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

19th Meeting of the Fachbeirat

Berlin, November 28th – 30th, 2017

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Max-Planck-Gesellschaft
Berlin

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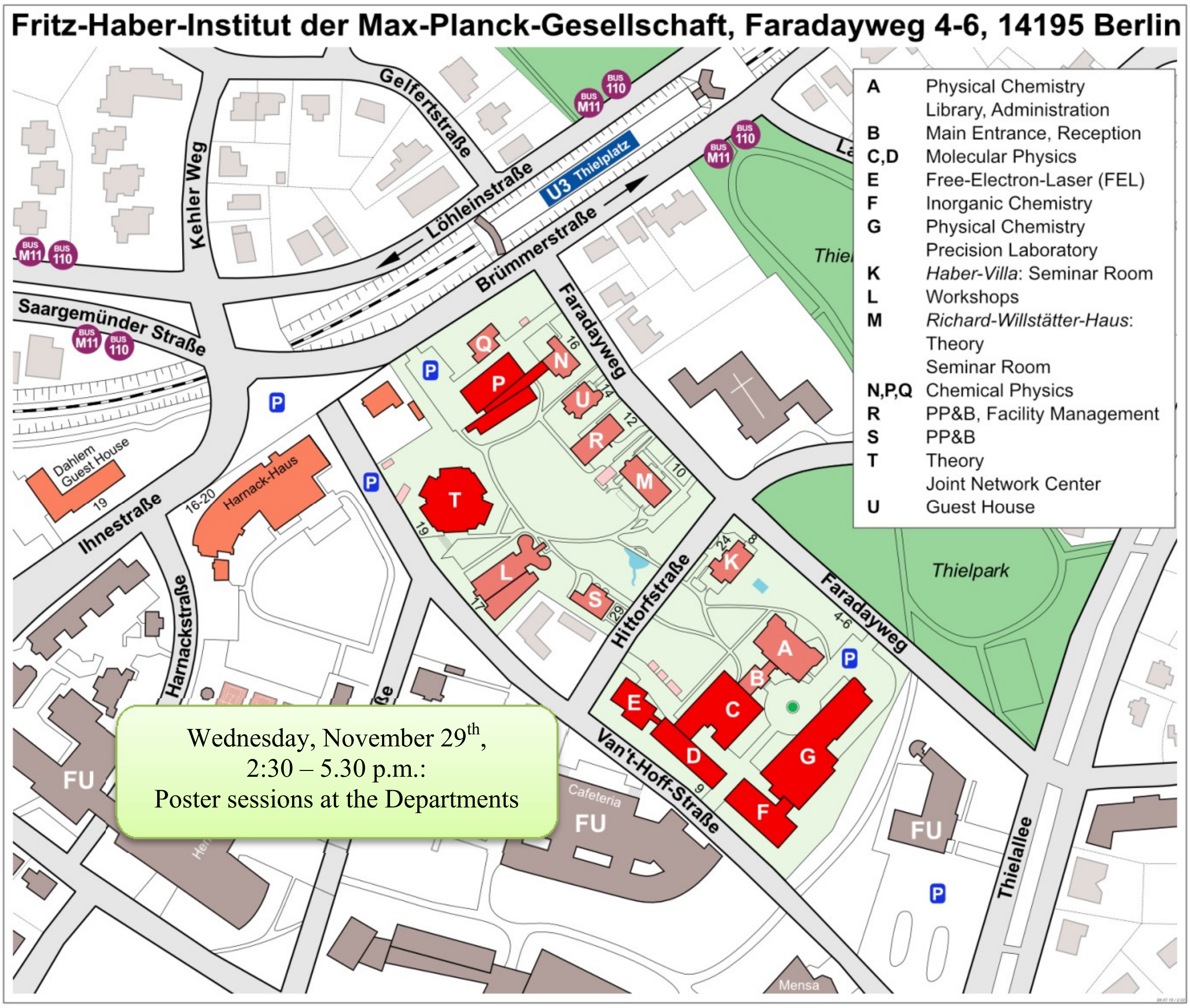
Poster Abstracts

Local Map


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

Wednesday, November 29th,
2:30 – 5.30 p.m.:
Poster sessions at the Departments

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Nanostructured Catalysts in Activation of Light Alkanes

The project deals with fundamental questions concerning the activation of small alkane molecules (C1-C4) over oxide catalysts.

The catalysts applied include binary model oxides, such as doped CaO for oxidative coupling of methane, and V_2O_5 or CeO_2 for activation of C2-C4 alkanes, as well as more complex mixed Mo-V-based oxides, transition metal molybdates, tungstates, and perovskites ABO_3 with La, Pr, Nd, and Sm used as A elements and the first row transition metal elements V, Cr, Mn, Fe, Co, and Ni applied as B elements.

Our aim is to investigate well-defined materials characterized by phase-purity and homogeneity with respect to bulk chemical composition, particle size and morphology. Predominating synthesis techniques are precipitation or solvothermal synthesis. Therefore, our work covers studies of polycondensation reactions in solution with the aim to master effective control of synthesis products in terms of their functional properties. Poster 1.1 summarizes our results in analysing the speciation of molybdates and vanadates in aqueous solution by ion mobility spectrometry-mass spectrometry (IMS-MS) as an example. The work is performed in collaboration with the group of Gert von Helden, Department Molecular Physics.

Partial oxidation reactions of light alkane molecules comprise a complex network of parallel and consecutive reactions responsible for the challenging selectivity issue in oxidation catalysis. Clarification of major pathways within the network and the link to catalyst bulk and surface structure will contribute to an improved understanding as a basis for the development of new approaches to rational catalyst design. In a kinetic study we contribute to the analysis of the reaction network in oxidation of propane over vanadium oxide-based catalysts by using labelled reactants, temperature-programmed experiments, and microcalorimetry. The results are summarized in Poster 1.2.

The activation of both the alkane molecule and the oxygen molecule may have an impact on selectivity. Therefore, we synthesized and analysed various oxides that differ in their properties with regard to alkane adsorption and oxygen activation including perovskites (Poster 1.3), cerium oxide (Poster 1.4), and vanadium oxide (Poster 1.5). The characterization of the model catalysts comprises advanced techniques of electron microscopy (Poster 3.4), synchrotron-based electron and X-ray absorption spectroscopy, as well as operando resonance Raman spectroscopy combined with theory (Poster 1.5).

Furthermore, we investigate whether structurally equilibrated species in a liquid film differ in activity and selectivity from rigid structural arrangements of metal oxide species at the surface of monolayer catalysts as a continuation of our studies concerning frustrated species in C-H activation reactions. In this respect we synthesized vanadium oxide-based supported liquid phase (SLP) catalysts and investigated their catalytic properties in propane oxidation as a function of the state of aggregation (Poster 1.6). In addition we analysed working Na-Mn-W-oxide-based catalysts in-situ and in operando at high reaction temperatures in the oxidative coupling of methane by XRD and Raman spectroscopy, respectively, (Poster 1.7).

Structural Determination of Molybdenum and Vanadium Oxide Nanoclusters Present in Early Condensation Stages

Sabrina Jung, Annette Trunschke, Mateusz Marianski,[a]
Jongcheol Seo[a] Gert von Helden[a], and Robert Schlögl

Reproducible synthesis of transition metal oxides used as catalysts in oxidation catalysis requires detailed knowledge of the polycondensation reactions in aqueous solutions that determine particle size, morphology, surface termination, and, hence, functional properties of the nano-structured materials. In the present work we deal with the structure of polyoxometalate species of vanadium and molybdenum in aqueous solutions that eventual condense to non-charged species, which are able to growth spontaneously.

Aqueous solutions of ammonium heptamolybdate $(NH_4)_4[Mo_7O_{24}]$ with Mo concentrations from 0.35 M to 0.07 mM and ammonium metavanadate NH_4VO_3 with V concentrations from 10 to 0.01 mM were adjusted to pH values from 2 to 9. The solutions have been analysed by Raman, infrared, and UV-vis spectroscopy in the condensed phase and a combination of ion mobility spectrometry-mass spectrometry (IMS-MS), and infrared multiple phonon dissociation (IRMPD) in the gas phase.[1] The interpretation of the spectra was supported by theory (DFT).

The results unravels diversity of polyoxomolybdate species present in the sprayed solution at pH 3 that features different topology (dimensionality) of clusters of various sizes, ranging from 1-dimensional chains for n = 1 and 3, ring-like structures for n = 4 and 5, to 3-dimensional clusters stemming from Lindqvist type structure for $n \geq 6$. The absence of such species in the solution sprayed at pH 9 suggests that condensation does not occur during evaporation but the precursors are present in the condensed phase. Moreover, ab initio molecular dynamics simulations suggest that the clusters are not rigid but can feature dynamic metal-oxide bond breaking/formation on the picosecond scale.

A wide distribution of vanadium oxide species has been found by IM-MS. Singly charged species follow either the protonated $[HV_mO_{(5m+2)/2}]^-$ (*m* even) or the deprotonated $[V_{m3(5m+1)/2}]^-$ (*m* odd) series, whereas doubly charged species follow the general formula of $[V_{2m}O_{(5m+1)}]^{2-}$. Radical species with the formula $[V_mO_{(5m/2)}]^{\cdot -}$ (*m* even) are also possible.

Mass spectrometry in combination with infrared spectroscopy and theory allows a more detailed insight into the structural diversity of polyoxometalate species in solution and in the process of desolvation that goes along with condensation. The observed dynamics may simulate elementary processes occurring in precursor formation and nucleation of molybdenum and vanadium oxide nanoparticles.

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Reaction Network in the Oxidation of Propane over Vanadium Oxide-based Catalysts

Pierre Kube, Sabine Wrabetz, Annette Trunschke, and Robert Schlögl

Mo-V oxide-based catalysts show high activity in the partial oxidation of ethane and propane. However, until today, the selectivity to desired olefins and oxygenates is too low due to undesired side, consecutive and total combustion reactions, and, therefore, corresponding selective oxidation processes have not yet been taken into account in industrial applications.[1] Insight into the reaction network and how rate constants of the elementary steps are linked to bulk and surface properties of the catalyst may render control over selectivity by targeted fine-tuning of material properties possible.

We analysed the reaction network in oxidation of propane over vanadium oxide-based catalysts by comparing crystalline MoVTeNb oxide (M1) with a silica-supported sub-monolayer vanadium oxide catalyst (V_xO_y/SiO_2) in a kinetic study using labelled reactants and temperature-programmed experiments. Microcalorimetry was applied to determine and strength and density of propane adsorption sites.[2,3]

M1 oxidizes propane to acrylic acid with high selectivity, while over V_xO_y/SiO_2 essentially propylene and carbon oxides are formed. Kinetic modelling of the obtained data applying a simple model-free time law indicates similarities in the reaction network over the two catalysts in the investigated range of reaction conditions implying that differences in the selectivity are the result of different rate constants of the individual reaction steps.[2] Differences in the overall reaction rate and the kinetic isotope effect measured for the abstraction of the first hydrogen atom are attributed to differences in the density of propane adsorption sites on the two catalysts.[3] A stepwise abstraction of hydrogen is observed over V_xO_y/SiO_2, whereas over M1 a quasi-simultaneous H-abstraction occurs due to the high density of oxidising sites present on this catalyst.

Temperature programmed reaction experiments confirm similar intermediates in the gas phase over the two catalysts.[3] Differences in acrolein formation in the low-temperature range ($T < 523$ K) suggest the presence of electrophilic oxygen species on the surface of V_xO_y/SiO_2, which do not play a significant role over M1. At $T > 573$ K acrolein seems to be formed via allylic oxidation over both catalysts. Experiments with ^{13}C labelled propane indicate that oxygen insertion into the CHO group of acrolein under formation of acrylic acid is faster over M1 than oxidation at the CH_2 group and decarbonylation to acetaldehyde, which occurs preferentially over V_xO_y/SiO_2. The origin of these differences is discussed in terms of differences in electronic and molecular structure.

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Synthesis of Perovskites for Oxidative Dehydrogenation of Propane at Low Temperatures

Gregor Koch, Pierre Kube, Thomas Lunkenbein, Detre Teschner, Frank Rosowski[a],
Annette Trunschke, and Robert Schlögl

The ABO_3 perovskites exhibit a wide range of combinations of A and B metal atoms, and are characterized by particular thermal stability. Therefore, perovskites are employed in many high-temperature applications, for instance in solid oxide fuel cells (SOFC) or as total combustion catalysts.[1,2] With the objective to get deeper understanding about the role of the A and B elements in oxygen and alkane (ethane, propane, and *n*-butane) activation, a matrix of perovskites was prepared including lanthanide elements La, Pr, Nd, and Sm used as A elements and the first row transition metal elements V, Cr, Mn, Fe, Co, and Ni applied as B elements.

The perovskites were synthesized via Pechini route using glycine as fuel and in selected cases by hydrothermal synthesis. XRD analysis showed phase purity of synthesized catalysts. The surface areas matched with crystallinity of the synthesized materials and ranged from 2 m^2/g to 30 m^2/g. The bulk structure of the catalysts is stable under reaction conditions of alkane oxidation.

The onset temperature in alkane oxidation was found to be below 200°C. Interestingly, not only the total combustion product CO_2 was observed in propane oxidation, but also a significant fraction of propene. The two molecules were the only products detected under all reaction conditions applied. In general, increasing temperature resulted in increasing activity of the perovskites, while only minor decrease in selectivity was observed. The B element determines the catalytic activity. Substituting La by Pr, Nd, and Sm leads to increased distortion of the structure and a decreasing M-O-M angle. This correlated with decreasing conversion rates of propane. Therefore, less distorted perovskite structures are apparently more active in conversion of propane.

The conversion of propane was also enhanced with increasing O_2 content in the feed indicating an important role of O_2 activation. After adding H_2O to the O_2 rich feed, a maximum selectivity to propene of about 40% was achieved using the $LaMnO_3$ perovskite. Contrarily, the selectivities to propene decreased in presence of steam employing for example $LaCoO_3$ and Fe-based perovskites. Only in the most selective $LaMnO_3$ catalyst a slightly shrinked lattice was observed indicating increased content of smaller Mn^{4+} compared to predominant Mn^{3+}. Redox and surface properties of selected catalysts have been studied by temperature-programmed methods, high-resolution electron microscopy, photoelectron spectroscopy, and vibrational spectroscopy and the results will be discussed in terms of activity and selectivity in propane oxidation.

