 and interact antiferromagnetically in MgO, in strong contrast to the previously predicted ferromagnetic half metal. Our calculations are corroborated by the fact that the impurity levels of concern lie well inside the wide band gap (although underestimated by LDA or GGA).

For the C doped ZnO, we find that the spin-polarized C_2 $pp\pi^*$ states resonate with the host conduction band and could thus mediate a long-range ferromagnetic interaction, see Fig. 1. This is supported by the Heyd-Scuseria-Ernzerhof hybrid functional calculations, which describe correctly the ZnO band gap and thus the impurity-host interaction.

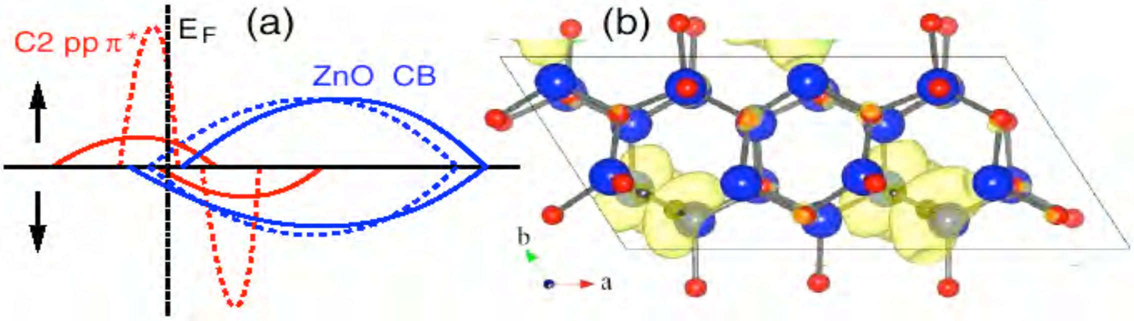


Fig. 1: (a) Level resonance and (b) spin-density isosurface for the C_2 dimers in ZnO

To conclude, open-shell impurity molecules (or defect complexes) and their level resonance with the host band are proposed as a possible route to the d^0 ferromagnetism in C or N doped oxides.

[1] H. Wu, A. Stroppa, S. Sakong, S. Picozzi, M. Scheffler, and P. Kratzer, *PRL* **105**, 267203 (2010).

Properties of free and size-selected metal clusters for bridging the gap between gas phase and surface

P. Fayet, L. D. Socaciu, T. Bernhardt, G. Santambrogio, K. R. Asmis,
and Ludger Wöste
Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

The very particular electronic features of metal clusters lead to extraordinary optical and dynamic properties, which occur, regardless if these particles are embedded in a matrix, deposited on a surface, or if they are free. Most promising chemical applications can certainly be expected from clusters, which are deposited on well chosen surfaces. Free metal clusters provide - on the other hand – the best access to study their dynamic properties experimentally and theoretically as a function of size, structure, charge and their environment. Even the assembly of mono-dispersed clusters on a surface leads across soft landing of size selected particles in the gas phase.

Already in 1985 we have performed - in order to identify the latent image spec of AgBr photographic plates - first soft landing experiments of size selected silver and gold clusters. This allowed us to identify the silver tetramer as the critical germ of the photographic elementary process. Later it was found by U. Heiz et al. that supported gold clusters containing few atoms up to nanometer size exhibit pronounced catalytic properties. In order to obtain more insights into the underlying processes, we performed reactivity experiments on corresponding systems in the gas phase. Combined with advanced calculations performed by U. Landmann et al. the approach allowed us to identify not only a complete catalytic cycle of CO-oxidation occurring on free Au_2^-, but also the structures of all its intermediates.

By using state-of-the-art cluster sources, we are now able to synthesize a rich variety of neutral, negatively and positively charged, pure and mixed metal clusters. These particles are then mass selected and introduced into an ion trap, which allows to perform systematic IR- absorption experiments. Among these we found striking similarities with spectra obtained on corresponding deposited particles. Our present activities focuses on preparing new architectures like "clusters on clusters", which allow us to mimic and investigate the situation of a size-selected cluster deposited on well defined surface element in the gas phase.

[1] *Latent Image Generation by Deposition of Monodisperse Silver Clusters*
P. Fayet, F. Granzer, G. Hegenbart, E. Moisar, B. Pischel, and L. Wöste: *Phys. Rev. Lett.* **55**, p. 3002-3004 (1985).
[2] *Catalytic CO Oxidation by Free Au_2: Experiment and Theory*
L. D. Socaciu, J. Hagen, T. Bernhardt, L. Wöste, U. Heiz, H. Häkkinen, U. Landman: *J. Am. Chem. Soc.* **125** p. 10437-10445 (2003).
[3] *Isomorphous Substitution in Bimetallic Oxide Clusters*
E. Janssens, G. Santambrogio, M. Brümmer, L. Wöste, P. Lievens, J. Sauer, G.Meijer, and K. R. Asmis: *PRL* **96**, p. 233401-1-4 (2006).
[4] *Gas phase vibrational spectroscopy of mass-selected vanadium oxide anions*
G. Santambrogio, M. Brümmer, L. Wöste, J. Döbler, M. Sierka, J. Sauer, G. Meijer, K. R. Asmis: *Phys. Chem. Chem. Phys.* **10**, 3992-4005 (2008).

