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

18th Meeting of the Fachbeirat

Berlin, 2nd - 4th November 2015

Poster Abstracts

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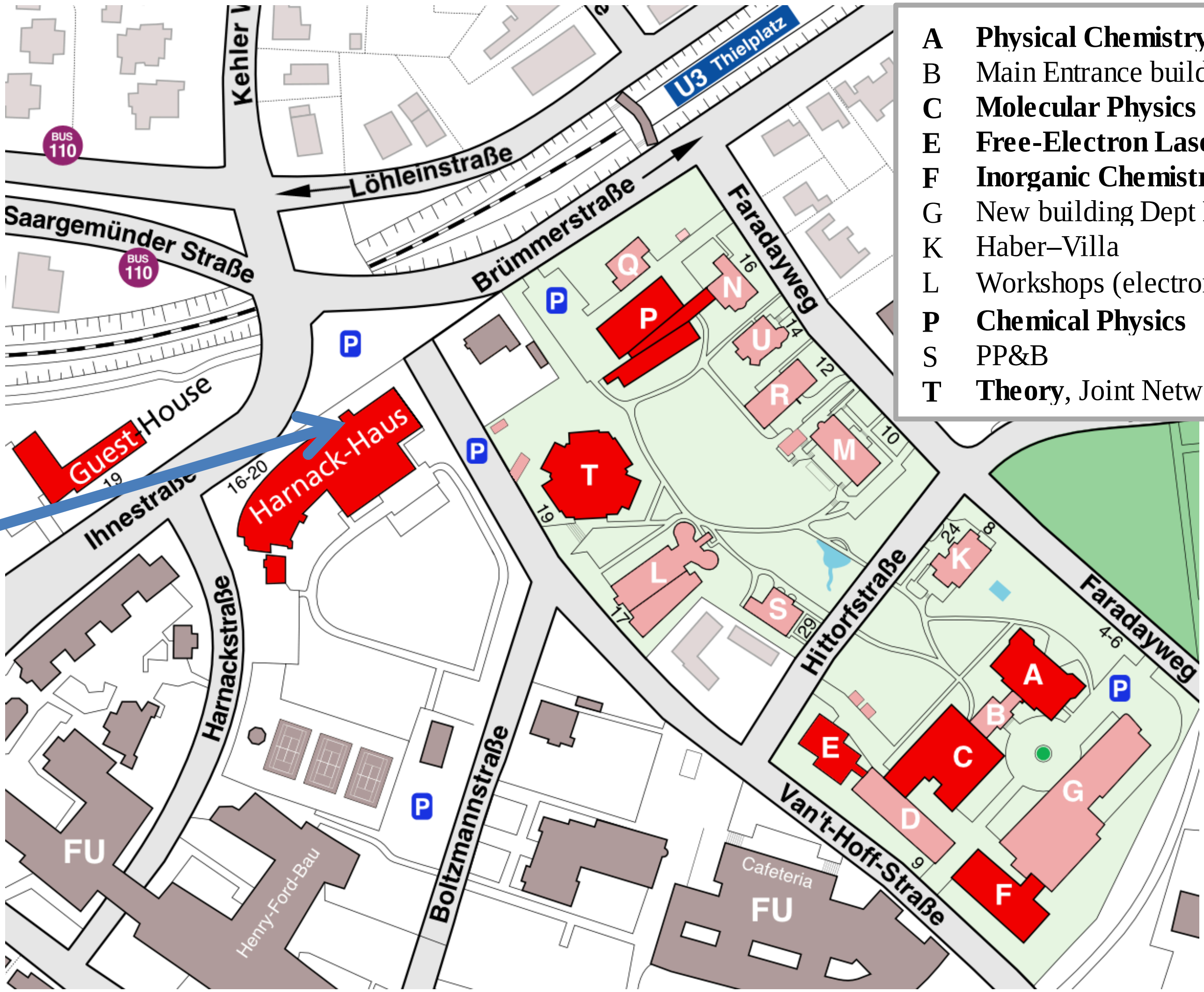

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Nanostructured Catalysts in Activation of Light Alkanes

Light alkanes abundant from natural gas and renewable resources have potential as alternative raw materials in the chemical industry, but the direct conversion into value added products is still a major challenge. We deal with fundamental questions concerning the activation of C1-C4 alkanes over oxide catalysts in particular in presence of oxygen.

To understand how alkane molecules are activated at the surface of metal oxides and which factors limit the selectivity towards the desired products, we synthesize structurally well-defined metal oxides. Pure and doped alkaline earth oxides are studied as model catalysts in the oxidative coupling of methane. The oxidation of ethane, propane and butane is investigated over molybdenum- and vanadium-based mixed oxides and nano-structured manganese tungstate catalysts (AC 1.1). Silica-supported monolayers of potentially relevant metal oxide species and molecular complexes serve as models for the surface of high-performing polycrystalline bulk materials.

Rational synthesis concepts have been implemented with the aim to detect key synthesis parameters that control the functionality of the catalyst surface. To describe the interaction of the substrate with the catalyst surface we investigate the adsorption of probe molecules and perform spectroscopy under operation conditions. Reaction networks have been analysed by the variation of operation parameters over a wide range (AC 1.2).

Selective Alkane Oxidation by Manganese Oxide: Site Isolation of MnO_x Chains at the Surface of $MnWO_4$ Nanorods

Xuan Li[a], Thomas Lunkenbein, Verena Pfeifer, Axel Knop-Gericke, Mateusz Jastak,
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Selectivity is a major challenge in the oxidation of alkanes to olefins and oxygenates most frequently studied over vanadium oxide catalysts.[1] Electronic and structural properties of V-containing phases determine the isolation of active sites at the catalyst surface with major impact on catalytic performance[2-3]. Dynamic changes of V oxidation state and elemental composition are frequently observed at the surface under reaction conditions[1]. We show that the concept of surface re-structuring is not restricted to V catalysts.

Deliberate use of hydrothermal techniques can turn Mn oxide, known as a typical combustion catalyst, into a selective catalyst for oxidative dehydrogenation of propane. Nano-structured, crystalline $MnWO_4$ serves as support that stabilizes a defect-rich MnO_x surface phase. Nanostructured $MnWO_4$ catalysts characterized by different aspect ratios of the nanoparticles have been prepared. XRD, Raman spectroscopy, and electron microscopy indicate phase purity, and high crystallinity of the bulk. Oxygen defects can be reversibly replenished and depleted at reaction temperature as shown quantitatively by temperature-programmed oxidation/reduction and confirmed by NEXAFS and UV-vis DR spectroscopy. The catalytic activity of the catalysts with different particle shapes is correlated to the abundance of terminating MnO_x zigzag chains on (010) crystal planes on the surface. Synchrotron-based in-situ XPS evidences Mn-enrichment at the surface that is confirmed by HAADF-STEM. Terminating MnO_x zigzag chains on (010) crystal planes are suspected to bear structurally site-isolated oxygen defects that account for the unexpected good performance of the catalyst in propane activation. Structural details of different terminations of the $MnWO_4$ (010) and (011) surfaces are examined also by ab initio DFT slab calculations including surface relaxation. The theoretical results for corresponding surface energies are consistent with the experimental findings.

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Surface Dynamics of Mixed MoV Oxides in Selective Oxidation of Alkanes

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Conceptual understanding of the mode of operation of bulk mixed oxides applied as catalysts in selective oxidation of alkanes is limited due to the often very complex structural and surface chemistry of this materials class. Activity and selectivity are frequently attributed to the crystal structure and the exposure of specific surface facets. One example is the *ab* plane of the so-called “M1 phase” (ICSD 55097) of MoVTeNb oxide. In the present work, crystalline MoVTeNb and MoV M1 oxides have been prepared by hydrothermal synthesis and precipitation. Phase purity of MoVTeNb M1 oxide was verified by XRD[1,2]. The crystal structure of MoV M1 oxide was analyzed by single crystal analysis applying synchrotron radiation at the MX 14.2 beam-line at BESSY II of the HZB (Helmholtz-Zentrum, Berlin) and electron microscopy[3]. MoVTeNb M1 oxide catalyzes the oxidation of propane to acrylic acid with high activity and selectivity, whereas the isomorphous MoV M1 oxide is unselective and transforms propane mainly into carbon oxides[1]. Even though phase purity represents an essential criterion with respect to catalyst stability[2], synchrotron-based near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) demonstrates that MoVTeNb M1 oxide is a self-supported monolayer catalyst[2]. Working M1 crystallites are covered by a thin layer in nm-dimension. The layer is enriched in V^{5+} and Te^{4+}. Elemental composition and oxidation state of V show dynamic response to changes in the feed. The V^{5+} content at the surface of the MoV oxide is significantly higher compared to MoVTeNb M1 oxide. Acrylic acid is also formed over MoV M1 oxide. But the high V concentration at the surface of this catalyst is responsible for consecutive reactions in which the desired product is largely further oxidized to carbon oxides. Our results demonstrate that the crystalline bulk structure has an impact on surface composition of Mo-based mixed oxides under operation in selective oxidation of propane, and, consequently, on the catalytic properties. The selective MoVTeNb oxide catalyst features dynamic site isolation due to segregation of Te, and is characterized by improved redox dynamics compared to the unselective catalysts composed of the same crystal structure.

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Structure and Reactivity of Oxygen in Particles of Catalytic Interest: DFT Studies on K[VO(O_2)Hheida] Compared with Infrared Spectroscopy and X-ray Absorption

Lili Sun, Klaus E. Hermann, Michael Hävecker[a], Johannes Noack, Olaf Timpe,
Israel E. Wachs[b], Annette Trunschke, and Robert Schlögl

The identification of structural details in catalyst particles is of paramount importance for a reliable description of structure-reactivity relationships in catalysis. In this study we consider an oxo-peroxovanadium(V) compound chelated with N-(2-hydroxyethyl) iminodiacetic acid, [VO(O_2)Hheida]. This complex is an efficient functional model for the vanadium haloperoxidase enzyme which acts as halide oxidant but also as a catalyst for sulfoxidation and alcohol oxidation. It includes oxygen species in very different local coordination next to vanadium: terminal vanadyl (V=O), dioxo (V-O_2), hydroxyl (V-OH), bridging V-O-C, and embedded C-O species. Thus, the [VO(O_2)Hheida] complex offers an ideal test case for examining differently coordinated oxygen in the same system and finding out about structure sensitivity of corresponding spectroscopies. DFT calculations are performed to determine the equilibrium geometry of the [VO(O_2)Hheida]$^-$ ion and the results agree nicely with experimental data for the K[VO(O_2)Hheida] single crystal. The analysis of vibrational modes, computed in harmonic approximation, allows an identification of differently coordinated oxygen species, such as vanadyl and di-oxo, although corresponding modes are not well localized. The theoretical spectrum agrees quite reasonably with experimental data from IR and Raman measurements. Further, theoretical O 1s NEXAFS spectra are evaluated for the [VO(O_2)Hheida]$^-$ complex. The corresponding partial NEXAFS spectra, providing a highly localized oxygen probe, show substantial differences amongst the different oxygen species which allows easy discrimination. These results can be compared with experimental O K-shell NEXAFS data obtained in this work. DFT calculations are also performed on reduced [VO(O)Hheida]$^-$ where oxidation reactions are assumed to remove one oxygen from the di-oxo site of the [VO(O_2)Hheida]$^-$ complex. The theoretical IR and O1s NEXAFS spectra show substantial differences between the two complexes, which can be compared with experimental data to help the interpretation of the spectral properties.

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Coin Metals

The discovery that gold nanoparticles (Au NPs) supported on metal oxides are active in low-temperature CO oxidation has inspired a considerable amount of research directed toward the understanding of the activity of Au catalysts. Interestingly, the activity in CO oxidation of Au supported on a metal oxide is sensitive to the gold particle size distribution. Au NPs on oxygen-free supports (HOPG, functionalized CNTs, Au foil) were studied. In-situ NAP-XPS measurements of the electronic structure of Au nanoparticles on oxygen-free supports were made during CO oxidation. Our results assume that the size reduction and the oxidation is not enough to activate Au. Finally, the Au NPs supported on transition metal oxides were synthesized by two different methods. We showed that the catalytic performance depends on the method of preparation.

Silver is the only metal capable of selectively epoxidizing ethylene. This unique ability is related to the intricate balance of two chemically distinct adsorbed oxygen species at oxygen chemical potentials typical for epoxidation, nucleophilic (O_{nucl}) and electrophilic (O_{elec}) oxygen. O_{nucl}, E_b(O1s)~528.1-528.4 eV, is thought to be required for ethylene adsorption, thereby allowing weakly bound O_{elec}, E_b(O1s)~530.5 eV, to react with ethylene and form the epoxide. A predominant hypothesis is that O_{nucl} is bound in surface reconstructions and O_{elec} is unreconstructed atomic oxygen. To test this hypothesis we performed a joint experimental and theoretical study of single crystals, (111) and (110), and powders, < 45 μm, under oxygen chemical potentials relevant for epoxidation. We also studied the dynamics of unreconstructed, reconstructed, and electrophilic oxygen on real catalysts with mircocalorimitry.

While silver is the only material known catalyze direct epoxidation well enough for use at industrial scale, recent studies have demonstrated that copper exhibits interesting epoxidation behavior and holds promise as a possible alternative or perhaps additive to silver catalysts. We have undertaken a study to examine copper's behavior under ethylene epoxidation conditions, using a combination of in-situ electron spectroscopy and in-situ electron microscopy to examine phenomena not accessible by ex-situ methods.

The industrially $Cu/ZnO/Al_2O_3$ catalysts in methanol synthesis are applied for almost 50 years, but still not completely understood. Cu is commonly regarded as the active phase, but the role of ZnO and Al_2O_3 is more than that of an inert support. Cu and ZnO exhibit a special synergistic effect, and Alumina as a promoter improves the morphology, stability and intrinsic activity of the catalysts. To study the promoter effect in more detail, we have prepared, characterized and tested model supports ZnO:M (M = Al, Ga, Mg; loaded with copper in a separated step) as well as high performance catalysts with low level Al doping and compared them with the unpromoted ones. By contactless conductivity measurements, EPR and UV-visible spectroscopy, we gained insights into the electronic structure of the ZnO:M model systems for a correlation with catalytic tests in rWGS and in methanol synthesis. Additionally, we investigated the high performance precatalyst in an ambient pressure NEXAFS study to clarify the role of Al during the reduction of the precatalyst.

Copper Oxides in Ethylene Epoxidation

Mark T. Greiner, Travis E. Jones, Katarzyna Skorupska, Jing Cao, Zhu-Jun Wang, Benjamin E. Johnson, Marc G. Willinger, Axel Knop-Gericke, and Robert Schlögl

Ethylene epoxidation is one of the most fundamental heterogeneously catalyzed partial oxidation reactions. Our understanding of the principles of heterogeneous catalysis benefits greatly from a clear understanding of this elementary process. Despite many decades of research into this topic, many peculiarities of the reaction remain unclear.

One such peculiarity is the role of copper as a promoter in silver-copper alloy catalysts.[1,] While silver is the de facto standard epoxidation catalyst, and has been the central focus of most research in heterogeneous ethylene epoxidation, copper has received comparatively little attention from the scientific community. In order to understand copper's role in a catalyst alloy, it is important to understand how it behaves under epoxidation conditions in its pure form.

When exposed to epoxidation conditions–i.e. a mixture of O_2 and C_2H_4 at temperatures of 150-300°C–copper corrodes, becoming covered with a copper oxide film. However, the oxides of copper exhibit interesting epoxidation catalyzing behaviour.

Copper forms two thermodynamically stable oxides, Cu_2O and CuO. Both oxides exhibit epoxidation activity at high temperatures (>300°C) with meagre selectivities of 2%. Interestingly, low-temperature (170°C) high-selectivity (25%) epoxidation is observed near the $Cu_2O \rightarrow CuO$ phase transition.

In-situ near-ambient-pressure photoemission spectroscopy and *in-situ* environmental scanning electron microscopy studies that suggest this unique epoxidation activity arises due to the presence of a meta-stable oxide phase. In such a phase, one would expect dynamic switching between Cu^{1+} and Cu^{2+} states, which could give rise to adsorbed activated oxygen species that are capable of epoxidizing ethylene.

This poster presents an experimental investigation of this low-temperature high-selectivity epoxidation reaction, as well as an in-situ characterization of the $Cu_2O \rightarrow CuO$ phase transition and a proposed mechanism for the reaction.

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The Role of the Promoter Al on Cu/ZnO Based Catalysts for CO_2 Conversion Reactions and Their Dynamic Behavior in Longtime Experiments

Julia Schumann, Maik Eichelbaum[a], Andrey Tarasov, Nygil Thomas[b],
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Thomas Lunkenbein, Malte Behrens[c], Elias Frei, and Robert Schlögl

For a knowledge-based catalyst design for moving from a fossil fuel based towards a sustainable future energy scenario, fundamental understanding of the materials properties and its influence on catalysis is necessary. The industrially $Cu/ZnO/Al_2O_3$ catalysts in methanol synthesis are applied for almost 50 years, but still not completely understood. Cu is commonly regarded as the active phase,[1] but the role of ZnO and Al_2O_3 is more than that of an inert support. Cu and ZnO exhibit a special synergistic effect, and Alumina as a promoter improves the morphology, stability and intrinsic activity of the catalysts.[2,3]

To study the promoter effect in more detail, we have prepared, characterized and tested model supports ZnO:M (M = Al, Ga, Mg; loaded with copper in a separated step) as well as high performance catalysts with low level Al doping and compared them with unpromoted samples. By contactless conductivity measurements, EPR and UV-visible spectroscopy, we gained insights into the electronic structure of the ZnO:M model systems for a correlation with catalytic tests in rWGS and in methanol synthesis. Additionally, we investigated the high performance precatalyst in an ambient pressure NEXAFS study to clarify the role of Al during the reduction of the precatalyst. A longtime deactivation experiment was conducted to monitor the dynamic character of the catalyst under working conditions.

Our studies reveal that tri-valent dopants have a strong influence on the electronic structure of the ZnO support. Lower activation energy and decrease of the reaction order of H_2 are found for the tri-valent promoters, whereas Mg has no effect on the reaction order or activation energy. In the high performance system, the precatalyst consists of $CuO/ZnO/Al_2O_3$ where ZnO is still undoped. The mechanism of incorporating Al in ZnO is part of the reduction process, where Al changes the coordination from octahedral (Al_2O_3) to tetrahedral (ZnO:Al) at temperatures of 150-250 °C. Thus, the reduction of the catalyst is a manifold process, where Cu metal and Al doped ZnO emerges. The Zn-containing phases of an industrially relevant catalyst show a dynamic behavior in 148 days time-on-stream in methanol synthesis. The growth of the coherent scattering ZnO domains gives experimental evidence for a catalyst deactivation process dominated by ZnO crystallization, emphasizing the importance of ZnO within the Cu/ZnO synergy for methanol catalysts.

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Identifying Active Sites for Oxidations Catalyzed by Noble Metals

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Despite their name, noble metals catalyze an array of important reactions. In particular, both Au and Ag are effective oxidation catalysts. While Ag has long been known to epoxidize ethylene under O_2, the ability of supported Au nanoparticles (NPs) to catalyze CO oxidation was discovered more recently. However, neither reaction mechanism is well understood due to the intricate relationships between the structure and function of multiple types of adsorbates. To unravel these links we studied Ag and Au using XPS and NEXAFS, at the ISISS beamline at HZB/BESSY, combined with microcalorimetry, microscopy, and DFT calculations. We have found new insights into the structure, function, and dynamics of the species active in oxidation on noble metals[1-3].

Previous studies of ethylene epoxidation on Ag have suggested two types of oxygen are required for epoxidation, O_{nucl} with $E_b(O1s)$~528.1-528.4 eV and O_{elec} with $E_b(O1s)$~530.5 eV. O_{nucl} is needed for ethylene adsorption, allowing O_{elec} to react with ethylene to produce ethylene oxide. Though the intricate balance of the two species mediates catalytic performance, their nature has remained elusive. To further our understanding of the active species we have identified a scaling relationship between an oxygen's $E_b(O1s)$ and its heat of adsorption, allowing us to demonstrate that O_{elec} is covalently bound and O_{nucl} is ionically bound. As examples we have seen that adsorbed atomic oxygen forms species with $E_b(O1s)$ in the range of O_{nucl}, while OH and SO_x form species with $E_b(O1s)$~530-531 eV.

To address the long-standing question over the nature of Au nanoparticle (NP) activation we performed in-situ XPS measurements of Au NPs on oxygen-free supports (HOPG, functionalized CNTs, Au foil) during CO oxidation. Our results show that size reduction and oxidation alone do not activate Au[2]. We went on to synthesize Au NPs supported on transition metal oxides by two different methods, XPS measurements which allowed us to show that active samples have two Au species (Au^0 and $Au^{\delta+}$) present on the surface[3]. The binding energy shift of the $Au^{\delta+}$ peak, relative to Au^0, depends on the support and is in a good agreement with calculated values for TiO_2.

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Chemical Electron Microscopy

The department of Inorganic Chemistry has a long tradition in the development and application of *in-situ* spectroscopic and diffraction techniques for the study of active catalysts. Meanwhile we have learned that catalysts are dynamic materials whose active centres are formed or transformed under reaction in response to the chemical potential of the surrounding gas phase.

Conventional high-resolution imaging by electron microscopy plays an important role in the structural and compositional analysis of catalysts. However, since the observations are generally performed under vacuum and close to room temperature, the obtained atomistic details concern an equilibrium state that is of limited value when the active state of a catalyst is in the focus of the investigation.

In the last couple of years, the electron microscopy group has therefore started to develop and implement methods for real-space and direct structural observation of catalysts under relevant catalytic conditions. The approach can be summarized as "Chemical electron microscopy" and means analytical electron microscopy with a strong focus on the chemical state of the investigated materials by spectroscopic analysis and especially, under consideration of catalytically relevant dynamic processes. The Electron Microscopy group is following different strategies for the study of reaction-induced surface and bulk modifications through *ex*- and *in-situ* observation.

We have continued to improve and implement environmental scanning electron microscopy as an *in-situ* technique for the observation of surface dynamics on active metal catalysts. A laser heating system was developed for drift and contamination free heating up to 1000 °C, the gas feeding and vacuum system have been improved and a mass spectrometer for gas phase analysis has been implemented. The set-up is now versatile and allows a wide range of *in-situ* experiments under different atmospheres, pressures and temperatures as well as the application of electrochemical potentials (see Poster AC 3.1). In parallel to the experimental development, investigations on contrast mechanisms and the processes of signal generation are conducted. The results are promising and demonstrate the potential of the ESEM technique as surface-science tool.

On the atomic scale, we have continued with the development of ambient- and high-pressure micro-reactors for the investigation of microscopic amounts of catalysts at pressures up to 30 bar by coupling *ex-situ* catalytic reaction to electron microscopic investigation *via* a sample transfer system. Using this approach, we are able to investigate identical particles before and after exposure to catalytically relevant conditions in the transmission electron microscope (TEM). Hence, limitations of environmental TEM in terms of pressure, selection of gases and the catalytic relevance of experimental conditions can be avoided (see Poster AC 3.2). Since the beginning of 2015 we are using a commercial TEM sample holder for *in-situ* experiments. Using a home build gas-feeding system, we can operate that holder under defined gas flow at pressures of up to 1 bar and temperatures of up to 900 °C. First experiments have shown that some of the assumptions that were published in the catalysis literature on the basis of TEM observations made in vacuum have to be revised.

In-Situ Investigation of Catalyst Surface Dynamics by Environmental Scanning Electron Microscopy

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During the last three years we have modified the set-up of a commercial environmental scanning electron microscope (ESEM) in order to enable observations of catalyst surface dynamics under controlled atmospheres, at pressures of up to 20 mbar, and temperatures of up to 1000 °C. Using this instrument, we are investigating metal catalysed chemical-vapour-deposition (CVD) growth of graphene and the dynamic response of metal catalyst surfaces to red-ox conditions during catalytic reactions.

In the case of graphene growth by metal catalysed CVD, we studied the growth modes of graphene on nickel, copper and platinum substrates. We were able to relate the different growth modes of graphene to the respective catalytic properties and bulk solubility of carbon. From the subsequent frame-by-frame analysis of movies that were recorded during the CVD process, we identified the critical steps that control the growth process in terms of island formation and island evolution dynamics[1]. Due to the high sensitivity of the secondary electron (SE) signal, slight changes in the work function and variations in charge transfer at the surface can be detected. As we know from our recent investigations on the graphene-substrate interaction, oxygen intercalation and de-intercalation between copper and graphene gives rise to an atmosphere composition- and temperature-dependent change in the coupling between graphene and the substrate[2,3]. This change in coupling was detected as a shift in the C 1s binding energy, measured by near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at BESSY, and can also be seen as contrast variation in SE images. We are thus able to visualize different degrees of graphene-substrate coupling in the ESEM.

In a further study on CVD growth of carbon structures, that was conducted in collaboration with the group of Prof. Leon Lefferts at the University of Twente, The Netherlands, we investigated conditions for carbon nano-fiber (CNF) and nano-tube (CNT) growth versus the formation of graphene and other forms of carbon deposits on nickel substrates during the catalytic decomposition of ethylene. On the basis of *in-situ* observations, we have now understood the conditions for optimized CNF/CNT growth.

Due to the ability of observing surface features at nanometre resolution in real time at high temperatures and controlled atmosphere, the ESEM provides a unique tool for the observation of the surface dynamics of metal catalysts during red-ox reactions. As it furthermore covers the same pressure range as the NAP-XPS setup at BESSY, the two instruments combined ideally complement each other by joining visual information to spectroscopic data (see Poster AC 2.1).

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Chemical Transmission Electron Microscopy for Heterogeneous Catalysis

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Walid Hetaba, Gerardo Algara-Siller, Marc G. Willinger, and Robert Schlögl

Modern transmission electron microscopes (TEM) enable the observation of the atomic arrangement and a simultaneous identification of atom kind and chemical state through a combination of different imaging and spectroscopic techniques. Recently, we could demonstrate that direct imaging of the oxygen sub lattice in a complex molybdenum vanadium mixed oxide reveals the distortion of the different metal oxygen octahedra. Using this information we were able to draw conclusions about the distribution of oxidation states of molybdenum and vanadium at different sites[1]. It is therefore possible to obtain chemical information by imaging. Regardless of the wealth of information that can be abstracted from the atomic arrangement, the requirement of a good vacuum inside the TEM column still places a serious limitation for the investigation of catalysts. Instead of describing the thermodynamic equilibrium state of an isolated material we are now moving forward, towards electron microscopic investigations of dynamic processes that occur in the interaction of a catalyst with its surrounding atmosphere. On one hand we have continued our development of TEM-grid micro-reactors for high and ambient pressure catalysis. The reactors allow a decoupling of the catalytic reaction from the imaging process. In addition, imaging at identical location before and after experiments in the micro–reactor allows following morphological, structural and chemical changes of precursors and catalytically active materials. Transport of the sample between TEM and micro-reactor is enabled via vacuum transfer holders and glove box without contact to ambient environment. Hence, restrictions with respect to pressure, atmosphere and electron beam are omitted.