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Morphology Effects in Oxidation Reactions over CeO_2

Teng Fu, Pierre Kube, Friedrich Seitz, Sabine Wrabetz, Meeseon Le, Detre Teschner, Annette Trunschke, and Robert Schlögl

Cerium oxide has been the subject of numerous investigations in heterogeneous catalysis mainly due to the oxygen storage capacity and acid-base properties of the material. Recent studies have shown that the morphology of cerium oxide affects the catalytic activity and, when used as support, the metal-support interactions. [1,2]

In this work, cerium oxide "nano-rods" and "nano-cubes" with varying particle size distribution have been synthesized through a hydrothermal approach. Precipitation was applied to prepare a morphologically less defined reference material denoted as "particles". The catalysts were studied in oxidation of CO and propane.

In both oxidation reactions a strong impact of the morphology on the reaction rate normalized to the specific surface area was observed. However, the trends in the reaction rates at 550 K differ. In oxidation of CO, the rate over cubes was higher compared to the rate over particles and rods. In contrast, the specific reaction rate in propane oxidation decreases in the order particle>rod>cube.

Neither hydrogen consumption nor the rate related to the reduction of surface oxygen species determined by temperature-programmed reduction (TPR) correlate well with the reaction rates in the two oxidation reactions indicating that surface oxygen species are less relevant in terms of the reaction rates. Adsorption of CO and propane were studied by FT-IR spectroscopy and microcalorimetry, while oxygen adsorption was investigated by Raman spectroscopy. Various carbonate species including unidendate, bidendate, polydendate, inorganic-like, and hydrogen carbonate were formed upon contact of CeO_2 with CO. Furthermore, the thermal stability of the different carbonate species was analysed by temperature-programmed desorption (TPD)-FTIR spectroscopy. The thermal stability of all carbonates decreases in the order rod≈cube>particle. A good correlation between the relative amount of carbonate species formed after CO adsorption at 298 K as well as the amount still present at 550 K and the specific reaction rates in CO oxidation suggests that the formation of carbonate species plays a critical role in CO oxidation over cerium oxide. The different trends in the reaction rates are discussed in view of the adsorption of the substrate molecules and oxygen on cerium oxide.

References

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Activation of Molecular Oxygen on Metal Oxide Surfaces

Yuanqing Wang, Anna Maria Wernbacher, Andrey Tarasov, Frank Rosowski[a],
Annette Trunschke, and Robert Schlögl

The activation of molecular oxygen at the surface of metal oxides is of fundamental importance to selective oxidation, solid oxide fuel cells and gas sensors.[1] Oxygen reduction has been generally understood as stepwise electron transfer forming electrophilic molecular oxygen species including superoxide O_2^-, and peroxide O_2^{2-} as intermediates. Finally, dissociation under formation O^- radicals and incorporation of nucleophilic O^{2-} into the oxide lattice occurs. Alkane molecules and intermediates in alkane oxidation react differently with nucleophilic and electrophilic species. However, there is no direct and convincing proof of the oxygen activation process at the atomic level until now, which makes proposed reaction mechanisms in hydrocarbon oxidation only hypothetical. The paramagnetic species O_2^- and O^- are EPR active and have been detected on numerous metal oxides at low temperature. Peroxide species O_2^{2-} are not paramagnetic, but can be observed by vibrational spectroscopy.

We installed a Raman system that uses nine different lasers (from near infrared laser to UV: 785, 633, 532, 488, 457, 442, 355, 325, and 266 nm) as excitation sources, which may facilitate the discovery of adsorbed oxygen species due to resonance effects. In an attempt to clarify the oxygen activation and correlate it with activity and selectivity in alkane oxidation, multi-wavelength Raman spectroscopy was applied in combination with Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, isotopic exchange experiments and DFT calculations in an continuation of our work on V_2O_5 as a model system.[2]

Small changes in the $V2p_{3/2}$ core level, the V3d levels, and the V L_3-edge have been observed by NAP-XPS and NEXAFS experiments in presence of reducing and oxidizing atmosphere at low pressures (0.25 mbar). However, reversible oxidation/reduction of vanadium was not detected under these experimental conditions, but shown by *in situ* UV/Vis spectroscopy and *in situ* conductivity measurements at atmospheric pressure. Feed composition (oxidizing or reducing) and temperature (300-550°C) determine the oxygen exchange mechanism in bulk V_2O_5 involving either V=O, twofold-, or threefold-coordinated oxygen atoms as evidenced by Raman spectroscopy. Furthermore, a surface VO_x species was found on V_2O_5 characterized by a band at 1030 cm^{-1}. The reactivity of the various oxygen species with propane and the implications on the reaction mechanism in alkane oxidation will be discussed.

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Oxidation of Lower Alkanes on Supported Liquid-Phase Catalysts

Hamideh Ahi, Frank Girgsdies, Detre Teschner, Andrey Tarasov, Yuanqing Wang,
Frank Rosowski,[a] Annette Trunschke, and Robert Schlögl

Oxidative dehydrogenation of propane (ODP) to propene has been extensively investigated over the last decades with the aim to develop a process in which propene is produced independent of other olefins.[1] Much of the attention has been devoted to supported vanadium oxide. However, no clear relations between the structure of surface vanadium oxide species and the properties of the catalysts have been identified so far. Applying the concept of supported liquid phase catalyst (SLP) we investigate whether structurally equilibrated species in a liquid film on the catalyst surface fulfill the requirements for selective alkane activation in comparison to more rigid structural arrangements of metal oxide species at the surface of monolayer catalysts.[2]

Silica-supported potassium pentavanadate has been chosen as a model system in the present investigation due to the appropriate melting point of this solid (410°C), which allows the investigation of catalytic performance both in solid and liquid states. As evidenced by differential scanning calorimetry (DSC), $K_3V_5O_{14}$ melts in air between 403 to 412°C both as pure substance and supported on silica. The V/K ratio of 1.33 determined by XPS indicates a slight enrichment of potassium on the surface. The ratio does not change significantly with increasing temperature verifying that K is not lost by evaporation or migration into the bulk of the support. The melting has been also observed by high temperature X-ray diffraction in air and *in-situ* Raman spectroscopy in the feed of 7.5 C_3H_8 : 7.5 O_2 : 85 N_2. The peaks due to crystalline $K_3V_5O_{14}$ in the diffraction patterns disappear above 400°C and the Raman spectrum changes in the range of V-O and V=O stretching vibrations above the melting point. All experiments confirm that a supported liquid phase is formed in the feed of the reactants at temperatures above 400°C.

The catalytic test in a fixed bed reactor exhibits an increase in selectivity towards propene by 20-40% after phase transition from solid to liquid at comparable conversion. At the same time a component at 500 nm in the *operando* UV-Vis spectrum of the catalyst due to the pseudo-octahedral coordination of V in the layered structure of $K_3V_5O_{14}$ decreases, and a peak at 330 nm most likely due to tetrahedral coordination of V increases. The experiments indicate that the transformation of a supported phase from solid to liquid has a positive impact on the selectivity in oxidative dehydrogenation of propane to propene due to structural changes in the local coordination around the vanadium atom highlighting the potential of SLP catalysts in selective oxidation of alkanes.

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The Relevance of Phase Transitions in Na-Mn-W-Oxide Catalysts for the Oxidative Coupling of Methane

Hamideh Ahi, Michael Geske,[a] Frank Girgsdies, Johannes Noack, Frank Rosowski,[b]
Robert Schlögl, and Annette Trunschke[b]

The Mn-Na_2WO_4/SiO_2 catalyst system for oxidative coupling of methane (OCM) has been extensively investigated over the last decades.[1] The reaction temperatures applied in OCM are usually above 730°C. Under these reaction conditions, liquefaction of an active component that contains alkali and transition metal oxides should be taken into consideration. To investigate the influence of sodium on the physical and catalytic properties of supported Na-Mn-W-oxide model catalysts, we have studied the thermal behaviour of supported and unsupported mixtures of sodium oxide and manganese tungstate applying thermal analysis, X-ray diffraction, *operando* Raman spectroscopy, and electron microscopy.

Mixtures of Na_2CO_3 and $MnWO_4$ have been prepared by grinding. The mixtures with or without steatite used as support (20 wt% loading) have been heated to 850°C for 1-16 h in flowing synthetic air (20 ml min^{-1}). Due to the use of $MnWO_4$ the Mn:W ratio was kept constant at 1:1, but the Na content was varied. The Na:Mn:W ratios ranges from 80:10:10 to 40:30:30.

Na_2WO_4 and $MnWO_4$ are the main supported phases formed. Phase composition varies depending on the composition of the mixtures. Thermal analysis reveals a complex melting behaviour showing two main endothermic events with on-sets at 570°C and 650°C, respectively. Based on the results of Raman spectroscopy these events are related to first order phase transition of Na_2WO_4 from the cubic structure to the orthorhombic structure, and to the melting point of Na_2WO_4, respectively. $MnWO_4$ melts at 1250°C.

The catalyst with the highest sodium content (80%) is characterized by the lowest activity and comparatively low selectivity. With increasing sodium content the activity increases. At comparable conversion the highest selectivity to C2 products (sum of ethane and ethene) has been achieved with the catalyst that contains the lowest amount of sodium.

Relations between the presence of a molten sodium tungstate and the onset of the activity in OCM have not been found. Under reaction conditions, significant changes in the Raman spectra of the catalysts occur that suggest substantial structural changes. The lattice vibrations of $MnWO_4$ disappear at 700°C. The observation is tentatively attributed to dissolution of $MnWO_4$ in molten Na_2WO_4, which seems to characterize the active state of the catalyst under reaction conditions of oxidative coupling of methane.

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Metals

The direct partial oxidation of ethylene to ethylene oxide (EO) over silver is one of the most well studied heterogeneously catalyzed partial oxidation reactions. The first plausible models dealing with selectivity appeared already in the 1940s. These postulated a special form of oxygen is involved in epoxidation, which became known as electrophilic oxygen. This oxygen species, characterized by an O 1s binding energy (BE) of ~530.5 eV is the only species known to produce epoxide during temperature programmed reaction, yet its structure remained elusive until we were able to show it is the oxygen in adsorbed SO_4 ($SO_{4,ad}$) that is part of a non-stoichiometric two-dimensional Ag/SO_4 phase where the sulfur is formally S(+V). (AC 2.3)

Ag supported on α-Al_2O_3 is used as catalyst for the industrial ethylene epoxidation. Promotors are added in order to reach EO selectivities up to 90% in the direct conversion of oxygen and ethylene. The knowledge gained about the functionality of the oxygen species present on the Ag surface under reaction conditions was used for the development of new synthesis concepts. A new promising class of catalysts, α-$AgAlO_2$ Delafossite systems was identified, and a novel synthesis route was established. (AC 2.4)

Alloying is a useful method for tuning a metal catalyst's electronic properties; however, mean-field behavior and scaling relationships impose limits on the catalytic performance that can be achieved with homogeneous alloys. We have found that certain dilute alloys can possess a unique electronic structure where the impurity state exhibits a free-atom-like electronic structure. In particular, we have found that AgCu alloys, dilute in Cu, exhibit weak wavefunction mixing between Ag and Cu *d*-states, resulting in free-atom-like anionic Cu 3*d* states. Density functional calculations show that this unique electronic structure has a strong influence on adsorbate bonding, whereby localized covalent bonding occurs that is akin to the bonding in molecular metal complexes. The adsorption behavior exhibits periodic trends that can be qualitatively predicted using simple graphical solutions to the Newns-Anderson-Grimley model of adsorbate binding. These results indicate that the adsorption trends stem from the unique combination of zero-dimensional and three-dimension properties that this alloy possesses. Screening of other Ag-based dilute alloys predicts a number of other compositions to have a similar electronic structure. (AC 2.2)

Silica supported Rh catalysts applied in ethanol synthesis from syngas have been characterized. In particular, the interaction of Rh with the promotors Fe and Mn promoters was studied. In-situ infrared spectroscopy led to new insights into the interaction of the adsorbed CO molecules with hydrogen. (AC 2.1)

Characterization of Mn- and Fe-promoted Rh Catalysts Supported on SiO_2 for Hydrogenation of CO to Ethanol

Maria Dimitrakopoulou, Xing Huang, Jutta Kröhnert, Maike Hashagen, Detre Teschner, Marc Willinger, Annette Trunschke, and Robert Schlögl

The need for alternative energy resources has led to the development of new types of catalytic systems for the synthesis of ethanol and other C_{2+} oxygenates from syngas.[1] Supported Rh-based catalysts are promising candidates since the selectivity towards the desired product can be tuned in a wide range by selection of either specific supports or promoters.[2,3]

The highest yields of ethanol have been achieved using manganese and iron as promoters. In the current work a silica-supported Rh catalyst containing 2.8 wt% Rh, 1.5 wt% Mn, and 0.5 wt% Fe was analyzed by in-situ infrared spectroscopy, electron microscopy, temperature programmed reduction, and X-ray photoelectron spectroscopy. The work was performed in the framework of the BasCat project. Catalysts and reference materials were synthesized by BASF. Kinetic studies, which confirmed the outstanding catalytic performance of the promoted catalyst, have been performed by hte, Heidelberg.

The findings reveal an intimate contact between Rh metal and the promoters. The elements are homogeneously distributed on the surface of the support in the calcined catalyst precursor forming complex mixed oxides. Reduction results in bimetallic Rh_xFe_y alloy particles that are partially covered by $Mn(Fe)O_x$ species containing Mn and Fe in low oxidation states. The statistical EDX measurements show the Fe/Rh mass ratios are 0.095 in the reduced alloy particles and 0.14 in the catalytically used Rh-Mn-Fe/SiO_2 catalyst. FTIR spectroscopy indicates metallic Rh is accessible to the reactants due to a perforated structure of the oxide shell. However, carbon monoxide adsorbed as a linear carbonyl species on the metal hardly reacts with hydrogen under 30 bar pressure at reaction temperature of 250°C, indicating that the free metal surface is less relevant in terms of catalytic activity.

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Free-atom-like *d*-States in Dilute Bimetallic Catalysts

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The bandwidth of metallic valence states plays an important role in chemisorption.[1,2] In general, the more narrow a valence band is, the more closely adsorbate bonding to that state resembles bonding in molecules. Metals generally have rather broad valence bands as a result of wave-function delocalization in the solid state. The narrowest of metallic valence bands are the d-bands of transition metals, with band widths ranging from ca. 3-10 eV.[3] Due to their narrow widths, d-bands have relatively strong interactions with adsorbate states, giving rise to the broad range of catalytic properties of transition metals. However, such valence bands are still wide enough that mean-field effects dominate and adsorption behavior is governed by average properties of the metal.