Metal-free photocatalyst g-C_3N_4 thin-films deposited on p-type semiconductors for water reduction under light illumination

Florent Yang[1]*, Steven Orthmann*[1]*, Christoph Merschjann*[1]*, Tobias Tyborski*[1]*,*
Michael Lublow[1]*, Sven Kubala*[1]*, Arne Thomas*[2]*, Thomas Schedel-Niedrig*[1]
[1]*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH,*
D-14109 Berlin, Germany
[2]*Technische Universität Berlin, Fakultät II, Mathematik und Naturwissenschaften,*
D-10623 Berlin, Germany

In the last few years, graphite-like carbon nitride (g-C_3N_4) has been intensively studied in photocatalytic processes for hydrogen and oxygen production from water splitting under visible light illumination in the presence of a proper sacrificial electron donor or acceptor, respectively [1]. The huge interest on this metal-free photocatalyst g-C_3N_4 is increasing because of the high chemical and thermal stability of this material. However, up to now, the photocatalyst g-C_3N_4 has been only studied as powder in several photocatalytic systems [2].

In this work, we will show that the deposition of g-C_3N_4 thin-films on p-type semiconductors like porous silicon and chalcopyrite substrates can be successfully achieved. These g-C_3N_4 thin-films have been obtained by two methods of preparation: (1) thermal condensation of dicyandiamide under inert gas atmosphere and (2) sublimation of g-C_3N_4 powder by physical vapor deposition. Morphological, structural and optical properties of g-C_3N_4 thin-films have been investigated using scanning electron microscopy, grazing incidence X-ray diffraction and photoluminescence techniques. Additionally, X-ray photoemission spectroscopy measured on these modified substrates reveals the same chemical composition as g-C_3N_4 powder while photo-electrochemical investigations clearly prove hydrogen evolution under visible light illumination. Moreover, the deposition of metal co-catalyst (Pt, Rh) on such photocathodes was observed to further enhance the evolution of hydrogen.

Financial support granted by the BMBF, project “Light2Hydrogen” 03IS2071F, is acknowledged.

[1] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nature Mat.* **8** (2009) 76.
[2] X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu, M. Antonietti, *J. Am. Chem. Soc.* **131** (2009) 1680.

LIST OF PARTICIPANTS

Heather L. Abbott	Kennesaw State University	USA	hlabbott@gmail.com
Igor Abrikosov	Linköping University	Sweden	igor.abrikoso@ifm.liu.se
Serguei Adamovski	Fritz-Haber-Institut der MPG, Berlin	Germany	adams@fhi-berlin.mpg.de
Katharina Al-Shamery	Carl v. Ossietzky Universität Oldenburg	Germany	katharina.al.shamery@uni-oldenburg.de
Paola Alippi	CNR	Italy	paola.alippi@ism.cnr.it
Consuelo Alvarez-Galvan	Fritz-Haber-Institut der MPG, Berlin	Germany	galvan@fhi-berlin.mpg.de
Ole K. Andersen	MPI f. Festkörperforschung, Stuttgart	Germany	oka@fkf.mpg.de
Wanda Andreoni	Ecole Polytechnique Federale de Lausanne	Switzerland	wanda.andreoni@epfl.ch
Heiko Appel	Fritz-Haber-Institut der MPG, Berlin	Germany	appel@fhi-berlin.mpg.de
Rosa Arrigo	Fritz-Haber-Institut der MPG, Berlin	Germany	arrigo@fhi-berlin.mpg.de
Viktor Atalla	Fritz-Haber-Institut der MPG, Berlin	Germany	atalla@fhi-berlin.mpg.de
Paul S. Bagus	University of North Texas, Denton	USA	bagus@unt.edu
Carsten Baldauf	Fritz-Haber-Institut der MPG, Berlin	Germany	baldauf@fhi-berlin.mpg.de
Sudipta R. Barman	UGC-DAE CSR Indore	India	barmansr@gmail.com
Ernst Bauer	Arizona State University	USA	ernst.bauer@asu.edu
Marcus Bäumer	Universität Bremen	Germany	mbaeumer@uni-bremen.de
Friedhelm Bechstedt	Friedrich-Schiller-Universität Jena	Germany	bech@ifto.physik.uni-jena.de
Jörg Behler	Ruhr-Universität Bochum	Germany	joerg.behler@theochem.ruhr-uni-bochum.de
Malte Behrens	Fritz-Haber-Institut der MPG, Berlin	Deutschland	behrens@fhi-berlin.mpg.de
Michael Bender	BASF SE, Ludwigshafen	Germany	michael.bender@basf.com
Giorgio Benedek	Universität Milano-Bicocca	Italy	giorgio.benedek@unimib.it
Hadj Mohamed Benia	MPI f. Festkörperforschung, Stuttgart	Germany	h.benia@fkf.mpg.de
Elizabeth C. Beret	Fritz-Haber-Institut der MPG, Berlin	Germany	beret@fhi-berlin.mpg.de
Adriana Bernal Osorio	Fritz-Haber-Institut der MPG, Berlin	Germany	adbeos@fhi-berlin.mpg.de
Richard Berndt	Christian-Albrechts-Universität zu Kiel	Germany	berndt@physik.uni-kiel.de
Jerry Bernholc	North Carolina State University	USA	bernholc@ncsu.edu
Erminald Bertel	University of Innsbruck	Austria	erminald.bertel@uibk.ac.at
Bjoern Bieniek	Fritz-Haber-Institut der MPG, Berlin	Germany	bieniek@fhi-berlin.mpg.de