Since the beginning of 2015 we are using a commercial gas-cell TEM holder in combination with a home built gas-feeding unit. We use this system in order to conduct *in-situ* experiments under catalytically relevant conditions, *i.e.*, under the criteria that a conversion can be detected. Due to the microscopic amount of catalyst, fulfilling this criterion is still challenging. We have therefore started with the investigation of nickel catalyzed chemical vapor deposition growth of carbon nano filaments. Here, the reaction product can directly be visualized. As a second system, we are currently studying the dynamic behavior of small Cu particles under red-ox conditions. Both experiments are complemented by *in-situ* experiments that we perform in the environmental scanning electron microscope under similar conditions, but different spatial resolution (see poster 2.1 and 3.1).

In order to participate in the development of *in-situ* methods for electron microscopy in the field of catalysis, we are actively collaborating with companies that are working on commercial solutions. We share our experience with Protochips, DensSolutions and started a joint development project with FEI, a world-leading producer of electron microscopes.

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Carbon Synthesis and Applications

Carbon is an inexpensive material of advantageous electric conductivity that can be produced in broad structural variety. For this reason, carbon materials play a major role in all future energy scenarios as the basis of electrode materials, energy storage devices, such as batteries and supercapacitors, or in their application as catalyst or catalyst support in the development of more efficient processes. The aim of our research is the knowledge-based development of advanced carbon materials consisting of a structured carbon backbone with specific functional groups that are either active intrinsically and/or have the ability to anchor the catalytically active metal component even as small metal clusters.

The variety of carbon synthesis strategies applied in the department ranges from two-dimensional graphenic modelstructures over nanostructures towards hierarchical structured bulk systems in 100 g scale. The latter are synthesized hydrothermally by molecular precursors in a bottom-up process, as documented in poster AC 4.1. In order to elucidate the complex structural properties of functional carbon materials the investigation of model and reference systems is required, as well as the application of multiple complementary analytical methods. Makroscopic properties are investigated by contact angle measurements, Van-der-Pauw conductivity tests, titration and electrochemical testing. Furthermore, the oxidative dehydrogenation (ODH) functions as test reaction for both oxidation stability and chemical spectroscopy of functional groups. Structural properties are studied by combining Raman, FT-IR, electron microscopy, TG-MS, XPS and EELS.

In addition to the specific choice of precursors in the bottom-up synthesis approach, O- and N-functional groups are incorporated by different post-treatments in liquid phase (in HNO_3, H_2SO_4, H_2O_2 or urea) or gas phase (O_2, H_2O, NH_3). The use of electrochemical oxidation and plasma-assisted functionalization completes the portfolio of functionalization methods (poster AC 4.1). For the depositions of metal(oxide) catalysts atomic layer deposition (ALD), wet impregnation and precipitation is applied.

The major fields of application for our carbon and carbon composite materials are batteries, electrode materials for OER and catalysts in ODH as documented in poster AC 4.2.

Within the carbon project several fruitful collaborations established over the last years with the Ruhr-University Bochum (Martin Muhler, Axel Rosenhahn, Achim von Keudell), University Duisburg-Essen (Philipp Wagener), Hochschule Niederrhein (Jürgen Schram), University of Cambridge (John Robertson, *Grafol*).

Functional Carbon Materials by Bottom-up Synthesis and Post-Functionalization

Natalia Kowalew, Jan W. Straten, Pascal Düngen, Marina Prenzel, Saskia Buller,
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Functional carbon materials were prepared in a bottom-up approach by hydrothermal carbonization of glucose. Depending on the initial synthesis pH, particles of different size and functionalization can be obtained. For lower initial synthesis pH, i. e. pH 0, extended carbonaceous structures were confirmed by Raman spectroscopy, whereas for pH>3 furanic structural entities from the 5-hydroxymethyl furfural intermediate remained the dominant structural motive of the carbon.[1] Upon thermal annealing at 900°C, the materials exhibit electrical conductivities suitable for electrochemical applications. Due to the advantageous binding properties of hydrothermal carbon (HTC), the materials can be pressed into pellets prior thermal treatment and thus yield individually functionalized disc electrodes.

For the introduction of different N-functional groups, urea, urotropine and imidazole were added as precursors. Up to 15 wt% N-incorporation could be detected by elemental analysis. By combining thermoanalytical techniques with FT-IR and EELS analysis precursor dependent distributions of pyrridinic, pyrollic and amine groups were detected. Whereas the addition of urea and imidazole resulted in rather planar carbon structures, the addition of urotropine yielded spherical particles, similar to nitrogen-free HTCs.

In collaboration with the Ruhr-University Bochum, the functionalization of carbon materials by oxygen- and nitrogen-plasma treatment was studied. As examined by XPS, up to 7 at% of nitrogen were incorporated into the surface of a glassy carbon reference disc by partial reduction of initial oxygen functional groups.

Furthermore, the functionalization of multi-walled carbon nanotubes (MWCNTs) was studied, as structured reference material. The differentiation of MWCNTs after functionalization was carried out by the evaluation of the corresponding Raman spectra. The in-house developed fitting procedure allows the examination of type and quantification of functional groups on graphitic carbon, when applied in combination with other analytical techniques, as thermal analysis, electron microscopy and XPS.[2]

Specific functional groups generated by the described procedures provide anchoring sites for possible catalytic active materials, which are deposited by differnet techniques like atomic layer deposition (ALD), wet impregnation and absorption of laser ablated colloids.

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Functional Carbon Materials as Support for Vanadium Oxide or Manganese Oxide Containing Compounds for Catalytic Applications

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Omar A. Mayorga, Marina V. Bukhtiyarova, Youngmi Yi, Sylvia Reiche,
Kevin Kähler, Saskia Buller, and Robert Schlögl

Functional carbon materials were synthesized by a hydrothermal process as reported in poster AC 4.1. These hierachical structured bulk materials exhibit excellent requirements for catalytic purposes, primarily electronic conductivity and well defined specific functional groups at the surface that are catalytically active itself or provide potential anchoring sites. Different methods to bind the metal oxides with the carbon support were applied. Vanadium oxide containing samples were used for the oxidative dehydrogenation (ODH) of Ethylbenze forming Styrene to monitor oxidation stability and active sites. The vanadium oxide deposition was fulfilled by atomic layer deposition (ALD) technique in a homebuilt setup. Manganese oxide containing samples are potential electrode materials and were tested electrochemically for oxygen evolution reaction (OER). The incorporation of manganese oxide species in the carbon structure was achieved through direct addition during the hydrothermal process.

Manganese oxides are well-known as active compounds for OER. α-MnO_2, α-MnO_2 (microemulsion) and γ-MnO_2 were synthesized and characteriszed before they were added to the initial solution for the hydrothermal process to perform the functional carbon materials. The obtained compounds were pressed into pellets and thermally annealed at 900°C for 4h to receive electrically conductive and mechanically stable disc electrodes. Structural differences between the manganese oxide containing samples and the pristine carbon material could be revealed by microscoy. Spherical particles dominate the structures of the synthesized materials on the microscopic scale, while the outer surface of the disc electrodes that contain manganese oxides are coalesced. Smooth surfaces with homogeneously integrated manganese oxides can be observed. The spherical particles can be found merely in the inside of the pellets. The electrochemical performance of these disc materials was tested in 0.1 M KOH. Linear sweep voltammetry as well as chronoamperometric measurments were performed to study the influence of the manganese oxide containing hydrothermal carbon (HTC) materials in comparison to the pure structured carbon material. Long term stability was proven by chronoamperometric measurements at 1.8 V for 12 and 24 hours. Manganese oxide containing materials show higher currents in comparison to pure hydrothermal carbon and only minor loss in current over 24 hours.

Vanadium oxide was deposited on HTC by ALD using vanadium(V) oxytripropoxide as precursor and water as co-reactant. Selective reactivity of the specific functional groups could be determined. Combined analysis by XPS, ESR and thermal analysis is applied. First ODH studies showed activities for the pure as well as for vanadium deposited HTC materials. The focus of our research is to elucidate structure reactivity correlations.

Electrochemistry, Charge Carrier Dynamics

The electrochemistry research group, hosted by the Department of Inorganic Chemistry of the FHI, is composed of a team of multidisciplinary scientists performing fundamental and applied experimental research framed within three research areas, namely energy storage, water electrolysis, and charge transport characterization across interfaces.

The development of electrochemical devices with high energy density accompanied by long cycling life is essential to store energy produced by intermittent and renewable energy sources. Contemporary efforts aim at substituting the remarkably stable graphite anode in lithium ion batteries by other solid state materials, such as silicon. This substitution has a significant impact on the electrochemical dynamics and stability of the electrode, and consequently on the energy accumulator. It is our principal aim to better understand the fundamental relationship between structural and electronic factors at the electrode-electrolyte interface and their influence on the mechanically and electrochemically irreversible mechanisms, *i.e.* the electrode stability and dynamics. Our working concepts, methodologies, custom made instrumentation, and selected results are presented on Poster AC 5.1. This work benefits from a fruitful collaboration with Volkswagen Research Centre, the Helmholtz-Zentrum Berlin and the Ruhr-Universität Bochum.

Accompanying the development of energy storage devices, electrocatalysis will play definitive role in energy storage technologies and energy conversion systems of the near future, such as water electrolysis. While the desired product of water splitting is hydrogen, which can be used as combustion gas or as a reactant to produce synthetic fuels, the limiting catalytic process is related to the oxygen evolution reaction (OER). In Poster 5.2 we are presenting our efforts to develop *in situ* near-ambient-pressure XPS and grazing angle XRD as analytical tools for the *in situ* studies of novel iridium based electrocatalysts for the OER. The objective of this research is to develop complementary *in situ* methods to improve our mechanistic understanding of the OER and of the electrode stability and dynamics under working conditions. This work is integrated within the Ekolyser project and benefits from collaboration with the Technische Universität Berlin.

At its most fundamental level, the transformation and storage of chemical energy, as well as the product formation in heterogeneous catalysis, is accompanied by a local displacement of charge carriers, often across an interface. Our group has developed a set of tools, based on the Microwave Cavity Perturbation Technique (MCPT) and Microwave Hall Effect (MHE) to characterize *in situ* and contactless the dielectric properties of materials including thermally activated catalysts, for example VPP or $MoVTeNbO_x$. More specifically, these powerful instrumental techniques enable us to characterize a catalyst’s conductivity, its charge carrier concentration and mobility. Poster 5.3 includes a presentation of our latest instrumental developments. Selected results will demonstrate the applicability of semiconductor physics and gas sensor theory to gain valuable mechanistic understanding of vanadium based catalysts using the MCPT technique complemented by near-ambient-pressure XPS and NEXAFS.

Electrochemical Stability and Dynamics of Silicon Based Anode Materials for Lithium Ion Batteries

Kathleen Nimmrich, Martin Pradel, David Klein, Sylvia Reiche, Sébastien Cap,
and Robert Schlögl

The development of electrochemical devices with high energy density accompanied by long cycling life is essential to store energy produced by intermittent and renewable sources. Since its first introduction on the market in the 1980s by Sony and despite a moderate specific charging capacity, graphite based anode materials are broadly used due to their remarkable electrochemical cycling stability. Among the candidate materials that can substitute graphite to achieve superior anode charging performance, silicon represents an attractive alternative as it reversibly alloys lithium at low potential (vs. Li/Li^+) with a specific charge capacity exceeding carbonaceous material by one order of magnitude. Unfortunately, silicon based anodes are limited by a poor electrochemical cycling stability that can be attributed to two irreversible processes, namely, the mechanical and the electrochemical degradation that affects the electrode stability and dynamics.

It is our principal aim to better understand the fundamental relationship between the structural and the electronic factors of the electrode-electrolyte interface and their influence on the mechanically and electrochemically irreversible mechanisms.

As a first step, we have specifically developed a versatile low pressure chemical vapor deposition (LP-CVD) reactor for this project, allowing to perform diverse surface treatments, in a single batch, on a broad range of substrates, *e.g.*, deposition of nano-metric silicon thin films followed by C deposition. The LP-CVD route used for both the substrate functionalization and the Si deposition represents a chemically clean and highly reproducible process compared to alternative wet chemical routes, *e.g.*, precursor calcination or electro-deposition.

As selected results, presented on the Poster AC 5.1, we are comparing the electrochemical stability and dynamic properties of electrodes for diverse silicon allotropic structures (crystalline, amorphous) as well as the electronic surface obtained by material doping or chemical functionalization. Based on the knowledge acquired from the layered model electrodes, a broad portfolio of nano-structured and surface functionalized carbonaceous materials have been systematically synthetized. It has been found that surface functionalization significantly alters the anode electrochemical properties and is often beneficial for the electrode cycling stability. Currently, we are investigating the fundamental factors responsible for such electrode stabilization.

This work contributes to a more comprehensive understanding of the Si-based anode material stability and the different charging/discharging dynamic mechanisms related to the interface structure and to the electronic properties with the ultimate aim to outline novel synthetic routes for the design of stable and high-performance silicon based anodes.

In situ Techniques for Monitoring IrOx-based Electrocatalysts for Water Oxidation

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Ir-based electrocatalysts are promising candidates for water electrolysis as they combine high activity with stability in the anodic oxygen evolution reaction (OER). Typically, metallic Ir is activated for the OER by potential cycling which leads to the formation of an amorphous overlayer with higher OER-activity than the bare metal. This electrochemically formed overlayer is likely composed of Ir-oxohydroxides, however, the origin of their increased OER-activity has remained elusive. Recent literature findings suggest that active hydrated, amorphous powder catalysts can be directly synthesized via wet-chemical methods[1,2,3]. Based on these observations, we have produced a portfolio of amorphous Ir-compounds using diverse synthesis routes. The synthetized electrocatalysts are then evaluated for their OER performance using classical electrochemical methods. Paralleling the electrochemical OER performance evaluation, our department has developed analytical tools adapted for electrocatalytic *in situ* studies of the surface structure and chemistry of Ir-based electrocatalysts. By combining these techniques, we aim to gain fundamental insights into the intricate relationships between the structure, function, and dynamics of oxygen-evolving Ir surfaces.

A prerequisite for the application of *in situ* techniques is the identification of the differences between OER-active and -inactive Ir oxides. For this task, we compared measured and calculated XPS and NEXAFS spectra of benchmark systems. We observe characteristic differences between the Ir 4f line shapes and the O K-edges of the active (amorphous) and inactive (crystalline IrO_2) materials that are indicative of additional oxygen-containing species in the more active amorphous catalyst. Combining these new insights with measurements made using our modified *in situ* XPS- and NEXAFS-cell[4] will help us identify the OER active Ir-sites.

For further *in situ* structural characterization of the Ir-catalyst surface, we have developed an *in situ* cell for grazing incidence x-ray diffraction and x-ray reflectometry. First “proof of principle” of the experimental setup was successful. We expect, through specific hkl-dependant measurements and electron density contrast variations visible in x-ray reflectometry, to provide further understanding of the structural changes at the surface while OER is proceeding.

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Investigation of Charge Transport at Interfaces Using the Contact-free and *in situ* Microwave Cavity Perturbation Technique

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and Robert Schlögl

The transfer of charge carriers between reactant molecules and catalysts is important for catalytic activity and selectivity. Hence, the study of the electrical conductivity, charge carrier concentration and mobility, and redox properties of heterogeneous catalysts under reaction conditions is of crucial importance for the understanding of the underlying mechanisms.

Owing to the semiconducting properties of these catalysts, concepts from semiconductor physics and gas sensor theory have been applied to gain mechanistic understanding of thermally activated catalysts. We have proven the applicability of these concepts to (selective) oxidation catalysts such as VPP, $MoVTeNbO_x$ (M1 phase) and V_2O_5 in a near-ambient pressure XPS study. The surface potential barrier height, which is caused by a charge transfer between the bulk and the surface of the catalysts, inducing a subsurface space charge region, is proposed as a physical descriptor for the selectivity of oxidation reactions of alkanes[1]. Near-ambient-pressure NEXAFS spectroscopy and conductivity measurements based on the custom designed *in situ* microwave cavity perturbation technique (MCPT)[2] complement these results.

Furthermore, our research aims to investigate the frequency dependent conductivity to elucidate the nature (free or bound) of the charge carriers, gaining novel insights into the conductivity mechanism. For this purpose we developed an *in situ* contact free multi frequency MCPT setup with several gold plated TM0n0 (n=1, 2) cavities. Our findings show that the frequency dependence behavior at room temperature can be described by bound charge carriers (Lorentz oscillator model), whereas at higher temperatures, while the catalytic process is in operation, the conductivity trend suggests the contribution of free charge carriers (Drude model) to the overall conductivity response.

In our latest instrumental development, a new bimodal cylindrical TE112 cavity system was constructed to observe the Hall effect of charge carriers at microwave frequencies under reaction conditions. The reactor was connected to a gas delivery manifold and a gas analysis system. With this setup, we simultaneously analyze the charge carrier mobility and the absolute charge carrier number with the aim to identify electronic structure-function relationships.

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CH_3OH and NH_3 Synthesis for Utilization of H_2 Produced From Renewable Energies

Marina V. Bukhtiyarova, Kevin Kähler, and Robert Schlögl

As the appearance of renewables like solar, wind, or hydro energy usually fluctuates, their storage is of special interest in terms of sustainable substitution of a hydro-carbon based energy supply. Electro- or photo-catalytic H_2 production is often discussed as a key technology. Numerous techniques to store the produced H_2 have been suggested including the generation of NH_3 and CH_3OH. Both substances offer the advantage of high H_2 contents and are easy to store as they are condensable.

Additionally, the capability of industrial exhaust gases as potential feed gases for NH_3 and CH_3OH synthesis is determined in the catalytic technology group. To elucidate the influence of impurities and to find out to which extent gas purification is needed, systematic reactivity and stability studies in methanol synthesis have been started. Feed gases consist of CO_2, hydrogen, and additionally trace components, like benzene as a representative of BTEX-aromatics. Long-term stability tests with an industrially used $Cu/ZnO/Al_2O_3$ catalyst show that the reaction rate stays in the same order of magnitude compared to benzene-free feed gas even after 230 h time on stream. A further purification step of the steel mill gases from BTEX aromatics does not seem to be necessary as the impurities do not affect the catalyst's stability and activity.

NH_3 synthesis represents an additional way to store H_2 produced with renewable energy sources. Nevertheless, the NH_3 synthesis catalyst is particularly prone for deactivation as only around 5% of the surface of a technical NH_3 synthesis catalyst would actively dissociate di-nitrogen and oxygenate impurities can bond firmly to the catalyst surface as catalyst poisons[1]. The development of catalysts with higher density of active sites may help to enhance the operation time of a technical catalyst. That is why different catalyst model systems are investigated including an $MgFe_2O_4$ system prepared by the group of M. Behrens in the University of Duisburg-Essen. At 425 °C the model catalyst achieves an ammonia production rate of 2.3 $\mu mol \cdot g_{cat}^{-1} \cdot s^{-1}$. As a multiple promoted Fe catalyst shows only less than 3.8fold higher activity compared to the unpromoted model catalyst the latter is an interesting starting point for further catalyst development.

Additionally, a special reactor was constructed allowing the disassembly of the catalyst without contact to the ambient. This may help to elucidate whether surface, subsurface, or bulk nitride species are generated during the reaction, which is still unclear[2]. Those analyses can be performed in close collaboration with the "X-Ray Spectroscopy" group of S. DeBeer as well as in the "Electronic Structure" group of A. Knop-Gericke.

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Catalytic Technology

In the catalytic technology group heterogeneously catalyzed reactions are investigated. Catalysis is of major importance for an energy-effective and sustainable conversion of reactants as it lowers the activation barrier of a chemical reaction by changing its reaction mechanism. In heterogeneous catalysis, usually, the catalyst is a solid, whereas the reactants exist in the surrounding fluid phase. A deeper understanding of catalytic processes can help to improve the efficiency of reactions and, therefore, help to save resources and lower the overall energy demand.

Nowadays, solar, wind, and hydro energy are often regarded as sustainable energy sources and can help to solve the shortage of hydro carbon-based energy sources in an environmentally friendly way. Electro-catalytic hydrogen production is investigated in the institute and is often discussed as key technology to store renewable energies. In the catalytic technology group reactivity studies are performed for catalytic processes binding the primary hydrogen onto carrier molecules such as CO_2 and N_2 to arrive at practically useful solar fuels.

Besides the electro-catalytic generated hydrogen different other source materials can play an important role in chemical industry for the future. In the catalytic technology group the capability of industrial exhaust gases as potential hydrogen, carbon oxide, and/or nitrogen sources for ammonia and methanol synthesis is determined. An extensive analysis of real exhaust gases from steel mill plants will be performed in collaboration with the ThyssenKrupp Company (see poster AC 8).

Systematic reactivity and stability studies in methanol synthesis have been started. The hydrogenation of CO_2 to methanol is recognized as one of the most promising processes to stabilize the atmospheric CO_2 level. Therefore, the optimal conditions for high methanol yields in the hydrogenation of pure CO_2 were elucidated. As a representative of trace components of real exhaust gases benzene was added to the feed gas and its influence on the catalyst’s performance was tested in methanol synthesis as shown in Poster AC 6.1.

In NH_3 synthesis different model catalyst systems are investigated with the aim to develop a catalyst with an increased density of active sites in the future as also presented on Poster AC 6.1. A special reactor was constructed allowing the disassembly of the catalyst inside a glove box without contact to the ambient. This may help to elucidate if surface, subsurface, or bulk nitride species are generated during the reaction.

Additionally, the oxidative dehydrogenation (ODH) of ethylbenzene is investigated in the catalytic technology group. This reaction is an energy saving candidate for the synthesis of styrene. Carbon materials are active in the ODH reaction and are, therefore, interesting and cost-effective materials. As distinct nucleophilic ketonic carbonyl groups and defect sites on graphene layers are considered as active sites, the ODH reaction can also be used as a complementary characterization method for the materials prepared in the carbon synthesis and application group (see poster AC 4.2).

MAXNET Energy

Alexander Auer and Robert Schlögl

The MAXNET Energy is a research cooperation as initiative of the Max Planck society, that focuses on the chemistry central to energy conversion. One of the key reactions in chemical energy conversion is the evolution of oxygen as the anode reaction of water splitting. In biochemistry, the function of the oxygen evolving complex is just being unravelled. In technological applications, few catalyst systems exist that are stable enough for large scale operation. However, in all cases the basic mechanisms are hardly understood.

The work within MAXNET energy aims at obtaining a deeper understanding of the complex mechanisms, the basic reaction steps and the influence of components and materials. The span of the projects within MAXNET Energy ranges from atomistic insight of catalytic reactions to details of engineering solutions for technical systems, from quantum simulation to synchrotron measurements and from synthetic chemistry to material science.

A unique feature of MAXNET Energy are two dedicated modes of cooperation: The shared mode includes cooperation by sharing expertise, samples and materials or resources. This way, the knowledge and facilities within MAXNET Energy are used in an optimal way and communication and cooperation are facilitated. In the joined mode, participants define and use common reference systems, standards and standard protocols for materials, systems and measurements. This way, each working group uses predefined common experimental parameters in order to guarantee the same experimental conditions and thus comparability and transferability of the results between all groups.

MAXNET Energy originated from the ENERCHEM initiative (2005-2011) of the Max Planck Society that has successfully brought together scientists within the MPS from different fields of chemistry, physics and engineering. Within the framework of the MAXNET Energy research association, researchers from 8 Max Planck Institutes are cooperating: the Max Planck Institute for Dynamics of Complex Technical Systems (Kay Sundmacher, Magdeburg), for Iron Research (Martin Stratmann, Düsseldorf), for Chemical Energy Conversion (Robert Schlögl, Frank Neese, Mülheim/Ruhr), for Chemical Physics of Solids (Yuri Grin, Dresden), for Coal Research (Ferdi Schüth, Mülheim/Ruhr), for Polymer Research (Klaus Müllen, Mainz), of Colloid and Interfaces (Markus Antonietti, Potsdam-Golm) and of the Fritz Haber Institute (Robert Schlögl, Berlin). Recently the Cardiff Catalysis Institute (Graham Hutchings) and the University of Virginia (T. Brent Gunnoe) joined as external members.

TREK / PLANCK

Jorge I. Salazar Gómez, Kevin Kähler, Marion Tiedtke, and Robert Schlögl

Within the transfer platform PLANCK (German: PLAttform für Nachhaltige Chemische Konversion) chemical energy conversion technologies are focused. These technologies require expertise in the fields of catalysis, process technology, energy systems, and system control. Knowledge base should be transferred into industrial application. Participants of PLANCK are industrial partners, university as well as research institutes. The aim of PLANCK is to generate technologies, which help to ensure the success of the energy transition and which enhance the reduction of CO_2 emissions in a way that sustainable production processes can be designed and industrially implemented.

To realize to focus the competences at a traditional heavy industry location the transfer platform will be installed by founding the non-profit enterprise TREK gGmbH.

The first project of PLANCK is regarded as a lighthouse project, because of its exceptionally strategic relevance and its excellent potentials to support the energy transition. It is called “Carbon2Chem” and focuses on the development of technologies for a sustainable operation of a steel mill plant.

Up to date blast furnace gases produced in the steel industry have been only used to preheat the ovens or to produce electricity in steam engines. The utilization as feedstock for chemical industry of the typical gases produced in the steel industry, such as coke oven gas, converter gas, and blast furnace gas, can be seriously compromised due to the high number of trace compounds. These compounds could act as a poison for any subsequent catalytic process. Although many trace compounds are found in these gases only in the lower ppm or ppb concentration range, they could deactivate a specific catalyst within minutes. Since until now, the detection of such low-concentration substances has been of little interest and a complete characterization would be time consuming and expensive, there is a lack of knowledge about their concentration fluctuations and their persistence after a conditioning process.

In a pre-project called HÜGAPROP the main task is to develop a methodology to characterize the gases of the steel industry in a container installed directly on-site, so that different catalysts for reactions, such as methanol synthesis can be tested under real conditions. For the analysis of trace compounds, a new generation of a mass spectrometer, the so-called Proton-Transfer-Reaction Quadrupole ion guide Time-of-Flight Mass Spectrometer (PTR-QiTOF-MS) will be used. This prototype is equipped with additional features like a Fast-GC for the identification of possible isomers. NDIR and gas chromatography will be used for the analysis of main components and the performance of the methanol catalysts. For comparison purposes, a parallel study of the methanol catalysts will be carried out under laboratory conditions. These analyses give additional information about the effect of the dynamic changes in pressure on the catalyst activity and help to evaluate to which extent regeneration is possible after controlled poisoning with the substances previously found in the blast furnace gases. As output, a database of the measurement methods will be generated together with the spectra of the identified trace compounds and their optimum ionization parameters.