In the present work, we have found that certain dilute alloys can exhibit extremely narrow d-bands on the minority element. This phenomenon was observed using valence band photoemission spectroscopy of dilute AgCu alloys (dilute in Cu). In this case, the d-band of Cu exhibits a free-atom-like electronic structure and bonding to adsorbates that is akin to bonding in molecular metal complexes. This finding opens up many new possibilities for tuning catalytic properties.

In-situ XPS, measured during a test reaction of methanol reforming, shows that the narrow d-band of Cu in AgCu is retained under reaction conditions, while activation energy tests show that such catalysts exhibit a 0.1 eV lower activation energy for methanol reforming. DFT calculation using DFT methods show that the decrease in activation energy is a result of the increased charge density on the Cu center. This phenomenon is predicted to be possible with several other alloy combinations and could prove to be a valuable new parameter in alloy catalyst design.

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Sulfur in Ethylene Epoxidation on Silver

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Understanding ethylene epoxidation over silver has been long a standing challenge in heterogeneous catalysis, where a major problem has been rationalizing silver's selectivity to the epoxide.[1] Decades of effort have revealed two classes of oxygen species form on the active surface and can be distinguished by their O1s binding energy (Eb).[1-3] One type, nucleophilic oxygen with Eb(O1s)~528.1-528.4 eV, participates only in combustion while the second type, electrophilic oxygen with Eb(O1s)~530.5 eV, is involved in epoxidation.[1-3] The structure of nucleophilic oxygen is now well-known, as it can readily be prepared under UHV conditions. Formation of electrophilic oxygen, however, typically requires high pressure O_2 treatment or exposing the surface to the reaction gas mixture, which has hampered detailed knowledge of its structure.[1-3] But recently a method of preparing electrophilic oxygen under clean conditions was developed[4]. Together with ab initio calculations, this preparation method has enabled us to solve the structure of electrophilic oxygen. Curiously we find that this selective species is the oxygen in adsorbed SO_4 ($SO_{4,ad}$). This adsorbate is part of a two-dimensional Ag/SO_4 phase, where temperature programmed reaction and computed minimum energy paths reveal that only the non-stoichiometric surface phase, with formally S(+V), facilitates selective transfer of oxygen to ethylene. With this detailed knowledge of electrophilic oxygen we have performed a variety of in-situ XPS experiments aimed at furthering our understanding of the reaction under more realistic conditions. These experiments have demonstrated that under mbar pressures and during surface titrations the epoxide selectivity tracks the coverage of $SO_{4,ad.}$ Furthermore, they have exposed a rich subsurface chemistry involving the exchange of dissolved and surface SO_x species that may play a critical role in mediating the coverage of $SO_{4,ad}$ and hence epoxide selectivity.

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Synthesis and Investigation on Ag-Catalysts for Ethylene Epoxidation

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Ag supported on, mainly, α-Al_2O_3 is used as a catalyst for industrial ethylene epoxidation. The careful addition of promoters allows epoxide selectivities of up to 90% to be reached for the direct conversion of oxygen and ethylene. These promoters influence the complicated Ag-oxygen interaction.[1] Our institute has contributed significantly to the understanding of these interactions by studying interplay between various oxygen species in and on the surface model catalysts (Ag foils) for the ethylene epoxidation.[2] However, for the development of new industrially relevant catalysts, the knowledge gained from such model studies has to be transferred into new synthesis concepts. For this purpose new materials and model systems have to be investigated and new methods must be applied.

A new promising class of catalysts, α-$AgAlO_2$ Delafossite systems, were identified and a novel synthesis was established. These systems allow a smart catalyst approach where, the catalytically active Ag component is segregated in-situ. The mechanism of segregation (exothermic or endothermic event) and the temperature range (100-800 °C) for Ag decoration is adjustable by the reductive potential of the reactants, leading to a controlled Ag content with particle sizes between 5-50 nm. These catalysts showed not only high activities and selectivities in ethylene epoxidation, but also in probe reactions for the character of the activated oxygen species and surface acidity, CO- and *iso*-Propanol-oxidation, respectively.

The impact of small (< 5 nm) Ag-nanoparticles on oxidation reactions is still under debate.[3] To further clarify this point, Ag supported on SiO_2 (Aerosil) with narrow size distributions of 3 nm were synthesized and tested in ethylene epoxidation and CO-oxidation. Under industrially relevant conditions these promoter-free catalysts show EO selectivity of 80 % at comparably low-temperatures (< 200 °C). This is in agreement with CO-oxidation results, that indicate oxygen activation already at 50 °C.

Due to the high oxygen/oxidic content of the supports/catalysts used in the aforementioned systems O1s XPS analysis is impossible. However, to identify different kinds of oxygen species in and on the Ag-catalysts a TDS setup was constructed, which enables us to quantitatively analyze the oxygen fingerprints of powdered samples. In combination with in-situ Raman spectroscopy all the main oxygen species on Ag powder and various supported catalysts were identified and correlated with their relevance in ethylene epoxidation and CO-oxidation.

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Chemical Electron Microscopy

The way in which we picture and describe active catalysts is largely built on indirect observations and conclusions that are drawn on the basis of smart experiments and theoretical modelling. Direct imaging of the atomic arrangement and local compositional analysis is possible by conventional high resolution electron microscopy. 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 relevance if the active state of a catalyst is in the focus of the investigation.

Indeed, it has been shown that catalysts often show rich structural rearrangements, some of which are oscillatory in nature.[1,2] In order to capture the dynamics that evolve in the active state, we have recently implemented commercially available sample holders for *in situ* studies under controlled atmosphere and temperature inside a transmission electron microscope. To furthermore relate local processes that occur on the nanometre scale with collective phenomena that involve fast movement of large numbers of atoms, we have adapted an environmental scanning electron microscope (ESEM) for the investigation of catalytically active surfaces.[3] Using these two instruments, we are now able to cover a pressure range from 10^{-4} to 10^{3} *mbar* and a spatial resolution ranging from the *mm* to the *sub-nm* scale. Both setups are equipped with mass spectrometers for analysis of the gas-phase composition and detection of catalytic conversion. The latter is important because it allows us to relate observed dynamics to catalytic function.

The influence of the electron beam, which is still required for the observations, is carefully evaluated in each experiment. Presently we investigate structural dynamics that are observed during oscillatory red-ox reactions on nickel, platinum and copper catalysts. Direct observations are complemented by identical-location, quasi-*in-situ* observations. The latter allows tracking the modifications of individual catalyst particles upon exposure to relevant catalytic conditions (AC 3.4).

The ability to directly image the active catalyst and associated morphological changes at high spatial resolution enables us to refine the interpretation of spatially averaged spectroscopic data that was obtained under otherwise similar reaction conditions, for example, during near-ambient-pressure *in situ* XPS measurements[4] (AC 2.2). Direct observation such as exemplified on poster AC 3.2 for the case of redox dynamics of metals and in poster AC 3.1 for the CVD growth of graphene will have an influence on the way in which we depict and describe active catalysts and help building refined models for theory.

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In Situ Observation of Metal Catalysed CVD Growth of Graphene

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We have modified the set-up of a conventional scanning electron microscope (SEM) in order to enable the observation of catalyst surface dynamics under controlled atmosphere and temperature.

Using this instrument, we perform *in situ* investigations on chemical vapour deposition (CVD) growth of graphene on different metal catalysts. Since the experiments are performed in the chamber of a microscope, it is possible to observe complete CVD processes starting from substrate annealing through graphene nucleation and growth and, finally, substrate cooling in real time at nanometer-scale resolution without the need of sample transfer. The nucleation and growth of single layer graphene can be investigated at temperatures of up to 1000 °C, while at the same time, surface dynamics of the active metal catalyst can be studied. Growth on polycrystalline substrates reveals grain orientation dependent growth dynamics and catalytic activity.[1] Due to the high sensitivity of the secondary electron signal to changes in the work function and charge transfer at the surface, we are able to visualize different degrees of graphene-substrate coupling.[2]

In the case of graphene growth on copper substrates, we investigated the growth dynamics during different stages of growth as well as the effects of grain dependent substrate dynamics. In the case of graphene growth on platinum substrates, we revealed the growth kinetics of different layers in few-layer graphene. Real-time imaging under well-controlled atmosphere enables the observation of the response of in-plane dynamics in few-layer graphene to changes in the chemical potential of the atmosphere. By switching between graphene growth and hydrogen etching it is possible to distinguish between graphene layers that are inserted underneath or forming on top of the initial layer and thus, to abstract information about the stacking behaviour directly from the observation of in-plane dynamics.[2,3]

Finally, it will be highlighted that *in situ* scanning electron microscopy completes the spectroscopic data that is provided by complementary *in situ* techniques that provide spectroscopic information, such as ambient pressure X-ray and Raman spectroscopy. It adds the visual information and delivers unprecedented and direct insights about the complex interplay between environment, catalyst and formed product.

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Multi-Scale Red-Ox Dynamics of Active Metal Catalysts Revealed by a Combination of *In Situ* Scanning and Transmission Electron Microscopy

Jing Cao, Ali Rinaldi, Ramzi Farra, Zhu-Jun Wang, Milivoj Plodinec, Gerardo Algara-Siller, Elena Willinger, Xing Huang, Mark T. Greiner, Robert Schlögl,
and Marc G. Willinger

Many efforts have been made in order to investigate catalyst under relevant working conditions, and it is known that the action of a chemical potential has to be understood in order to describe the function and state of an active catalyst.[1,2]

In order to make the transition from imaging in vacuum to observation under relevant catalytic conditions, we have modified a conventional environmental scanning electron microscope (ESEM) and implemented MEMS-based gas-flow holders for *in situ* observation in the column of a conventional FEI Titan transmission electron microscope (TEM). Both set-ups are connected to home-built gas-feeding stations and mass-spectrometers for analysis of the gas-phase composition and detection of catalytic conversion. The two complementary instruments allow us to study dynamic processes under defined conditions at the µm to Å scale at pressures ranging from 10^{-2} to 10^{3} Pa. In this way, local observations that are made in the TEM can be related to observations that capture collective processes at reduced spatial resolution in the ESEM. Furthermore, direct visual observation of the active catalyst can be complemented by *in situ* electron energy loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDXS) and electron diffraction, which are available as analytical tools of the TEM.

We use the two set-ups to investigate the influence of the chemical potential of a gas phase on the composition, structure and dynamics of metal catalysts. One example is the observation of oscillatory red-ox dynamics during hydrogen oxidation on polycrystalline nickel, copper and platinum foils.

It will be shown how the combination of complementary *in situ* imaging and spectroscopic tools, including *in situ* NEXAFS and XPS[3], provides a unique insight on the rich structural and compositional dynamics and how the catalyst surface and bulk dynamics are controlled by the chemical potential of the gas phase.

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Identifying Key Structural Features of OER Active IrO_x Catalysts

Elena Willinger, Cyriac Massué, Robert Schlögl, and Marc G. Willinger

Large scale production of hydrogen by electrochemical water splitting faces enormous challenges that are related to reactions taking place at the anode side.

So far, X-ray amorphous iridium (hydr)oxides have been identified as most promising catalysts for the oxidation of water. Considering the importance of the reaction, a genuine understanding of the catalyst structure−function relationship is required. Although comprehensive spectroscopic and theoretical studies[1] have provided some insight on its electronic structure, information about the arrangement of relevant structural units within the amorphous phase is missing. Here we present a detailed comparative structural investigation of amorphous iridium (hydr)oxides that show distinct differences in their catalytic properties. Using real-space atomic scale imaging in combination with analysis of the atomic pair distribution function abstracted from electron diffraction, we are able to identify key structural motifs that are linked to the high activity in water splitting. Furthermore, the electronic structure resulting from the structural arrangement is investigated by electron energy loss spectroscopy (EELS) and compared to reference phases. Our results indicate that high activity is related to the presence of interconnected, single unit cell sized hollandite-like structural domains. These units are cross-linked through under-coordinated oxygen/iridium atoms.

The less active and unstable IrO_x reference sample contains, besides the hollandite-like structural domains a substantial amount of rutile-like structural motifs. The latter are thermodynamically more stable and known to be catalytically less active.[2] Compared to the flexible hollandite-like framework, the rutile phase results in a faster structural collapse and deactivation.

Our findings promote a rational synthesis of amorphous IrO_x hydroxides that contain a favourable arrangement of structural units for improved performance in catalytic water splitting.[3]

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Exploring Structural Complexity by Quasi *In Situ* TEM: Local Structures in Complex Mo and V Mixed Oxides

Liudmyla Masliuk, Klaus Hermann, Annette Trunschke, Marc G. Willinger, Thomas Lunkenbein, and Robert Schlögl

Heterogeneous catalysis has emerged to a ubiquitous technology, whose products promote our everyday life. Parallel optimizations of catalytic and synthetic protocols of solid catalysts, have rendered this technology into the future chemical approach for efficient energy conversion. Those solid catalysts are intrinsically composed of defects in their bulk and surface structure, which can significantly alter the catalytic performance. Defects, however, are often treated as white spots on the catalytic landscape since they are, due to the lack of translational symmetry, hard to pinpoint. Qualitative and quantitative defect estimation could reflect important defect- activity correlations, which will boost the understanding in heterogeneous catalysis and will simplify a prospective catalyst tailoring. Using scanning transmission electron microscopy (STEM) we explore local structural variations in orthorhombic $(Mo,V)O_x$.[1,2]

Up to 19 different structures were observed in orthorhombic $(Mo,V)O_x$ that can be listed and classified into different structural motifs, intergrowth, channels, interstitial regions, and inclinations. The observed defects can be composed of Mo or V enriched metal sites and are expressed by the rearrangement of the $\{(Mo)Mo_5O_{27}\}$ building blocks. Furthermore, the evaluation of 31 orthorhombic $(Mo,V)O_x$ crystals yields an average defect concentration of 3.3% and indicates the absence of identical particles. In addition, we have observed 54 of these rearranged structural motifs close to the surface of one $(Mo,V)O_x$ particle (100x50 nm^2). A detailed analysis of the atomic arrangement at the surface of this particle suggests a surface composition of $(Mo_{610}V_{230}M_{70})O_x$ (M= Mo and/or V). We are currently expanding the principle of cataloging local nano-structures to a quantitative analysis of dynamic surface structures mimicking calcination and catalytic operation conditions of the catalyst by exploiting quasi *in situ* TEM techniques.

The knowledge of the diversity of defects generated by nano-structuring combined with a quantitative analysis will establish new defect-activity correlations that will allow explaining trends in heterogeneous catalysis in greater detail.