Silke Biermann	Ecole Polytechnique, Palaiseau	France	biermann@cpht.polytechnique.fr
Dieter H. Bimberg	Technische Universität Berlin	Germany	bimberg@physik.tu-berlin.de
Volker Blum	Fritz-Haber-Institut der MPG, Berlin	Germany	blum@fhi-berlin.mpg.de
Piotr Boguslawski	Institute of Physics PAS, Warsaw	Poland	bogus@ifpan.edu.pl
Jorge A. Boscoboinik	Fritz-Haber-Institut der MPG, Berlin	Germany	bosco@fhi-berlin.mpg.de
Alex M Bradshaw	MPI für Plasmaphysik und Fritz-Haber-Institut	Germany	amb@ipp.mpg.de
Matthew Brown	ETH Zurich	Switzerland	matthew.brown@chem.ethz.ch
Harald Brune	Ecole Polytechnique Fédérale de Lausanne	Switzerland	harald.brune@epfl.ch
Christin Büchner	Fritz-Haber-Institut der MPG, Berlin	Germany	buechner@fhi-berlin.mpg.de
Kieron J. Burke	University of California, Irvine	USA	kieron@uci.edu
Marilia J. Caldas	University of São Paulo	Brazil	mjcaldas@usp.br
Roberto Car	Princeton University	USA	rcar@Princeton.EDU
Christian Carbogno	Fritz-Haber-Institut der MPG, Berlin	Germany	christian.carbogno@fhi-berlin.mpg.de
Esther Carrasco Burgos	Instituto de Estructura de la Materia (CSIC), Madrid	Spain	Ecarrasco@iem.cfmac.csic.es
Fabio Caruso	Fritz-Haber-Institut der MPG, Berlin	Germany	caruso@fhi-berlin.mpg.de
Marco Casadei	Fritz-Haber-Institut der MPG, Berlin	Germany	casadei@fhi-berlin.mpg.de
Welchy L. Cavalcanti	Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung (IFAM)	Germany	welchy.leite.cavalcanti@ifam.fraunhofer.de
Wael Chibani	Fritz-Haber-Institut der MPG, Berlin	Germany	chibani@fhi-berlin.mpg.deb
Sucismita Chutia	Fritz-Haber-Institut der MPG, Berlin	Germany	chutia@fhi-berlin.mpg.de
Horst Conrad	Fritz-Haber-Institut der MPG, Berlin	Germany	conrad@fhi-berlin.mpg.de
Andreia Luisa da Rosa	University of Bremen	Germany	darosa@bccms.uni-bremen.de
Juarez L. F. Da Silva	The University of Sao Paulo	Brazil	dasilva_juarez@yahoo.com
Jan-Christoph Deinert	Fritz-Haber-Institut der MPG, Berlin	Germany	deinert@fhi-berlin.mpg.de
Bernd Dillmann	Xapollo AG, Uitikon Waldegg	Switzerland	bernd.dillmann@xapollo.ch
Karl-Heinz Dostert	Fritz-Haber-Institut der MPG, Berlin	Germany	dostert@fhi-berlin.mpg.de