MANGAN – Standardized Measurements of Catalysts for the Oxygen Evolution Reaction

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Chinmoy Ranjan, Cyriac Massué,
Sébastien Cap, Justus Masa[a], Wolfgang Schuhmann[a], and Robert Schlögl

In the quest for non-noble metal-based catalysts for the electrochemical splitting of water, materials based on manganese have received considerable attention in recent years. A systematic fundamental study on structure-function relationships is, however, lacking. The BMBF-funded cluster project MANGAN aims at establishing such understanding in the most comprehensive way focussing on the oxygen evolution reaction. A deeper understanding of the stability of manganese-based materials is explicitly included as one of the main targets of the project. Ultimately, the project aims at answering the question whether manganese-based materials have the technical potential to be employed as electrodes in large-scale electrochemical water splitting.

Project partners are the Fritz Haber Institute, the Helmholtz Center, the Max Planck Institute for Chemical Energy Conversion and the Max Planck Institute for Iron Research, the universities of Bochum, Duisburg-Essen, Erlangen-Nürnberg, Freiburg, Gießen, and Mainz as well as the technical universities of Aachen, Berlin, and Darmstadt, and BASF as an industrial partner. Expertise of the partners covers synthesis from biomimetic complexes to composites and new electrode materials as well as analysis from fundamental electrochemistry to high-end spectroscopic techniques and theoretical modelling. Consequently, the consortium is well-equipped to tackle the given systemic complexity.

A core piece of the project is a database that compiles all measurements and analyses carried out on the respective samples. Such a unique compilation of structural and functional data will allow for a fact-based argumentation in favor or against manganese as a catalyst. As mentioned above, a common method for testing is prerequisite for the evaluation of materials produced via diverse synthetic approaches. Studies on oxygen evolution catalysts do, however, lack a commonly accepted standardized protocol for the characterization of the electrocatalytic properties. Hence, a focus of the project is to develop and to apply such a protocol. Drawing from existing approaches, a sequence of electrochemical measurements was designed making use of a relatively simple rotating disk electrode methodology. The protocol allows for an evaluation of both the catalytic activity and stability of the electrode under study. An electrode based on commercially available nickel cobalt oxide functions as a standard in alkaline media against which new compounds are measured. For neutral and acidic media, standard catalysts will be defined in the near future. Compounds which define the benchmark set by the standard are subjected to further in-depth analysis.

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EMIL - Exploring Electrochemical Reactions Under Aqueous Conditions by means of Photoelectron Spectroscopy

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One of the main goals in electrochemistry is the characterization of electrode-electrolyte interfaces under operating conditions, to capture their electronic structure and chemical composition when it is in contact with the electrolyte and in the presence of applied electrical bias[1]. However, the lack of surface sensitive techniques able to monitor the electronic structure under reaction conditions in aqueous environment hinders the total understanding of such processes. Recently, the advent of reaction cells based on electron transparent membranes at low kinetic energy (i.e. high surface sensitivity) has found much interest. Using similar approach, we have investigated the local electronic structure of electrodeposited cobalt and its interaction with graphene[2]. In addition to providing a direct insight into the Cobalt-graphene reaction by means of X-ray photoelectron spectroscopy, our method opens the way for studies of virtually any solid-liquid, gas-phase interface, which was not possible with techniques such as X-ray absorption in fluorescence mode used until now. Results and potential applications will be given.

Access to tunable X-ray sources with best matching properties regarding photon energy range and photon flux is indispensable to facilitate these *in situ* studies of gas/solid and liquid/solid interfaces, in particular for experiments with electrochemical background. EMIL, the Energy Materials *In-situ* Laboratory Berlin at BESSY II is a joined project of Helmholtz-Zentrum Berlin (HZB) and Max Planck Society represented by FHI and MPI CEC seizes this need. This novel facility includes a new laboratory building hosting beamlines providing an unusual broad photon energy range from the soft X-ray regime up to the tender/hard X-ray regime, i.e. between 80eV–8000eV in one spot.

In addition to that the HZB, the Technical University of Darmstadt and the FHI/CEC will implement a joined lab at BESSY hosting tree beamlines providing Synchrotron radiation the in energy range from 10 eV – 10 KeV dedicated for energy research.

Modern *in situ* spectroscopy requires reaction cells that are adapted to the demands of the scientific goal and a specific problem. We have developed concepts that provide modularity at various levels and thus fulfill these demands for flexibility. Some of these concepts will be discussed. The AP-XPS spectrometer can be equipped with modules that are optimized e.g. for electrochemical experiments. Furthermore, these modules form self-contained units that can be operated detached from the spectrometer to test reaction conditions etc. Sample stages follow a unified design concept without losing the necessary flexibility. For instance: static and flow through cells, cells that allow XPS or XAS measurements. All can be mounted to the very same sample stage.

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CO_2 Activation: A Joint Project

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Since CO_2 is identified as the main source for global warming issues, its transformation into value added products is of superior interests. The common strategy is the hydrogenation of CO_2 to either alcohols or hydrocarbons. The most popular candidates are methanol (partially reduced) and methane (fully reduced). In both cases CO_2 has to be activated, oxygen has to be removed as water and the reactions are highly exothermic. Another approach of industrial relevance is the combination of CO_2 and CH_4 (dry reforming of methane, DRM) to syngas as gaseous intermediate for the Fischer-Tropsch based chemistry.

The methanol synthesis from CO_2 is an extensively studied reaction with $Cu/ZnO/Al_2O_3$ as the catalyst of choice. This ternary system shows a complex interplay of structural and electronic properties, which enables the activation of the reactants and guides the product selectivity. Using a binary Cu/MgO system, the catalyst loses instantly its activity for CO_2 activation, but shows an enormous CO hydrogenation potential. It has been shown, that by impregnating the Cu/MgO catalyst with ZnO, the capability of activating CO_2 is recovered. ZnO seems to be the key for CO_2 activation in Cu-based catalysts[1]. The special character of ZnO under a defined hydrogen atmosphere (“metallic ZnO”) and its relevance for CO_2 activation will be investigated for model systems by the **Physical Chemistry Department (Julia Stähler, Martin Wolf).**

The methanation of CO_2 (Sabatier reaction) is generally conducted with Ni-based catalysts. The critical parameter of this reaction is to avoid the formation of by-products through side reactions like the Boudouard reaction, the reverse water-gas-shift reaction and coke formation. NiO/MgO solid solutions are examples for non-coking, high selective catalysts, which show at low loadings an isolation effect. It is another object of this project to combine both strategies of CO_2 activation to alcohols and hydrocarbons, to steer the product selectivity away from full reduction of CO_2 to higher alcohols and/or hydrocarbons ($n \leq 3$), including an additional C-C coupling. The doping of MgO with transition metals as electronic promotors will be evaluated under reductive working conditions in collaboration with the **Chemical Physics Department (Shamil Shaikhutdinov, Hans-Joachim Freund)[2].** Investigating the electronic and structural properties of these systems on the surface and in the bulk, supported by calculations of the **Theory Department (Sergey Levchenko, Matthias Scheffler)**, will provide further insights to the mechanism of the hydrogenation chemistry of activated CO_2.

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Department of Chemical Physics

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Modification of $TiO_2(110)$ by Vanadium – Methanol Partial Oxidation Studies

Xin Song, Helmut Kuhlenbeck, and Hans-Joachim Freund

V+Ti mixed oxide layers were prepared on rutile $TiO_2(110)$ with the aim of learning about the modification of the surface reactivity by vanadium with respect to the partial oxidation of methanol. A Ta+Ti mixed oxide layer between the V+Ti mixed oxide surface layer and the $TiO_2(110)$ substrate blocks the diffusion of vanadium atoms into the substrate. The concentration of vanadium was typically in the range of a few percent in order to prevent the agglomeration of vanadium-based aggregates. Room temperature STM, XPS and thermal desorption spectroscopy were applied in this study, which concentrated on structural aspects as well as on the effect of the presence of vanadium onto the partial oxidation of methanol at the surface.

The V+Ti mixed oxide system is highly reducible: annealing at just 800 K in UHV leads to a significant reduction of the oxide as evidenced by the formation of many bridging oxygen vacancies and even a (1x2) structure as known for heavily reduced $TiO_2(110)$. On pure $TiO_2(110)$ the latter is often prepared by annealing at T>1100K or by sputtering followed by annealing. We assign this effect to the larger reducibility of V^{4+} ions ($V^{4+} \rightarrow V^{3+}$) as compared to Ti^{4+} in the TiO_2 lattice, as shown by XPS. The vanadium atoms are located below the surface under such conditions and the main effect of them is an enhanced density of surface structures related to oxygen loss (bridging oxygen vacancies, 1x2 reconstruction). The reactivity of the mixed oxide surface with respect to the partial oxidation of methanol is under such conditions essentially the same as for reduced pure $TiO_2(110)$.

The situation is different under oxidizing conditions. For pure $TiO_2(110)$ the methanol TPD spectra depend on the oxidation conditions, probably due to the dependence of the surface structures formed by the oxidation of reduced Ti ions on the oxidation conditions[1]. In V+Ti mixed oxide layers part of the vanadium atoms are located at the surface or in near-surface layers under such conditions. The vanadium atoms in the layer have two effects: (1) the presence of oxygen vacancies at elevated temperature even in an oxygen ambience due to the high reducibility of the mixed oxide, which results in TPD structures typical for oxygen vacancies and (2) a modification of the oxidation-induced surface structures which exhibit a modified chemical activity. An atomic picture of the effect of the presence of vanadium cannot yet be presented – structural data (STM), reactivity spectra (TPD) and XPS data do exist, but calculations still need to be performed.

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Setup of an Apparatus for Action Spectroscopy of Deposited Clusters and Surfaces

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Helmut Kuhlenbeck, and Hans-Joachim Freund

Action spectroscopy is a spectroscopic tool often employed to measure vibrational spectra of small aggregates in the gas phase. The basic idea of this method is to use an action resulting from the excitation of a vibration in the aggregates as an indicator for the excitation. In the case of the vibrational spectroscopy of aggregates in the gas phase the action is often the desorption of rare gas atoms which are weakly bound to the aggregates and desorb when the clusters heat up due to absorption of energy from an infrared beam (often from a free electron laser).

We have constructed an apparatus which applies this experimental method to deposited clusters and solid surfaces using light from the free electron infrared laser of the Fritz Haber Institute. The two main components are a highly sensitive mass spectrometer for the detection of desorbing rare gas atoms and a low temperature AFM/STM system, which will be used to image the surface structure, the rare gas atoms, and to identify areas from which rare gas atoms have desorbed due to the action of the IR beam.

Scientific questions where this method may be helpful are:

- *Vibrational spectra of deposited clusters.*
  Vibrational spectra in combination with computed vibrational level schemes are a key to the elucidation of the cluster structure, which is an important parameter for the chemical activity. Essentially all types of deposited small aggregates (pure metal, mixed metal, dielectric) can be investigated with this approach. Vibrational spectra of deposited aggregates cannot easily be obtained with standard surface science methods due to the low cross section of such vibrations (in the case of metals) and the often limited cluster density.
  At present, the lowest photon energy of the free electron laser is too high for the study of metal-metal vibrations, especially of heavy atoms like gold. An upgrade to the FEL to the THz range would make such vibrations accessible.
- *Vibrational spectra of dissolved atoms in clusters.*
  Dissolved atoms in clusters may have a significant impact on the catalytic performance as catalytic modifiers or by taking actively part in the reaction. Vibrational spectra may help to identify such atoms and their embedding into the cluster lattice. An example is the case of hydrogen in deposited Pd clusters which are relevant for hydrogenation reactions (Schauermann et al, Acc. Chem. Res. 46, 2013, 1673). Carbon atoms modify the hydrogen uptake of the clusters.
- *Vibrational spectra of impurities, dopants and defect sites.*
  The sample can be illuminated with IR light in the STM/AFM system which opens up the possibility to study the effect of irradiation laterally resolved. One application of this possibility is the study of vibrations of impurities, dopants and defect sites by the laterally resolved observation of rare gas desorption. Structural information about the absorbing site may be derived from this information.

Ultra-thin Zinc Oxide Films on Metal Supports

Bo-Hong Liu, Shamil Shaikhutdinov, and Hans-Joachim Freund

The attention to ZnO (wurtzite) thin films has recently been reinforced since theoretical predictions, corroborated by a surface x-ray scattering study, of that (0001)-oriented thin films adopt a hexagonal boron nitride like structure, with the O and Zn layers being almost co-planar. Apparently, the driving force for such reconstruction is the polar instability of either Zn- or O- terminated surfaces of ZnO(0001).

In this Poster, we report on preparation, surface structure, and thermal stability of ultrathin zinc oxide films grown on Pt(111), Ag(111) and Cu(111) using physical vapor deposition.

The ZnO films on Pt(111) grow in a layer-by-layer mode, basically converging to the surface structures obtained on single crystals at film thicknesses above ~ 5 monolayers. A variety of structures was observed for the (sub-) monolayer films. In addition, the structures may transform into each other depending on the exposure conditions. In contrast, monolayer films were not observed on Ag(111) and Cu(111) surfaces, on which the films grow up as bilayer from the onset.

Although prepared in pure oxygen ambient, the films on Pt(111) exposed hydroxyls, regardless of the film thickness. In contrast, the bilayer films on Ag(111) do not exhibit OH species, not even upon dosing of hydrogen or water. Apparently, hydrogen is provided by the Pt support via hydrogen dissociation and subsequent diffusion of H atoms on the surface through the film. Thermal stability of the OH-terminated surfaces depends on the film thickness. De-hydroxylation of a monolayer film proceeds through water desorption, and may be accompanied by hydrogen spillover onto more stable multilayer structures.

The results show that the atomic structures of thin ZnO films are more complex than considered so far for bulk ZnO crystals, and additionally depends on the film thickness and the nature of a metal support. Stabilization of the polar ZnO surface on the metal supported films seems to be a delicate balance between interlayer relaxation and hydroxylation.

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Reactions on Metal-supported Double-Layer Silicates: Towards Chemistry in Confined Space

Emre Emmez, Shamil Shaikhutdinov, and Hans-Joachim Freund

The structural motif of well-ordered silicate films grown on a metal substrate is a hexagonal layer of corner-sharing [SiO_4] tetrahedra. On noble metal surfaces, such as Ru(0001), Pt(111), and Pd(110), a double-layer (or bilayer) silicate sheet may be formed, which is O-terminated on either side and hence weakly bound to the underlying support. In this case, reaction of ambient molecules may occur at its surface as well as underneath the silicate sheet, as a relatively large space between the silicate and the metal support allows, in principle, small molecules to intercalate the interface and react on the metal surface.

We address reaction of CO, hydrogen, and oxygen with a double-layer silicate film grown on Ru(0001) using infrared reflection absorption spectroscopy and temperature programmed desorption. A general scenario for a silicate/metal system exposed to ambient gases includes: (i) penetration of molecules through “pores” in the film; (ii) chemisorption on the metal surface right behind the pore and subsequent diffusion across the metal surface; (iii) surface reactions, and finally (iv) desorption of products (if any) back through the pores in the film.

The results referring to CO and D_2 exposure showed that gas transport primarily occurs through “pores” in the silicate, associated with structural defects in the hexagonal network, and subsequent adsorption and diffusion across the metal surface. Note, however, that CO exposure at elevated pressures and/or temperatures (1 mbar, 400 K) may result in carbonaceous deposits which react with a silicate sheet upon heating in vacuum.

The silicate film stays essentially intact upon exposure to oxygen at high pressures (up to 10 mbar) and temperatures (750 K), and oxygen in the film does not exchange with oxygen in the ambient. O_2 molecules readily penetrate the film and dissociate on the underlying Ru surface. The silicate layer does however strongly passivate the Ru surface towards RuO_2(110) oxide formation, which readily occurs on bare Ru(0001) under the same conditions. The results indicate considerable spatial effects for oxidation reactions on metal surfaces in the confined space at the interface.

Metal-supported bilayer silicate films, which combine an ultrathin “membrane” and a chemically active metal surface underneath, may be interesting hybrid materials, in particular in catalysis as the silica is a robust material in catalytically relevant atmospheres.

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Surface Structure Effects on Strong Metal/Support Interaction of Pt with Magnetite

Ke Zhang, Earl M. Davis, Shamil Shaikhutdinov, and Hans-Joachim Freund

Strong metal-support interaction (SMSI), often observed for metal particles supported on reducible oxides, is mostly discussed in terms of encapsulation of the metal by the oxide. An atomic description of how a metal particle becomes covered by an oxide is still missing. Another interesting, yet poorly studied, issue is whether SMSI effects are structure sensitive, that is dependent on the surface structure of the oxide. To gain a fundamental understanding of the SMSI effects, model studies are carried out, in which metal nanoparticles are deposited in a controllable manner on well-defined oxide surfaces. In particular, our previous studies of Pt deposited on Fe_3O_4(111) thin films showed the formation of hemi-spherical nanoparticles exposing (111) top facets. Upon UHV annealing, the Pt particles exhibit encapsulation by a FeO(111) single layer.[1]

Here we focus on the interaction of Pt with a Fe_3O_4(100) surface, following expectations of a large difference in reactivity when compared to the (111) surface. We first studied the preparation of well-ordered thin Fe_3O_4(001) films on a metallic substrate, in this case Pt(100). The preparation must include deposition of an Fe buffer layer as previously suggested for the growth on MgO(001). Two stable surface terminations were observed, both exhibiting a $(\sqrt{2}\times\sqrt{2})R45^0$ reconstruction. Several intermediate, Fe-rich terminations were also observed during the annealing process of an initially dimer-like structure. The process critically depends on the thickness of the buffer layer, which can be used as a tuning parameter for surface structures.

STM results of Pt deposited on the $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstructed surface of Fe_3O_4(001) thin films showed that, at low and medium coverages, Pt preferentially adsorbs monoatomically on the so-called “narrow” sites. Vacuum annealing above 700 K leads to Pt sintering and concomitant re-shaping (at ~1000 K) into the cuboid Pt nanoparticles. In addition, high-temperature annealing suppresses CO adsorption on Pt, clearly manifesting the SMSI effect. The combined LEED, STM and TPD results provide evidence for an encapsulating overlayer to be identified as FeO(111), i.e. as observed for a Pt(001) single crystal substrate.[2]

The comparison suggests that the SMSI effect via encapsulation is insensitive to the surface structure of oxide, although the latter strongly affects the particle morphology.

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Exploring the Luminescence Characteristics of Zinc Oxide Thin Films: The Role of Defects, Impurities and Metal Ad-Particles

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and Hans-Joachim Freund

Due to their important role in applications, zinc oxide thin films have gained substantial interest in surface science during the last decades. In addition, zinc oxide is a unique material that exhibits semiconducting and transparence properties, making it as a promising candidate for the fabrication of optoelectronic and electromechanical devices. We have investigated the structural properties and the optical luminescence of ZnO/Au(111).

The first aspect of this work discussed concerns the growth modes of ZnO on Au(111). Whereas a layer-by-layer growth is reveled in oxygen excess, formation of oxide nanorods with large height-to-diameter ratio prevails at lower oxygen chemical potentials. We attribute the formation of 3D nanostructures in the latter case to traces of gold atoms on the surface that promote trapping and dissociation of the incoming oxygen molecules. On the other hand, for the case of thin films growth, ZnO develops a (0001)-oriented coincidence lattice that gives rise to a well ordered hexagonal Moiré pattern with 2.2 nm periodicity, which, in turn, is explained by the lattice mismatch with the gold substrate beneath. The superstructure disappears at 4 ML and films thicker than 10 ML already exhibit bulk properties in terms of conductance and light emission.

The second aspect of this work provides new insights into the local photon emission of the ZnO thin films. STM-based luminescence reveals bandgap recombination as well as sub-band-gap peaks due to the presence of defects in the wurtzite lattice. To understand their nature, we systematically change the preparation conditions, e.g. by laser radiation, high temperature annealing as well as hydrogen reduction. By analysing the variation in the emission response, we assign the sub-band-gap peaks to specific zinc and oxygen defects in the lattice. Aiming at a study of the n-type conductivity of ZnO, we also prepare nitrogen-doped ZnO films. The intensity of the oxygen defect peak increases when growing the film at reducing conditions or inserting nitrogen into the oxide lattice. This fact suggests that not the nitrogen impurities but oxygen vacancies are responsible for the defect emission and that the nitrogen incorporation only facilitates the formation of oxygen defects.

The last part of the work concerns the modification of the optical spectra and is studied by growing and embedding silver metal particles on top of the films. The influence on both (1,0) and (1,1) plasmon resonances with focus on the shape and dielectric environment of the particles is presented.

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Silica: A Novel 2D Material

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Novel two-dimensional (2D) materials have garnered significant scientific interest due to their potential technological applications. Crystalline materials, such as graphene and hexagonal BN, are already well understood. The properties of a new class of 2D amorphous materials need to be studied. For amorphous materials, a detailed understanding of the complex structure is necessary.

Here we present a study of a bilayer thin film of SiO_2 on a Ru(0001) substrate. It has been grown in both amorphous and crystalline configurations. The ordered and vitreous variety can be prepared as an atomically flat film in our UHV setup[1]. Atomic structure has been determined with a dual mode atomic force microscopy (AFM) and scanning tunneling microscopy (STM) sensor, revealing a network of different rings sizes for amorphous 2D films[2]. By analyzing the sizes of neighboring rings, characteristic arrangements of rings within the amorphous structure have been identified and their relative prevalence has been quantified. Typical ring arrangements, such as the Stone-Wales defect, are compared with other atomic scale, molecular scale, and macro-scale two-dimensional amorphous systems[3]. Notably, similar 2D ring arrangements are observed across systems with diverse length scales. Ring cluster configurations within two dimensional amorphous network structures are influenced by the space-filling requirements for two-dimensions. In the crystalline domain, six-membered rings are the only building blocks, apart from domain boundaries. Grain boundaries consisting of 5-7 membered ring combinations and of 5-5-8 ring combinations are observed. These boundaries relate to the film strain and to the influence of the underlying Ru substrate.

Liquid AFM provides high resolution imaging, yielding atomic resolution for samples such as mica, graphite, and calcite. Thus enables ex-situ characterization of the silica film structure. Silica films are grown and characterized in vacuum and subsequently transferred to air. The silica film has been found to be robust against a number of liquid treatments with common solvents including ethanol, water, and acetone. The stability of the silica film is indicated by the observation of certain structural features observed in both UHV and liquid AFM.

Weak interaction between silica films and the Ru(0001) substrate enable avenues for developing free standing films. Silica has been lifted off of the substrate using a polymer coating as a transfer substrate. Successful liftoff is confirmed with low-energy electron diffraction and Auger spectroscopy.

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Combining High-Resolution Scanning Probe Microscopy Studies with Reactivity Experiments

Stefanie Stuckenholz, Christin Büchner, Hendrik Ronneburg, Gero Thielsch,
Markus Heyde, and Hans-Joachim Freund

Magnesium oxide (MgO) is a widely studied model catalyst. We use thin metal supported MgO films to understand the correlation between morphology, electronic structure and reactivity of the oxide on the atomic scale.

For the atomic scale investigation of our sample systems we operate a scanning tunnelling microscope (STM) and noncontact atomic force microscope (nc-AFM).

We prepared Mo(001) supported thin MgO films and used AES and LEED to pre-characterize the films. With our dual mode microscope the morphology was studied and spectroscopic measurements, field emission resonance (FER) and Kelvin probe force microscopy (KPFM) performed. Measurements in varying distance between tip and sample show the confined spacial influence of the defect sites on the local electronic structure. The spectroscopic data show the influence of a thin MgO film on the Mo(001) local work function, as well as differences between pristine terrace sites and line defect sites.[1] This work not only complements previous studies in the department on MgO on Mo(001)[2], but is a direct continuation of workfunction measurements on point defect sites of MgO on Ag(001)[3].

To connect the findings of the dual mode microscope with reactivity studies we integrated a low temperature thermal desorption spectroscopy (TDS) experiment into the existing UHV-setup. Here, desorption of gaseous species, e.g. CO, from MgO are studied. This reaction serves as a model for the interaction of CO with an ionic surface. CO desorption measurements of bulk MgO(001)[4] and of Mo(001) supported thin MgO films[5] could be confirmed with our new TDS setup. Additionally, STM images of the same sample surfaces, before and after TDS measurements, can now be provided. We observed that the surface morphology is unaffected by the TDS measurements.

Next to STM, FER and KPFM measurements of line defects, first measurements of the low temperature TDS setup will be presented.

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Supported Au Nanoparticles and the Oxide-Metal Interface: Adsorption and CO_2 Activation

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Small metal particles on oxide surfaces are pivotal elements in heterogeneous catalysis as they serve as active centers in catalytic reactions. It has been suggested by various calculations and indirectly inferred experimentally that the presence of an oxide-metal interface enhances the reactivity of nanocatalytic systems, but until now no definite proof has been reported at the atomistic level. Furthermore, quantum size effects of ad-particles, lying in the nonscalable size regime, lead to a quantization of the electronic structure and the opening of an energy gap at the Fermi level that crucially affect various properties of the nanostructures, such as their behavior towards molecular adsorption and consequently their performance in catalytic reactions.

Scanning tunneling microscopy (STM) and spectroscopy has been employed to analyze the impact of molecular adsorption on the quantized electronic structure of individual metal nanoparticles containing between 50-300 atoms. For this purpose, isophorone and CO_2, as prototype species for physisorptive and chemisorptive binding, were dosed onto monolayer Au islands grown on MgO/Ag(001) ultrathin films[1]. Whereas isophorone, being a saturated hydrocarbon, is expected to bind weakly to the clusters, an activation of CO_2 is known to require the transfer of an electron to the molecule, thus forming CO_2^-. The molecules attach exclusively to the oxide-metal boundary, in consistency with the high localization of excess charges (0.2 e per atom)[2]. The Au quantum well states experience distinct energy shifts upon molecular adsorption, whereby adjacent states move apart in the CO_2 case but move together in the isophorone case. Additional infrared reflection absorption spectroscopy (IRAS) measurements reveal a fully reversible activation process of gas-phase CO_2 to oxalate species ($C_2O_4^{2-}$) at the rim of the clusters, induced by electron-transfer processes between the Au islands and molecules[3]. On the other hand, the vibrational data of isophorone adsorbed on the Au clusters show no indication of a dissociative adsorption. Further density functional theory (DFT) calculations on the molecule-cluster systems corroborate a physisorptive binding mechanism of isophorone, but a chemisorptive scenario for CO_2.