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Activities of the Electrochemistry Group

The development of electrochemical devices with high energy densities accompanied by long cycling life is essential to store energy produced by intermittent and renewable energy sources. Si represents an attractive anode material for the next generation of lithium ion batteries (LIBs) owing to its capacity to charge up to ten times more Li than currently used carbonaceous materials (3578 for Si versus 372 mAh/g for graphite). However, due to severe irreversible mechanical and electrochemical degradation mechanisms, and despite intense research over two decades, Si based anode technology is still hampered from a large scale commercialization. We are investigating Si deposited by a low pressure chemical vapour deposition technique on both carbonaceous powder substrates and on model electrodes. The use of model Si-anodes is expected to disentangle the fundamental cause of capacity reduction and irreversible degradation mechanisms upon electrochemical cycling and derive structure-function relationships. These may in the future facilitate a rational development of novel, industrially applicable and powder based Si-anode materials, see posters AC 4.1 and 4.2. This work benefits from a fruitful collaboration with Volkswagen Research Centre and the Helmholtz-Zentrum Berlin.

Accompanying the development of energy storage devices, electrocatalysis will play a defining role in energy storage technologies and energy conversion systems of the near future, particularly in water electrolysis. The performance of water splitting systems is limited by the stability of the anodic electrocatalysts. Our group has accomplished a major breakthrough in this field by producing an amorphous Ir-oxohydroxide via a rapid hydrothermal microwave synthesis.[1,2] The catalyst achieved an unrivalled activity and 33 times longer than the best commercial Ir benchmark, both as the neat compound, and supported by antimony-doped tin oxide.[3] In addition, we have suggested a fundamental working scheme for this novel class of OER electrocatalysts.

Charge transfer at interfaces plays a decisive role in materials science and is of particular relevance in energy storage devices (batteries), energy conversion processes (water splitting) and heterogeneously catalyzed reactions. Our group has developed a set of tools based on the Microwave Cavity Perturbation Technique (MCPT) and recently completed a Microwave Hall Effect (MHE) setup to characterize the dielectric properties of catalysts *in situ* and contactless. These powerful instrumental techniques were used to characterize the charge carrier properties of selective oxidation and CO_2 hydrogenation catalysts (AC poster 4.3) and the MHE technique was successfully applied in the characterisation of a series of Al^{3+} promoted Cu/ZnO catalysts (AC poster 4.4). This latter pioneering and challenging work unequivocally demonstrated the invaluable analytical capabilities of the MHE technique for heterogeneous catalysis.

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Investigation of Irreversible Processes of Silicon Deposited by Low Pressure Chemical Vapor Deposition on Carbonaceous Materials as a High Performance Anode for Lithium Ion Batteries

Kathleen Lamoth, David Klein, Andrey Tarasov, Wiebke Frandsen, Xing Huang, Marc G. Willinger, Sébastien Cap, and Robert Schlögl

Today, efforts are being made to design anode materials based on silicon, as this element reversibly forms alloys with Li at low potential (vs Li^+/Li) with a specific charge capacity exceeding the one of carbonaceous materials by one order of magnitude. However, silicon-based anodes have a poor cycling stability, which is speculated to be related to two distinct irreversible processes, namely the mechanical and the electrochemical degradation. It is our aim to investigate the fundamental cause of capacity fade decrease and the irreversible degradation mechanism upon lithiation and delithiation of Si-based anodes through the comprehensive synthesis of a series of Si-carbon anode materials and their exhaustive characterization. Ultimately, we aim to derive structure-function relations that affect the electrode stability and dynamics useful for the development of novel Si-based anode materials.

As a major milestone of this research, a Low Pressure Chemical Vapor Deposition reactor (LPCVD) was developed to homogenously deposit Si on numerous morphologically different carbonaceous materials (graphite, multi-walled carbon nanotubes, carbon black) in a single batch. Compared to wet chemical approaches, the LPCVD process has several advantages: it is clean, reproducible and allows the synthesis of series of materials whose material properties, *e.g.*, crystallinity, can be systematically varied with exceptional control.

Si was deposited on a high surface area graphite while varying deposition time, temperature and gas composition. Subsequently, the samples were compared to a standard commercially available material composed of a mixture of Si nanoparticles (SiNPs) and graphite. The LPCVD deposition of Si from neat silane (SiH_4) decomposition revealed the formation of Si nanodroplets. Post mortem analysis demonstrated that the adhesion of these Si nanodroplets to the graphitic surface is superior compared to standard SiNPs-graphite composite materials. In addition, amorphous Si produced at low deposition temperatures (< 550°C) showed different charging behaviour than the SiNP-graphite composite and has improved electrochemical cycling characteristics. Currently, photoemission spectroscopy is being used to compare the electrolyte decomposition products between selected synthetized materials and relate them to their electrochemical performances.

We have furthermore investigated the effect of a thin protective layer of carbon deposited onto Si-graphite materials on the electrochemical performance. From these results, we have defined an optimum carbon thickness for reducing the irreversible degradation and have critically discussed the effect of a native SiO_x layer on the anode electrochemical cycling performance.

Model Based Investigation of Irreversible Degradation Processes of Silicon Thin Films as Anode Material for Next Generation Lithium Ion Batteries

David Klein, Kathleen Lamoth, Wiebke Frandsen, Adnan Hammud, Xing Huang, Walid Hetaba, Marc G. Willinger, Sébastien Cap, and Robert Schlögl

Si based anodes represent attractive materials for the next generation of lithium ion batteries (LIBs), owing to their capacity to charge up to ten times more Li than current carbonaceous materials (3578 for Si versus 372 mAh/g for graphite). However, due to severe mechanical and electrochemically irreversible degradation mechanisms, and despite intense research over two decades, Si based anode technology is still hindered from large scale commercialization. The vast majority of current Si-based anode research is performed by mixing Si-compounds, conductive carbonaceous additives, and binder and casting the mixture on a metallic current collector. Such an approach has proven to be cost efficient for the production of anodes, though their intrinsic complexity leads to challenging fundamental research. It is our aim to investigate model Si electrodes, where fundamental processes are expected to be easier to disentangle. The fundamental cause of capacity decay as well as irreversible degradation mechanisms upon cycling are investigated, in order to derive structure-function relations/relationships/correlations, for the development of novel, industrially relevant Si based anode materials.

For this specific purpose we developed a Low Pressure Chemical Vapor Deposition (LPCVD) reactor which allows the deposition on both planar substrates (used as model electrodes) and carbonaceous powders. This methodology allows in a single batch the production of reproducible scientifically and industrially oriented samples. A key step of this research consisted defining a suitable metallic current collector which does not form silicides during high temperature (>500°C) Si deposition using the LPCVD reactor. As a further experiment, an electron beam evaporation technique was used to deposit well defined thin films of amorphous H-free Si, on previously defined current collectors and under ultra-high vacuum conditions. This electrode defines our internal benchmark for the Si model anode system, see Poster 4.2.

Based on the above, we have deposited Si thin films on metallic current collectors in order to evaluate the experimental parameters affecting the electrochemical cycling stability by numerous varying parameters. In this work, we investigated the variation of, Si thin film thickness, electrolyte composition, electrochemical cycling protocols, Si thermal annealing and Si surface functionalization. The obtained results were used to develop a concept of Si based anode degradation mechanisms in the aim to derive a first principle degradation model. Furthermore, taking into account the conclusions of this study, an innovative Si thin film based anode was synthetized on a porous metallic conductor which demonstrated outstanding electrochemical cycling performances, technologically suitable for an immediate large-scale deployment.

Investigation of Charge Transfer at Interfaces Using the Contact-free and *In Situ* Microwave Cavity Perturbation Technique

Elisabeth H. Wolf, Anna M. Wernbacher, Maria Heenemann, Marie-Mathilde Millet,
Thomas Risse, Elias Frei, Sébastien Cap, and Robert Schlögl

Charge transfer across interfaces plays a decisive role in several research fields, such as energy storage/conversion processes, and in heterogeneously catalysed reactions. Charge carrier properties are typically evaluated using contact-based methods, *e.g.*, the Van der Pauw method, which is used to quantify the materials' conductivity, or to evaluate the Hall coefficient of the material. While these contact methods have proven to be effective, in the case of a powder sample electrode-material and grain boundary resistances impede an accurate, quantitative, and sensitive investigation of the charge carriers. To circumvent these limitations, our group has successfully developed a contact free Microwave Cavity Perturbation Technique (MCPT) which allows the evaluation of the materials' dielectric properties at various temperatures and gas atmospheres. As an example, MCPT was successfully applied to characterize the charge transfer between bulk, surface, and gas phase of selective alkane oxidation catalysts.[1]

Methanol is an essential feedstock for the chemical industry and can play a central role as a future carrier of sustainable energy. Methanol is produced over a $Cu/ZnO/Al_2O_3$ catalyst from syngas, but the fundamental role of Cu and ZnO in this reaction is still under debate. In the present contribution, we aim to report our latest achievements in the charge carrier characterization of the Cu/ZnO system under catalytically relevant conditions. By characterising electronic contributions in this reaction, we ultimately aim to contribute to a better understanding of the catalyst, facilitating a rational synthetic approach.

In this effort, we have completed the instrumental development of the MCPT setup by the design of several resonant cavities, giving us the ability to investigate the frequency dependence of the materials' conductivity. This instrumental achievement allowed us to gain insight into the nature of charge carriers, *e.g.*, free or bound charges, of unpromoted and promoted (Mg, Al, Ga) polycrystalline ZnO. As a next step, we have expanded the use of the MCPT technique to samples more conductive than wide band gap semiconductors, and defined experimental methods and limitations. This methodological basis was used to provide additional experimental data to critically discuss the direction of charge transfer between Cu and ZnO, considering a series of Cu/ZnO samples with increasing amount of Cu. To address this latter question, we use MCPT alongside complementary techniques including TEM, DR-UV-vis spectroscopy, and EPR. Our findings of changes in the effective conductivity under reaction conditions support the hypothesis of a charge transfer in the direction from Cu to ZnO with results detailed in AC poster 4.3.

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In situ Charge Carrier Characterisation Using the Microwave Hall Effect Technique

Maria Heenemann, Thomas Risse, Reinhard Stößer, Elias Frei, Annette Trunschke,
Sébastien Cap, and Robert Schlögl

The very successful use of the MCPT to investigate *in situ* changes of dielectric properties of catalysts (see AC poster 4.3) has endeavored our group to develop an *in situ* Microwave Hall Effect (MHE) technique. The Hall effect has been discovered over a century ago and is nowadays routinely used to measure electronic properties of a vast range of materials with applications ranging from biology to aerospace engineering. Similarly to MCPT, the MHE technique is a contact free method, thereby avoiding ambiguities related to contacts between the electrode and the material being investigated and variable intragranular electronic connections. The acquisition of the MHE technique is very desirable, as it allows us to discriminate between the contributions of charge carrier mobility and density, which information, evaluated while the catalyst is in operation, is of invaluable analytical interest for heterogeneous catalysis. The poster AC 4.4 describes the detailed achievements of the MHE instrument development from its conception to the latest *in situ* measurements.

The MHE instrument is based on a bimodal cavity which is currently the most sensitive method to characterize charge carriers. A bimodal cavity has two degenerate orthogonal modes at identical resonant frequency, which we name excitation and sensing mode. The sample to analyze is positioned in the maximum of the electric field common to both modes. Under ideal conditions, and without applied external magnetic field, no energy is transferred between the two orthogonal modes. However, in presence of an external continuous magnetic field, charges will be accelerated according to the Lorentz force law and transfer energy to the "sensing" orthogonal mode. The amount of power coupled from the excitation mode to the sensing mode is proportional to the charge carriers' mobility. Subsequently, we have thoroughly validated the MHE setup using doped Si, Ge and intrinsic ZnO single crystals and extended the validation to ZnO powder. We have additionally adapted and validated an *in situ* plug flow reactor setup, whose design is based on the MCPT setup, for the measurement of the MHE signal of ZnO powder at elevated temperatures.

As a major and latest accomplishment, the constructed and validated MHE setup was used to characterize the promoting effect of Al^{3+} on the charge carrier density of a Cu/ZnO model catalyst under reverse water-gas shift reaction conditions. We have determined the electrical conductivity, charge carrier mobility and absolute number of charge carriers. We are reporting an increase of charge carrier density with increasing concentration of Al^{3+}, as well as a strong correlation with the CO formation, see poster AC 4.4 for more details.

This pioneering and challenging work unequivocally demonstrated the invaluable analytical capabilities of the MHE technique for application in heterogeneous catalysis.

Carbon Based Electrode Materials

Saskia Heumann (née Buller)[a], Youngmi Yi[a], Pascal Düngen [a], Jan Straten[a], Yang-Ming Lin[a], Yuxiao Ding[a], Fabian Wachholz[a], and Robert Schlögl

It is well-known that efficient, cheap, abundant, environmentally friendly alternative electrode materials for water splitting are required to overcome a global demand for energy conversion and storage systems. The knowledge-based development of electrode materials of our research is focused on compound materials of carbons as conductive base material and the deposition of transition metals as nanostructured catalytic active sites.[1]

Carbon materials fulfill the requirements of a conductive support that provides high surfaces areas as well as specific functional groups that are able to anchor catalytic active metal oxides. Systematic changes of the synthesis parameter, like pH or the addition of manganese salts or urotropine for the incorporation of heteroatoms in the graphitic layers, are performed. Variations of the initial pH mainly influence the degree of condensed graphitic layers that are performed during the autoclave process.[2] The initial synthesis conditions therefore influence the electrocatalytic performance of these.

The characterization of carbon support materials by Raman spectroscopy was revised for high graphitic carbon materials like multi-walled carbon nanotubes (MWCNT). The single phonon resonance fitting procedure allows the thorough determination of defect formation.[3] Thermal analysis was refined to gain better qualitative and quantitative knowledge about the surface functional groups. This isothermal heating approach allows the detailed investigation of functional groups that can act as anchoring sites that are required for the deposition and stabilization of metal species.

The electrochemical performance of the carbon based electrode materials was mainly investigated for the oxygen evolution reaction (OER) in alkaline or acidic media. Long-term stability measurements in different electrolyte media revealed that the oxidation mechanism of carbon materials is pH dependent.[4] Surface oxide formation and accompanying dissolution can be observed in alkaline media whereas bulk oxide formation can be determined in acidic media.