Rhys M. Dowler	Fritz-Haber-Institut der MPG, Berlin	Germany	dowler@fhi-berlin.mpg.de
Wolfgang U. Eberhardt	Technische Universität Berlin	Germany	wolfgang.eberhardt@helmholtz-berlin.de
Holger Eisele	Technische Universität Berlin	Germany	ak@physik.tu-berlin.de
Gerhard Ertl	Fritz-Haber-Institut der MPG, Berlin	Germany	ertl@fhi-berlin.mpg.de
Robert Fenger	Humboldt-Universität zu Berlin	Germany	robert.fenger@chemie.hu-berlin.de
Janaina Fernandes Gomes	Universidade de São Paulo	Brazil	Janainafg@iqsc.usp.br
Kristen A. Fichthorn	The Pennsylvania State University	USA	fichthorn@psu.edu
Andre Fielicke	Fritz-Haber-Institut der MPG, Berlin	Germany	fielicke@fhi-berlin.mpg.de
Vincenzo Fiorentini	Università di Cagliari	Italy	vincenzo.fiorentini@dsf.unica.it
Laura Foglia	Fritz-Haber-Institut der MPG, Berlin	Germany	lafoglia@fhi-berlin.mpg.de
Hans-Joachim Freund	Fritz-Haber-Institut der MPG, Berlin	Germany	freund@fhi-berlin.mpg.de
Martin Friak	Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf	Germany	m.friak@mpie.de
Bretislav Friedrich	Fritz-Haber-Institut der MPG, Berlin	Germany	brich@fhi-berlin.mpg.de
Cynthia M. Friend	Harvard University, Cambridge MA	USA	Cfriend@seas.harvard.edu
Yuichi Fujimori	Fritz-Haber-Institut der MPG, Berlin	Germany	fujimori@fhi-berlin.mpg.de
Johanna I. Fuks	University of the Basque country, San Sebastian	Spain	Johannafuks@gmail.com
Maria Veronica Ganduglia-Pirovano	Institute of Catalysis and Petrochemistry-CSIC, Madrid	Spain	vgp@icp.csic.es
Francesca Genuzio	Fritz-Haber-Institut der MPG, Berlin	Germany	fgenuzio@fhi-berlin.mpg.de
Luca M. Ghiringhelli	Fritz-Haber-Institut der MPG, Berlin	Germany	luca@fhi-berlin.mpg.de
Javier B Giorgi	University of Ottawa	Canada	jgiorgi@uottawa.ca
Vivekanand V. Gobre	Fritz-Haber-Institut der MPG, Berlin	Germany	gobre@fhi-berlin.mpg.de
Claude F. Goldsmith	Fritz-Haber-Institut der MPG, Berlin	Germany	cfgoldsmith@fhi-berlin.mpg.de
Anastasia Gonchar	Fritz-Haber-Institut der MPG, Berlin	Germany	gonchar@fhi-berlin.mpg.de
Nuria Gonzalez-Garcia	Fritz-Haber-Institut der MPG, Berlin	Germany	garcia@fhi-berlin.mpg.de
Irene Groot	Fritz-Haber-Institut der MPG, Berlin	Germany	groot@fhi-berlin.mpg.de

E.K.U. Gross	Max Planck Institut for Mikrostrukturphysik Halle	Germany	hardy@mpi-halle.mpg.de
Axel Groß	Ulm University	Germany	axel.gross@uni-ulm.de
Frank Grosse	Paul-Drude-Institut für Festkörperelektronik, Berlin	Germany	frank.grosse@pdi-berlin.de
Mathis Gruber	Fritz-Haber-Institut der MPG, Berlin	Germany	gruber@fhi-berlin.mpg.de
Michael Grunze	University of Heidelberg	Germany	apc@pci.uni-heidelberg.de
Chunsheng Guo	Fritz-Haber-Institut der MPG, Berlin	Germany	chunsheng@fhi-berlin.mpg.de
Gary L. Haller	Yale University	USA	gary.haller@yale.edu
Heiko Hamann	Universität Oldenburg	Germany	heiko.hamann@uni-oldenburg.de
Dan J. Harding	Fritz-Haber-Institut der MPG, Berlin	Germany	harding@fhi-berlin.mpg.de
Volker Heine	Cavendish Lab	England	vh200@cam.ac.uk
Klaus Heinz	Universität Erlangen-Nürnberg	Germany	klaus.heinz@physik.uni-erlangen.de
Stefan Heinzel	Rechenzentrum Garching der MPG	Germany	stefan.heinzel@rzg.mpg.de
John C. Hemminger	University of California, Irvine	USA	jchemmin@uci.edu
Uwe Hergenhahn	Max-Planck-Institut für Plasmaphysik Garching	Germany	uwe.hergenhahn@ipp.mpg.de
Klaus E. Hermann	Fritz-Haber-Institut der MPG, Berlin	Germany	hermann@fhi-berlin.mpg.de
Markus Heyde	Fritz-Haber-Institut der MPG, Berlin	Germany	heyde@fhi-berlin.mpg.de
Stefan Hildebrandt	Wiley-VCH Berlin	Germany	shildebr@wiley.com
Werner Hofer	University of Liverpool	UK	whofer@liverpool.ac.uk
Oliver Hofmann	Fritz-Haber-Institut der MPG, Berlin	Germany	hofmann@fhi-berlin.mpg.de
Karsten Horn	Fritz-Haber-Institut der MPG, Berlin	Germany	horn@fhi-berlin.mpg.de
Mahboubeh Hortamani	Institute of Applied Physics, University of Hamburg	Germany	Mahboubeh.Hortamani@physnet.uni-hamburg.de
Qing-Miao Hu	Institute of Metal Research, Chinese Academy of Sciences	China	qmhu@imr.ac.cn
Anastasija Ichsanow	PSI/ETH Zürich	Switzerland	anastasija.ichsanow@psi.ch
Francesc Illas	Universitat de Barcelona	Spain	francesc.illas@ub.edu
Gerd Illing	Laser- und Medizin-Technologie GmbH, Berlin	Germany	g.illing@lmtb.de
Joel Ireta	Universidad Autónoma Metropolitana-Iztapalapa	México	iret@xanum.uam.mx
Akira Ishii	Tottori University	Japan	Ishii@damp.tottori-u.ac.jp