In summary, the molecular species at the cluster perimeter have been identified locally by STM, chemically by IRAS and their formation verified by DFT calculations, thus demonstrating the importance of synergetic efforts from different experimental and theoretical approaches in the atomistic understanding of heterogeneous catalysis.

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Characterization of Point Defects in Thin MgO(001) Films Using a W-band EPR Spectrometer

Damien Cornu, Laxman Kankate, Werner Hänsel-Ziegler, Thomas Risse,
and Hans-Joachim Freund

EPR spectroscopy has proven to be a valuable tool for the characterization of paramagnetic centers at single crystal surfaces such as point defects or metal atoms. Up until now these experiments were performed at X-band (10 GHz). The experiments at X-band sometimes suffer from a lack in spectroscopic resolution as well as intrinsic problems with respect to the implementation of modern pulse spectroscopic techniques. Changing the operating frequency by a factor of 10 (W-band, 94 GHz) would resolve the resolution issues and would provide the prospect to go beyond continuous wave spectroscopy. For the characterization of single crystalline surfaces by EPR at W-band a commercially available spectrometer was integrated into a UHV setup comprising additionally STM, IRAS, LEED, Auger, TPD as well as preparation facilities. This poster will focus on the latest development of the instrumentation and results obtained for paramagnetic defects on single crystalline MgO films.

EPR spectra of 30 ML thick MgO(001) films prepared at room temperature taken at 94 GHz will be discussed. The spectra show a doublet of lines with a maximal splitting if the magnetic field is oriented along <110> equivalent direction of the MgO film, while the doublet collapses into a single line in case the field is aligned with a <100> equivalent direction. The splitting that is not observed in X-Band clearly demonstrates the ability of W-band EPR spectroscopy to provide additional information on the nature of the underlying centers not available from investigations at X-band. The collapse of the two lines with the magnetic field being oriented along the <100> direction is a direct consequence of the g-tensor orientation. To account for this behavior the principal components of the g-tensor have to be aligned with the <110> directions of the film. This is in contrast to expectations for electron centers being located in domain boundaries of the film, which run along the <100> directions of the film, but suggests that the unpaired electron is trapped at sites, which have a local symmetry corresponding to kinks of the domain boundaries. In addition to these experiments on electron trapping sites, the poster will discuss the EPR characteristics of paramagnetic transition metal centers, namely Cr3+, used as dopants of the MgO oxide films.

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Pd Adsorption on 2D Silica: Influence of Substrate Hydroxylation and Catalyst Preparation Method

Sascha Pomp, William E. Kaden, Martin Sterrer, and Hans-Joachim Freund

The hydroxylation-dependent permeability of bilayer SiO_2 was investigated by XPS studies in a temperature range of 100 K to 600 K. For this, the thermal behavior of Pd evaporated at 100 K, which results in surface and sub-surface (Ru-supported) binding arrangements,[1,2] was examined relative to the extent of pre-hydroxylation. Samples covered in thick ice-layers predictably resulted in the complete blockage of Pd diffusion pathways through the film, and thus resulted in the nucleation of silica-bound particles as temperatures were increased beyond the threshold for multilayer ice desorption. By contrast, samples containing only defect-mediated hydroxyl groups formed by thermally desorbing ice layers from the pristine Pd/SiO_2 system showed no effect on Pd diffusion on and through the film at low temperature. If, instead, the ice-covered samples were exposed to a flux of high energy electrons prior to thermal desorption of the multilayers, the films were left with a greatly enriched concentration of strongly bound hydroxyl groups and associated weakly bound water molecules, which, in turn, resulted in decreased Pd diffusion through the film via a combination of pore-blocking and metal-anchoring effects. Above room-temperature, all samples showed similar behaviour, reflective of particle nucleation above the film and eventual agglomeration with any metal-atoms initially binding beneath the film.

The stability of bilayer SiO_2 upon exposure to aqueous solutions was found to be similar as for bulk silica, showing no dissolution at room temperature at any pH, but partial dissolution with increasing rates in more basic solutions and at elevated temperature. Binding of Pd-complexes from solution onto the silica film was achieved by exposure to $Pd(NH_3)_4Cl_2$ at strongly basic pH (pH 12) following an electrostatic adsorption mechanism. The thermal decomposition of the adsorbed precursor resulted in the formation of metallic Pd nanoparticles on the silica surface. In contrast to the UHV deposition of Pd, no diffusion of Pd through the film was observed in the solution-based preparation of Pd-silica model catalysts.

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Polyalcohol Chemistry on Clean and Oxidized Metals

Florencia Calaza, Martin Sterrer, and Hans-Joachim Freund

Glycerol, which is the major byproduct in biodiesel production, is of industrial interest as it may serve as feedstock for a variety of chemical products. The search for new processes for its upgrade is reflected by the increasing number of applied catalysis work published during the last decade. By contrast, surprisingly little work about the fundamental interaction of glycerol with catalytic surfaces is available. Here we present an IRAS, XPS and TPD investigation of glycerol chemistry on clean and oxygen-covered Pd(111) and Au(111) single-crystal model surfaces. When the polyalcohol is adsorbed on the metallic Pd surface, it primarily decomposes into H_2 and CO, thus presenting promising results for its use in reforming reactions. On the other hand, on Au(111) surface it interacts very weakly with no indications for showing decomposition. In the presence of chemisorbed oxygen or surface oxides, the interaction with both surfaces can be tuned towards different products (Pd showing more aldehyde production by selective oxidation). Chemisorbed oxygen leads to a strong enhancement of the reactivity of Au(111), where formation of carboxylates as intermediates towards total combustion were observed. These latter results are of interest in understanding the mechanistic processes of selective catalytic oxidation of glycerol. Results from IR spectroscopy upon adsorption of the molecule at low temperatures show that its adsorption geometry and the cleavage of specific intra/intermolecular hydrogen bonds are key parameters dictating the decomposition pathways observed for the polyalcohol at higher temperatures.

For the case of upgrading glycerol to 1,2-propylene glycol, the process goes through two steps, the dehydration to acetol followed by its hydrogenation to the final product. We present results for the interaction of the intermediate, acetol, with metal surface from our in-house PM-IRAS set-up, where we follow vibrational features of adsorbed intermediates from UHV up to ambient pressures, and combine this with results from NEXAFS and ambient pressure XPS studies (Dr. Hendrik Bluhm, LBNL, Berkeley, USA). Acetol interaction with metal single crystals, such as Ru(0001) and Pd(111), shows Pd is more active than Ru towards decomposition of Acetol. We observed that the adsorption of intact acetol molecules at ambient pressure and that this may be related to the presence of coadsorbed carbon and/or oxygen.

Interaction of Water with CaO(001)

Yuichi Fujimori, Xiang Shao, Xun-Hua Zhao[a], Sergey Levchenko[a], Niklas Nilius,
Martin Sterrer, and Hans-Joachim Freund

The interaction of water with the surface of CaO has been rarely investigated in the past, despite its importance and relevance in applications such as desulfurization, carbon capture and heterogeneous catalysis. With the introduction of a CaO(001)/Mo(001) thin film model system,[1] detailed experimental investigations of fundamental processes on CaO surfaces have become possible. In the present study, infrared reflection absorption spectroscopy (IRAS), X-ray photoelectron spectroscopy (XPS), scanning tunnelling microscopy (STM) and density functional theory (DFT) have been employed to reveal details about the interaction of water with CaO(001) in a wide range of water vapour pressure and at temperatures ranging between 100 K and 300 K. Different hydroxyl structures are obtained at different water dosing conditions. In particular, a unique development of 1D water/hydroxyl chains aligned along the CaO[110] directions is observed in STM at sub-monolayer water coverage at UHV conditions. Their atomic structure is identified with IRAS combined with DFT. The latter exploit an ab initio genetic algorithm linked to atomistic thermodynamics to determine low-energy H_2O configurations on the oxide surface. The development of 1D structures on the C_{4v} symmetric CaO(001) is triggered by symmetry-broken water tetramers and a favourable balance between adsorbate−adsorbate versus adsorbate−surface interactions at the constraint of the CaO lattice parameter. At higher water coverage, the ordered CaO(001) surface transforms into a disordered state, which is characterized by partially solvated Ca^{2+} ions. Finally, interaction of CaO(001) with water at elevated pressure (sub-mbar range) leads to partial bulk hydroxylation and structural transformation into brucite-like $Ca(OH)_2$.

In addition, we address the correlation between the presence of dissociated water on oxide surfaces and the thermal behaviour of amorphous solid water including its phase transition to crystalline ice using MgO(001), hydroxylated MgO(001) and CaO(001) as model surfaces and provide first evidence that water dissociation on ultrathin CaO(001)/Mo(001) films is strongly suppressed.

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Chemoselective Partial Hydrogenation of Acrolein over Pd Model Catalysts

Karl-Heinz Dostert, Casey P. O‘Brien, Wiebke Ludwig, Aditya Savara,
Swetlana Schauermann, and Hans-Joachim Freund

Atomistic–level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. Chemoselective partial hydrogenation of α,β-unsaturated ketones and aldehydes represents an important class of reactions resulting an broad class of valuable intermediates for practically-relevant processes such as e.g. unsaturated alcohols. Generally, thermodynamics favors hydrogenation of the C=C bond in these compounds to form the unwanted product, i.e. saturated aldehydes or ketones. Therefore chemoselective hydrogenation of the C=O bond requires manipulation of kinetic effects by means of a suitable catalyst. This represents challenging problem and asks for fundamental studies.

We present a detailed mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) and Pd nanoparticles supported on an oxide support – under well-defined UHV conditions. Being the smallest α,β-unsaturated aldehyde, acrolein was chosen as a simple proxy to investigate the selective hydrogenation chemistry at the atomistic level. In previous studies on powdered supported Pd catalysts, acrolein was reported to be hydrogenated almost exclusively on the C=C bond forming propanal. In our studies, we showed for the first time that selective hydrogenation of the C=O bond in acrolein with nearly 100% selectivity is possible over Pd(111). However, this process requires a very distinct modification of the Pd(111) surface with a spectator species that turns the metal surface selective towards unsaturated alcohol formation. This spectator species is formed from acrolein during the initial stages of surface reaction and builds up a densely packed overlayer. By applying a combination of pulsed multi-molecular beam experiments and *in situ* infrared reflection-absorption spectroscopy (IRAS) we were able to identify the chemical nature of the spectator and the reactive surface intermediate and for the first time experimentally follow the simultaneous evolution of the reactive intermediate on the surface and formation of the product in the gas phase. With this study it has been possible to directly identify the reaction intermediate that leads to the formation of the unsaturated alcohol as a final product and obtain atomistic-level insights into the chemoselective hydrogenation chemistry of acrolein. Spectator species were found to play an important role in governing chemoselectivity – the observation that might be of great interest for development of new selective powdered catalysts such as e.g. ligand-modified nanoparticles.

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Water Interaction with Model Iron Oxide Surfaces

Petr Dementyev, Jan Seifert, Karl-Heinz Dostert, Casey P. O’Brien,
Francisco Ivars-Barceló, Francesca Mirabella, Swetlana Schauermann,
and Hans-Joachim Freund

Interaction of water with iron oxides is of crucial importance for many technological and environmental applications as it strongly affects the structure of these materials and their reactivity in surface chemical processes. Particularly for magnetite (Fe_3O_4), there is a limited knowledge on the nature of the surface species formed upon water adsorption and dissociation. Even though infrared vibrational spectroscopy of adsorbed water layers on well-defined model Fe_3O_4 surfaces provides some evidences for the formation of hydroxyl groups in the past, the spectra reveal rather high complexity and are not understood. Particularly, it is not clear if the simplest model suggesting formation of two individual hydroxyl groups upon dissociation of one water molecule – usually discussed in the literature – is valid.

In this study, we investigate interaction of water with well-defined model Fe_3O_4(111)/Pt(111) and Fe_3O_4(100)/Pt(1000) surfaces by employing a newly developed single crystal adsorption calorimetry (SCAC) set up to determine the adsorption and dissociation energies of water on these oxides with high accuracy. Complementary, we employed infrared reflection adsorption spectroscopy (IRAS) in combination with molecular beam techniques to identify the nature of the surface species formed upon water adsorption and to find detailed correlations between the adsorbates’ structures and the energetics of their formation

We show that water dissociation energy on Fe_3O_4(111) (101 kJ/mol) is considerably higher than all previously reported values obtained by the indirect desorption-based methods. By employing IRAS on isotopically labeled water and Fe_3O_4, we experimentally prove that the generally accepted simple model of water dissociation to form two individual OH groups is not correct. By combing experimental observations and theoretical calculations carried out in the group of Prof. J. Sauer (HU, Berlin), we show that OH groups formed upon water dissociation build a very stable complex with molecular water. We could unambiguously rule out formation of two individual spatially separated OH groups upon water dissociation. Calculated spectroscopic vibrational signatures and formation energy of an OH-water complex were found to be in excellent agreement with the experimental data. The adsorption behavior of water on Fe_3O_4(100) was found to be similar to Fe_3O_4(111) but the adsorption energies exhibit somewhat lower values.

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Ultrathin Silica and Iron-Silicate Films on Ru(0001)

Hagen W. Klemm, Gina Peschel, Alexander Fuhrich, Ewa Madej, Dietrich Menzel,
Thomas Schmidt, and Hans-Joachim Freund

For the understanding of very complex material systems like Zeolites and their relationship between structure and reactivity, ultrathin SiO_2 and metal doped silicate layers on Ru(0001) offer possibilities for use as model systems[1,2]. The crucial preparation conditions to get well-defined and homogeneous films were studied at mesoscopic scale using the aberration corrected spectro-microscope SMART, located at the synchrotron light source BESSY II in Berlin. It enables a comprehensive *in situ* and *in real time* characterization of surface processes by high-resolution XPEEM, µXPS, valence band mapping and LEEM / LEED. Here, the chemical composition, crystalline structure and the topography of two material systems were studied, pure Silica (SiO_2) and mixed Iron-Silica (Fe/SiO_2).

For SiO_2 on Ru(0001) investigations have already shown that the deposited amount and the annealing conditions strongly influence the crystallographic and electronic structure. The SiO_2 bilayer film is of special interest, because it is only Van de Waals bound to the Ru(0001) surface and therefore lifts off the support. We show[3] that it is possible to prepare a fully oxidized, homogenous film at a micron scale; however holes in the film seem to be unavoidable. They are important to consider for averaging experiments that investigate migration and reaction of molecules between Silica and Ru(0001)[4]. Also, the phase transition from a crystalline to a vitreous film was observed *in situ* and *in real time* in LEED, showing a continuous transformation from an ordered (2x2) structure into a diffuse ring. The dark field mode of our microscope shows that the vitreous film is smooth and homogenous.

Deposition of iron onto SiO_2 films transforms the initial (2x2) structure into a ($\sqrt{3}$x$\sqrt{3}$) R30° structure with a Moiré pattern. The composition of the layers depends on the preparation conditions: depositing silicon and iron at room temperature with subsequent annealing in oxygen leads to separated domains of iron-silicate and silica. In contrast, the *in situ* preparation of a FeO layer at 630°C in oxygen atmosphere, followed by silicon deposition at 760°C, also in oxygen atmosphere, produces a homogenous iron-silicate film[5]. For both systems structural models are discussed.

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SMART-II: An Aberration Corrected LEEM/PEEM with Space Charge Compensation and a New Type of Electrostatic Omega Filter

Francesca Genuzio, Helder Marchetto, Thomas Schmidt, and Hans-Joachim Freund

The SMART (Spectro-Microscope with Aberration correction for many Relevant Techniques) combines electron spectroscopy with electron microscopy at high lateral and energy resolution to obtain spatially resolved information about the morphology, chemical distribution, work function and structural properties at nano-metric scale. The basic instrument is a Low Energy Electron Microscope (LEEM) and Photo-Emission Electron Microscope (PEEM) equipped with an imaging energy analyzer and an aberration corrector, compensating simultaneously for both spherical and chromatic aberrations. In LEEM, this leads to an outstanding lateral resolution of 2.6 nm[1] which is twice as good as for an uncompensated system. In energy filtered XPEEM we demonstrated a resolution of 18 nm[2], the best value achieved with this kind of instrument. The clear difference between these two modes is due to space charge effects caused by the pulsed time structure of the exciting synchrotron light. Currently we are setting up a new instrument, called SMART-II. The aims of the new instrument are the improvement of lateral and energy resolution in XPEEM (5 nm and 75 meV, respectively) and a routine operation with easy handling. Compared to the optical design of SMART-I, the SMART-II will use (a) intensity reducing apertures and slits to limit the space charge and (b) the magnetic Ω-filter will be replaced by an electrostatic analogous instrument which allows to float the analyzer potential on the sample potential, leading to much higher electronic stability.

The new designed beam splitter implements field apertures and high pass filtering slits to cut away electrons outside the field of view and secondary electrons, i.e. electrons not needed for imaging but blurring the image by its charge. The new Omega filter is optimized for both, lateral and energy resolution better than 2 nm and 100 meV, respectively. The majority of the possible second order aberrations are already compensated by the intrinsic symmetry. The dominating residual aberrations are fully corrected by four multipoles; so the lateral resolution is determined by the unavoidable third order aberrations; the effect of which is reduced by an adequate design for the deceleration-acceleration optics in combination with optimized pass energy.

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Laser Beam Profiling and Further Improvements to the FHI-FEL

Heinz Junkes and Mike Wesemann

A mid-infrared FEL has been established at the Fritz-Haber-Institut in Berlin. It is used for spectroscopic investigations of molecules, clusters, nanoparticles and surfaces. The oscillator FEL is operated with 15 - 50 MeV electrons from a normal-conducting S-band linac equipped with a gridded thermionic gun and a chicane for controlled bunch compression[1].

The EPICS software framework was choosen to build the control system for this facility. In an effort to support the various experimenters two different Laser Beam Profiling cameras have been integrated. Here, the areadetector framework with Genicam integration is used.

The control system was also expanded with fast digitizers (SIS3316) but connected via Ethernet instead of using a VMEbus crate controller to get a higher flexibility.

A new EPICS Archiver Appliance was installed. The system was developed by a collaboration of SLAC, BNL and FRIB to allow the archival of millions of PVs, mainly focused on data retrieval performance. It offers the ability to cluster appliances and to scale by adding appliances to the cluster. Multiple stages and an inbuilt process to move data between stages facilitates the usage of faster storage and the ability to decimate data as it is moved. Our Long Term Storage is based on cost-effective Linear Tape File System technology

An iPad app for monitoring completes the enhancement.

This poster presents design and implementation aspects of the upgrade, its capabilities, and lessons learned during the development.

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Department of Molecular Physics

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MP 10 Spectroscopy of Strongly Bound Binary Clusters and Cluster Complexes

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MP 11 Separation of Oligosaccharide and Glycopeptide Isomers Using Ion Mobility-Mass Spectrometry

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MP 1

Supersymmetry and Topology of the Quantum Pendulum

Burkhard Schmidt[a] and Bretislav Friedrich

We applied the apparatus of supersymmetric quantum mechanics (SUSY QM) to analyze the problem of the quantum pendulum, i.e., that of a rigid rotor under a cosine potential and/or its variants. It belongs to prototypical problems in quantum mechanics and lurks behind numerous applications in chemical and molecular physics.[1] A general solution of the eigenproblem relies on numerical diagonalization of a truncated infinite-dimensional Hamiltonian matrix. The matrix elements are functions of dimensionless parameters η and ζ that characterize, respectively, the strengths of the pendulum's orienting ($\propto\eta \cos\theta$) and aligning ($\propto\zeta \cos^2\theta$) interactions (where θ is a polar angle). For arbitrary non-zero values of the η and ζ parameters, there are no analytic, closed-form solutions to the pendular eigenproblem. Following upon our previous studies of both planar[2] and spherical[3] pendula, we were concerned with the topology of the eigenenergy surfaces spanned by the interaction parameters η and ζ for all values of the projection quantum number m as well as with the supersymmetry of the eigenproblem as a means for identifying its analytic solutions – if any.

Topology. We found that the loci of all intersections that arise among the eigenenergy surfaces of the quantum pendulum are accurately rendered by a simple formula, $k= \eta/(2 \zeta^{1/2})$, with k=1, 2, 3, ... Since this formula is independent of the eigenstate, the energy levels exhibit a general pattern that only depends on the value of k, termed the topological index: for each k, there are k single states, followed, in ascending order, by all other states which are nearly doubly degenerate. All the intersections are avoided, as they only occur between opposite-parity levels coupled by the parity-mixing orienting interaction.

Supersymmetry. We have identified two sets of conditions (termed cases 1 and 2) under which SUSY QM can be applied to the pendular eigenproblem. In particular, these conditions imply a certain ratio of the interaction parameters η and ζ and, thereby, a certain value of the topological index k. This made it possible to identify each case with a particular topology: case 1 with $k = \mp m + 1$; case 2 with $k = 1$ form > 0. In most cases SUSY QM enabled us to obtain analytic expressions for the ground-state wave functions. For one case, we were able to find the excited-state wave function as well.

We emphasize that the condition for analytic solvability as identified by SUSY QM coincides with the loci of the avoided eigensurface intersections, which only arise for the combined orienting and aligning interactions whose parameters η and ζ span the eigensurfaces. So far, no SUSY analytic solution has been found for either of these interactions alone. The origin of the connection between eigensurface topology and exact solvability will be the subject of a further investigation.

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Quantum Computing with Ultracold Polar Paramagnetic Molecules

Mallikarjun Karra, Ketan Sharma, and Bretislav Friedrich

Arrays of trapped ultracold molecules represent a promising platform for implementing a universal quantum computer. DeMille[1] has detailed a prototype design based on polar $^1\Sigma$ molecules trapped in a one-dimensional optical lattice, partially oriented in an external electric field, and coupled by the electric dipole-dipole interaction.

In our present work, we consider an array of polar paramagnetic molecules (exemplified by polar $^2\Sigma$ molecules) as qubits, entangled likewise by the electric dipole-dipole interaction, but subject to various combinations of concurrent homogeneous and inhomogeneous electric and magnetic fields. For $^1\Sigma$ molecules, the Stark effect is second-order; therefore, a sizable external electric field is required to produce the requisite dipole moments in the laboratory frame.[2] Polar $^2\Sigma$ molecules (which are inherently paramagnetic) offer advantages resulting from a nearly first-order Stark and Zeeman effects when subject to combined electric and magnetic fields.[3] That permits the use of lower external field strengths in addressing the qubit sites. Moreover, for a particular choice of qubits, the electric dipole interactions become isomorphous with the well-studied NMR systems, which are amenable to a wide repertoire of radiofrequency techniques developed for quantum information processing.

We characterized the eigenstates of the array, including their mutually induced directionality, by evaluating their eigenproperties via numerical diagonalization of the appropriate Hamiltonian matrix, whose elements we found analytically. We also evaluated the concurrence of the states as a measure of their entanglement in the presence and absence of fields. Our findings led us to propose two novel schemes for implementing an optically controlled CNOT gate operation: Scheme I comprises five steps, including an adiabatic switching of the magnetic field, while Scheme II consists of only a single step. The schemes will be further tested by invoking multi-target optimal control theory as a means of optimizing the initial-to-target transition probability via a controlling laser field and of evaluating the fidelity attainable for the schemes.

Of key importance is the ability to resolve the transition frequencies involved in the optical control of the gate operations – in the face of broadening due to dipole-dipole coupling and the inhomogeneity in the electric and magnetic fields. We also demonstrate that the former dominates over the latter, thus setting the criteria for the feasibility of the schemes.

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Unzipping of Gas Phase Proteins - Similar Secondary Structures at High Charged States

Ana Isabel González Flórez, Eicke Mucha, Doo-Sik Ahn, Kevin Pagel[a],
and Gert von Helden

The structure and dynamics of a protein is determined by a subtle balance between various intra- and intermolecular interactions. When investigating charged proteins in the gas phase, intermolecular interactions are explicitly absent. Under such conditions, attractive forces such as hydrogen bonding as well as Van der Waals interactions tend to drive a protein into a compact shape. This is counter acted by repulsive coulomb forces, which want to maximize the distances between charges. Indeed, in a hallmark experiment, gas-phase ion mobility methods were used to observe the transition from folded compact shapes to extended shapes when the charge on the protein increases [1]. However, while ion mobility is sensitive to the global shape and structure, it gives little information on the local structure - a gap that infrared spectroscopy can fill.

In an IR spectroscopic study on mass/charge selected cytochrome c, a protein consisting of 104 amino acids, the appearance of a new and unexpected "mystery" band near 1480 cm^{-1} is observed for high charge states [2] and no conclusive assignment could be performed. Here, we reinvestigate cytochrome c as well as ubiquitin (76 amino acids) by performing IR spectroscopy for a wide charge state range. For improved spectral resolution, the experiments are performed in an ultracold environment, inside liquid helium droplets. For this, we have developed an experimental setup in which mass-to-charge selected ions are accumulated inside a hexapole ion trap and picked up by a traversing beam of helium droplets. Once embedded inside the droplet, the ion is cooled down to an equilibrium temperature of ~ 0.37 K *via* evaporative cooling. Further downstream, the ion-doped helium droplets are probed using the Fritz Haber Institute IR-free-electron-laser and detected in a time-of-flight mass spectrometer.

With increasing charge state, the appearance of the above mentioned mystery band is observed and its growing intensity comes at the cost of the regular Amine-II (N-H bending) band. Comparing the spectra with theoretical models clearly shows, that this band is an indicator for the coulomb repulsion induced stepwise unzipping of helical structures to form extended structures.

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Infrared Spectroscopy of Complex Carbohydrates in the Gas Phase

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and Gert von Helden

Besides the well-known function of carbohydrates as energy source, smaller sugars – often referred to as oligosaccharides – are essential in processes like cell-cell-communication, inflammation, molecular recognition or immunity.[1] In comparison to other biopolymers such as DNA and proteins, oligosaccharides are largely under-studied, which is predominantly a result of their structural diversity. While DNA and proteins are exclusively assembled in a linear fashion, oligosaccharides are additionally branched and exhibit a complex stereochemistry. As a result, their in-depth structural analysis represents a significant challenge to date.

One step towards understanding the function of carbohydrates is to gain knowledge about their intrinsic structural properties, which can for example be probed by infrared spectroscopy in the gas phase. Using this approach, vibrational spectra of smaller carbohydrates at room temperature showed a limited resolution, making the investigation of larger species rather difficult. In this work, we investigated complex carbohydrates *via* infrared spectroscopy using the Fritz Haber Institute free-electron laser (FHI-FEL). In our present experimental setup[2] carbohydrate ions are accumulated inside a hexapole ion trap and picked up by a traversing pulsed beam of helium droplets. Embedded ions are cooled down to the equilibrium temperature (~0.37 K) of the superfluid helium droplets and transported to the detection region. Here, the absorption of resonant laser photons can lead to the ejection of the ion which is then detected in a time-of-flight mass spectrometer. This approach of investigating ultra-cold molecules in the gas phase provides high resolution spectra that allow to differentiate structurally very similar carbohydrates.