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EMIL: Bridging the "Pressure Gap" in Electron Spectroscopy

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The EMIL project (Energy Materials In-Situ Laboratory Berlin) of HZB and MPG at the BESSY synchrotron aims to contribute to a better understanding of processes that take place at solid-gas and solid-liquid interfaces. Electrified interfaces are relevant in general to electrochemistry and in particular to chemical energy conversion and storage. However, the number of methodologies able to provide information of the reactions taking place on the surface of electrified electrodes is rather limited. This applies in particular to soft X-ray techniques that require high vacuum for their operation. The discrepancy between low pressure during X-ray spectroscopy characterization and higher operating pressures is known as the "pressure gap". The EMIL beamlines expand the available photon energy range from 80eV to up to 8000eV allowing photoelectrons at higher kinetic energy to be utilized as a probe of the interfaces.[1,2] Two canted undulators serve as a source for two plane grating monochromators and one liquid nitrogen cooled double crystal monochromator to make this wide photon energy range available in one overlapping focus. In combination with a small entrance aperture of a differentially pumped electron spectrometer ("ambient pressure–XPS") a high operation pressure can be achieved. It becomes feasible to study liquid electrolyte films of several tens of nanometers thickness due to the fact that the vapor pressure of water (~20 mbar at room temperature) can be established during the XPS experiments. The high kinetic energy assures that the photoelectrons generated at the solid-liquid interface can penetrate the thin film of liquid and can be detected before they are inelastically scattered. Hence, the EMIL facility allows XPS under liquid environments.

A different methodological approach makes use of an ultrathin photoelectron transparent membrane based on a graphene layer to separate the liquid in thermodynamic equilibrium at room temperature from the vacuum where the analyzer is located.[3] Combined with an array of micro holes as a support structure for the graphene, the mechanical stability issue of free standing graphene covering large open areas can be overcome while still providing high transmission for low kinetic energy electrons and allowing operation pressures up to 1.5 bar. Using this approach it was possible to fabricate an electrochemical liquid flow cell which refreshes the electrolyte due to a continuous flow of liquid allowing the investigation of several processes that take part at solid-liquid electrified interface. Using a similar approach it became feasible to investigate relevant solid-gas interfaces at atmosphere pressure under reaction conditions with simultaneous on–line reaction product analysis.

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Materials for Catalytic Oxygen Evolution

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The MAXNET Energy is research cooperation is 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 (OER).[1] Two groups of catalytic materials for OER have been the subject of the current research.

The first group represents Pt-based intermetallic compounds. OER performance is examined for binary PtAl and ternary PtHfAl systems as anode material. Activity, stability and corrosion are examined in electrochemical flow cell coupled with ICP-MS. XPS and SEM reveal oxidation of Al during OER reaction and its partial leaching into solution. Pt is found in +2 and +4 oxidation state after OER. Compositional changes in near surface region are confirmed with product analysis of the outflow. The catalyst´s stability in OER agrees well with corrosion rate.

The second group comprises amorphous Ir-based oxohydroxides for OER electrocatalysis. The generation of a solid Ir compound through hydrothermal synthesis is determined by the complex chemistry of solvated Ir at basic conditions. The type of base and metal to base ratio affects the microstructure of the amorphous Ir-based material and catalytic performance in OER of the final catalyst.[2] Ir-OH species accommodated in particular $Ir^{III/IV}$ environment render as OER-related structural features.[3] *In-situ* XPS investigation of amorphous Ir compounds points out the presence of OER-relevant nucleophilic O species.[4,5] Alkali metal cations present in smaller amounts are thought to play a major role in stabilizing a high-performance Ir oxohydroxide phase. SEM shows formation of porous sponge-like morphology for Li - base route and flat surfaces in presence of K^+ cation. A set of complementary thermoanalytical methods applied for quantification of oxohydroxo surface groups indicates decrease in the reactivity of the active oxygen species for $K^+>Na^+>Li^+$. This trend is consistent with OER performance.

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Electronic Structure of Mn Based Catalysts Relevant for the OER

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In nature the oxygen evolution reaction (OER) is carried out by photosystem II and takes place at the oxygen evolving complex (OEC), also known as the water oxidation complex (WOC), with a [Mn4Ox:Ca] core structure.[1] The obvious resemblance of the OEC with inorganic manganese oxides makes the latter interesting candidate catalysts for the OER. [2, 3]

Birnessite, a layered manganese based oxide, is known to be active in the OER.[4, 5] We will compare the properties of Ca-birnessite powder with screen-printed electrode layers on FTO[6] and the changes following oxygen evolution in 0.1M phosphate buffer pH7. The results suggest dynamic ion exchange within a very porous Ca-birnessite anode during water oxidation. The intensity ratio of Mn 2p to Ca 2p shows that the concentration of calcium in the birnessite catalyst decreases during the applied procedures. Deconvolution of the XPS P 2p line for the sample after electrochemical treatment shows remnants of the phosphate buffer interacting with the manganese based catalyst that could act as a proton acceptor. The modification of the material during OER was also confirmed by SEM / TEM. The calculated NEXAFS and XPS spectra of calcium using a configuration-interaction cluster model including the full atomic multiplet theory suggest a covalent interaction of the calcium ions with the oxygen ligands after electrochemistry in phosphate buffer under OER condition. This development will be related to the reversible changes in oxidation state of manganese under oxidation conditions which were studied by Mn L-edge.

We will briefly report on the development of manganese oxide based electrodes for the OER designed for in-situ measurements. This is the optimal, but also very challenging way, to understand the role of catalytic centers under realistic reaction conditions. The first approaches and issues recording Mn K- and L-edges during the in-situ electrochemical deposition of manganese oxides on silicon nitride membranes followed by their characterization under OER conditions will be discuss.

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CO_2 Activation on Model Catalysts: From Fundamental Understanding to Catalyst Design

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The hydrogenation of CO_2 to value-added products is a key process for a sustainable energy concept.[1,2] This modern and heavily-used term "value-added products" slightly conceals the real scientific challenge behind it. Activating CO_2 opens a chemical pathway to a complex reaction network with various target molecules, such as CO, CH_3OH, and CH_4, among others. The control of product selectivity is a demanding interplay of multiple parameters like reaction conditions (H_2:CO_2 ratio, temperature, pressure) and of course the catalyst used. For a knowledge-based catalyst development, a fundamental understanding of the CO_2 activation and the catalytic material is crucial. For this purpose we investigated the reverse water-gas-shift reaction (rWGS, as a first hydrogenation step in CO_2 to CO and H_2O) on two series of model catalysts.

Using a solid solution approach, a series of NiO/MgO catalysts were successfully synthesized with varying Ni content. The isolated character of Ni is retained until 10 at.-% leading to single atoms embedded in a MgO matrix, available for the adsorption of CO_2. Ni is preferentially located at steps and corners of MgO and, as a consequence, the catalysts surface is rich in defects. The degree of substitution (Ni_{Mg}) correlates directly with the CO_2 adsorption capacity quantified by microcalorimetry (adsorption energies 1.2-1.3 eV). This is in perfect agreement with calculations from the Theory Department, with calculated adsorption energies of CO_2 at the MgO (110) surface, and at the O-terminated octopolar reconstruction of the polar MgO (111) surface (TH 20).[3] Moreover, with the increasing number of adsorption sites for CO_2, the activity in the rWGS reaction increases, evidencing a direct correlation between the concentration of single atoms of Ni on surface and the catalytic performance.

A combined quantitative charge carrier analysis and catalytic activity investigation of Cu/ZnO:Al (Al 0-1.7 wt.-%) model catalysts was performed. We show for the first time that the contact-free and operando microwave Hall effect technique is able to measure charge carriers in Cu/ZnO-based model catalysts under rWGS reaction conditions. This method allows analyzing the electrical conductivity, charge carrier mobility, and absolute number of charge carriers. An increase in charge carrier concentration with increasing Al^{3+} content as well as its direct correlation to the catalytic activity for CO formation is found. The increased availability of charge carriers plays a key role in the CO_2 activation and CO formation processes, which finds additional support in a concurrent decrease of the apparent activation energy and increase in the reaction order of CO_2. Complementary to our studies, the interaction of CO_2 with a single crystal (10-10) surface is investigated in the PC department. Time-resolved photoelectron spectroscopy suggests that CO_2 is reduced upon adsorption and by cross-bandgap photo-excitation of ZnO (PC 28).

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CP 14 **Data Acquisition in Science. A General Approach**

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Heinz Junkes, Markus Heyde, Patrik Marschalik, and Wieland Schöllkopf

Resolving Dynamic Processes in Real Space with Variable-Temperature High-Speed Scanning Tunneling Microscopy

Zechao Yang, Patrik Marschalik, Jens Hartmann, Heinz Junkes, Gero Thielsch,
Burkhard Kell, Markus Heyde, and Hans-Joachim Freund

Silicon is the most abundant element in the earth's crust. Its oxide, silica (SiO2) is the basis for most minerals of the earth's crust, and also for a number of technological applications ranging from window glass, via electronics to catalysis. However, until recently, a real space image of a bulk silica glass with atomic resolution had not been recorded.

Scanning probe microscopy (SPM) techniques have been applied to metal supported thin silica films. It has been possible to clearly resolve individual atomic sites of both crystalline and vitreous silica network structures in real space.[1,2] Recently, atomic rearrangements in this film system were observed by transmission electron microscopy (TEM) under the impact of an electron beam.[3] Our study aims to resolve dynamic processes between the amorphous phase and the crystalline phase via a liquid phase (or vice versa) as a function of temperature in real space. For this purpose, we are developing a high speed scanning tunneling microscope (STM) that will be operated over a large temperature range from cryogenic temperatures to approximately 1200 K.

A compact, highly symmetric microscope body will be attached to a continuous flow cryostat with a temperature range from 4 to 500 K. This combination optimizes the temperature stability, thermal drift and vibrational noise during scanning. A built-in e-beam heater is designed for the sample holder, which is used for annealing during silica film preparation and heating to trigger transitions during measurements. To ensure efficient high-speed scanning, the piezo will move in the Lissajous scanning mode.[4] A hybrid-electronics solution will be used for the measurements beyond video-rate, which will be realized by a combination of a typical commercial SPM control unit (Nanonis control system) with custom-made high-speed electronics Versa Module Eurocard bus (VMEbus) technology. Furthermore, an atom-tracking program will be developed to automatically correct the thermal drift caused by the temperature ramp.

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The Atomic Structure of a Metal-Supported Thin Germania Film

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Germanium oxide (GeO_2), or germania, is a highly insoluble thermally stable germanium source used in engineering optical materials such as windows and lenses for night-vision technology, luxury vehicles, and thermographic cameras. Germania can be prepared in both crystalline and amorphous forms,[1] and it is mechanically stronger than other infrared (IR) transparent glasses, making it more reliable in harsh environmental conditions.

Analyzing the atomic structure of germania plays a critical role in the understanding of its material properties. In this study we investigated structures within a germania film on a ruthenium, Ru(0001), substrate. The samples were grown in an ultra-high vacuum chamber. A structure study by LEED-*IV* (Low energy electron diffraction) analysis was combined with high-resolution real-space imaging by scanning tunneling microscopy (STM). Atomically flat monolayer germania films have been prepared allowing to resolve in clear and detailed STM images the individual network and domain boundary structures.

Throughout the structural analysis, LEED measurements were taken over an energy range of 60 and 550 eV with steps of 1 eV. 42 diffraction spots were recorded and averaged over 6 symmetry equivalent spots, leading to a total energy range of 2500 eV. The experimental curves were compared to modeled diffraction pattern intensities from suggested test structures based on density functional theory (DFT) calculations. The individual preparation steps from the clean Ru(0001) substrate,[2] the oxygen pre-covered Ru(0001)[3] and finally the deposited germania films on Ru(0001) were separately analyzed. For the germania films the best agreement has been achieved with DFT structures where the germanium atoms sit preferentially on atop and fcc hollow sites of the Ru(0001) substrate.

From the STM images, we found that a series of ring networks are formed from germanium and oxygen atoms on this 2D film. The size of a particular ring is defined by the number of germanium atoms in the ring. Ideal crystalline regions contain only six-membered rings, while domain boundaries and defects introduce other ring sizes. We identify a variety of domain boundaries within monolayer germania structures from STM data, discuss characteristic properties of the sample that result from these defects, and develop atomic models for the relationship between domain boundaries and the substrate. Initial results from germania films with coverage larger than 1ML reveal that both crystalline and amorphous configurations of germania might exist.

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Resolving Atomic Structures at Silica-Water Interfaces

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Silica and silicate surfaces are ubiquitous in nature, science and technology with occurrence in fields like geology, medical research (silicosis), device technology, biomineralization and heterogeneous catalysis. Despite this, detailed understanding is frequently prohibited by lacking information on surface structure and chemistry.

Here we present atomic scale atomic force microscopy (AFM) results recorded in liquid.[1,2] Image data from an ultrahigh vacuum (UHV) grown 2D silica bilayer film[3,4,5,6] is compared to high resolution air and liquid AFM results from corresponding bulk silica (c-SiO_2(0001), i.e. α-quartz(0001) and v-SiO_2, i.e. quartz-glass) surfaces. In contrast to the UHV grown films the bulk samples have been prepared either by high temperature annealing (1100°C) in air or by etching in acid or base solutions. This aims at preparations above or below the structural phase transition between α-quartz and β-quartz at 573°C as well as portability of the preparation to the quartz glass surfaces.

On α-quartz(0001) air annealing produces nicely ordered terraced surfaces. AFM in moist air reveals coverage by three stripe domains (compare to[7,8]) which vanish or cease to be detectable in liquid AFM. Etched surfaces have so far proven less successful with disordered overlayers seemingly covering the surface. Additionally, the morphology of such surfaces is altered by numerous etch pits at dislocations. However, small scale, high resolution, liquid AFM data from both bulk crystal preparations show hexagonally ordered stripes or rows of rings, which match quartz bulk termination in their spacing and symmetry. Surfaces of the amorphous bulk silica samples have been prepared with analog high and low temperature procedures. The structures are discussed in comparison to the crystalline surfaces.

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2D Silica Films: Applications, New Polymorphs and Network Modifications

D. Kuhness, H. J. Yang, K. M. Burson, Z. Yang, C. Büchner, M. Heyde,
and H.-J. Freund

The structure and chemical nature of thin silica films have been investigated intensively in the recent years. In the case of the silica bilayer film, its extraordinary properties, related to the large band gap and the high thermal stability, have gathered the interest of more application-related research. Control of synthesis and understanding of the various observed phases at the atomic scale have therefore become of crucial interest.[1,2]

The silica bilayer phase has been found to represent a two dimensional (2D) van-der Waals solid. It is stable upon transfer from one sample to another and seems therefore suitable for the toolbox of future nano-devices.[2]

A new metastable silica film structure has been prepared, besides the well-known monolayer and bilayer films on Ru(0001). This new silica polymorph can be transformed upon annealing into a patched bilayer silica film. The detailed knowledge about this intermediate phase is of great importance, because it might allow us to gain further insights into the growth modes of silica films as wells as a better understanding of structural transitions between crystalline and amorphous film structures. Based on high resolution scanning tunneling microscopy (STM) images revealing zig-zag line-shapes, we propose a structure model with a rectangular unit cell. From low energy electron microscopy (LEEM) and low energy electron diffraction (LEED) measurements taken by the group of Thomas Schmidt a glide mirror plane in the structural unit cell has been identified. In addition, the group of Shamil Shaikhutdinov has measured infrared finger prints of such film preparations. Currently the group of Prof. Martin Schütz together with Prof. Joachim Sauer is working on reasonable structural models in accord with our experimental observations.