Karl Jacobi	Fritz-Haber-Institut der MPG, Berlin	Germany	`friedrich-karl.jacobi@t-online.de`
Julius Jellinek	Argonne National Laboratory	USA	`jellinek@anl.gov`
Hong Jiang	Peking University	China	`h.jiang@pku.edu.cn`
Ling Jiang	Fritz-Haber-Institut der MPG, Berlin	Germany	`ljiang@fhi-berlin.mpg.de`
Christian Joas	Fritz-Haber-Institut der MPG, Berlin	Germany	`joas@fhi-berlin.mpg.de`
Werner Jürgens	Fritz-Haber-Institut der MPG, Berlin	Germany	`werner.juergens@fhi-berlin.mpg.de`
Osman Karslioglu	Fritz-Haber-Institut der MPG, Berlin	Germany	`osman@fhi-berlin.mpg.de`
Adam Kiejna	University of Wroclaw	Poland	`kiejna@ifd.uni.wroc.pl`
Jürgen Kirschner	Max-Planck-Institut für Mikrostrukturphysik	Germany	`sekrki@mpi-halle.mpg.de`
Alexander Kleinsorge	former FHI	Germany	`aleks@physik.tu-berlin.de`
Thorsten Klüner	University Oldenburg	Germany	`thorsten.kluener@uni-oldenburg.de`
Helmut Knözinger	University of Munich	Germany	`helmut.knoezinger@cup.uni-muenchen.de`
Peter Kratzer	University Duisburg-Essen	Germany	`Peter.Kratzer@uni-due.de`
Dominik Kröner	Universität Potsdam	Germany	`Dominik.Kroener@uni-potsdam.de`
Helmut Kuhlenbeck	Fritz-Haber-Institut der MPG, Berlin	Germany	`kuhlenbeck@fhi-berlin.mpg.de`
Vijay Kumar	Dr. Vijay Kumar Foundation, Gurgaon	India	`kumar@vkf.in`
Karel Kunc	Max-Planck-Institut für Festkörperforschung	Germany	`karel.kunc@upmc.fr`
Karolina Kwapien	Humboldt-Universität zu Berlin	Germany	`kwapienk@chemie.hu-berlin.de`
Doron Lahav	Academic Pixel	Germany	`contact@academic-pixel.de`
Florian Lazarevic	Fritz-Haber-Institut der MPG, Berlin	Germany	`lazarevic@fhi-berlin.mpg.de`
Hermann Lederer	Rechenzentrum Garching der MPG	Germany	`lederer@rzg.mpg.de`
Sergey V. Levchenko	Fritz-Haber-Institut der MPG, Berlin	Germany	`levchenko@fhi-berlin.mpg.de`
Wei-Xue Li	Dalian Institute of Chemical Physics	China	`wxli@dicp.ac.cn`
Jörg Libuda	Friedrich-Alexander-Universität Erlangen-Nürnberg	Germany	`libuda@chemie.uni-erlangen.de`
Leonid Lichtenstein	Fritz-Haber-Institut der MPG, Berlin	Germany	`lichtenstein@fhi-berlin.mpg.de`
Wei Liu	Fritz-Haber-Institut der MPG, Berlin	Germany	`wliu@fhi-berlin.mpg.de`
Bo-Hong Liu	Fritz-Haber-Institut der MPG, Berlin	Germany	`bhliu@fhi-berlin.mpg.de`