Six synthetic trisaccharide-isomers that differ in the composition, connectivity or configuration of only one building block were analyzed. These similar carbohydrates clearly show unique signatures in their vibrational spectra and demonstrate the potential of this experimental approach. Extending the scope to monosaccharides, disaccharides and more complex systems may lead to the identification of characteristic bands or patterns that allow to deduce structural information encoded in their spectra.

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Gas-Phase Infrared Spectroscopy of Ion Mobility-Selected Amyloid Intermediates

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Amyloidogenic peptides and proteins play a crucial role in a variety of neurodegenerative disorders such as Alzheimer´s and Parkinson disease.[1] The involved proteins undergo a spontaneous transition from a soluble, often partially folded form into an insoluble, β-sheet rich amyloid fibril. The underlying assembly pathway is not fully understood to date, but there has been increasing evidence that oligomeric folding intermediates that occur during the transformation process are the toxic species in the afore mentioned diseases. Understanding the structural details of those oligomers is therefore the key for successful drug development.

However, amyloid oligomers are polydisperse, *i.e.* they do not exhibit a defined oligomerization state but rather form a dynamic equilibrium of multiple species. In addition, amyloid oligomers are also polymorph, *i.e.* for one and the same oligomeric state multiple conformers can coexist. As a result of this complexity, traditional condensed-phase methods are of limited use for the characterization of intermediates, because they typically only provide average properties of the ensemble. A promising method to obtain detailed structural information about individual oligomeric species is ion mobility-mass spectrometry (IM-MS)[2] Here ions are separated according to their size and shape as well as their mass and charge, which enables a simultaneous disentangling of polydisperse and polymorph species. In addition, direct secondary structure information of individual oligomers can be obtained for mass and shape selected ions using gas phase infrared (IR) spectroscopy.

Here, we demonstrate the potential of IM-MS coupled to free electron laser-based IR spectroscopy as a tool for deducing the self-assembly process of amyloidogenic intermediates. We synthesized three isomeric hexapeptides, which are composed of the same amino acids and only differ in their sequence. One of these peptides does not form amyloid fibrils and can be used as an ideal reference for a non-fibril forming system; the other two peptides readily assemble into amyloids, but differ significantly in their tendency to aggregate. Our data reveal that already early oligomers consisting of four to nine peptide subunits can contain a significant amount of β-sheet. In addition, we provide first evidence for a correlation between an increase in collision cross-section and elevated β-sheet content.

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Matter-wave Diffraction of Helium Atoms, Dimers, and Trimers; Observation of the Elusive Efimov State in He_3

B. S. Zhao[a], Lee Young Kim[a,b], and W. Schöllkopf[b]

We have continued our experimental studies based on matter-wave diffraction of molecular beams. Two lines of experiments have been pursuit since the last Fachbeirat meeting: (i) an investigation of the helium trimer; and (ii) a study of diffraction of He, He_2, and D_2 from a quantum reflection grating.

(i) He_3, the van der Waals bound trimer of ground-state He, represents a unique quantum system, because it is arguably the only naturally occurring 3-body system to possess an *Efimov state*. In 1970 Vitaly Efimov predicted universal behaviour of a 3-body system (trimer), if the corresponding 2-body system (dimer) is sufficiently weakly bound. Efimov's theory predicts an infinite number of 3-body excited states at resonance, *i.e.* in the limit of vanishing 2-body bond strength. Unlike classical excited vibrational states Efimov states are predicted to disappear successively when the 2-body interaction strength is increased starting from resonance conditions. For atomic helium it just happens that the He_2 binding energy of ~100 neV is sufficiently weak to support just one such Efimov state in He_3. The grating diffraction method, which allowed us to detect He_3 in its ground state, did not reveal evidence for the expected Efimov state.

We have been collaborating with the group of Prof. Dörner at Frankfurt University combining their *COLTRIMS* reaction microscope with the diffraction method. To this end, part of our diffraction setup was installed at the *COTRLIMS* setup in Frankfurt. This permits to first separate He_3 from He and He_2, and then to selectively image the wave-function of He_3 by *COLTRIMS*. This approach has turned out to be very fruitful and allowed us to image the structure of the pure and mixed-isotope trimer systems $^4He_3$ and $^3He^4He_2$, respectively, thereby confirming the wave-function of $^3He^4He_2$ to form a quantum halo[1]. In addition, it also made it possible to observe, for the first time, the long-sought Efimov state in $^4He_3$[2]. Observation of the wave-function of the Efimov state is not only an experimental confirmation of Efimov's theory, but it also serves as a sensitive benchmark test for quantum chemistry calculations.

(ii) In the second line of experiments we have been studying diffraction of helium and deuterium beams *quantum reflected* from a blazed grating. We observed universal behaviour; different atoms and molecules show diffraction patterns of identical relative peak intensities, only depending on the particle's de Broglie wavelength. This is in contrast to previous matter-wave diffraction experiments where the particle specific interaction with the diffracting element (be it a material grating or a light wave) was observed to significantly alter and, possibly, suppress the diffraction peak visibility. By applying a secondary scattering model we traced the universal behaviour back to the peculiar principles governing quantum reflection[3].

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The IR FEL Facility at the FHI: Review of the First Two Years of Operation and Future Prospects

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The FHI free-electron laser (FHI FEL) started regular user operation in November 2013. First results were reported already at the last Fachbeirat meeting in spring 2014. As of August 1st, 2015 a total of 172 user shifts (full days) have been provided to 6 FHI user groups. In addition, machine shifts have been used to maintain, characterize, and continuously improve the performance of the FHI FEL. Here, we present the current FEL installation, give an overview of results from user groups gained with the FEL in the first 2 years of operation, and discuss a possible future system upgrade.

The FHI FEL is driven by an electron accelerator providing a final electron energy adjustable from 15 to 50 MeV at more than 200 pC bunch charge with a bunch repetition rate of 1 GHz [1]. Currently, the FEL provides powerful, pulsed laser radiation at any wavelength continuously tunable from 3.5 to 50 µm covering the mid-infrared wavelength range. The IR pulses consist of 5 to 10 µs long pulse trains (macro-pulses) of up to ~100 mJ energy containing thousands of short (~1 ps) micro-pulses of about 10 µJ energy separated by 1 ns [2]. The Fourier transform limited relative bandwidth is, typically, about 0.5% FWHM. By fine tuning the FEL cavity length it is possible to adjust the micro-pulse length down to less than 0.5 ps accompanied by a corresponding increase of the relative bandwidth to several percent (see Poster PC 2 by the Paarmann group for details of the micro-pulse shape measurements).

Furthermore, we provide a brief review of results from user experiments indicating how the FEL has opened up new possibilities for the ongoing research at the FHI in gas phase spectroscopy, surface science, and physical chemistry. This includes, for instance: spectroscopy of bio-molecules either conformer selected by ion mobility spectrometry (Poster MP03) or embedded in superfluid helium nano-droplets at 0.4 K (MP02); gas-phase vibrational spectroscopy of mass-selected metal-oxide clusters and protonated water clusters (MP09) and of transition-metal carbonyl clusters (MP10); as well as nonlinear solid-state spectroscopy such as second harmonic phonon spectroscopy (SHP) and sum-frequency Raman (SFR) spectroscopy (PC 1).

In addition, we describe a possible future machine upgrade: By setting up a second FEL branch the wavelength range can easily be extended into the far-infrared and Terahertz region beyond 100 µm wavelength. In addition, we lay out a proposal to modify the existing electron accelerator and beamline system such that simultaneous operation of both FEL branches becomes possible, thereby allowing generation of synchronized FEL radiation at two independently tunable wavelengths. This approach can open the door to 2-color pump-probe experiments in the infrared regime.

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Measuring and Manipulating the Temperature of Cold Molecules Trapped on a Chip

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Gerard Meijer[d], and Gabriele Santambrogio[a]

The manipulation of polar molecules using the electric fields created by microscopic electrodes on the surface of a chip is a new and fascinating research field. Microscopic electrodes allow for the creation of large field gradients, i.e., large forces for polar molecules, using only moderate voltages applied to the electrodes. Present-day microelectronics technology makes it possible to integrate multiple tools and devices onto a compact surface area, like lenses, decelerators and traps for polar molecules but also integrated detection elements like radiation sources and optical cavities.

We have demonstrated that rotational transitions can be induced while the molecules are above the chip. Due to the very narrow bandwidth (kHz) of the microwave radiation that is used for these experiments, the electric fields on the chip have to be switched off at the moment that the transition is induced to circumvent Stark-broadening of the spectral lines. After the microwave excitation, the electric fields are then switched on again and the rotationally excited molecules are recaptured in the traps above the chip[1]. Apart from rotational transitions, vibrational transitions can be induced in heteronuclear diatomic molecules, like CO, as well. For this, we have upgraded an available table-top pulsed IR laser system with a frequency down-conversion unit such that we can reach the fundamental $v=1 \leftarrow v=0$ transition in metastable CO around 5 μm. The bandwidth of the pulsed IR radiation is nicely matched to the width of the Stark-broadened ro-vibrational transitions and the electric fields can therefore stay on while the excitation is performed, i.e. the excitation is really performed on molecules while these are trapped above the chip[2].

We have designed and constructed an ion-imaging setup with a cylindrical ion-lens with which we have been able to record two-dimensional images of the distribution of CO molecules on the chip with a spatial resolution of about 20 μm along the molecular beam axis (and about 0.5 mm perpendicular to that) after planar (1+1)-REMPI. The time-resolved spatial imaging that we applied allows for the analysis of the phase-space distribution of the molecules and for direct measurement of their temperature[3]. We have used this to study an adiabatic expansion process of the molecules trapped on the chip in which the temperature of the ensemble was lowered from 16 to 5 mK.

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Gas Phase Vibrational Spectroscopy of Size-selected Aluminium and Iron Oxide Clusters: Structure, Stability and Reactivity

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Wieland Schöllkopf,[a] Sandy Gewinner,[a] Joachim Sauer[c] and Knut R. Asmis[a,b]

Metal oxides are currently attracting much attention due to their use such as ceramics, abrasives, absorbents, catalysts and catalyst support. In order to design oxides with desirable properties a detailed understanding of their interaction with water, which determines oxide formation and dissolution, is indispensable. However, a molecular level understanding of their physical and chemical properties is far from complete. Our study aims at characterizing the structure, stability and reactivity of mass-selected metal oxide cluster ions of increasing size and complexity in the gas phase.[1,2] This project is part of the Collaborative Research Centre 1109 “Understanding of Metal Oxide/Water Systems at the Molecular Scale: Structural Evolution, Interfaces, and Dissolution”, where the interaction of water with metal oxides is studied at different dimensions ranging from small clusters, to nanoparticles all the way to bulk materials. We use infrared photodissociation (IRPD) spectroscopy in combination with the intense and widely-tunable radiation from the IR free electron laser FHI-FEL[3] (215-2500 cm^{-1}) or a nanosecond IR tabletop laser (600-4000 cm^{-1}) to study the structure and reactivity of bare aluminium and iron oxide clusters as well as their complexes with water. Structures are assigned based on the comparison of the IRPD spectra to simulated IR spectra from electronic structure calculations. The IRPD spectra of small aluminium oxide anions (AlO_{1-4}^-, $Al_2O_{3-6}^-$) and iron oxide cations ($(Fe_2O_3)_{1-5}^+$) in the mid-IR range (400-1200 cm^{-1}) allow understanding their vibrational signature, determining scaling factors and identifying typical binding motifs in the smaller cluster ions. We find that some of the electronically open shell cluster anions readily react with the H_2. Most oxide compounds, however, feature the metal in its highest oxidation state. Hence, we then focused on a systematic study of nominally fully oxidized, electronically closed-shell clusters, i.e. $(Al_2O_3)_{1-6}AlO_2^-$ and $(Fe_2O_3)_{1-4}FeO^+$, which serve as model systems for characterizing the initial steps in the formation and growth of metal oxides. The interaction of fully oxidized $Fe_3O_4^+$ with one to four water molecules is characterized by measuring in the O-H stretching (3000-3800 cm^{-1}) as well as in the mid-infrared region (350-1800 cm^{-1}). The IRPD spectra reveal that the water molecules remain intact and suggest that a hydrogen bond network forms upon addition of the third water molecule.

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Spectroscopy of Strongly Bound Binary Clusters and Cluster Complexes

David Yubero Valdivielso[a], Philip Jäger[a], and André Fielicke[a]

In the past years our group has established different variants of infrared spectroscopy as tools to unravel the structures of gas-phase clusters and cluster complexes in different charge states, including neutral species. These studies heavily rely on the availability of intense and widely tuneable infrared radiation produced by Infrared Free Electron Lasers. The experimental findings provide valuable reference data for the evaluation of quantum chemical methods, which still have difficulties with reliable prediction of cluster structures and their related properties from first principles. Here we summarize some of the first investigations we have performed with the new Infrared Free Electron Laser at the Fritz-Haber Institute.

Recently we have implemented in our experiment a dual target laser ablation cluster source that allows the well-controlled preparation of binary clusters. As one of the first studies we have synthesized boron doped silicon clusters starting with two separate solid targets of silicon and boron. We obtained the IR spectra for selected neutral Si/B clusters using the infrared-UV two colour ionization technique. Comparison of the experimental spectra with results of DFT calculations reveals that the boron atoms essentially substitute Si in the cluster structure, although significant distortions occur due to shorter Si-B bond length compared to Si-Si (collaboration with O. Dopfer, TU Berlin).

A second aspect that has been studied using the dual target source are the chemical properties of binary metal clusters. As examples we analyze the activation and binding of molecular hydrogen by aluminum clusters doped by single (or two) atoms of transition metals (Co, Rh, V), a process possible relevant for hydrogen storage applications. While pure cationic Al clusters do not, or very slowly, react with H_2, the transition metal dopant facilitates binding of H_2, its activation, leading finally to dissociation. The resulting different binding motifs of H are probed by infrared multiple photon dissociation spectroscopy (collaboration with E. Janssens, KU Leuven, Belgium).

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Separation of Oligosaccharide and Glycopeptide Isomers Using

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Complex carbohydrates are of great importance for a variety of biological functions. They can be linked to proteins as post-translational modifications or exist as free oligosaccharides, for example in milk. Currently, the vast majority of carbohydrates are characterized using mass spectrometry-based techniques (MS) that are directly descending form those established in proteomics. Measuring the molecular weight of a sugar, however, immediately poses a fundamental problem: entire classes of the constituting monosaccharide building blocks exhibit an identical atomic composition and, consequently, an identical mass. Therefore, carbohydrate MS data can be highly ambiguous and often it is not possible to clearly assign a particular molecular structure.

A promising approach to overcome the above-mentioned limitation is to *implement* an additional gas-phase separation step using ion mobility-mass spectrometry (IM-MS). Here, ions travel through a gas-filled cell aided by an electric field and are separated according to their mass, charge, size and shape. While the drift time of an ion depends on instrumental conditions, the collision cross section (CCS) is a molecular property that can be compared and calculated theoretically.

Here, we demonstrate the potential of IM-MS to be used as a tool for the separation and identification of isomeric carbohydrates and glycopeptides. First, six synthetic carbohydrate isomers that differ with respect to their composition, connectivity, or configuration were analyzed individually and as mixtures. Our data reveal that carbohydrate linkage- and stereoisomers, which are difficult to distinguish using established techniques such as liquid chromatography or NMR, can be separated and unambiguously identified on basis of their CCS. When mixed, even minor isomeric components with relative concentrations as low as 0.1% are still clearly detectable.[1]

Second, we extended our investigations to glycopeptides. First data show that the position of the carbohydrate within the peptide sequence can be clearly identified using IM-MS when multiple glycosylation sites exist. More importantly, however, our data reveal that also glycopeptides, which merely differ in the regiochemistry of the attached glycan can be distinguished using fragmentation and subsequent IM-MS analysis. These results indicate that IM-MS is an exceptionally effective tool for the structural analysis of oligosaccharides. The full benefit of the method will become apparent once CCS data of oligosaccharides and their fragments are deposited in databases.[2]

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Poster List

PC 1 **Mid-Infrared Nonlinear Solid State Spectroscopy Using the FHI Free Electron Laser**

Alexander Paarmann, Ilya Razdolski, Christopher Winta, Alexey Melnikov, Sebastian Mährlein, Riko Kießling, Sandy Gewinner, Wieland Schöllkopf, Joshua D. Caldwell, Tobias Kampfrath, and Martin Wolf

PC 2 **Ultrashort Pulse Operation of the FHI Infrared Free-Electron Laser**

Alexander Paarmann, Hans Christian Schewe, Riko Kießling, Sandy Gewinner, Wieland Schöllkopf, and Martin Wolf

PC 3 **Ultrafast Dynamics of Solvated Electrons at the D_2O/Cu(111) Interface**

Clemens Richter, Jan-Christoph Deinert, Daniel Wegkamp, Martin Wolf, and Julia Stähler

PC 4 **Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces**

Jan-Christoph Deinert, Laura Foglia, Lea Bogner, Clemens Richter, Sesha Vempati, Lukas Gierster, Martin Wolf, and Julia Stähler

PC 5 **Photoinduced Phase Transitions in Strongly Correlated Systems: When Does the Electronic Band Gap Collapse?**

Marc Herzog, Daniel Wegkamp, Selene Mor, Claude Monney, Angel Rubio, Martin Wolf, and Julia Stähler

PC 6 **CDW Formation and Dimensionality in Quasi-one Dimensional Metal Wires Probed by ARPES**

Christopher W. Nicholson, Claude Monney, Michele Puppin, Moritz Hoesch, Ulrich Krieg, Christoph Tegenkamp, Herbert Pfnür, Ralph Ernstorfer, Karsten Horn, and Martin Wolf

PC 7 **Ultrafast Dynamics of Correlated Materials Probed by Time-resolved HHG-based ARPES**

Christopher W. Nicholson, Claude Monney, Michele Puppin, Cephise Cacho, Robert Carley, Martin Weinelt, Ralph Ernstorfer, and Martin Wolf

PC 8 **Development of an Ultrafast 500 kHz XUV Source**

Michele Puppin, Yunpei Deng, Johannes Feldl, Niels Schröter, Marcel Krenz, Martin Wolf, and Ralph Ernstorfer

PC 9 **Femtosecond Low-energy Electrons Probing Currents and Atomic Structure in Nanomaterials**

Melanie Müller, Thomas Vasileiadis, Vasily Kravtsov, Markus Raschke, Alexander Paarmann, and Ralph Ernstorfer

PC 10 **Time-domain Separation of Optical Properties from Structural Transitions in Phase Change Materials**

Lutz Waldecker, Roman Bertoni, Timothy Miller, Simon Wall, and Ralph Ernstorfer

PC 11 **Electron-lattice Interactions in Transition Metal Dichalcogenides, Clusters and Bulk Materials**

Roman Bertoni, Lutz Waldecker, Thomas Vasileiadis, Ilya Razdolski, Alexey Melnikov, Dawn Wells, Richard Palmer, Jan Vorberger, and Ralph Ernstorfer

PC 12 **Ultrafast Charge Currents at the Surface of the Topological Insulator Bi_2Se_3**

Lukas Braun, Luca Perfetti, Gregor Mussler, Markus Münzenberg, Martin Wolf, and Tobias Kampfrath

PC 13 **Ultrafast Spin-lattice Coupling in a Model Ferromagnetic Insulator**

Sebastian Mährlein, Ilie Radu, Pablo Maldonado, Alexander Paarmann, Michael Gensch, Peter M. Oppeneer, Martin Wolf, and Tobias Kampfrath

PC 14 **Probing and Tailoring of Spin Transport in Magnetic Metals at Terahertz Frequencies**

Tom Seifert, Lukas Braun, Jürgen Henrizi, Ulrike Martens, Gerhard Jakob, Martin Jourdan, Markus Münzenberg, Mathias Kläui, Martin Wolf, and Tobias Kampfrath

PC 15 **Excitation and Propagation of Spin Currents in Fe/Au/Fe/MgO(001): Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescale**

Ilya Razdolski, Alexandr Alekhin, Nikita Ilin, Jan Meyburg, Detlef Diesing, Vladimir Roddatis, Tim Wehling, Ivan Rungger, Maria Stamenova, Stefano Sanvito, Uwe Bovensiepen, and Alexey Melnikov

PC 16 **Aligning Polar Molecules in Liquids by Strong THz Electric-Field Pulses**

Mohsen Sajadi, Martin Wolf, and Tobias Kampfrath

PC 17 **Probing Molecular Structure, Dynamics and Thermodynamics at the Air/Water Interface**

Yujin Tong and R. Kramer Campen

PC 18	**Characterizing Elementary Processes at Electrochemical Interfaces** Yujin Tong, Francois Lapointe, Martin Wolf, and R. Kramer Campen
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Mid-Infrared Nonlinear Solid State Spectroscopy Using the FHI Free-Electron Laser

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The intense, narrowband, and widely tunable mid-infrared (mid-IR) pulses generated by the FHI Free-Electron Laser (FEL) provides a unique opportunity to study low-energy resonant nonlinear optical processes in the solid state. We have developed two novel types of mid-IR nonlinear spectroscopy: (i) second harmonic phonon (SHP) and (ii) sum-frequency Raman (SFR) spectroscopy. SHP spectroscopy is demonstrated for bulk silicon carbide (SiC)[1], and applied to study field localization of sub-wavelength confined surface phonon polaritons[2]. The SFR effect is introduced as a novel excitation pathway for Raman-only active phonons and exemplified for diamond.

(i) *Second harmonic phonon spectroscopy:* Optical phonon resonances are traditionally studied using Raman or reflectance spectroscopy. Additionally, vibrational sum-frequency generation is now established to study phonons in bulk crystals with broken inversion symmetry, as well as surface and interface phonons as inversion symmetry is broken at surfaces and interfaces[3]. We have developed an alternative second-order mid-IR spectroscopy based on resonant second harmonic (SH) generation employing the FHI FEL. For SiC, we observe two distinct phonon-resonances in the SH yield, originating from enhancement of the nonlinear susceptibility and the Fresnel transmission, respectively[1]. Furthermore, we exploit the high sensitivity of the SH yield to resonant field localization by performing SHP spectroscopy of a nanophotonic model system where surface phonon polaritons in SiC are confined in sub-wavelength nanostructures[2].

(ii) *Sum-frequency Raman spectroscopy:* Optical lattice vibrations that modulate the polarizibility of a solid can be excited by the Raman effect. Usually, the Raman excitation is realized with incident photon energies much higher than that of the phonon (difference frequency Raman excitation)[4]. Here, we introduce a novel scheme of Raman excitation using a sum-frequency process with intense mid-IR radiation at half the phonon frequency. The process is demonstrated experimentally for infrared inactive optical phonons in diamond with two complementary approaches: (a) time-domain coherent phonon spectroscopy[4] after excitation with broadband, phase-stable THz fields from a table-top laser and (b) two-photon absorption spectroscopy employing tunable FEL excitation.

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Ultrashort Pulse Operation of the FHI Infrared Free-Electron Laser

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The FHI infrared Free-Electron Laser (FEL) delivers exceptional spectral power densities, tunable throughout the whole mid-infrared spectral region from 3.5 to 50 µm, enabling high-resolution spectroscopy of optically thin samples. Due to the picosecond duration of the electron bunches, the FEL naturally produces macro-bursts of ultrashort optical micropulses with respectively high peak intensities, which allows to efficiently perform nonlinear and time-resolved spectroscopy. Here, we characterize the different regimes of ultrashort pulse operation of the FEL, as well as the related nonlinearities in the lasing process itself. We also report the development of a synchronization system for femtosecond near-infrared (NIR) laser pulses to the FEL micropulses. All these features are crucial for the ongoing efforts to develop nonlinear and time-resolved solid-state spectroscopy approaches using the FEL.

Temporal characterization of the FEL micropulses is achieved using a specifically designed second harmonic (SH) autocorrelator[1]. Using a geometric beam splitter and reflective SH generation from CdTe, the autocorrelator can be operated over the full tuning range of the FEL. By varying of the FEL cavity length, we are able to continuously tune the pulse duration from <8 cycles (<320 fs at 12 microns) to > 80 cycles (>3.2 ps at 12 microns), with the respective Fourier-limited spectral bandwidth. Thus, the cavity length detuning presents itself as an excellent parameter to balance signal strength and spectral resolution in nonlinear spectroscopy experiments.

The FEL naturally generates radiation at higher harmonics simultaneously with the fundamental frequency[2], which is sensitive to the steering of the electron beam in the FEL. By implementing a ZnSe prism-based harmonic separator the intensity distribution and temporal structure of the high harmonic radiation has been characterized up to the 11th harmonic. Additionally, the intrinsic phase-coherence between the fundamental and the SH radiation of the FEL is tested, potentially allowing to use the SH as local oscillator for heterodyne detection in FEL-based SH spectroscopy.

Finally, we present the concept of the timing infrastructure in order to synchronize a NIR table-top laser to the mid-infrared (MIR) FEL micropulses. The 3 GHz FEL master oscillator signal is transferred by a stabilized fiber-optic link from the FEL source to the experimental user station, to be incorporated in a minimal timing jitter electronic synchronization system. Two-color cross correlation by difference-frequency generation in a nonlinear crystal will be used to determine the arrival time of the FEL pulses[3]. This synchronization system will allow for sub-picosecond resolution in MIR pump-NIR probe spectroscopy.

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Ultrafast Dynamics of Solvated Electrons at the D_2O/Cu(111) Interface

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Excess electrons in solution play a crucial role in physics, chemistry, and biology, especially in aqueous environments, as water is the ubiquitous solvent in nature. The solvent molecules reorient their dipoles in order to stabilize the excess charge, thus forming a solvated electron (SE). SEs are a long-known, highly reactive species and play a key role in charge-transfer reactions in various branches of chemistry. However, despite continuing efforts, the vertical binding energy (VBE) of the excess electron en route to the SE state has been unknown for decades.

Following a surface science approach, time-resolved two-photon-photoelectron (2PPE) spectroscopy was applied to amorphous solid water (ASW) layers adsorbed onto a metal surface. With this technique, it is possible to gain insight into the unoccupied electronic structure as well as in the ultrafast dynamics of electron solvation and charge-transfer at the D_2O/Cu(111) interface.