Besides this new silica polymorph the group has started initial work on incorporating Mg atoms into silica bilayer film systems.[3,4] So far the department has introduced different network forming agents such as Al or Fe, which substitute for Si in the silica film. In contrast, Mg represents a network modifying agent, which is expected to affect the structure morphology significantly.

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Surface Action Spectroscopy with Neon Messenger Atoms

Zongfang Wu, Agata Płucienik, Felix E. Feiten[a], Matthias Naschitzki, Walter Wachsmann, Sandy Gewinner, Wieland Schöllkopf, Volker Staemmler[b], Helmut Kuhlenbeck, and Hans-Joachim Freund

In model catalysis and general surface science studies the vibrational characterization of surfaces is usually performed with HREELS (high resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample.

Action spectroscopy with rare gas messenger atoms[1] is a method for the vibrational spectroscopy of gas phase clusters and does not have these disadvantages. Rare gas atoms attached to gas phase clusters may desorb when the infrared radiation illuminating the clusters is in resonance with a cluster vibration. The fragmentation rate as monitored with a mass spectrometer represents a vibrational spectrum, which can be used to draw conclusions regarding the structure.

Clusters, in this case deposited on surfaces, are also very relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both, cluster shape and size matter. With this topic in mind we have constructed an apparatus for the application of action spectroscopy to solid surfaces and studied V_2O_3(0001)/Au(111) (~10 nm thick) and a TiO_2(110) single crystal surface as first test systems.[2] The machine is situated at the free electron laser of the Fritz Haber Institute which is able to provide intense and wide-range tunable infrared radiation. For V_2O_3(0001)/Au(111) the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. We assume that anharmonic vibrational coupling between the primary excited vibration and the rare gas vs. surface vibration is the process leading to desorption, which explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the TiO_2(110) single crystal also rare gas desorption resulting from warming of the crystal by absorbed IR radiation could be observed. This led to new findings regarding a polaronic trap state in rutile.

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Well-ordered Iron Sulfide Layers on Au(111)

Earl Davis, Giulia Berti, Helmut Kuhlenbeck, and Hans-Joachim Freund

The iron-sulfur world hypothesis of G. Wächtershäuser is an origin-of-life theory which proposes that early life may have formed at the surface of sub-marine iron sulfide compounds[1]. This involves the activation of carbon dioxide to form simple organic molecules. Theoretical and experimental studies[2] show that the mineral greigite (Fe_3S_4) should be active for this.

With the idea to activate CO_2 in mind we have started a project to prepare ordered iron sulfide layers. After several tries we found that such a layer can be prepared on Au(111) by deposition of iron in an atmosphere of S_2 molecules, which are produced by an electrochemical sulfur source. In order to avoid a sulfur contamination of the experimental chamber, the preparation is performed in a dedicated chamber. According to XPS the layer is sulfur terminated and STM shows a homogeneous, well-ordered surface with a hexagonal symmetry. The same symmetry is found in LEED patterns and the hexagonal lattice parameter fits to what is expected for Fe_3S_4(111). I/V LEED curves were measured in order to determine details of the structure and I/V LEED calculations are presently running. Parallel to this, first CO_2 activation experiments have been carried out. They have not yet been successful, probably due to the terminating sulfur layer. However, it could be shown that it is possible to hydrogenate the surface which might offer routes to hydrogenation reactions.

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Beyond Pure Silica: Iron-Silicate and Germania Ultrathin Films

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

The Silica system on Ru(0001) has been intensely studied by different techniques.[1,2] However, the modification of these ultrathin films by using additionally iron or using germanium instead of silicon offers many interesting opportunities. Iron-silicate can be seen as a model system for zeolites which are of great importance for catalysis. Germania catalyses poly-ethylene-terephthalate (PET) polymerisation reactions.[3]

The experiments have been performed with LEEM and (μ-) LEED. In addition the iron-silicate films were studied also by XPEEM and XPS. These techniques offer measurements of ultrathin oxide films in-situ and in real-time on mesoscopic scale (field of view between 1 μm and 20 μm) with high surface sensitivity (less than one nanometer) and good lateral resolution (better than 3 nm).

Our studies reveal that on Ru(0001) surfaces the formation of iron-silicate is energetically favoured compared to a phase separation of pure iron-oxide and silica domains. XPS and LEED results fit well to a model with silica on top of iron-oxide (FeO-like) whereas silica orders as a $(\sqrt{3}\text{x} \sqrt{3})\text{R}30°$ structure regarding the FeO layer, which itself arranges as a Moiré structure on Ru(0001). Iron-silicate was prepared as complete and incomplete films and with different preparation methods. Here, the nature of the initial iron-oxide layer influences the silicate. When starting with incomplete FeO films the deposition of silicon and subsequent oxidation causes iron to migrate from the centre to the outside of forming iron-silicate islands, indicating that the FeO layer in the iron-silicate contains less Fe than the initial FeO film. In some cases the diffusing iron forms an iron-silicate rim, surrounding the individual islands, leading to an enlargement of the silicate island.

Germania films were prepared on Ru(0001) and Pt(111) surfaces with two different recipes: (A) Ge was deposited in UHV at 540 K and subsequently oxidized at slightly higher temperatures in $1 \cdot 10^{-6}$ mbar O_2. (B) Ge was deposited in $1 \cdot 10^{-7}$ mbar oxygen at RT onto the 3O-(2x2)-Ru(0001) and Pt(111) surfaces. Then the partially oxidized Ge was oxidized in $1 \cdot 10^{-6}$ mbar O_2. The preparation condition controls the domain size of the GeO_2 films on Ru(0001). Whereas method A yields in domain sizes up to micrometer, preparation B forms small domains in the range of only a few nanometer on 3O-(2x2)-Ru(0001). This is due to low diffusion of Ge on the 3O-(2x2)-Ru(0001) surface. However, both preparations result in the same crystalline film structure, as shown in the same LEEM-IV and sharp (2x2) LEED pattern. Up to now there is no evidence for a vitreous Germania phase on Ru(0001).

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Silica Bilayer Supported on Ru(0001): a Model System for Crystalline to Vitreous Transition and Chemistry in Confined Space

Hagen W. Klemm, Mauricio J. Prieto, Feng Xiong, Daniel Gottlob, Dietrich Menzel, Thomas Schmidt, and Hans-Joachim Freund

Ultra-thin oxide films are interesting candidates as model systems for either catalytic material, in the case of active phases, or as supporting material for active phases with catalytic properties.[1] In our department, ultrathin silica films have been the subject of many studies in the last years, aiming the fundamental structural characterization and its physicochemical properties with the application of techniques such as LEED, LEEM, XPS, XPEEM, TPD, IRAS, STM and AFM (see e.g. [2-4]). Among the different types of SiO_2 films characterized in the department, the SiO_2 bilayer supported on Ru(0001) has proven to be quite versatile in the sense that it can be produced in both crystalline and amorphous forms,[5] both being completely decoupled from the Ru substrate. The detachment of the silica film leads to the formation of a confined space between the SiO_2 bilayer and the Ru(0001) surface where molecules can intercalate.[6]

We used the aberration corrected spectro-microscope SMART[7] at the synchrotron light source BESSY-II in Berlin, applying LEEM, XPEEM, µXPS, and µLEED, to study in-situ and in real-time the growth and phase transitions of a SiO_2 bilayer and to investigate chemical reactions in confined space. The starting point of the preparation was silicon deposited on 3O-(2x2)-Ru(0001) at RT, forming a disordered and only partially oxidized film. Annealing in oxygen leads to a complete oxidation at 625 K, but film ordering does not happen below 1070 K. At this temperature, silica exhibits a well ordered hexagonal crystalline structure which transforms into a vitreous phase upon further annealing. The temperature dependence of the conversion rate yields a activation energy of 4.2 eV in agreement with a Stone-Wales mechanism for this transformation. When the completely oxidized but not yet ordered film is annealed in UHV, a new well-ordered rectangular structure is observed, which can be converted to the hexagonal structure via oxidation.

Regarding the study of chemical reactions in confined space, H_2 oxidation under a silica bilayer has proven to proceed as a moving front, causing a sudden change in image contrast in LEEM. The activation energy for the process can be evaluated from the temperature dependence and is about half the value reported for bare Ru(0001), thus indicating the effect of confinement on the chemical reaction for the first time in the SiO_2/Ru(0001) system. The role of SiO_2 film structure in the H_2 intercalation process will be discussed. Also, the real-time observation of CO intercalation, its potential oxidation under silica thin films and the influence of different film structures/morphologies will be discussed.

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CO Oxidation on Metal-Supported Ultrathin FeO Films

Xuifei Weng, Khe Zhang, Qiushi Pan, Linfei Li, Shamil Shaikhutdinov,
and Hans-Joachim Freund

A continuously growing body of experimental and theoretical results indicates that ultrathin oxide films may exhibit interesting catalytic properties in their own right, which may not be observed on thicker films or respective single crystal surfaces. In particular, a thin FeO(111) film grown on Pt(111) was found active in CO oxidation in the mbar pressure range at low temperatures.[1] Comparative studies on ultrathin films of transition metal oxides showed that binding energy of the most weakly bound oxygen (WBO) species may serve as a good descriptor for the reaction.[2] Furthermore, the reaction rate showed the film coverage effect when supported on metals that strongly adsorbs CO, hence suggesting that the reaction takes place on oxide/metal interface, and the CO binding energy may be considered as another descriptor. The Poster addresses the support and film coverage effects for CO oxidation on FeO(111) films grown on Pt(111) and Au(111).

The results showed that the initial FeO(111) bilayer structure is inert, whereas the FeO_{2-x} trilayer structure shows substantial CO_2 production that reaches a maximum at about 40 % coverage at both UHV and near-atmospheric pressure ($CO/O_2 = 1/5$, totally 60 mbar, He balance) conditions. In addition to that FeO_{2-x} boundaries expose WBO species, as suggested by DFT calculations, strong binding of CO to Pt in proximity favours the reaction at the FeO_{2-x}/Pt interface.[3] To verify this scenario, we performed studies on FeO(111) grown on an inert Au(111) surface.[4] Enhanced reactivity was only observed if the FeO films showed WBO species that are formed upon oxidation at elevated pressures. The reaction rate was found to correlate with the total amount of WBO measured in the films by TPD. However, the rate showed a maximum at about 100% film coverage. When compared to FeO(111)/Pt(111), WBO species on FeO(111)/Au(111) desorb at a much lower (i.e., by ~ 200 K) temperature, but also in much smaller amounts. STM studies showed that the FeO(111) layer on Au(111) is fairly stable towards high pressure oxidation in the low coverage regime, but undergoes substantial reconstruction at near-monolayer coverages, thus resulting in poorly-defined structures.

Comparison of structure-reactivity relationships observed for Au(111) and Pt(111) supported FeO(111) films revealed the complex role of a metal support on reactivity. While a strong interaction with the Pt(111) surface stabilizes a planar, FeO(111)-derived structure for the active oxide phase, in the case of a more weakly interacting Au(111) surface, the reaction atmosphere induces structural transformations governed by the thermodynamic phase diagram of the iron oxide, albeit it seems crucial to have a dense FeO(111) film as the precursor.

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Metal Supported Silicate Thin Films

Linfei Li, Heloise Tissot, Xuifei Weng, Shamil Shaikhutdinov,
and Hans-Joachim Freund

Well-defined thin silica films grown on metal substrates are considered as good model systems for studying chemical reactions at silica surface. The structural motif of the silica films is a layer of corner-sharing SiO_4 tetrahedra, which form either a strongly bound monolayer or a weakly bound bilayer film depending on the metal support used. "Doping" the bilayer film with Al results in an aluminosilicate film exposing highly acidic Si-OH-Al species as in zeolites,[1] whereas Fe (and Ti) prefers to form a layered silicate/iron oxide structure as in clay minerals.[2] This Poster reports our most recent studies on the preparation, atomic structure and adsorption properties of silicate bilayer films.

We studied preparation of Fe-containing aluminosilicate films[3] to address the Fe states in zeolite catalysts like Fe-ZSM5. The results show that even at low concentrations Fe does not randomly substitute Si(Al) cations in the silicate framework, but segregates into a pure aluminosilicate phase and an Fe-silicate phase. At high Fe/(Si+Al) molar ratios, the resulting films showed two phases depending on the annealing temperature. In both phases, the surface exposes a silicate layer and the bottom layer is dominated by FeO. The results suggest that the formation of in-frame Fe species in silicalites and zeolites is thermodynamically unfavorable. Interestingly, doping with Fe had a strong impact on the large-scale crystallinity of the resulted films making them much better ordered than the pure silicate films. STM study revealed that the Fe-silicate domains trigger the formation of the crystalline pure silicate, which propagates in the same orientation as a "crystallization wave" outwards the Fe-silicate.[4] By using transition metal as a "seed" one may, therefore, improve crystallinity and lower the preparation temperature, which may be critical for future applications of the ultrathin silica films in nanotechnology.

To further elucidate the role of a metal support, we studied preparation of a silicate film on Pd(111).[5] All structural characteristics were found to be virtually identical to those we have previously reported for Pt(111) supported films, both showing exclusively a "two-dimensional glass" structure. In addition, the films were examined towards adsorption of CO and D_2. The results show that the bilayer film is permeable for the molecules thus allowing to study in more details chemical reactions in confined space under the silicate film. Such materials which combine an ultrathin "membrane" and a chemically active metal surface underneath, may become interesting hybrid systems for catalytic applications.[6]

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Towards Modeling the Phillips (Cr/SiO_2) Polymerization Catalysts

Qiushi Pan, Linfei Li, Shamil Shaikhutdinov, and Hans-Joachim Freund

The Phillips catalyst (Cr/SiO_2) is successfully used in the large-scale production of polyethylene and has attracted a great interest in catalytic community over the last sixty years. However, the atomic structure of the active site(s) and the reaction mechanism remain controversial, in particular due to the structural complexity and surface heterogeneity of the amorphous silica surface. The Poster reports first attempts to fabricate a planar model Cr/SiO_2 catalyst which is well-suited for "surface science" tools by using a well-defined, atomically flat silica film as a support offering the opportunity to investigate the chemical reactions at the atomic scale.