Sönke Lorenz	Kanzlei Gulde Hengelhaupt Ziebig & Schneider	Germany	soenke.lorenz@gmx.de
Steven G. Louie	University of California at Berkeley	USA	sglouie@berkeley.edu
Frantisek Maca	Institute of Physics ASCR, Praha	Czech Republic	maca@fzu.cz
Claudia Mangold	Fritz-Haber-Institut der MPG, Berlin	Germany	mangold@fhi-berlin.mpg.de
Helder Marchetto	Fritz-Haber-Institut der MPG, Berlin	Germany	marchetto@fhi-berlin.mpg.de
Yulia Martynova	Fritz-Haber-Institut der MPG, Berlin	Germany	martynova@fhi-berlin.mpg.de
Gerard Meijer	Fritz-Haber-Institut der MPG, Berlin	Germany	meijer@fhi-berlin.mpg.de
Dietrich Menzel	Technische Universität München	Germany	dietrich.menzel@ph.tum.de
Ingrid Mertig	Martin-Luther-Universität Halle-Wittenberg	Germany	mertig@physik.uni-halle.de
Hakim Meskine	(formerly) Fritz-Haber-Institut der MPG, Berlin	Germany	Hakimmeskine@gmail.com
Horia Metiu	UC Santa Barbara	USA	metiu@chem.ucsb.edu
Randall J. Meyer	University of Illinois at Chicago	USA	rjm@uic.edu
Jan Mitschker	Carl von Ossietzky Universität Oldenburg	Germany	jan.mitschker@uni-oldenburg.de
Nikolaj Moll	IBM Research Zurich	Switzerland	nim@zurich.ibm.com
Martin Muhler	Ruhr-University Bochum	Germany	muhler@techem.rub.de
Barbara Müller	Generalverwaltung der MPG, München	Germany	barbara.mueller@gv.mpg.de
Lydia Nemec	Fritz-Haber-Institut der MPG, Berlin	Germany	lnemec@fhi-berlin.mpg.de
Jörg Neugebauer	Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf	Germany	neugebauer@mpie.de
Konstantin M. Neyman	ICREA and Universitat de Barcelona	Spain	konstantin.neyman@icrea.es
Horst Niehus	Humboldt-Universität Berlin	Germany	horst_niehus@yahoo.de
Niklas Nilius	Fritz-Haber-Institut der MPG, Berlin	Germany	nilius@fhi-berlin.mpg.de
Marek Nowicki	University of Wroclaw	Poland	Nowicki@ifd.uni.wroc.pl
Gianfranco Pacchioni	UniversitÃ Milano Bicocca	Italy	gianfranco.pacchioni@unimib.it
Julia Pach	Fritz-Haber-Institut der MPG, Berlin	Germany	THsecretary@fhi-berlin.mpg.de
Joachim Paier	Humboldt Universität Berlin	Germany	joachim.paier@chemie.hu-berlin.de
Sokrates T. Pantelides	Vanderbilt University, Nashville	USA	Pantelides@Vanderbilt.Edu

Leandro Pascua	Fritz-Haber-Institut der MPG, Berlin	Germany	`pascua@fhi-berlin.mpg.de`
Anastassia Pavlovska	Arizona State University	USA	`pavlovska@asu.edu`
Rossitza Pentcheva	LMU Munich	Germany	`rossitzap@lmu.de`
Mats O. Persson	University of Liverpool	United Kingdom	`mpersson@liv.ac.uk`
Matthias Peter	Fritz-Haber-Institut der MPG, Berlin	Germany	`peterm@fhi-berlin.mpg.de`
Lars G.M. Pettersson	Stockholm University	Sweden	`lgm@fysik.su.se`
Earl Ward Plummer	Louisiana State University	United States	`Wplummer@phys.lsu.edu`
Johannes Pollmann	Universität Münster	Germany	`pollman@uni-muenster.de`
Elena Primorac	Fritz-Haber-Institut der MPG, Berlin	Germany	`primorac@fhi-berlin.mpg.de`
Hengshan Qiu	Fritz-Haber-Institut der MPG, Berlin	Germany	`Qiu@fhi-berlin.mpg.de`
Lavanya Ramaniah	Bhabha Atomic Research Centre	India	`lmrjgd@gmail.com`
Rampi Ramprasad	University of Connecticut, Storrs	USA	`rampi@uconn.edu`
Christian Ratsch	UCLA Los Angeles	USA	`cratsch@math.ucla.edu`
Xinguo Ren	Fritz-Haber-Institut der MPG, Berlin	Germany	`xinguo@fhi-berlin.mpg.de`
Karsten Reuter	TU München	Germany	`karsten.reuter@ch.tum.de`
Neville V. Richardson	University of St Andrews	Scotland, UK	`master@st-andrews.ac.uk`
Norina A. Richter	Fritz-Haber-Institut der MPG, Berlin	Germany	`richter@fhi-berlin.mpg.de`
Karl-Heinz Rieder	EMPA Swiss Federal Laboratories for Materials	Switzerland	`karl-heinz.rieder@empa.ch`
Patrick Rinke	Fritz-Haber-Institut der MPG, Berlin	Germany	`rinke@fhi-berlin.mpg.de`
Thomas Risse	Freie Universität Berlin	Germany	`risse@chemie.fu-berlin.de`
Oscar Rodriguez de la Fuente	Universidad Complutense	Spanien	`oscar.rodriguez@fis.ucm.es`
Jutta Rogal	Ruhr-Universität Bochum	Germany	`jutta.rogal@rub.de`
Matti Ropo	Fritz-Haber-Institut der MPG, Berlin	Germany	`matti.ropo@fhi-berlin.mpg.de`
Mariana Rossi	Fritz-Haber-Institut der MPG, Berlin	Germany	`rossi@fhi-berlin.mpg.de`
Harm H. Rotermund	Dalhousie University	Canada	`harm.rotermund@dal.ca`
Angel Rubio	Universidad del Pais Vasco UPV/EHU	Spanien	`angel.rubio@ehu.es`
Victor G. Ruiz Lopez	Fritz-Haber-Institut der MPG, Berlin	Germany	`ruiz@fhi-berlin.mpg.de`
Günther Rupprechter	Institute of Materials Chemistry, TU Wien	Austria	`Grupp@imc.tuwien.ac.at`