2PPE measurements with strongly improved time-resolution compared to previous works enable a detailed characterization of all involved elementary processes launched by photoexcitation of the metal and the creation and decay of solvated electrons. Quasi-instantaneous photoinduced electron injection leads to (i) population of the D_2O-conduction band (CB) where (ii) rapid carrier relaxation to the CB minimum with a rate of 4 meV/fs takes place, followed by (iii) localization of the electron in pre-existing trapping sites with a time constant of 22 fs and subsequent (iv) energetic stabilization via solvent molecule reorientation with a significantly slower rate of 0.27 meV/fs[1]. These results do not only provide insight into the processes involved in electron solvation, but also explain the inaccessibility of the VBE of the CB of water: The ultrashort lifetimes of the delocalized electron in the CB and its rapid localization inhibited the measurement of the CB VBE by techniques with too low time-resolution. Furthermore, our investigation of the electron population dynamics suggests that the fast relaxation dynamics in the CB as well as the electron localization (steps i & ii) are unaffected by the presence of the metal substrate, thus possibly rendering the electron dynamics in ASW representative for bulk ice and/or liquid water.

Current investigations make use of the SE as a tool to determine the mean free path of low kinetic energy electrons in ASW. In these measurements the SE, which is located 2-3 BL from the D_2O/Cu(111) interface, is photoexcited above E_{vac} and the photoemission intensity monitored for different ASW film thicknesses. These experiments will provide important information about the mean free path of highly reactive low kinetic energy electron which is particularly relevant in radiation chemistry, notably with regard to the length scales in radiation damage.

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Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces

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The functionality of hybrid inorganic/organic systems (HIOS) is governed by (i) the static interfacial electronic properties and, consequently, the resulting energy level alignment, and (ii) the resulting charge and energy transfer rates (CT/ET). Both are investigated by a combination of complementary fs time-resolved techniques: two-photon photoelectron spectroscopy (tr-2PPE), transient excited state transmission (tr-EST) and time-resolved electronic sum frequency generation (tr-eSFG).

ZnO is an ideal candidate for a cheap, abundant and optically transparent inorganic semiconductor for HIOS. We show that hydrogen renders both mixed- and oxygen-terminated surfaces metallic by inducing strong downward surface band bending and, as a consequence, a charge accumulation layer at the surface. This is accompanied by a reduction of the work function by up to 1.6 eV. Our 2PPE measurements are supported by DFT calculations from the theory department which demonstrate that the associated changes to the electrostatic potential remain localized almost exclusively at the adsorption site for low hydrogen coverages[1]. Above band gap excitation is followed by hot electron relaxation to the Fermi level E_F and the formation of a surface exciton (SX) within 200 fs, which exhibits a remarkable stability and lifetime up to nanoseconds[2]. Tr-eSFG spectra of the non-centrosymmetric bulk of ZnO reveal three excitonic resonances of the dielectric function associated with the split valence bands of ZnO, which show picosecond dynamics, probably due to the hot-carrier relaxation at the band edges. Furthermore, we observe dynamics associated with the formation of bulk excitons on a 200 ps timescale.

With regard to HIOS, we present first tr-2PPE results on the formation of a CT exciton at the ZnO interface with 5-phenyl-pyridine. The interfacial electronic structure is modified by adsorption[3] of the pyridine endgroup, elucidating the CT excitation mechanism. It decays through decay to the ZnO conduction band within 90 fs, indicating strong electronic coupling. Furthermore, we investigate the interface of ZnO with the organic dye 2,7-bis(biphenyl-4-yl)-2',7'-ditertbutyl-9.9'-spirobifluorene (SP6) by tr-EST. We observe two excited states populated for hundreds of ps, of which, remarkably, only one is depleted by charge transfer to the ZnO, showing that only one excited state diffuses to the interface. The charge separation competes with intersystem crossing to the SP6 triplet state and luminescence. Moreover, we detect unexpected electron emission due to triplet-triplet annihilation of triplet states on microsecond timescales.

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Photoinduced Phase Transitions in Strongly Correlated Systems: When Does the Electronic Band Gap Collapse?

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Strong electron correlations can drastically modify the electronic properties of solids as compared to what the single-particle picture would predict. For example, electron repulsion may open an insulating band gap transforming a metal into a Mott insulator or strong electron-hole interaction may lead to exciton condensation to form an excitonic insulator (EI). The insulator-to-metal transition can often be induced by ultrashort laser pulses and monitored by femtosecond time-resolved spectroscopy. We present results of pump-probe experiments on two material systems of different nature:

(1) Since the discovery of the insulator-metal transition in vanadium dioxide (VO_2) at $T_C \approx 340$ K it is highly debated whether a Mott or a Peierls mechanism causes the insulating band gap. We addressed this question by following the femtosecond electron dynamics in the gap region after laser pulse excitation using time-resolved photoelectron spectroscopy. We find a quasi-instantaneous collapse of the insulating band gap which suggests strong electron correlations as its cause[1]. In order to identify the microscopic mechanism we performed first-principles many-body perturbation theory calculations. After a charge redistribution simulating the laser excitation, the calculations reveal a massively enhanced Coulomb screening mainly due to localized V 3*d* photoholes. The screening effect fully closes the band gap without the need of ionic motion evidencing the pivotal role of electron correlations in the PIPT of VO_2.

(2) At $T_C \approx 328$ K, the ternary chalcogenide Ta_2NiSe_5 (TNS) is suspected to undergo a transition to the theoretically predicted EI phase, but an experimental proof is yet missing. Also at T_C, a structural phase transition takes place, consistent with the emerging EI phase. We identify several phonon modes, especially a 4 THz mode characteristic of the EI phase, using temperature-dependent Raman scattering and time-resolved all-optical pump-probe techniques. We observe a saturation threshold of the photoinduced response at very low excitation densities. Also the lifetime of the 4 THz phonon strongly decreases and saturates at the same threshold. Time-resolved photoelectron spectroscopy of the occupied and unoccupied band structure proofs that this saturation is due to a complete bleaching of pump pulse absorption at the top valence band. Our findings *do not* show any sign of a photoinduced melting of the low-temperature phase band gap. Instead, TNS appears to protect itself from a PIPT through the absorption bleaching at higher excitation densities.

The discussed cases exemplify the diversity of PIPT and represent two limiting cases: the phase transition in VO_2 can be successfully triggered by photoexcitation while a PIPT in TNS seems to be hindered by absorption bleaching.

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CDW Formation and Dimensionality in Quasi-one Dimensional Metal Wires Probed by ARPES

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Electrons confined to low dimensions display a wide variety of phenomena resulting from enhanced electronic interactions and quantum effects which can be probed directly by angle resolved photoemission (ARPES) to gain access to many-body interactions and correlations via the single particle spectral function.

$NbSe_3$ is one of the few materials that exhibits all the ingredients of a charge density wave (CDW) and its transport and diffraction results serve as a benchmark[1]. However $NbSe_3$ is extremely challenging to work with, as single crystals grow as fragile micro-ribbons and thus very few studies of the electronic structure exist. We have performed detailed high energy resolution ARPES measurements, including Fermi surface mapping, in order to address a number of outstanding issues. We present the first detailed temperature dependence of this material and show that a pseudo-gap gradually develops at the Fermi level around 200K, which exhibits a power law dependence; one of the ingredients of Luttinger-Liquid behaviour. In addition, we find two band gap openings due to the CDW formation resolving the origin of the anomalous dispersion[2]. The CDW wave vectors are found not to match the quasi-one dimensional Fermi surface implying that CDW formation in $NbSe_3$ is not driven by a nesting mechanism but rather originates from a structural transition.

Self-assembled metal nanowires on semiconducting substrates are an important model system for low-dimensional materials providing versatile and tuneable environment. We apply ARPES to the Ag/Si(557) nanowire system (at a coverage of 1ML), which exhibits signatures of a quasi-1D electron gas in electron energy loss spectra [3]. Doping by Ag or residual gas induces 2D metallic states at the Fermi level, which appear to obey the super-periodicity imposed by the terrace/step edge structure perpendicular to the wire direction. Evidence of a super-periodicity along the wires is also found. By considering the electronic coherence length we reconcile the seemingly conflicting views of the dimensionality in this and other nanowire systems probed by photoemission spectroscopy, and the dispersion of collective excitations as detected by electron energy loss spectroscopy (EELS).

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Ultrafast Dynamics of Correlated Materials Probed by Time-resolved HHG-based ARPES

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Many-body effects can lead to rich phase diagrams in correlated materials. The underlying interactions and elementary excitations imply characteristic timescales for relaxation dynamics back to equilibrium if the system is perturbed on an ultrashort timescale. Combining the energy and momentum resolution of angle-resolved photo emission (ARPES) at XUV photon energies with ultrafast time resolution via high harmonic generation (HHG) provides access to the relevant parts of the electronic band structure involved in ultrafast laser-driven phase transitions and to the natural timescales of relaxation processes.

The nature of the charge density wave (CDW) transition in $TiSe_2$ – a layered transition metal dichalcogenide – has remained elusive, although recent work hinted at an excitonic insulator driven phase.[1,2] Here, we unravel the specific mechanism of the charge density wave instability in $TiSe_2$ by using time-resolved XUV ARPES at the Artemis facility[b] and focussing on the high-temperature fluctuation regime, which precedes the CDW instability. Our observations suggest that the momentum- and energy-resolved relaxation times reveal the material's self-energy[3] and that the screened Coulomb-mediated electron-hole interaction between the valence and conduction bands is the dominant mechanism leading to the CDW instability of $TiSe_2$.

As a textbook example of a spin density wave (SDW) transition, we have studied chromium – an antiferromagnet based on the pairing of itinerant electron and hole states with opposite spins around the Fermi level.[4] Using HHG-based ARPES[c] we unravel the evolution of the band structure in thin epitaxial Cr films after laser excitation and probe the excitation and recovery of the SDW ordering. We disentangle non-equilibrium chemical potential contributions to the dynamics of the band structure from those intrinsic to the phase transition. This enables us to track the order parameter through the ultrafast phase transition, and reveal that it follows the non-equilibrium electronic temperature. This is consistent with the purely electronic driven nature of the SDW formation in contrast to CDWs.

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Development of an Ultrafast 500 kHz XUV Source

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Ultrashort laser pulses are invaluable tools for the investigation of photo-induced processes in matter. In particular, time- and angle-resolved photoemission spectroscopy (trARPES) reveals electronic coupling, scattering and correlation effects by gaining access to the temporal evolution of the out-of-equilibrium electronic structure on the femtosecond time scale. While high harmonic generation (HHG)-based extreme ultraviolet (XUV) sources provide access to the electronic structure in the entire Brillouin zone in photoemission experiments, the laser intensities required for driving HHG so far has limited the repetition rate of these light sources to 10 kHz.

We advance this approach through a novel high-average power ultrashort laser system capable of generating spectrally narrow XUV pulses with 500 kHz repetition rate for trARPES. The key component of this approach is an optical parametric chirped-pulse amplifier (OPCPA), which provides intense ultrashort pulses, tunable both in wavelength (700-900 nm) and in bandwidth (50 - 300 nm)[1]. Up to 15 W of output power (30 µJ pulse energy) are used for HHG. In the XUV generation process, the single-atom yield scales with respect to the driver wavelength approximately with λ^{-5}. In order to exploit this favourable effect, the wavelength of the source is up-converted to 400 nm by second harmonic generation in a vacuum chamber. The resulting sub-30 fs near-UV pulses are tightly focused in a 150 µm diameter nozzle connected to a Krypton gas line. A plateau harmonic at 21.7 eV with 100 meV bandwidth is selected by a combination of XUV multilayer mirror and thin foil metal filters. An intensity contrast between the selected and neighbouring harmonics exceeding 100:1 is achieved. A photon flux on the sample $>10^{10}$ ph/s is expected. Up to now, trARPES is either based on high repetition rate femtosecond UV sources or low-repetition rate XUV sources. The reported XUV light source closes this technology gap.

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Femtosecond Low-energy Electrons Probing Currents and Atomic Structure in Nanomaterials

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We report a novel concept for femtosecond point-projection microscopy (fsPPM) and femtosecond low-energy electron diffraction (fsLEED) utilizing laser-triggered electron emission from metal nanotips as pulsed electron source, delivering either divergent or collimated femtosecond electron wave packets in the sub-kV energy range[1]. Due to the large scattering cross-section of low-energy electrons and their high sensitivity to electric fields, our hybrid approach is ideally suited to probe ultrafast currents and electric fields in nanoobjects as well as atomic structure in low-dimensional materials with femtosecond time resolution.

Using fsPPM, we investigate femtosecond currents in axially p-i-n doped Indium Phosphide nanowires (NWs) with few tens of nanometer spatial resolution[2]. We image the local electric field distributions along the NW surface and map the transient change of the projected NW diameter upon laser excitation. We measure fast initial, spatially inhomogeneous changes in the projected NW diameter after photoexcitation with different femtosecond rise times for the p- and n-doped segment, respectively. The observed effect can be explained by radial separation of photoexcited charge carriers due to surface electric fields, leading to radial photocurrents. Quantitative information can be obtained by comparison with numerical simulations. With these proof-of-principle experiments, we demonstrate that fsPPM is a sensitive tool for the investigation of photoinduced currents in nanoobjects.

The capability of our setup to study ultrafast structural dynamics in low-dimensional systems is demonstrated by probing the atomic structure of free-standing monolayer graphene[2]. Our electron gun design allows propagation distances of the collimated electron beam down to the 100 µm range, minimizing temporal broadening to the 100 fs range and thus facilitating real-time measurements on structural dynamics in monolayer 2D materials.

We further realize plasmon-driven sub-10 femtosecond electron emission from a gold nanotip as novel femtosecond electron point source. Electron emission is triggered by the optical near field at the tip apex after laser excitation and subsequent nanofocusing of a surface plasmon polariton[3]. Due to the remote laser illumination 20 µm away from the tip apex, this conceptually new electron source will significantly improve the temporal and spatial resolution in fsPPM, and will allow for performing femtosecond low-energy electron holography.

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Time-domain Separation of Optical Properties from Structural Transitions in Phase Change Materials

Lutz Waldecker, Roman Bertoni, Timothy Miller[a], Simon Wall[a], and Ralph Ernstorfer

Phase change materials, such as $Ge_2Sb_2Te_5$ (GST), have several metastable amorphous and crystalline phases at room temperature with vastly different optical and electronic properties. The fast and reversible optically-induced switching between those states has found numerous applications in modern data storage technology. Despite the extensive research on tuning material properties for applications, many aspects of the microscopic origin of the optical contrast and the ultrafast response to femtosecond light pulses are still subject to debate. Specifically, the existence of predicted non-thermal pathways for ultrafast amorphisation remained an open question[1].

We investigate the evolution of optical and structural properties of crystalline GST upon excitation with a femtosecond laser pulse by applying two complementary pump-probe techniques[2]. We follow the transient optical properties by femtosecond optical spectroscopy and directly probe the response of the lattice with time-resolved electron diffraction.

We excite the material below and above the threshold for inducing the structural phase transition. At low excitations, we observe large and quasi-immediate changes in the optical properties, which are independent of the dynamics of the lattice. The lattice heats by incoherent scattering processes on the few-picosecond timescale. Above the switching threshold, we use single-shot optical and diffraction measurements to follow the transient properties of GST during the phase transition. In the initial optical response, we observe a saturation in the photo-induced change when crossing the fluence for permanent switching. In earlier work, this has been attributed to an ultrafast phase transition[3] or non-thermal melting[4], respectively. We show that the contrast in the early optical response is purely related to electronic excitation and melting of the material only takes place on a few-picosecond timescale.

Our experiments reveal a transient state exhibiting up to 30% change in the dielectric function with preserved crystalline long-range order. The pronounced changes of the optical properties are assigned to photo-induced depopulation of resonantly bonded electrons exhibiting large polarizability.

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Electron-lattice Interactions in Transition Metal Dichalcogenides, Clusters and Bulk Materials

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Fundamental aspects of the electron-lattice interaction in crystalline materials are investigated with time-resolved electron diffraction[1]. This technique gives access to the energy redistribution from optically excited electrons to the lattice via the emission of phonons. We investigate basic aspects of electron-phonon coupling in materials of varying dimensionality ranging from bulk crystals to clusters.

First, we present a combined experimental-theoretical study of electron-phonon coupling in the free-electron metal aluminium[2]. As first principles calculations reveal a phonon-branch dependence of the electron-phonon coupling, we propose a non-thermal lattice model describing the energy transfer between electronic and vibrational degrees of freedom in non-equilibrium states. This model allows for non-thermal phonon distributions, beyond the widely applied two-temperature model.

Transition metal dichalcogenides (TMDC), made of covalently bound single-crystalline layers of transition metal atoms sandwiched by two planes of group VI elements and van der Waals interlayer interaction, offer fascinating properties rendering possible new concepts for optoelectronic, spintronic or valleytronic devices[3]. The strong structural anisotropy results in quasi-two-dimensional electronic wave functions located at the corners of the Brillouin zone. At these particular points, semiconducting TMDCs exhibit pronounced excitonic effects. We use time-resolved diffraction to investigate the interaction between excitons and the lattice. Employing optical spectroscopy, we show that optical pumping in resonance with the excitonic band leads to the emission of optical phonons related to a fully symmetric vibrational mode, indicating strong exciton-lattice coupling.

Finally, we discuss structural dynamics of Au nanoclusters synthesized with a very precise structure and number of atoms[4]. In such ‘magic clusters’, where the translational symmetry spans over few unit cells only, the Bloch description of electrons and phonons breaks down and their electronic, vibrational and optical properties acquire more molecular-like characteristics[5]. The effect of such strong spatial confinement in the electron-phonon coupling mechanism is a demanding and still open question that we aim to resolve experimentally through time-resolved electron diffraction.

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Ultrafast Charge Currents at the Surface of the Topological Insulator Bi_2Se_3

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and Tobias Kampfrath

Topological insulators (TIs) are new class of matter, exhibiting an insulating bulk but gapless (metallic) surface states protected by time-reversal symmetry. In this project, we aim at gaining insight into elementary processes of ultrafast charge transport on the surface of the model TI Bi_2Se_3. As electron scattering processes occur on a femtosecond time scale, we make use of ultrashort laser pulses to launch and detect transport. Recent work[1,2] has indicated that optical excitation of TIs can induce surface currents, but the time resolution was no better than 300 fs.

To resolve the initial, ultrafast steps of photocurrent relaxation, we excite n-doped Bi_2Se_3 crystals (Fermi energy at 300 meV above bulk conduction band minimum) with a laser pulse as short as 20 fs (center photon energy 1.5 eV). The resulting photocurrent gives rise to the emission of an extremely broadband terahertz (THz) electromagnetic pulse (1 to 30 THz) whose transient electric field is detected by means of electrooptic sampling[3]. We have developed a method that allows us to extract the transient current $j(t)$ from the measured field $E(t)$. The AC photocurrents are found to be dominated by shift currents[4] (due to the optically induced shift of electron density along the Se-Bi bonds) and drift currents (driven by the space-charge field along the surface normal). Our findings render previously suggested scenarios[1] of photocurrent generation in TIs unlikely.

To determine the extent to which the observed shift current is localized at the TI surface, we study the temporal development of THz emission from a freshly cleaved TI sample over a time interval of 2 h. Our data strongly indicate that the shift current is generated in a surface layer with a thickness as small as 3 nm.

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Ultrafast Spin-lattice Coupling in a Model Ferromagnetic Insulator

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Michael Gensch[c], Peter M. Oppeneer[b], Martin Wolf, and Tobias Kampfrath

Terahertz (THz) spectroscopy is routinely used to investigate electron and phonon dynamics in numerous physical systems. So far, however, only a minor part of THz work has focused on the manipulation of magnetic systems. In this study, we use intense THz pulses to investigate how fast the magnetization of a spin-ordered solid can be quenched by resonantly exciting the crystal lattice. The remarkable attention to this general question not only arises from application potential in future magnetic data storage technology, but also from the fundamental interest to unveil the interaction mechanisms of spins with the lattice and electron degrees of freedom.

Since the first discovery of ultrafast demagnetization two decades ago[1], in most studies, ultrashort optical pulses have been used to induce a non-equilibrium distribution of hot electrons in a metallic ferro- or ferrimagnet. In all cases, a subsequent reduction of the magnetization on a sub-picosecond time scale has been observed, yet the underlying complex interaction processes of spins, electrons and lattice are still controversially debated.

Here, we make an attempt to reduce the complexity of previous studies by pumping selectively few optical phonon (lattice) modes of an insulator in which the electron orbital degrees of freedom are frozen out. More precisely, we resonantly excite the high-frequency oxygen-iron phonon modes (at ~19 THz) of the insulating ferrimagnet $Y_3Fe_5O_{12}$ (YIG) using intense THz pump pulses (fluence of ~50 mJ/cm^2, duration of ~150 fs). As the pump photon energy (80 meV) is much smaller than the electronic band gap (2.85 eV), such pumping enables the exclusive excitation of phonons, while leaving the electrons unaffected in their ground state. A subsequent weak probe pulse (duration of 8 fs, photon energy of 1.6 eV) interrogates the transient magnetization change by means of Faraday rotation and ellipticity, on multiple time scales ranging from tens of femtoseconds to hundreds of microseconds.

We find an unexpectedly fast quenching of the magnetization with a time constant as short as (1.2±0.2) ps. The resulting magnetization quenching of ~1% persists over a timescale of 1 µs. Given the long spin-lattice relaxation times in YIG (nanoseconds to microseconds)[2], the observation of such fast phonon-driven demagnetization process is highly surprising, and indicates a highly efficient energy transfer between certain optical phonon- and magnon-modes. Supported by ab initio calculations, we present a new microscopic mechanism of spin-lattice coupling and the dynamics observed. These results reveal THz-pulse-driven phonon modes as a novel and efficient pathway to manipulate and possibly control the spin degree of freedom.

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Probing and Tailoring of Spin Transport in Magnetic Metals at Terahertz Frequencies

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Spin-orbit interaction (SOI) is a fundamental interaction in condensed matter and of central importance for future spin-based electronics (spintronics) because it permits, for example, the conversion of charge currents into spin currents and vice versa. It is highly interesting to study SOI-based effects at terahertz (THz) frequencies for applied and fundamental reasons. First, to be competitive with circuitry based on the electron charge as information carrier, spintronic devices should operate as fast as possible, eventually at THz rates. Second, the THz photon energy (4 meV at 1 THz) is comparable to the SOI energy in many magnetically ordered solids, thereby potentially making THz radiation a sensitive probe of SOI.

Here, we use two complementary approaches to address the interplay of SOI, electron and spin transport at THz frequencies. In the first scheme, we employ broadband THz time-domain ellipsometry[1] to measure the complex conductivity tensor of various magnetic metals from 1 to 40 THz. Our results show that the anomalous Hall effect is operative also at THz frequencies. Supported by *ab initio* calculations[2], we discuss the spectral dependence of the anomalous Hall angle in terms of SOI.

In a second experiment, we use femtosecond laser pulses (800 nm, 10 fs, 2 nJ) to launch ultrafast spin currents in magnetic heterostructures whose dynamics is monitored by taking advantage of the inverse spin Hall effect and broadband THz emission spectroscopy[3]. By tuning various sample parameters, we have built THz emitters that provide gapless emission from 1 to 15 THz, thereby outperforming standard emitters such as ZnTe in terms of bandwidth while having comparable or even better conversion efficiency.

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Excitation and Propagation of Spin Currents in Fe/Au/Fe/MgO(001): Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescale

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Ultrafast spin dynamics is the key for development of data storage and spintronics devices. Of particular interest is the development of generation, control, and monitoring techniques for ultrashort spin current (SC) pulses[1] and the study of their subsequent spin transfer torque (STT) action on a ferromagnet (FM). The later is a promising and elegant way to excite magnetization dynamics: when spin-polarized hot carriers (HC) reach FM layer, the magnetization experiences a torque and starts moving out of the equilibrium. SC can be produced by temperature gradients in a bulk of FM metal[2] or across interfaces to normal metal[3], which is known as the spin Seebeck effect. Here we demonstrate the ultrafast spin Seebeck effect based on spin-dependent interface transmission for non-equilibrium HC. With *ab initio* calculations, we show that the transmission of Fe/Au interface for majority electrons is much larger than for the other HC, which provides a spin flux from Fe to Au forming a pulse of superdiffusive SC. The SC pulse duration is determined by the HC thermalization time on the order of 200 fs: once the HC relax towards the Fermi level the transmission difference vanishes and the HC emission stops.

We excite non-equilibrium HC in a top 16 nm-thick Fe layer of a Fe/Au/Fe/MgO(001) structure by 14 fs-long 800 nm laser pulse and monitor the SC with the second harmonic generation (SHG) in a back pump-front probe scheme[1] developing a technique to pick up the SHG contribution which is directly proportional to the SC. We demonstrate the generation of about 300 fs-long SC pulses characterizing their shape after passing the 55 nm-thick Au layer and study the SC reflection from the Au/Fe interface to the 15 nm-thick bottom Fe layer. In particular, we show that the SC polarized orthogonally to the Fe magnetization **M** looses the orthogonal component upon the reflection and becomes polarized anti-parallel to **M**, which indicates the quantum-mechanical origin of spin transmission/reflection. With the magneto-optical Kerr effect, we monitor subsequent picosecond precessional dynamics of **M** excited in the second Fe layer by the STT. We show that owing to a spatially non-uniform STT, on top of the uniform precession[4], several lowest standing spin wave modes can be excited. Spectral analysis of the excited modes allows for an estimation of the spin accumulation depth in Fe $\lambda < 4$ nm.

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Aligning Polar Molecules in Liquids by Strong THz Electric Field Pulses

Mohsen Sajadi, Martin Wolf, and Tobias Kampfrath

Controlling the alignment or orientation of molecules in liquids is important in many chemical reactions. Usually, optical laser pulses are employed for ultrafast alignment, and the torque required is mediated by the electrons of the molecule which rectify the rapidly (~400 THz) oscillating laser field. However, alignment can also be achieved by static electric fields acting on the permanent dipole moments of polar molecules. In an attempt to engage both electronic and nuclear degrees of freedom for molecular alignment in liquids, we use intense THz fields, oscillating much slower than optical fields yet still being shorter than the relaxation dynamics of the liquids.

In our comparative experiments, we apply intense pulses at ~1 THz (field strength >2 MV/cm) to various liquids and probe their impact by measuring the transient optical birefringence of the sample. As a comparison to this so-called THz Kerr effect (TKE)[1], we also measure the optical Kerr effect (OKE) by pumping the sample with optical laser pulses (wavelength 800 nm). We compare the transient birefringence of three liquids, namely nonpolar toluene and the polar liquids dimethyl sulfoxide (DMSO) and chloroform.

Interestingly, apart from amplitude differences, both optical (OKE) and THz excitation (TKE) cause identical time-dependent signals once the pump pulse has left the sample. For toluene, this nuclear relaxation dynamics has even identical amplitude (normalized to the pump intensity) because in both cases, torques applied to the molecules originate solely from the induced electronic dipole moments. In sharp contrast to toluene, the TKE signals from the polar liquids DMSO and chloroform are either enhanced (DMSO) or reduced (chloroform) as compared to the OKE data. This difference is assigned to the different torques caused by THz fields (which can couple to both the permanent molecular dipole moment and the induced electronic dipole moment) and optical radiation (which couples only through the electronic polarizability). Note that the electronic polarizability anisotropy of DMSO and chloroform has opposite sign, consistent with the, respectively, enhanced and reduced TKE signals found in these liquids. The enhancement/reduction of the relaxation tail in TKE signals can also be explained semi-quantitatively using a simple perturbative model.[2]

Our study can be considered a primary step toward alignment of relatively large solute molecules in solution.