In this approach, Cr was deposited using physical vapor deposition onto the hydroxylated silica film surface.[1] Structural characterization and adsorption studies were performed by infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD). The results show that hydroxyl groups serve as anchoring cites to Cr ad-atoms which were deposited at low temperatures to minimize their clustering. As monitored by IRAS, hydroxyls consumption correlated with the appearance of the new band at ~ 1010 cm^{-1} typical for Cr=O vibrations. In addition, CO titration experiments suggested also the presence of "naked" Cr sites, which transforms into mono- and di-oxo chromyl species and their aggregates upon oxidation treatments.

Ethylene adsorption experiments at low temperatures under UHV conditions showed the formation of butane as one of the main products. The resultant surfaces are thermally stable, at least, up to 400 K which allows to further investigate ethylene polymerization under more realistic conditions.

In addition, in order to mimic powdered catalysts preparation, we are now performing experiments using chemical vapor deposition of volatile Cr precursors such as $Cr(OC(Me)_2CH_2OMe)_3$, provided by the group of Prof. Coperet (ETH Zurich).

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Surface Termination and Water Adsorption on Magnetite $Fe_3O_4(111)$

Francesca Mirabella, Eman Zaki, Francisco Ivars Barcelo, Jan Seifert, Xiaoke Li[a],
Joachim Paier[a], Joachim Sauer[a], Shamil Shaikhutdinov, and Hans-Joachim Freund

Although the (111) surface of Fe_3O_4 (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination proposed on the basis either of structural (LEED, STM) or adsorption studies, in particular of CO and water. The Poster revises old and provide new experimental results which in combination with DFT calculations led to a unified picture in which the $Fe_3O_4(111)$ surface is terminated by a $^1/_4$ monolayer of tetrahedrally coordinated Fe^{3+} ions on top of a close-packed oxygen layer as determined by I-V LEED and favored also by the DFT-derived stability diagram.[1] This finding lead us to revisit our previously proposed scheme for water adsorption based on octahedrally terminated surface.

The $Fe_3O_4(111)$ films were prepared on a Pt(111) substrate under well-controlled conditions. CO and water adsorption experiments were studied by TPD, IRAS, and a single crystal microcalorimetry, and carried out in several UHV chambers. Thorough precautions have been taken in order to cross-check the results obtained in different setups.

TPD spectra of water exposed at 100 – 300 K revealed multiple desorption peaks before the multilayer (“ice”) formation sets in, which were analyzed within different models. Thus obtained desorption energy considerably decreases with the water coverage, from ~ 90 to ~ 50 kJ/mole, in nice agreement with the results of microcalorimetry measurements which allow to directly measure the heat of adsorption. Combined IRAS and TPD results suggest water dissociation first to occur which is, at increasing coverage, accompanied by molecular water adsorption, that may even result in ordered (2×2) ad-layer structure as judged by LEED. Further IRAS experiments using isotopic labelling of oxygen in the water and in the films revealed more complex adsorption behavior which is, however, generally consistent with the “classical” water dissociation mechanism resulting in terminal OH on top of Fe and H on top of lattice oxygen.

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H Species inside $CeO_2(111)$ and $CeO_{2-x}(111)$ Thin Films

Kristin Werner, Xuefei Weng, Florencia Calaza, Thomas Kropp[a], Joachim Paier[a],
Joachim Sauer, Katsuyuki Fukutani[b], Markus Wilde[b], Shamil Shaikhutdinov,
and Hans-Joachim Freund

Cerium oxide (CeO_2) has been shown to be an efficient catalyst in alkyne hydrogenation. This behavior is unique among oxides and seems surprising, since these are primarily used in oxidation reactions. We aim at identifying the precise reaction mechanisms for hydrogenations on CeO_2.

CeO_2 is only an efficient hydrogenation catalyst when present in the oxidized state. The activity and selectivity deteriorate quickly under reducing conditions. This difference in performance might be linked to a different chemical nature of H species on oxidized and reduced CeO_2. To identify the H species present on both surfaces, we performed model studies on the interaction of H_2 with an oxidized $CeO_2(111)$ and a vacancy-rich, reduced $CeO_{2-x}(111)$ thin film.

We assessed the oxidation state of both films before and after H_2 exposure using X-Ray Photoelectron Spectroscopy (XPS). During H_2 exposure, we followed OH vibrations on the oxide surface using Infrared Reflection Absorption Spectroscopy (IRAS). Furthermore, we performed Nuclear Reaction Analysis (NRA) to study the spatial distribution of H species on and inside the oxide films.[1] We study by Density Functional Theory (DFT) calculations how H_2 dissociates on CeO_2 and in which chemical form it is most stable within the oxidized and the reduced films.

We found that after H_2 dissociation, H species are present on both films. On oxidized $CeO_2(111)$, H species are stable on the surface and in the shallow subsurface region. On reduced $CeO_{2-x}(111)$, however, H species are distributed also in the bulk phase. Surprisingly, the oxidation state of the reduced Ce^{3+} ions on $CeO_{2-x}(111)$ changes to Ce^{4+} after H_2 treatment. This could not be observed when $CeO_{2-x}(111)$ was exposed to atomic H.

Our DFT calculations show in agreement with previous literature that H_2 dissociates heterolytically, forming first an OH and a hydride (Ce-H) group. On oxidized $CeO_2(111)$, Ce-H is unstable and will form a second OH group, transferring an electron to Ce^{4+}. We show that this second OH group may be formed in the subsurface region. On the reduced $CeO_{2-x}(111)$ film, in contrast, the Ce-H group can be stabilized by O vacancies in the bulk phase. We attribute the differences in the spatial distribution of H species inside both films to their different chemical nature - OH within $CeO_2(111)$ and OH and Ce-H in $CeO_{2-x}(111)$.

Further studies in the department will focus on the direct identification of these hydride species by High Resolution Electron Energy Loss Spectroscopy (HREELS) and on reactivity studies on both model thin films.

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Data Acquisition in Science. A General Approach

Heinz Junkes

Reliable and well understood data acquisition is essential to get high data quality in physical and chemical experiments. Unfortunately, it is often underestimated by scientists. They are accustomed to using black box systems with little information on the exact operations (no source code available, closed hardware) within these boxes. To acquire high quality data (multiple sources, synchronous, realtime triggered) it is necessary to know some facts like Nyquist-Shannon sampling theorem, aliasing, bandwidth and one has to be able to comprehend these basics in the hardware and software. This can only be achieved by a hardware and operating system independent software system with the following features:

- Distributed system
- Scalable
- Realtime, Timestamp-Support
- Available in source code with Version control

This poster presents the necessary components of such a system.

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Data Acquisition with the EPICS Framework at the FEL and CRYVISIL Projects

Heinz Junkes, Markus Heyde, Patrik Marschalik, and Wieland Schöllkopf

The use of the EPICS framework is demonstrated at the two FHI projects FEL and Cryvisil. EPICS is a set of software tools and applications which provide a software infrastructure for use in building distributed control systems to operate devices such as particle accelerators, major telescopes, or other large experiments. Such distributed control systems typically comprise tens or even hundreds of computers, networked together to allow communication between them and to provide control and feedback of the various parts of the device from a central control room, or even remotely over the internet. However, medium and small measuring systems nowadays consist of many individual devices (vacuum pumps and valves, cameras, spectrometers, digitizers, etc.) all of which must be controlled and monitored. This can best be realized with a distributed approach.

EPICS uses Client/Server and Publish/Subscribe techniques to communicate between the various computers. Most servers (called Input/Output Controllers or IOCs) perform real-world I/O and local control tasks, and publish this information to clients using the Channel Access (CA) network protocol. CA is specially designed for the kind of high bandwidth, soft real-time networking applications that EPICS is used for, and is one reason why it can be used to build a control system regardless of the number of devices.

This poster presents example setups and lessons learned.

Department of Molecular Physics

Department of Molecular Physics

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MP 2 **Ion mobility-mass spectrometry and gas phase spectroscopy of amyloid oligomers**

W. Hoffmann, J. Seo, S. Warnke, X. Huang, S. Gewinner, W. Schöllkopf, M.T. Bowers, G. von Helden, and K. Pagel

MP 3 **Vibrational spectroscopy of model carboxylates trapped in Helium nanodroplets: From prototypical hydrogen bonds to exotic molecular species**

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MP 4 **Ion mobility-mass spectrometry of glycans and glycoconjugates**

J. Hofmann, C. Manz, A. Stuckmann,H. S. Hahm, H. Hinneburg, W. B. Struwe, D. Kolarich, P. H. Seeberger, and K. Pagel

MP 5 **Cold-ion spectroscopy of oligosaccharides and glycosyl cations**

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MP 6 **Activation of carbon dioxide by anionic transition metal clusters**

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MP 10 **Structure of molecular complexes prepared and probed in superfluid He droplets**

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MP 11 **Matter-wave diffraction and quantum reflection of atomic and molecular beams**

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MP 16 **The FHI-FEL Facility: User operation, synchronisation with table-top lasers, planned facility extension & machine upgrade**

W. Schöllkopf, S. Gewinner, W. Erlebach, H. Junkes, R. Kießling, A. Liedke, A. Paarmann, G. von Helden, and G. Meijer

MP 17 **One hundred years of chemical warfare: Research, deployment, consequences**

B. Friedrich, D. Hoffmann, J. Renn, F. Schmaltz, and M. Wolf

IM-MS and IRMPD spectroscopic study of amino acid clusters

J. Seo, W. Hoffmann[a], S. Malerz, S. Gewinner, W. Schöllkopf, M.T. Bowers[b],
K. Pagel[a], and G. von Helden

Many small biological molecules can self-assemble and form aggregates, having a variety of shapes and structures. The propensity to do so, as well as the structures that are generated, are non-trivially linked to the structures and properties of the corresponding monomeric units. Getting a better understanding of this relationship is thus an important topic in biophysics. One of the simplest models for biomolecular assembly are clusters of amino acids.

Here, the combination of ion mobility spectrometry-mass spectrometry (IM-MS) and infrared multiple photon dissociation (IRMPD) spectroscopy is used to investigate the structure of various amino acid clusters and the interactions within those clusters. IM-MS can determine the geometrical size of each isolated amino acid cluster by measuring their collision cross-section. In addition, IM-MS can also be used as a filter to isolate conformationally-pure cluster ions for a subsequent analysis by IRMPD spectroscopy. To do so, a home-built IM-MS instrument is coupled to the Fritz Haber Institute free electron laser (FHI-FEL) to perform IRMPD spectroscopy in the 500 cm^{-1} –2000 cm^{-1} region. The resulting data can be used to deduce structural details of amino acid cluster ions.

In initial experiments, the structures and pairwise interactions of the smallest amino acid clusters, the protonated amino acid dimers, are investigated and the data gives a clear picture of the influence of the respective side chains on the dimer structures.[1] For larger clusters, our data reveals that those species are composed of zwitterionic monomer units. Of special interest are clusters of the amino acid serine. Due to its apparent high stability and unique homochiral nature, the serine octamer has been one of the icons in supramolecular self-assembly for nearly two decades and yet its structure is still not understood. Using a combination of IM-MS and IRMPD, we elucidated the structures of two magic-sized serine octamers ($\mathrm{Ser_8Cl_2}^{2-}$ and $\mathrm{Ser_8H}^{+}$). For the anionic $\mathrm{Ser_8Cl_2}^{2-}$ cluster, a highly symmetric, homochiral, and very stable structure consisting of eight zwitterionic serines was identified.[2] In addition, a structure of the highly stable cationic $\mathrm{Ser_8H}^{+}$ consisting of both zwitterionic and non-zwitterionic serines is proposed.

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Ion Mobility-Mass Spectrometry and gas phase spectroscopy of amyloid oligomers

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Amyloidogenic peptides and proteins play a crucial role in a variety of neurodegenerative disorders such as Alzheimer's and Parkinson's disease. The involved proteins undergo a spontaneous transition from a soluble, often partially folded form into insoluble, β-sheet rich amyloid fibrils. There has been increasing evidence that highly dynamic, polydisperse folding intermediates, which occur during fibril formation are the toxic species in the afore-mentioned diseases. One promising approach to obtain structural information about individual oligomeric species is ion mobility-mass spectrometry (IM-MS). Here ions are separated according to their size and shape as well as mass and charge and therefore quaternary structure information can be obtained for a single species in a complex mixture. IM-MS can also serve as a filter for a subsequent analysis by gas-phase infrared (IR) spectroscopy, which provides additional secondary structure information of individual oligomeric species.

We used IM-MS coupled to free electron-laser based IR spectroscopy to deduce the self-assembly process for three isomeric, amyloidogenic hexapeptides.[1] One of these peptides does not form amyloid fibrils and is therefore used as an ideal reference for a non-fibril forming system; the other two readily assembly into fibrils, but differ in their aggregation rate. Our data reveal that oligomers, which consist of four to nine peptide strands, can already contain a significant amount of β-sheet. In addition, our data show that the more extended variants of each oligomer generally exhibit increased β-sheet content.

In another study, soluble oligomers of the hexapeptide NFGAIL, derived from the human islet amyloid polypeptide (hIAPP), have been investigated.[2] Our data reveal that at neutral pH NFGAIL follows a nucleation-dependent mechanism to form amyloid fibrils. During the lag phase, highly polydisperse, polymorph, and compact oligomers (oligomer number n=1-13) as well as extended intermediates (n=4-11) are formed. IR secondary structural analysis reveals that compact conformations adopt turn-like structures, whereas extended oligomers exhibit a significant amount of β-sheet content. Previous molecular dynamic simulations suggest that the formation of unordered NFGAIL oligomers and their subsequent dissociation are crucial steps to form larger, structured aggregates. The NFGAIL intermediates probed here are therefore likely on-pathway oligomers occurring during amyloid formation.

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MP 3

Vibrational spectroscopy of model carboxylates trapped in Helium nanodroplets: From prototypical hydrogen bonds to exotic molecular species

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Helium nanodroplets provide an ideal environment for vibrational spectroscopy due to their extremely low equilibrium temperature (~0.4 K) and minimal matrix-induced spectral perturbation. In this work, the high-resolution, ground-state vibrational spectroscopy of ions trapped in helium nanodroplets is applied to the study of illustrative carboxylate molecules.