Jacinto P. Sa	ETH Zurich	Switzerland	`jacinto.sa@psi.ch`
Peter Saalfrank	Universität Potsdam	Germany	`petsaal@rz.uni-potsdam.de`
Alessandro Sala	Fritz-Haber-Institut der MPG, Berlin	Germany	`sala@fhi-berlin.mpg.de`
Biswajit Santra	Fritz-Haber-Institut der MPG, Berlin	Germany	`santra@fhi-berlin.mpg.de`
Joachim Sauer	Humboldt Universität Berlin	Germany	`js@chemie.hu-berlin.de`
Swetlana Schauermann	Fritz-Haber-Institut der MPG, Berlin	Germany	`schauermann@fhi-berlin.mpg.de`
Matthias Scheffler	Fritz-Haber-Institut der MPG, Berlin	Germany	`scheffler@fhi-berlin.mpg.de`
Arno Schindlmayr	Universität Paderborn	Germany	`Arno.Schindlmayr@uni-paderborn.de`
Robert Schlögl	Fritz-Haber-Institut der MPG, Berlin	Germany	`acsek@fhi-berlin.mpg.de`
Dieter Schmeißer	Brandenburgische Technische Universität Cottbus	Germany	`susanne.masch@tu-cottbus.de`
Thomas Schmidt	Fritz-Haber-Institut der MPG, Berlin	Germany	`schmidtt@fhi-berlin.mpg.de`
Wolf-Dieter Schneider	Ecole Polytechnique Fédérale de Lausanne (EPFL)	Switzerland	`wolf-dieter.schneider@epfl.ch`
Eckehard Schöll	TU Berlin	Germany	`schoell@physik.tu-berlin.de`
Kurt E. Schönhammer	Universität Göttingen	Germany	`schoenh@theorie.physik.uni-goettingen.de`
Franziska Schubert	Fritz-Haber-Institut der MPG, Berlin	Germany	`schubert@fhi-berlin.mpg.de`
Manfred E. Schuster	Fritz-Haber-Institut der MPG, Berlin	Germany	`manfred@fhi-berlin.mpg.de`
Pierre Schwach	Fritz-Haber-Institut der MPG, Berlin	Germany	`schwachp@fhi-berlin.mpg.de`
Oliver Seiferth	Hydro Aluminium Rolled Products GmbH, Bonn	Germany	`oliver.seiferth@hydro.com`
Ari P. Seitsonen	Universität Zürich	Switzerland	`Ari.P.Seitsonen@iki.fi`
Shamil Shaikhutdinov	Fritz-Haber-Institut der MPG, Berlin	Germany	`Shaikhutdinov@fhi-berlin.mpg.de`
Abhishek K. Singh	Indian Institute of Science	India	`Abhishek@mrc.iisc.ernet.in`
Mojmir Sob	Masaryk University, Brno	Czech Republic	`mojmir@ipm.cz`
Peter C. Stair	Northwestern University, Evanston	USA	`Pstair@northwestern.edu`
Elisabeth Stankewitz	Fritz-Haber-Institut der MPG, Berlin	Germany	`stankewitz@fhi-berlin.mpg.de`
Fernando Stavale	Fritz-Haber-Institut der MPG, Berlin	Germany	`stavale@fhi-berlin.mpg.de`