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Probing Molecular Structure, Dynamics and Thermodynamics at the Air/Water Interface

Yujin Tong and R. Kramer Campen

Gaining experimental molecular-level insight into the air/water interface is important both because of its environmental ubiquity and because of the potential insight such understanding affords into hydrophobic solvation more generally. Moreover, recent work has just begun to clarify that solutes at the air/water interface may have dramatically different reactivity and structure than in bulk water (*e.g.* both the molecular forms of HCl and HNO_3 are predicted to be stable at the air/water interface[1]). Clearly molecular-scale probes of both water and solute structure, and their relationship, would be useful.

From the water structure perspective, creating an air/water interface requires termination of bulk water's hydrogen bond network without possibility of forming new hydrogen bonds with the adjoining phase. To link this termination of the bulk network to interfacial properties we require a probe of intermolecular interactions in interfacial water. Here we characterize, for the first time, the highest frequency of water's intermolecular modes, the libration, using the interface-specific technique vibrational sum frequency (VSF) spectroscopy. The frequency of the libration, *i.e.* the stiffness of the rotational potential, of interfacial water is strongly blue-shifted relative to bulk liquid water and resembles that in ice. Evidently from this perspective, although not from many others[2], interfacial water is *ice-like*.

From the solute structure perspective we show, using VSF spectroscopy to probe Cl-O modes in perchlorate, that (a) ClO_4^- is interface active (b) it adsorbs to the air/water interface with a free energy of 2.2 kJ/mol (c) in solutions of perchloric acid it forms an ion pair (intermediate between molecular and dissociated acid) at concentrations > 10x lower than those at which such pairing is observed in bulk water. The accurate description of such interface induced ion pairing seems likely to be significant in understanding phenomena from the Hofmeister series, to the reactivity of this anion in atmospheric and electrochemistry.

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Characterizing Elementary Processes at Electrochemical Interfaces

Yujin Tong, Francois Lapointe, Martin Wolf, and R. Kramer Campen

Many important devices, *e.g.* batteries, solar cells, reactors for hydrocarbon conversion, rely on chemistry that occurs at electrified solid/liquid electrochemical interfaces. Optimizing this chemistry requires insight into the relevant reaction mechanisms. However, characterizing reaction mechanisms at the electrified metal/liquid interface is challenging for, at least, two reasons: a lack of methods capable of probing molecular species that simultaneously exist at the interface and in much larger concentrations in the adjoining liquid, and a lack of detailed knowledge describing species that exist only transiently (on picosecond timescales) following electron transfer to/from the solid.

Here we address these challenges by employing the laser-based, interface-specific nonlinear optical technique, vibrational sum frequency (VSF) spectroscopy in two experiments. Firstly, we show that by constructing an appropriate thin film cell we can monitor interfacial species on the Pt(100) surface during the electrooxidation of formic acid in water. This ability to quantitatively correlate voltammetry and interface-specific spectroscopy allows us to identify, previously unobserved, weakly adsorbed formic acid at the metal surface and understand how its population relates to the oxidation reaction[1]. Secondly in a UV pump / VSF probe experiment we directly probe optically induced electron transfer from a gold electrode to the electrolyte solution and the resulting short lived radical species.

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Understanding how Water Interacts with α-Al_2O_3(0001)

Harald Kirsch, Jonas Wirth[a], Yanhua Yue, Yujin Tong, Martin Wolf, Peter Saalfrank[a],
and R. Kramer Campen

α-Al_2O_3 surfaces are ubiquitous in engineered applications and useful models for environmentally common aluminosilicate surfaces. The properties of these surfaces – e.g. their conductivity, reactivity, and structure – are strongly influenced by the presence of even small amounts of water. Experimentally characterizing water/α-Al_2O_3 interaction is challenging because the problem is inherently multi-scale: while the thermodynamics and kinetics of a single water molecule interacting with an α-Al_2O_3 surface are important, the macroscopic properties of liquid water/α-Al_2O_3 interfaces cannot be recovered by adding single molecule effects. To overcome this problem experimental tools that characterize interfacial water, and α-Al_2O_3 surface, structure and dynamics over $> 10^{10}$ mbar in water pressure are required. We here address this problem for the most thermodynamically stable α-Alumina surface, the α-Al_2O_3(0001), using all-optical, interface-specific vibrational spectroscopy, vibrational sum frequency (VSF) spectroscopy, in three types of experiments.

(1) We characterize unimolecular water dissociation pathways via the OD (of D_2O) spectral response at submonolayer water coverages in UHV. In so doing we provide the first experimental evidence for theoretically predicted unimolecular dissociative adsorption pathways and constrain the kinetics of the interconversion of the resulting surface species.[1] (2) We characterize the structure of the α-Al_2O_3(0001) surface in ambient air by optically probing surface phonons. These results demonstrate a novel probe of surface structure applicable to solid surfaces outside of UHV and the characterization of oxide surface chemistry from the perspective of the solid.[2] (3) We characterizing water structure at the α-Al_2O_3(0001) / liquid water interface by probing the vibrational relaxation dynamics of surface hydroxyls with interfacial specificity (in an IR pump / VSF probe scheme). This work demonstrates that interfacial water at the α-Al_2O_3(0001)/liquid water interface is *hydrophobic*: it interacts only very weakly with bulk liquid.

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Graphene: Functionalization and Interface Effects

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The storm of activities concerning graphene, has changed and widened to include a large range of 2D materials which, when thinned down to the monolayer or few layer regime, exhibit similarly unusual properties. The combinations of stacked monolayers of these materials may open a new field of electronics. Even though large scale practical applications of graphene are still only just emerging, functionalization of graphene by adsorbates, and the effect of interfaces remain a challenging field of study. Hydrogenated graphene ("graphane") has been examined as a derivative with the desired fundamental band gap, but the structural order does not extend beyond a few C-C bond distances. Here we show that fluorination of graphene grown epitaxially on SiC(0001) leads to highly ordered fluorine-carbon bonds on a single side of graphene, and this material has a large band gap. Moreover, exposure to extreme ultraviolet photons induces a metastable phase with a much smaller band gap. This phase reverts to the stable phase under (thermoluminescent) emission of blue light; in both phases, the density of states vanishes at the Fermi level[1].

Molecular adsorption may also lead to functionalization; we show, for example, that an oxidized graphene sheet is formed by NO_2 or SO_2 adsorption and subsequent photodissociation. Adsorption on graphene grown on Ir(111) leads to a strong rehybridization of the unoccupied π^* states and the appearance of new features in the C 1s core level line. This is a reversible process, such that pristine graphene can be recovered by thermal treatment. The formation of oxidized graphene by NO_2 is sensitive to the photon flux, resulting in an intermediate phase of oxidized graphene[2]. These processes may provide an interesting pathway towards lithographic patterning in graphene.

Metals can be roughly grouped according to the impact they have on the electronic structure of graphene. Copper is a special case since the metal bands have sharp signatures in photoemission; hence the interaction with the graphene bands can be examined in great detail. Through a comparison with DFT calculations we arrive at a complete picture of band gap opening on the basis of hybridization between each d band and the graphene π band[3]. Using x-ray magnetic circular dichroism, we study an interesting case of graphene-ferromagnet interaction, i.e. emerging ferromagnetism in thin cobalt films intercalated between graphene and Ir(111). Magnetic ordering appears beyond monolayer coverage, and the orientation of the magnetic moment is out-of-plane. This moment is partly transferred onto the graphene π states, inducing an antiparallel moment compared to that of the cobalt layer[4].

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Precise Control of Intramolecular H-atom Transfer by Using Scanning Probe Microscopy

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H-atom or proton dynamics are related to a wide range of chemical and biological processes. Intramolecular H-atom transfer (tautomerization) provides a unique opportunity to study the fundamental mechanism, and it is also directly related to chromism and enzymatic reactions. More recently, tautomerization has gained increasing attention in nanoscale science and technology because the process resembles molecular switching. Accordingly, tautomerization of phthalocyanine and porphyrin derivatives has been investigated by using low-temperature STM[1,2]. However, the impact of the local enviroment of a molecule, which may strongly affect molecular processes, remains imperfectly understood. To provide microscopic insight, we have studied tautomerization of porphycene by using low-temperature STM and nc-AFM. Because of relatively strong H-bonds in the molecular cavity, porphycene is an intriguing model system to examine H-bond dynamics.

We present the direct observation and precise control of tautomerization of a single porphycene molecule on Cu(110). Porphycene molecules adsorb in the *cis* tautomer on the surface and the reversible *cis* ↔ cis tautomerization can be induced either by thermal activation, or STM-excitation[1]. Remarkably, the tautomerization behavior can be precisely controlled either by placing a single Cu atom nearby a molecule, or by changing the tautomeric state of neighboring molecules in one-dimensional oligomers[2]. Furthermore, it was found that the tautomerization occurs when approaching the tip towards a molecule even without energetic tunneling electrons. We measured the interaction between the tip apex and molecule during this atomic-force-induced process by using nc-AFM. The force curves measured over a molecule show submolecular spatial resolution and the tautomerization can be precisely controlled by the tip position during approach. The mechanism is rationalized by anharmonic coupling between the force induced molecular distortion and tautomerization coordinates through the H-bond. These findings highlight the impact of the local surroundings on a molecular process and demonstrate the potential to precisely control single-molecule switching by environmental modifications on the atomic scale.

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Direct Observation of Photo-induced Intramolecular H-atom Transfer on Cu(111)

Hannes Böckmann, Shuyi Liu, Leonhard Grill[a], Martin Wolf, and Takashi Kumagai

Photo-induced hydrogen transfer plays a crucial role in several important chemical and biological processes, and a variety of experimental and theoretical studies have been devoted to unveil the fundamental mechanism[1]. However, the transfer dynamics remain imperfectly understood at the single-molecule level. The intramolecular H-atom transfer (tautomerization) provides a unique opportunity to investigate the elementary steps. Furthermore, tautomerization of single molecules has attracted increasing attention in nano science, due to the possible applicability for molecular switching devices[2,3]. In our group, tautomerization within a single porphycene molecule, which is a structural isomer of free-base porphyrin, has been studied by using low-temperature STM[4]. The intramolecular H-bond in the molecular cavity makes porphycene an intriguing model system to explore H-bond dynamics.

We present the direct observation of photo-induced tautomerization of porphycene molecules on a Cu(111) surface by using a combination of low-temperature STM and laser excitation ranging from the UV to NIR region. Porphycene molecules adsorb on the surface as isolated monomers in the thermodynamically stable *trans* state which can be unidirectionally converted to the metastable *cis* tautomer by laser excitation. The wavelength dependence of the tautomerization cross-section shows a clear onset at about 2 eV and a maximum of $\sim 3\times10^{-19}$ cm^2. It is found that the spectral features are correlated with the electronic structure of the molecule covered substrate, which was measured using UPS. This result suggests that a hot hole transfer from the substrate to the molecule triggers the tautomerization, and the onset of the spectral feature corresponds to the *d–sp* interband excitation threshold. Our approach enables us to directly observe the photo-induced tautomerization within a single molecule and provides microscopic insight into the excitation mechanism. Additionally, the efficiency of this switching process is found to be exceptionally high, while the molecule can retain its molecular frame upon switching, making this system a promising building block for molecular devices.

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Tip-Enhanced Raman Spectroscopy of Graphene Nanoribbon on Au(111)

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Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level[1]. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces[2,3]. TERS could therefore provide unique and heretofore unprecedented insight on the adsorbate reactions o at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well-defined surface sites and as well as monitoring vibrational spectra to provide bond specific information about the reaction.

We investigated tip-enhanced Raman spectroscopy of graphene nanoribbons (GNRs) fabricated on Au(111) by on-surface polymerization technique under ultra-high vacuum conditions[4]. The 0.74 nm wide armchair GNRs are directly observed by scanning tunneling microscopy at room temperature and the characteristic vibration modes of GNRs appear in both, the far- and near-field (tip-enhanced) Raman spectra. The Raman scattering is enhanced by up to 4×10^5 in the near-field, while a strong intensity fluctuation (blinking) frequently emerges in the time series of the near-field spectra. From the STM observation of a stable adsorption structure of GNRs under the laser illumination and statistical analysis of the intensity fluctuation we attribute the origin predominantly to thermal fluctuations of the effective radius of the Au tip apex that induces the localized plasmonic field. The intensity distribution is qualitatively reproduced with a simple theoretical model in which the tip apex is approximated by ideal metal sphere.

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Hydrodynamic Collective Effects of Active Proteins in Water Solutions and in Biological Membranes

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Diffusion of particles in the interior of biological cells is known to strongly depend on ATP supply[1,2]. So far, this has been interpreted as an effect of non-equilibrium fluctuations in active gels formed by actin filaments and myosin motors in the cell. Recent *in vivo* diffusion measurements[2] of microinjected submicron tracers within biological cells in the group of D. Weitz in the Harvard University show however that this explanation is not sufficient: The diffusion coefficient is reduced by only about 10% if the activity of myosin motors is chemically inhibited, but ATP supply is maintained. However, the diffusion is dropping down below the measurement limit when ATP supply is stopped. Moreover, substantial diffusion dependence on substrate supply has recently been observed[3] *in vitro* in the experiments with water solutions of some enzymes, in absence of any molecular motors characteristic for a living cell. This suggests that a different, and general, mechanism is involved.

Not only molecular motors, but many other active proteins in a biological cell (including various protein machines and most of enzymes) are repeatedly changing their shapes in each ATP hydrolysis or catalytic turnover cycle. As we show[4], all such active proteins behave as oscillating force dipoles, giving rise to strong non-thermal hydrodynamic fluctuations in the solvent. Stochastic advection in such fluctuating flows leads to diffusion enhancement and this is enough to explain the observed effects. Additionally, directed drift of particles in gradients of protein concentration or of ATP supply should take place.

Similar effects are predicted for active protein inclusions in bio membranes. On sub micrometer length scales, lipid bilayers are known to behave as two-dimensional fluids. Hydrodynamic interactions in 2D systems are however ultra-long ranged and this leads to pronounced differences as compared to the 3D case. Most importantly, the effects become non-local, so that diffusion enhancement and drift are determined collectively by all active proteins and by their spatial distribution over the entire membrane.

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Theory Department

Poster List

Recent work done in the Theory Department is displayed on 22 posters. For this book we selected 17 poster abstracts, but kept the numbering of the full display.

All posters are displayed in building T and the poster site is given below.

The superscript^{ERC} marks the work of A. Tkatchenko’s ERC group.

Poster Site	*Poster Title and Authors*
New Concepts, Methods, and Techniques	
TH 1	**Kohn-Sham Approach to Quantum Electrodynamics** Johannes Flick, Christian Schäfer, Camilla Pellegrini, Heiko Appel, Michael Ruggenthaler, Ilya V. Tokatly, and Angel Rubio
TH 3	**Time-Evolution of Tensor Networks in Quantum Electrodynamics** Teresa Reinhard, Wilhelm Bender, Heiko Appel, and Angel Rubio
TH 4	**Correlation Consistent Basis Sets and Explicitely Correlated Wavefunctions in a Numerical Atom-Centered Framework** Salih Akbudak, Arvid C. Ihrig, Volker Blum, Patrick Rinke, Igor Ying Zhang, and Matthias Scheffler
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Kohn-Sham Approach to Quantum Electrodynamics

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Time-dependent density-functional theory (TDDFT) has been successfully applied to a large variety of problems, such as calculations of absorption spectra, excitation energies, or dynamics in strong laser fields. On the other side, many-body perturbation theory (MBPT) opens the possibility to construct approximations to every desired order of a 'weak' interacting system. Here, the drawback is an in general non-local interaction in space and time, and it is therefore a demanding task to apply it to 'real' systems. In the framework of quantum electrodynamics (QED), we have recently generalized TDDFT to also describe electron-photon systems (QED-TDDFT)[1,2]. In this approach matter and light are treated on an equal quantized footing.

The optimized effective potential (OEP), derived by inversion of the Sham-Schlüter equation, is a natural connection between local density functional theory and MBPT. In principle, this variationally best local potential reduces the problem to solving a simple system of Kohn-Sham equations combined with the solution of the OEP integral equation. However, converging the full set of OEP equations is quite challenging and is in practice rarely tackled. The Krieger-Li-Iafrate (KLI) approximation reduces the integral equation to an analytically solvable one via a dominant orbital approximation.

In this work, we present the first numerical calculations in the framework of QED-TDDFT. We show exact solutions for fully quantized prototype systems placed in optical high-Q cavities and coupled to quantized electromagnetic modes, both for model systems heavily used in Quantum Optics, as well as for 1D soft-Coulomb systems in real-space. We focus on the electron-photon exchange-correlation contribution by calculating exact Kohn-Sham potentials in real-space using fixed-point inversions and present the performance of the first approximated exchange-correlation potential based on an optimized effective potential approach for a Jaynes-Cummings-Hubbard Dimer[3]. Furthermore, we extend the OEP and KLI approaches to the case of electron-photon interactions in quantum optics and quantum electrodynamics. Here an effective electronic interaction is transmitted via transversal photons. We present first static and time-dependent results for the OEP[3] and KLI approximations of the Rabi and 1D-hydrogen model and compare with the exact configuration-interaction solution and the corresponding exact Kohn-Sham potentials[2].

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Time-Evolution of Tensor Networks in Quantum Electrodynamics

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Due to the high intensities and small wavelengths in modern light sources such as free electron lasers, a non-pertubative and beyond-dipole description of the coupling of electrons and photons is necessary. To describe the dynamics in such coupled quantum systems, time-dependent density-functional theory was recently extended to include quantum-electrodynamical effects (QEDFT)[1].

Like all density-functional approaches, this description is formally exact. However, for current approximate QEDFT functionals, no error bars for the deviation from the exact solution of the Schrödinger equation are known. In order to develop such error bars, we construct systematically improvable approximations for the wavefunction of lattice quantum-electrodynamics. In our work, we expand the many-body wavefunction in terms of a tensor network[2]. For quantum electrodynamics this naturally leads to two different strategies.

First, we employ the Lanczos algorithm in order to compute the dynamical evolution of the system in terms of generalized matrix-product states. If all the symmetries of the Hamiltonian and of the initial state are exploited, we find from our analysis that only a few possible states have to be retained to describe the whole dynamics of the system.

Second, we consider a tensor network in discrete space and time variables. Globally optimizing this tensor network according to the the McLachlan variational principle[3], we detemine states which are equivalent to stationary solutions of the action principle of quantum electrodynamics.

In both cases, we analyze the entanglement of the involved states and compare our approach to QEDFT. The amount of entanglement is the only approximation that is inherent in the tensor networks that we consider. Since this quantity can be converged by increasing the bond dimension of the network, we can assess the deviation from the exact solution of the problem with an asymptotic analysis.

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Correlation Consistent Basis Sets and Explicitely Correlated Wavefunctions in a Numerical Atom-Centered Framework

Salih Akbudak[a], Arvid C. Ihrig, Volker Blum[b], Patrick Rinke[c], Igor Ying Zhang,
and Matthias Scheffler

Methods like second-order Møller-Plesset perturbation theory (MP2) and the random-phase approximation (RPA) suffer from a slow basis set convergence due to the inaccurate modeling of the inter-electronic cusp. One popular strategy to alleviate this problem are complete basis set (CBS) extrapolation schemes as e.g. Dunning's correlation consistent (CC) Gaussian type orbital (GTO) basis sets[1]. Compared to Gaussian or plane-wave basis sets, numeric atom-centered orbitals (NAO) are more compact and transferable, thus they are appealing for the CC basis-set construction, as we have already demonstrated for light elements from H to Ar[2]. However, finding efficient and accurate CC basis sets for transition metals remains an open challenge for both GTOs and NAOs.

The RPA correlation of the 3*d* transition metals exhibits a significantly different convergence behavior compared to light elements. Based on this observation, we develop new CC basis sets for copper and several other 3*d* transition metals. The quality of CC strategies can be assessed by the energy difference from the counterpoise corrected and bare extrapolation, because the superposition error vanishes in the CBS limit. For the copper dimer, our new basis set yields an energy difference of about 10 meV, while the best available but considerably more expensive GTO basis set has a discrepancy of 91 meV.

Another approach is the introduction of an explicit dependence on the inter-electronic distance into the wave-function (F12 strategies[3]). However, the explicit dependence on inter-electronic distances gives rise to new matrix elements, which yield computationally expensive three and more electron integrals. We present an efficient evaluation scheme for these integrals in the NAO-framework using our recently developed maximally localized variant of the resolution of identity technique[4]. For the example of MP2 we demonstrate the improved convergence with the basis set size. In combination with CC basis sets, the F12 approach yields the prospect of reaching CBS-converged total energies for transitions metals with computationally affordable basis sets.

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Tailored Cascade Genetic Algorithms for the Study of the Thermodynamical Stability of Metal-Oxide Clusters and their Structure-Property Relationships

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Sergey V. Levchenko, Matthias Scheffler, and Luca M. Ghiringhelli

Materials at nanoscale size show unusual properties that have prompted extensive studies of clusters and that are generally attributed to the presence of undercoordinated atoms. However, in the presence of a reactive atmosphere, clusters can adsorb species from the gas phase, changing their stoichiometry. Thus, in order to understand the functional properties of clusters and in general nanostructures in a reactive atmosphere, it is important to know which structures and stoichiometries are energetically accessible.

We introduce a robust first-principles methodology[1] for the determination of (meta)stable structures at realistic environmental conditions. First, the *ab initio* potential-energy surface is scanned by means of a global-optimization technique, i.e., a massive-parallel cascade genetic algorithm (cGA) for which the choice of all settings is validated against higher-level methods. In particular, we validate (a) the criteria for selection and combination of structures used for the assemblage of new candidate structures, and (b) the choice of the exchange-correlation functional. In the second step, the low-energy structures are analyzed by means of *ab initio* atomistic thermodynamics in order to determine compositions and structures that minimize the Gibbs free energy at the temperature and pressure of the reactive atmosphere.

We demonstrate our cGA by exploring O-vacancy and O/O_2-ad-species defects at steps and corners at MgO surface. The defects are modeled using MgO clusters, described at the hybrid-functional level and embedded into a field of norm-conserving pseudopotentials and point charges. The long-range response of the oxide to the charge carriers trapped at the defects is taken into account using a polarizable force field. Unexpectedly, we find that O-ad-species rather than O-vacancies are dominating defects at realistic conditions. The stability of the O-ad-species over O-vacancies and pristine corners is explained by an interplay between bond-breaking, bond-making, and charge-carrier trapping.

Furthermore, we extend the cGA by including the optimization of properties different form energy, in order to allow for the understanding of the structure-property relationship of desired properties of (nano)materials, e.g., large electron affinity (EA) and small ionization potential (IP). This extension is demonstrated by applying it to $(TiO_2)_n$ clusters (n = 3−10, 15, 20), where we identify correlations between electronic properties (large EA, small IP) and structural features (number and distribution of dangling-O atoms)[2]. A tailored cGA can provide insight for the understanding of "design rules" of targeted metastable materials, in experiments and practical applications where quantities other than energy can be optimized (e.g., selection of clusters having a large EA in photoemission spectroscopy experiments).

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Wavelike Nature of van der Waals Interactions at the Nanoscale

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Van der Waals (vdW) interactions crucially influence the structure and properties of molecular clusters, soft-matter solids and heterogeneous material interfaces, thus driving applications from drug design to electronics to catalysis. With the increasing focus on supramolecular chemistry and nanostructured materials, vdW interactions are being employed and probed at increasingly larger scales and decreasing dimensionality. However, our current understanding of these interactions is largely based on small model systems and idealized, mostly pairwise-additive London dispersion picture. As a result of this inconsistency, predictions of both static and dynamic properties of nanoscale structures may fail in quantitative and sometimes even qualitative manner[1,2].

Here, we demonstrate that in supramolecular complexes and low-dimensional nanostructures, vdW correlations are more naturally described in terms of coupling between fluctuating dipole waves. This wavelike nature stems from the coupling between initially localized fluctuations, which lose their individuality due to strong interatomic interactions. This leads to several nontrivial effects in vdW interactions that cannot be explained by perturbative dispersion corrections and non-local functionals based on the electron density, but that are correctly captured by the infinite-order many-body dispersion (MBD) model[3,4]. In linear chain structures and 2D materials, the interaction energy is described by a combination of power laws that can vary widely between pairwise insulating and delocalized metallic limits. For molecules interacting through nanostructures, we observe a regime in which their interaction energy *increases*, instead of decreasing as naively expected from the conventional dielectric screening model. Further application to carbon-based supramolecular complexes demonstrates that omitting wavelike vdW fluctuations leads to differences in association constants of up to five orders of magnitude where there should be degeneracy according to high-level quantum Monte Carlo calculations.

Taken together, our findings indicate that the wavelike nature of vdW interactions provides a hitherto unexplored avenue that could be used for tailoring the assembly of complex polarizable systems at the nanoscale.

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First-Principles Simulations of Polarons in Oxides: Insights and Challenges

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The formation and migration of polarons plays an important role for many properties of functional materials, e.g., optical spectra and electrical conductivity[1,2]. However, a systematic first-principles assessment of the underlying electron-phonon (e-ph) coupling still faces severe challenges – especially in the case of oxides[3,4] such as ZnO, MgO, and TiO_2.

Foremost, we demonstrate that the e-ph interaction can be very sensitive to errors associated with the use of approximate exchange-correlation (XC) functionals in density-functional theory (DFT). Our results show that the stability of polarons can be decisively affected by small changes in parameters, e.g., the fraction of exact exchange included in hybrid functionals such as PBE0 and HSE06. We discuss how these uncertainties can be reduced by enforcing the XC functional to satisfy certain constraints that an exact functional would fulfill[5]. We investigate how the approach depends on the finite size of the employed supercell and the type of the lattice distortion (from small atomic displacements to O and cation vacancies).

Furthermore, we show that obtaining the correct atomic distortions of polarons proves to be more challenging than naively expected. On the one hand, strong e-ph coupling can result in small polarons that are localized within a few unit cells and that can therefore be treated in a supercell approach. Several types of small polarons with different atomic displacements but similar energies can co-exist, depending on the point group of the perfect crystal. On the other hand, weak e-ph coupling can result in large polarons that span several thousand atoms, defying a supercell treatment. In this case, analytic but approximate models can be used to estimate the polaron formation energies, e.g., by evaluating the renormalization of the band edges due to the zero-point motion of the atoms from first-principles[6] or by estimating the interactions in the elastic limit with the Fröhlich model[7]. We critically review and compare the available techniques, and investigate to which extent they allow us to bridge the gap between the localized and delocalized states. In particular, we show that in the intermediate coupling-strength regime neither of the first-principles techniques is able to achieve qualitatively correct results[1].