Hans-Peter Steinrück	Uni Erlangen	Germany	hans-peter.steinrueck@chemie.uni-erlangen.de
Martin Sterrer	Fritz-Haber-Institut der MPG, Berlin	Germany	sterrer@fhi-berlin.mpg.de
Ivan Stich	Inst. of Physics, Slovak Academy of Sciences	Slovakia	ivan.stich@savba.sk
Stefanie Stuckenholz	Fritz-Haber-Institut der MPG, Berlin	Germany	stuckenholz@fhi-berlin.mpg.de
Sefik Suzer	Bilkent University, Ankara	Turkey	suzer@fen.bilkent.edu.tr
Alexandre Tkatchenko	Fritz-Haber-Institut der MPG, Berlin	Germany	tkatchen@fhi-berlin.mpg.de
Mira Todorova	Max-Planck-Insitut für Eisenforschung, Düsseldorf	Germany	m.todorova@mpie.de
Jan Peter Toennies	MPI for Dynamics and Self-Organization, Göttingen	Germany	jtoenni@gwdg.de
Eberhard Umbach	Karlsruher Institut für Technologie	Germany	eberhard.umbach@vorstand.fzk.de
Stefan Vajda	Argonne National Laboratory	USA	vajda@anl.gov
Chris G. Van de Walle	University of California, Santa Barbara	USA	Vandewalle@mrl.ucsb.edu
Jean Pol Vigneron	University of Namur	Belgium	jean-pol.vigneron@fundp.ac.be
Elwira Wachowicz	University of Wroclaw	Poland	Elwira@ifd.uni.wroc.pl
Jörg M. F. Wambach	Paul Scherrer Institut, Villigen	Schweiz	joerg.wambach@psi.ch
Huifeng Wang	Fritz-Haber-Institut der MPG, Berlin	Germany	wang@fhi-berlin.mpg.de
Kazuo Watanabe	Tokyo University of Science	Japan	Kazuo@rs.kagu.tus.ac.jp
Jonas Weissenrieder	Royal Institute of Technology, Kista	Sweden	jonas@kth.se
Wolf Widdra	Universität Halle	Germany	wolf.widdra@physik.uni-halle.de
Jürgen Wieferink	Fritz-Haber-Institut der MPG, Berlin	Germany	wieferink@fhi-berlin.mpg.de
Markus Wilde	University of Tokyo	Japan	wilde@iis.u-tokyo.ac.jp
Frank Willig	Fritz-Haber-Institut der MPG, Berlin	Germany	willig@fhi-berlin.mpg.de
Malgorzata M. Witko	Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Science, Krakow	Poland	ncwitko@cyf-kr.edu.pl
Alec M. Wodtke	Max-Planck-Institut für biophysikalische Chemie	Germany	alec.wodtke@mpibpc.mpg.de
Wolfgang Wöger	retired from PTB	Germany	wolfgang.woeger@ptb.de

Martin Wolf	Fritz-Haber-Institut der MPG, Berlin	Germany	Wolf @fhi-berlin.mpg.de
Till Wolfram	Fritz-Haber-Institut der MPG, Berlin	Germany	wolfram@fhi-berlin.mpg.de
Christof Wöll	Karlsruhe Institute of Technology	Germany	christof.woell@kit.edu
Ludger H. Wöste	FU Berlin	Germany	ludger.woeste @fu-berlin.de
Hua Wu	University of Cologne	Germany	wu@ph2.uni-koeln.de
Yong Xu	Fritz-Haber-Institut der MPG, Berlin	Germany	yongxu@fhi-berlin.mpg.de
Qimin Yan	University of California at Santa Barbara	USA	qimin@engineering.ucsb.edu
Bing Yang	Fritz-Haber-Institut der MPG, Berlin	Germany	byang@fhi-berlin.mpg.de
Florent Yang	Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin	Germany	florent.yang @helmholtz-berlin.de
Jie Yu	University of California at Santa Barbara	USA	jieyuthu@gmail.com
Xin Yu	Fritz-Haber-Institut der MPG, Berlin	Germany	xinyu@fhi-berlin.mpg.de
Maxim Yulikov	ETH Zurich	Switzer-land	maxim.yulikov @phys.chem.ethz.ch
Guoxu Zhang	Fritz-Haber-Institut der MPG, Berlin	Germany	zhang2@fhi-berlin.mpg.de

Organization

Horst Conrad
Christa Hermanni
Karsten Horn
Gerard Meijer
Elisabeth Stankewitz

Logo design by Steffen Kangowski
Web design by Mike Wesemann