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Modeling Quantum Nuclei with Perturbed Path Integral Molecular Dynamics

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The quantum nature of nuclear motions can play an important role in the structure, stability, and thermodynamics of molecules and materials. Whenever interatomic forces are strong, nuclear quantum fluctuations (NQF) can be fairly pronounced at room temperature and even above it. The standard approach to model NQF in chemical and biological systems is path-integral molecular dynamics (PIMD). Unfortunately, conventional PIMD simulations can have exceedingly large computational cost due to the need of employing an excessive number of coupled classical subsystems (beads) for quantitative accuracy. More sophisticated approaches have been developed[1,2,3], but they either require extensive parameterization or inadequately sample the phase space, which limits their applicability to realistic molecules and materials. Hence, the development of a parameter free method for NQF that is both accurate and efficient would be desirable.

To achieve this challenging goal we combine perturbation theory[4] with the Feynman-Kac imaginary-time path integral approach[5] to quantum mechanics and derive improved non-empirical partition function and estimators to calculate converged quantum observables. Our *perturbed path-integral* (PPI) method requires the same ingredients as conventional approaches, but increases the efficiency of path integral simulations by an order of magnitude. Any kind of phase sampling technique and any thermostat or barostat can be utilized. The *converged* observables can be obtained either *on-the-fly* or *a posteriori* from conventional PIMD simulations, which form the base of the developed PPI approach.

Applications are presented for the thermodynamics of the quantum harmonic oscillator and the double-wall potential, empirical water model containing 256 water molecules within periodic boundary conditions, *ab initio* simulations of nitrogen and benzene molecules, and graphene. For all of these examples, our PPI approach with 4 to 8 classical beads recovers the nuclear quantum contribution to the total energy and heat capacity at room temperature within 3% accuracy, paving the way toward accurate modeling of nuclear quantum fluctuations in realistic molecules and materials.

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Thermal Conductivities in Solids from First Principles: Accurate Computations, Qualitative Insights, Rapid Estimates

Christian Carbogno and Matthias Scheffler

The development of materials with suitable thermal conductivity is crucial for a variety of applications, e.g., for the optimization of thermoelectric elements or for the design of novel thermal barrier coatings for gas and airplane turbines[1]. Since an assessment of vibrational heat transport in solids requires detailed knowledge of the anharmonic dynamics on macroscopic time and length scales, an accurate calculation of thermal conductivities is conceptionally and computationally challenging: On the one hand, approaches based on the *Boltzmann Transport Equation* (BTE) allow a computational efficient assessment in reciprocal space by utilizing the phonon properties (dispersions, group velocities, etc.) valid in the harmonic approximation at zero Kelvin. However, these approaches fail at elevated temperatures and/or for strongly anharmonic systems, since the anharmonicity is only accounted for perturbatively in terms of phonon lifetimes. On the other hand, molecular dynamics (MD) techniques using the *Green-Kubo* formalism[2] naturally capture the full anharmonic dynamics in real space. For the exact same reason, however, they can become prohibitively costly to converge in time and size – even when numerically rapid force fields are used to approximately model the inter-atomic interactions[3].

In this work, we developed a formalism that seamlessly bridges the gap between these two approaches so that both the BTE and the GK formalism can be evaluated via MD simulations. For this purpose, we determine the *effective* quasi-harmonic potential the atoms experience during the MD simulation[4], the associated temperature-dependent phonon properties, and the respective fluctuations in the phonon occupation numbers from the MD trajectory[5]. Besides facilitating a systematic quantitative comparison of the BTE and MD approach, this enables to extrapolate MD calculations to macroscopic time and size scales by applying interpolation techniques in reciprocal space. This accelerates such *Green-Kubo* simulations by several orders of magnitude and thus enables an accurate assessment of thermal conductivities within the limited time and length scales accessible in *ab initio* MD. For both force-field and *ab initio* MD, we carefully validate and critically discuss the involved conceptional and numerical approaches by investigating heat transport in silicon and zirconia, two materials known for their particularly harmonic and anharmonic character.

Eventually, we show how the developed techniques facilitate reasonable estimates of thermal conductivities from existing phonon or MD calculations at virtually no additional computational cost, how they enable qualitative insights in the mechanisms and properties promoting/hindering heat transport[6], and how they lay the founding for systematic data-mining approaches in this field.

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Electronic Properties of Molecules, Surfaces, and Interfaces with a Self-Consistent Interatomic van der Waals Density Functional

Nicola Ferri, Robert A. DiStasio Jr.[a,b], Alberto Ambrosetti[c], Roberto Car[a],
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Long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems, ranging from small dimers to complex hybrid inorganic/organic interfaces (HIOS). However, how strong is the effect of vdW interactions on the electronic properties of molecules and extended systems? It is often argued that the vdW energy has a small, or even negligible, influence on the electron density, $n(\mathbf{r})$, and derived electronic properties, since the vdW energy represents only a tiny fraction (0.001%) of the total electronic energy.

To answer the question posed above, we derived a fully self-consistent (SC) implementation of the density-dependent interatomic vdW functional of Tkatchenko and Scheffler[1] and its extension to surfaces[2]. Not surprisingly, vdW self-consistency leads to tiny modifications of the structure, stability, and electronic properties of molecular dimers and crystals. However, unexpectedly large effects are found in the binding energies, distances and electrostatic moments of highly polarizable alkali metal dimers. Most importantly, vdW interactions produced complex and sizable electronic charge redistribution in the vicinity of metallic surfaces and at organic/metal interfaces. As a result, for several coinage metal (111) surfaces, self-consistency induces modifications in the surface dipole, leading to an increase of up to $0.30\,\mathrm{eV}$ in the computed workfunctions. Furthermore, in the case of HIOS, SC vdW entails modifications of up to $0.22\,\mathrm{eV}$ in the shift of the interface workfunction, a property induced by molecular adsorption. The underlying mechanism responsible for the workfunction modifications stems from an interplay between two effects driven by SC vdW interactions: (i) the modification of the interface dipole, and (ii) a reduction in the charge transfer between the molecule and the surface.

In conclusion, the analysis of SC vdW effects performed in this work demonstrates the importance of vdW interactions on the electronic properties of different classes of systems, with self-consistency systematically improving the agreement between the theoretical predictions and the experimental measurements. Our study reveals a nontrivial connection between electrostatics and long-range electron correlation effects[3].

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Adsorbate-Adsorbate Interactions at Realistic Conditions: Cluster Formation of Adsorbates and Coverage-Dependent Chemistry

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Adsorbate-adsorbate interactions play an important role in adsorption and chemical reactions on metal and metal oxide surfaces, even at low coverage. In particular, such interactions can lead to the formation of dense adsorbate structures or networks. Inside such structures, the chemical properties of adsorbates are determined by both adsorbate-adsorbate and adsorbate-substrate interactions. A high coverage of co-adsorbed species will also affect the reaction barriers.

The first part of our work focuses on the atomic structure of adsorbed complexes that appear on alkaline-earth metal-oxide (001) surfaces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory with the HSE06 hybrid functional[1] combined with the self-consistent many-body dispersion approach[2] is used to calculate total energies. The most stable adsorbed water structures are obtained using a first-principles genetic algorithm. Thermodynamically stable adsorbed water phases are then determined using *ab initio* atomistic thermodynamics. We find a range of H_2O chemical potentials where ordered one-dimensional (1D) adsorbed water structures are thermodynamically stable on CaO(001). This result is in agreement with scanning tunneling microscopy and infrared spectroscopy studies of CaO films exposed to water vapor[3]. On MgO(001) and SrO(001), thermodynamically stable 1D adsorbed water structures are not found. We show that the formation of the 1D structures on CaO(001) is due to a balance between adsorbate-adsorbate and adsorbate-surface interactions, which is largely determined by the substrate lattice constant.

In the second part of our work, we investigated effects of hydrogen co-adsorption on the adsorption and reactions of CH_x (x = 0-4) species on Ru(0001) at realistic temperatures and hydrogen pressures. We find that co-adsorbed hydrogen qualitatively changes the preferred site and the stability of CH_2 species, which is crucial for understanding the mechanism of Fischer-Tropsch synthesis. Our results explain the recent observation of CH_2 species on methane-dosed Ru(0001) surface[4]. Moreover, hydrogen co-adsorption is found to have a profound influence on the C-C coupling reactions: While it generally reduces all the coupling reaction barriers, some reaction paths become more favored in the presence of the co-adsorbed hydrogen. Our study of the hydrocarbon chemistry on Ru(0001) surface at realistic conditions both explains the new observations[4] and resolves some of the controversies between existing theoretical and experimental studies.

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Pressure Dependent Electronic Properties of Organic Semiconductors from First Principles

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The electronic properties of organic semiconductors such as band gaps, effective masses, and conductivities typically exhibit a significant dependence on the strain, stress, and pressure, i.e., on the growth conditions during fabrication[1,2]. As shown in this work for two prototypical examples (anthracene, *trans*-polyacetylene), assessing these effects within density-functional theory (DFT) is challenging. First, DFT calculations at a semi-local level of theory suffer from a self-interaction error and from missing long-range, non-local van der Waals interactions. Both these shortcomings can critically affect the properties of organic systems, so that the employed description of exchange and correlation has to be carefully validated with respect to higher levels of theory. Second, the strain derivatives of the total energy, i.e., the stress tensor, are needed in order to investigate materials under pressure. We have implemented[3] these derivatives – including the terms that stem from van der Waals corrections and the exact exchange used in hybrid functionals – in the numeric atom-centered orbitals based all-electron electronic structure code FHI-aims[4].

We find that incorporating van der Waals corrections is pivotal for anthracene, a molecular organic semiconductor, since these interactions determine the binding between the constituent molecules and their arrangement in the crystal. In turn, this critically influences the electronic band structure, since the intermolecular interactions lead to a splitting of the valence and conduction bands that increases under pressure. In the case of *trans*-polyacetylene, we find again that van der Waals interactions are most influential for the binding between the individual polymer chains. Furthermore, the structure of the chains itself is critically affected by the self-interaction error. While semi-local functionals fail to reproduce its broken symmetry ground state, hybrid functionals yield the qualitatively right geometry. Quantitatively, however, the properties of *trans*-polyacetylene critically depend on the fraction α of exact exchange included in the calculations. Again, this is qualitatively consistent with previous high-level quantum chemical studies (CCSD(T)) of one isolated chain[5]. Our calculations reveal that the geometry, the electronic band structure, and the band gap of crystalline *trans*-polyacetylene do not only depend on α and on the symmetry breaking in the individual chains, but are at least as much influenced by interchain interactions, which lead to a pressure-dependent splitting of valence and conduction band as in the case of anthracene.

Eventually, we compute the pressure-dependent charge carrier concentrations and electronic transport coefficients for both organic semiconductors using the Boltzmann transport equation in the constant relaxation time approximation and point out how these macroscopic thermodynamic properties of intrinsic and doped systems are affected by changes in the band structure under pressure.

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Towards a Quantitative Description of the Energetics of Peptide-Cation Interactions

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Metal cations are essential to life by shaping the three-dimensional structure of proteins or in the active centers of nature's catalysts. One-third of the proteins in the human body require a metal cofactor for biological function[1,2]. Peptides in complex with cations undergo significant conformational changes that may alter important properties, e.g. binding sites, catalytic properties, and biological functions. On the negative side, it is hypothesized that metal cations promote protein misfolding of Aβ-amyloid peptides into aggregated senile plaques inside the human brain of Alzheimer patients[3]. Importantly, however, the accuracy of ion-peptide interactions in empirical simulation frameworks ("force fields") is anything but clear and, in fact, can be grossly misleading. Accurate electronic structure based validation data are thus a critical need, but here, too, the accuracy of a given method must be comprehensively established.

From a large-scale structure search effort, we present a structural data set[4] of 20 proteinogenic amino acids and their amino-methylated and acetylated (capped) dipeptides with and without divalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+}). Different protonation states of the backbone as well as varied side chain protonation states were considered. All systems were calculated on equal first-principles footing, applying the PBE generalized gradient density-functional approximation (DFA) corrected for long-range van der Waals interactions with the pairwise Tkatchenko-Scheffler scheme (DFT-PBE+TS). The database covers the conformational hierarchies of 280 systems in a wide relative energy range of up to 4 eV (390 kJ/mol), providing a total of more than 45k stationary points on the respective potential-energy surfaces. Experimentally established gas-phase relative ion binding propensities correlate well with DFT-PBE+TS energies. Given the vast space of conformations covered, the data base is thus a solid foundation for future validation work of higher-level electronic structure methods and lower-level force fields alike. We use examples from our curated data[4] and of Zn^{2+}-histidine complexes to first assess the performance of DFAs *vs.* CCSD(T) for a wide range of amino acids and cations. Secondly we also compare classical (OPLS-AA, Amber99, and Charmm22) and advanced polarizable (Amoeba-Bio-2009) force fields. Force fields fail to accurately describe the peculiarities of the test systems, indicated by large errors of relative energies of conformers compared to coupled-cluster calculations. The use of DFAs substantially reduces these errors, but a quantitative description requires the use of hybrid functionals, e.g. PBE0, in conjunction with a van der Waals correction.

In future steps, the foundation established here will enable us to suggest modifications to force fields for bare peptide-cation interactions. If successful, the overall effort can fundamentally enhance a critical piece of biomolecular simulation infrastructure and represent a key simulation tool to accurately study health-relevant processes at atomic resolution.

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Reduced Molecular Potential-Energy Surfaces from First Principles

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Flexible organic molecules and biomolecules can adopt a variety of energetically favorable conformations. We propose a method to construct a reduced potential-energy surface from low-energy local minima and selected transition states. It is computationally efficient enough to be used with first-principles energy functions in order to study the dynamics of conformational ensembles.

First, we assessed a genetic algorithm-based search with Fafoom (Flexible algorithm for optimization of molecules, available from https://github.com/adrianasupady/fafoom)[1] to sample the molecular conformational space. The algorithm was designed to work with first-principles methods, facilitated by the incorporation of local optimization and by blacklisting conformers to prevent repeated evaluations of very similar structures. Conformational transitions of molecules happen via bond rotations. The orientation of minima in structure space relative to each other can be resolved by estimating their distance by means of the root-mean-square deviation of torsion angles (tRMSD). We assume that short distances in torsion angle space are a characteristic of direct transitions between pairs of minima and consequently apply a tRMSD threshold to select direct transitions. With this, we build a network where the nodes represent conformers and the edges the tRMSD between adjacent minima. For each edge in the network connecting a pair of conformers, we suggest a transition path that is subsequently optimized by the aimsChain routine developed by Y. Yao and L. M. Ghiringhelli. With the identified transition states and the local minima, barrier trees[2] can be drawn for the investigated systems.

For the peptide Ac-Ala$_3$-NMe we use the force field Amber99sb as energy function and compare a barrier tree of the reduced potential-energy surface to a free-energy surface representation (Markov-chain model) constructed from long molecular dynamics simulations. The main features of the converged free-energy surface are already present in the potential-energy surface barrier tree. We investigate another system, a well-characterized synthetic peptide[3], exclusively with first principles (PBE+MBD*) and present a potential-energy surface that matches the experimental results.

Our approach provides a reduced, and thereby understandable, representation of the potential-energy surface. The sampling for stationary points (minima and transition states) can be performed with first-principles methods and can be fully automated. The outcome represents an ideal starting point to investigate free energy by, for example, constructing stochastic models or performing biased MD simulations along the known transitions.

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Anomalous Electron-Phonon Coupling in Thermoelectric Clathrates and Skutterudites

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Over the last decades, inclusion compounds have attracted considerable interest in different fields, since their electronic and vibrational properties can be tuned by doping the host and/or by filling the cages with guest atoms. For these reasons, clathrates and skutterudites have been identified as particularly promising materials for thermoelectric applications[1]. In this work, we use first-principles calculations to elucidate how electron-phonon (e-ph) coupling affects the thermodynamic properties of these compounds.

For clathrates, we find fundamentally different formation energies and distortions for (charged) vacancies in Si_{46} and Ge_{46} – in spite of their isoelectronicity. While an anomalous e-ph coupling suppresses vacancy $\square$ formation in Si, it favors it in Ge. For the exact same reason, these clathrates also behave differently upon addition of guests: While the Si host framework remains intact upon filling with K or Ba, the most favorable phases for fully filled Ge clathrates are $\mathrm{K}_8\mathrm{Ge}_{44}\square_2$ and $\mathrm{Ba}_8\mathrm{Ge}_{43}\square_3$, featuring two and three vacancies $\square$, respectively. Accordingly, controversial experimental discussions regarding the vacancy formation in these compounds and the underlying mechanism are resolved by our calculations.

Furthermore, we have extended these investigations to ternary clathrates such as $(\mathrm{Sr}, \mathrm{Ba})_8\mathrm{Al}_x\mathrm{Si}_{46-x}$ by developing a cluster-expansion code capable of treating such large unit cells (> 40 atoms). This enables studies of the thermodynamic stability with respect to competing phases, which sheds light onto the narrow ($x \simeq 10$) and wide ($x < 15$) stability range found for Sr and Ba guests, respectively[2].

For CoSb_3 and CoAs_3 skutterudites, we perform a systematic analysis of the vibrational properties depending on the type of guest (Ga, In, Sn, etc.) and its concentration. In this case, an anomalously strong e-ph coupling translates into a sensible dependence of the electronic properties on the geometries[3]. This gives rise to drastically different vibrational dynamics for different guests, ranging from coherent phonon modes to the formation of localized polarons.

In all cases, we validate the choice of the exchange-correlation functional (semi-local and hybrid functionals), in particular in view of the e-ph coupling strength. Furthermore, we use the *harmonic* approximation and *ab initio molecular dynamics* to investigate the temperature-dependent changes in the electronic and vibrational structure. We confront our findings with experimental results from our collaborators, the group of J. Grin at the MPI for Chemical Physics of Solids, and we discuss the implications of our findings for the synthesis of novel thermoelectric materials with improved transport properties.

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The FHI-aims Project

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The FHI-aims all-electron code, based on numeric atom-centered basis sets, is the flagship of code developments in the FHI theory department. Begun over ten years ago at the FHI, FHI-aims has developed into a key platform for new developments in and applications of electronic structure theory at the FHI and in many other groups around the globe. The core strength of FHI-aims is its ability to supply accurate, numerically converged calculations without hard-wired *a priori* approximations. This is feasible for both traditional and advanced electronic structure algorithms, for large systems, and exploiting massively parallel computer architectures efficiently where necessary. FHI-aims has proven itself as a high-accuracy framework on par with the best available benchmark codes in numerous past applications, most recently in the community-wide “Delta test” benchmark of solid $E(V)$ curves[1]. Here, FHI-aims provides essentially the same accuracy as benchmark (linearized) augmented plane wave codes such as Wien2k or exciting, the “gold standard” of accuracy for DFT. However, FHI-aims is significantly faster than the latter class of all-electron codes and offers far greater flexibility in terms of system types and methods beyond DFT. In terms of usability, FHI-aims is essentially as easy to use as pseudopotential codes due to the availability of a predefined hierarchy of basis sets and reliable numerical settings.

This contribution highlights recent achievements and future directions in FHI-aims. With the continued evolution of its community, the FHI-aims development has now diversified into numerous active centers outside the FHI, including Duke University (Blum), Munich (Reuter, Lederer), Hefei (Ren), Helsinki (Rinke, Havu), London (Catlow group), and many others. We highlight important new developments including: Periodic all-electron random-phase approximation (RPA), second-order Møller-Plesset perturbation theory (M- P2), and G_0W_0 for electronic excitations; a screened second-order exchange correction to GW; spin-orbit coupling, essential for electronic levels in any material beyond light elements; new metaGGA based and orbital-dependent level-5 density functionals; many-body dispersion method[2]; “embedding” localized regions into explicit (atomistic)[3] or implicit (continuum-like) electrostatic environments; density-functional perturbation theory, e.g., for phonons; efficient, localized “resolution of identity” treatment of the Coulomb operator for heavy elements and “beyond-DFT” approaches such as MP2 and RPA[4]; and range-separated hybrid functionals for molecular electronic properties.

Not least, FHI-aims now features a strong connection to QuantumWise's (Copenhagen) graphical and python based interface "Virtual NanoLab"[5]. This combination provides a foundation for easy integration of FHI-aims into industrial workflows, where electronic structure theory is playing an increasingly important role.

Important next steps to chemical accuracy in FHI-aims are thus implemented both based on the DFT paradigm and based on quantum chemical approaches. MP2 reference results for solids are obtained based on an efficient memory-distribution strategy with near-perfect parallelization efficiency and are available online. On the DFT side, the new *strongly constrained and appropriately normed (SCAN) meta-GGA*[6], constructed by satisfying all 17 known possible exact constraints, is implemented in FHI-aims. Likewise, a non-empirical *screened* second-order correlation functional based on the *Bethe-Goldstone equation (BGE), termed sBGE2* is available, offering accurate descriptions of significant problem cases such as H_2^+ and H_2 dissociation. The sBGE2 functional is used as a building block to construct a non-empirical doubly-hybrid functional termed ZRS0. This functional distinguishes itself by a satisfactory description of particularly challenging dissociation cases such as N_2 or C_2.

In short, FHI-aims is now an active and vibrant platform with a high degree of technical maturity, emerging as a source of a broad range new developments for electronic structure theory in general. We foresee that this trend will only accelerate in the next few years.

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Big Data of Materials Science: Critical Role of the Descriptor

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Statistical learning of materials properties or functions so far starts with a largely silent, nonchallenged step: the introduction of a set of descriptive parameter (a multidimensional descriptor). However, when the scientific relationship of the descriptor to the actuating mechanisms is unclear, causality of the learned descriptorproperty relation is uncertain. Thus, scientific advancement, trustful prediction of new promising materials and identification of anomalies is doubtful. We discuss and analyze this issue and define requirements for a descriptor that is suited for statistical learning of materials properties and functions.

Compressed sensing is a method[1,2], originally developed for signal processing, that finds sparse solutions of systems of linear equations which are in general undetermined, i.e., the number of descriptive parameters (the input information, that builds the feature space) is (much) smaller than the number of data (sampling) points. In practise, with compressed sensing a (small) subset of the input parameters is identified as a stable input set for the linear mapping from the descriptor to the sampled property. The size of the selected subset is controlled by the desired accuracy in the mapping

Here, we show how a meaningful descriptor can be found systematically, by means of compressed sensing techniques, which allow for an unbiased and robust model selection among many competing descriptive models.

These concepts are demonstrated for solving problems in materials science: i) prediction of the relative stability of zincblende/wurtzite vs. rocksalt octet binary semiconductors[3], and ii) prediction of their band gaps, by using simple atomic input and/or simple binding models (e.g., tight binding) for building the descriptor, and iii) prediction of other mechanical and elastic properties.

The causal character and predictive capability of the found descriptor(s) are discussed in terms of the robustness of the learned model with respect to perturbation applied to the data and cross validation.

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The Novel Materials Discovery (NoMaD) Center of Excellence: Big-Data Storage, Search, and Analysis

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The development of modern commercial products may it be from the health and environment, clean energy, heavy industry, information or communication technology sector depends strongly on the development and design of new and improved materials. However, identifying the best materials for a particular application is a significant challenge. Of key importance are the characteristics of the materials at the atomic and molecular levels, which determine their properties and behavior at the macro scale.

Computational materials science uses computers to investigate, characterise, and predict materials at the atomic level, and thus to provide insight into materials properties and functions and into the design and development of new materials to meet specific requirements. A huge number of materials has been and is being investigated using computational materials science methods employing either quantum mechanics (solving the Schrödinger equation for the electrons of the material) or a classical description via force fields or combination of both.

Since many years, the materials science community has been producing an enormous amount of data by CPU-intensive calculations. However, most of this data is not used in our target-oriented research and way of publishing. For optimal exploitation of the significant information content inherently inside all materials data, we need the willingness of the community to share, and we need repositories that allow for the long-term storage and access of all data.

Following this spirit, the NoMaD (Novel Materials Discovery) Repository[1] has been established, promoting the idea of storing open-access data, sharing, and enabling data reuse and repurposing. Open access implies that data can be used by anyone, not just by the experts who develop or run advanced codes. These include computer scientists, applied mathematicians, analytic condensed matter scientists, and more. Therefore, the future reuse of the stored data may be unpredictable, probably through the employment of tools that the present computational materials community does not even know. At present, we support major community codes, like ABINIT, CASTEP, CRYSTAL, exciting, FHI-aims, GAUSSIAN, octopus, Quantum ESPRESSO, VASP, and WIEN2k; this list is still increasing in order to incorporate more important electronic-structure codes and soon including also the force-field based codes.

The NoMaD Repository stores raw data, as they are output by the supported codes. Data can be retained private for up to 3 years after their upload to the repository, then they are made open access. Of course, they can be made open access earlier by the owner of the data. Simple searches for chemical composition, electronic structure code, basis set, exchange-correlation treatment, authors, and DOI help locate the desired entry in the repository, that can be downloaded even without registration.

The NoMaD Repository is a solid basis for the NoMaD Center of Excellence (CoE)[2], a unique collaboration between eight computational materials science groups and four high-performance computer centers. The goal of this CoE is to get scientific insight into the vast amount of existing data by extracting (often hidden) information in various ways.

In a first step, a code-agnostic (-independent) database will be created, where all data will be stored in a uniform, robust, and extensible representation. This will allow for making data as computed by different methods and codes comparable. This is achieved by implementing a *translation layer*, that transforms the data from the raw output contained in the repository into a code-agnostic format that uses HDF5 and json file formats. The HDF5 file format uses a flexible classification system that can be easily extended, to describe the data stored. In this way, scalar quantities as energies, vectors like forces and positions, functions like electronic or phonon density of states, and scalar fields like electronic densities and wavefunctions can be efficiently stored and searched.

Building on the database, a *Materials Encyclopedia* will be developed, based on Apache Flink[3] (a fast large-scale data-processing engine). This will be used to efficiently perform queries on the extracted data, allowing for either a comprehensive characterization of a material or trends across a class of materials or even all materials in the database. Besides this *Materials Encyclopedia*, an infrastructure will be established to develop advanced *big-data analytics* tools aiming at finding correlations between materials, their properties, and functions. The queries can be simple, e.g., a search for a material that has the band gap within a certain range while having a specific weight below a given threshold. They can be more complex, i.e. involving machine-learning algorithms. For example, pattern recognition (similarity among atomic structures, band structures, type of defects, etc.), identification of outliers, and more.

Illustrative examples of the queries and data analytics enabled by the developed infrastructure, and in particular of their scalability, are demonstrated.

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