Carboxylate proton-bound dimers of the form $\mathrm{RCO_2^-{-}H^+{-}{}^-O_2CR}$ represent excellent model systems to study the properties of the short, strong hydrogen bonds involved in shared proton systems. Questions including the symmetry of proton sharing, the coupling of proton motion to that of adjoining moieties, and the influence of neighboring functional groups are valuable for understanding processes ranging from catalysis to ion solvation. To assess these attributes, the homo- and hetero-dimers of formate, acetate, and trifluoracetate were studied by vibrational spectroscopy in the range of 400-1900 $\mathrm{cm^{-1}}$. For the formate homodimer, $\mathrm{HCO_2^-{-}H^+{-}{}^-O_2CH}$, a dominant feature at 605 $\mathrm{cm^{-1}}$ is assigned to the parallel motion of the shared proton, demonstrating the highly anharmonic character of the potential well. Theoretical calculations predict that the proton is equally shared between the two formate moieties and reveal a strong dependence of the fundamental vibrational frequency on the O–O distance. For the formate-trifluoroacetate heterodimer, in contrast, a large difference in the relative acidity of the two carboxylates leads to proton localization at the formate moiety, and the spectrum resembles that of the more strongly acidic trifluoroacetate.

Expanding the study of intriguing carboxylate systems, fluoroformate ($\mathrm{FCO_2^-}$) was generated *via* the gas-phase reaction of $\mathrm{CO_2}$ with $\mathrm{F^-}$ and characterized by vibrational spectroscopy. The predicted C–F bond length of 1.48 Å is significantly longer than that of typical $\mathrm{Csp^2{-}F}$ bonds (~1.34 Å), and the electrostatic potential illustrates that the central carbon is highly electrophilic, priming the molecule for nucleophilic attack. Indeed, a prominent peak corresponding to $\mathrm{FCO_2^-{+}H_2O}$ is observed in the mass spectrum, suggesting formation of a highly stable species. Vibrational spectroscopy of this ion indicates that several structures are present simultaneously following ion trapping and pickup in helium nanodroplets.

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Ion Mobility-Mass Spectrometry of glycans and glycoconjugates

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Glycans are essential for a variety of biological functions such as cell-cell-recognition, immune response or protein folding. They can be linked to proteins as post-translational modification or exist as free oligosaccharides. Glycans consist of monosaccharide building blocks that can form branched structures with complex regio- and stereochemistry. This often results in the presence of isomers, which pose a large challenge for their structural analysis. In the last years ion mobility-mass spectrometry (IM-MS) emerged as a promising tool for the analysis of biomolecules. In IM-MS, ions are guided by an electric field through a gas-filled cell, where they are separated according to their mass, charge, size and shape. While the drift time of an ion depends on the underlying instrument conditions, it can be converted into a collision cross section (CCS), which is a molecular property that can be universally compared and calculated theoretically. Here, we demonstrate the potential of IM-MS for the separation and identification of isomeric glycans and glycoconjugates.

In a systematic study of six synthetic trisaccharide isomers it was shown that IM-MS is able to distinguish glycans, which only differ in their regio- and stereochemistry.[1] Especially for negatively charged ions large CCS differences were observed that also allowed a separation of isomeric mixtures. With increasing size of oligosaccharides it naturally becomes more difficult to identify small structural changes and separate isomers. However, it was shown that small fragments of *m/z*-selected ions often have more diagnostic CCSs than the intact precursor ions. This was demonstrated by analyzing several common glycan motifs such as Lewis and blood group epitopes. By measuring the *m/z* and CCSs of the intact ions and their fragments characteristic fingerprint data were generated.[2] The obtained fingerprint was then used to identify those glycan motifs in N-glycans and milk oligosaccharides. In addition, fragment data can be used to identify special features in glycoconjugates. In particular, a trisaccharide fragment was found that enables the identification of α2→3 and α2→6 linked N-acetylneuraminic acids within synthetic glycopeptides as well as tryptic digests of glycoproteins.[3] The described IM-MS/MS approach is thus an extremely versatile technique, because structural assignments are purely based on diagnostic fragment CCSs and independent of the investigated glycan or glycoconjugate. In the future, the storage of such CCS data will be highly beneficial for the development of automated data analysis and glycan identification that allow a routine analysis by IM-MS.

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Cold-ion spectroscopy of oligosaccharides and glycosyl cations

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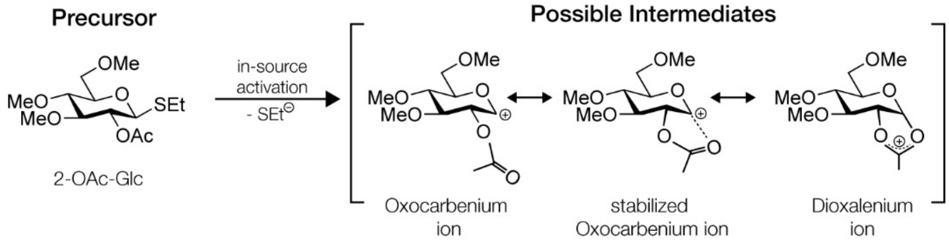
The immense structural diversity of glycans enables them to convey key-roles in virtually every biological process. However, this structural diversity at the same time poses a formidable challenge for their analysis. The identification of a complex oligosaccharide typically relies on highly sophisticated mass spectrometry-based techniques, chemical derivatization or, most recently, ion mobility-mass spectrometry. Gas-phase infrared (IR) spectroscopic methods, on the other hand, were limited to smaller glycans due to poor spectral resolution that results from their conformational flexibility and thermal activation during photon absorption.

Here, we overcome this limitation by using cold-ion spectroscopy. The optical signatures of complex carbohydrates in superfluid helium nanodroplets proved to contain a wealth of well-resolved absorption features. Even minute structural variations result in remarkable spectral differences providing the basis for an identification of glycans using their spectral fingerprints.[1] The remarkable structural information extracted from IR fingerprints also provides insight into the structural details of glycosyl cations - reactive intermediates that occur during chemical synthesis. These extremely short-lived species are a key species in the glycosylation reaction that links carbohydrates to each or to other molecules. Usually, attempts are made to control the stereochemical outcome of the reaction using neighboring group effects. The molecular details and the exact mechanism, however, are still barely understood. To address this problem systematically, a set of O-acetylated glycan precursors was used to generate different glycosyl cations using in-source fragmentation. The obtained cold-ion IR signatures as well as theoretical data derived from density-functional theory calculations revealed that reactive intermediates with adjacent acetyl protecting groups predominantly exist as dioxalenium ions.

In conclusion, cold-ion IR spectroscopy offers a new framework to gain understanding of structure formation in carbohydrates and disentangle the relation between their sequence and the three-dimensional structure they adopt.



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Activation of carbon dioxide by anionic transition metal clusters

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Metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of surface reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behaviour. Using vibrational spectroscopy of gas-phase clusters one can obtain information about the clusters' structure or the behaviour of adsorbed species. The latter provides valuable insights into the binding geometry, the activation of bonds within the ligands or reactions occurring on the clusters' surface. Cluster size specific data can be obtained using infrared multiple photon dissociation (IR-MPD) spectroscopy.

Emission control of carbon dioxide (CO_2), recognized as the primary greenhouse gas, is a major challenge for realizing a sustainable society. A promising approach to this issue is the catalytic conversion of the chemically inert CO_2 molecule into useful, value-added compounds. One possible activation mechanism is a reduction via the transfer of an electron into the LUMO of CO_2 which has C-O antibonding character. Furthermore, it breaks the degeneracy of this $2\pi_u$ orbital leading to a bent ground state structure of the CO_2^- anion. IR spectroscopy is sensitive to these structural changes as for instance the IR-inactive symmetric stretching mode of CO_2 becomes IR-active after symmetry lowering. Anionic metal clusters can serve as electron source for such activation mechanism.

Here we present results of the study of the reactions of CO_2 with anionic cobalt, rhodium, and platinum clusters. While the IR-MPD spectra of the anionic complexes between CO_2 and Rh clusters show all the typical fingerprint of metal-bound CO_2^-, the IR spectra of the Co cluster complexes are rather different but can be explained by dissociation of the CO_2 into O and CO. Indeed the only bands observed in the IR spectra are very close to the positions found for complexes between CO and the anionic Co clusters.[1] Theoretical investigation on the level of density functional theory confirm that this dissociation is energetically feasible. CO_2 binding to small anionic Pt clusters shows a cluster size dependent behaviour with certain sizes promoting dissociation of CO_2 like seen in the case of Co while for other sizes the presumably initially formed CO_2^- species can be identified. The role of energetics and activation barriers for the CO_2 dissociation on the Pt clusters is currently under investigation.

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Photo-Electron Circular Dichroism (PECD) of anionic metal complexes

Jenny Triptow[a], Gerard Meijer, and André Fielicke

Determination of absolute chirality, enantiomer differentiation and determination of enantiomeric excess for gas-phase species are topics within a currently very active research field.[1] A general problem in such studies is the low particle density in the gas phase and that the absorption circular dichroism usually is a very small effect. More recently, new methods have been developed to investigate the circular dichroism in the photoionization of chiral molecules and in the spatial distribution of the photoelectrons. In this case the dichroism can be orders of magnitude larger than the one observed in photoabsorption spectra.

We are extending this approach to anionic gas-phase systems. This not only allows for obtaining mass-specific information but usually also the electron affinities of neutral molecules are much lower than their ionization energies, such that they are in the range of the photon energies of common UV/vis table-top lasers.

Here, complexes between metal anions and chiral molecules are prepared in a molecular beam, mass selected and subsequently Velocity Map Imaging (VMI) is used to obtain the Photoelectron Angular Distributions (PADs). First results are presented for the electron detachment from chiral complexes of the atomic gold anion and of the chiral anion alaninolate.

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Vibrational spectroscopy of water adsorption on metal oxide clusters

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Metal oxides are currently attracting much attention due to their industrial use 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 of the products formed by the reaction of aluminum, iron and titanium oxide clusters with a controlled number of water molecules providing a molecular model for the chemistry taking place on the metal oxide surface.

Here, we present results on the interaction of $Fe_3O_4^+$, $Al_3O_4^+$ and $(TiO_2)_{2-4}^-$ clusters with one to four water molecules[1,2]. We use cryogenic ion trap vibrational spectroscopy in combination with the intense and widely-tunable radiation from the IR free electron laser FHI-FEL (215-3000 cm^{-1}) or a nanosecond IR tabletop laser (600-4000 cm^{-1}) to access the nearly the complete vibrational signature of the metal oxide framework as well as that of the adsorbed water molecules. Structures are assigned based on the comparison of the infrared photodissociation (IRPD) spectra to simulated IR spectra from electronic structure calculations. We find that dissociative water adsorption is favored in all cases. Characteristic IR absorption regions for O-H(D) stretching, M-O stretching and M-O-H(D) bending modes as a function of the M- and O-atom coordination are determined and compared to recent spectroscopic results on the dissociative water adsorption to metal oxide surfaces.

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Analytic solvability and eigenenergy-surface topology of problems related to molecules subject to electromagnetic fields

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Burkhard Schmidt[a], and Bretislav Friedrich

The scarcity of analytic solutions to problems arising in quantum mechanics has not only spurred the development of techniques to find their numerical solutions instead, but also impelled attempts to search for a type of analytic solutions that only obtain for a subspace of the parameters that specify a given eigenproblem. So, for instance, while the harmonic oscillator problem is analytically (or exactly) solvable for all values of the parameter on which it depends (the reduced force constant), the quantum pendulum one is not, i.e., its Schrödinger equation does *not* possess closed-form solutions that cover the entire spectrum of the problem's Hamiltonian. Rather, the pendulum eigenproblem is only conditionally quasi-exactly solvable, i.e., its closed-form solutions only exist for finitely many eigenvalues of the pendular Hamiltonian (quasi-exact solvability, QES), and, moreover, only obtain if the problem's interaction parameters satisfy a particular set of conditions (conditional quasi-exact solvability, C-QES), i.e., only for a subspace of the parameters that specify it. A polar and polarizable molecule subject to an electromagnetic field is a realization of the quantum pendulum. It is specified by the orienting and aligning parameters that determine its interactions with an electromagnetic field.

In our work, we found a number of analytic solutions and identified conditions under which they obtain for both the full-fledged three-dimensional – *spherical* – pendulum (9 solutions) and the one-dimensional – *planar* – pendulum (40 solutions). Our analysis of the planar pendulum eigenproblem revealed that the relationship between analytic solvability and eigenenergy surface topology, established in our earlier work[1], can be traced to the structure of the tridiagonal matrices representing the symmetry-adapted pendular Hamiltonian and the degeneracy properties of the Whitakker-Hill equation. Furthermore, an analogous analysis of the hyperbolic counterpart of the planar pendulum, the Razavy problem[2], which is also C-QES, showed that it is anti-isospectral with the pendular eigenproblem. Of key importance for both eigenproblems proved to be the topological index κ, as it determines the loci of the intersections (genuine and avoided) of the eigenenergy surfaces spanned by the aligning and orienting parameters. It also encapsulates the conditions under which analytic solutions to the two eigenproblems obtain and provides the number of analytic solutions. At a given κ, the anti-isospectrality occurs for single states only (i.e., not for doublets), like C-QES holds solely for integer values of κ, and only occurs for the lowest eigenvalues of the pendular and Razavy Hamiltonians.

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Structure of molecular complexes prepared and probed in superfluid He droplets

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We examine the binding by dispersion forces of Phthalocyanine (Pc) based molecular complexes such as Pc-(H_2O) and $(Pc)_2$ prepared and probed in superfluid helium nanodroplets.[1] The experimental technique of choice is high-resolution electronic spectroscopy capable of resolving the structure of complexes of well-defined stoichiometry. A superimposed Stark field aids in identifying the various isomeric variants of the complexes formed. By making use of optical spectroscopy, the investigations also provide access to electronically excited states of the complexes. A simultaneous theoretical analysis based on quantum chemistry computations serves to affirm the structural information on the clusters as revealed by the optical Stark spectra. To this end, global structure optimization based on the DoDo genetic algorithm followed by a local CC2 treatment is used to furnish the dipole moments for the ground and first electronically excited states along with the gas phase geometries/moments of inertia for a number of theoretically predicted configurations. The DoDo genetic algorithm program available within the TURBOMOLE[2] package is used as a search heuristic to pin down the most stable structures of the complex in the gas phase. The local-correlation coupled cluster second-order perturbation theory with the density fitting approximation (DF-LT-LCC2) is one of the best tools available to calculate the ground and excited state energies and dipole moments of large molecular systems. This scheme is well implemented in the MOLPRO[3] package. Despite possible inaccuracies in the transition frequencies, the important output from this step is a well-optimized geometry of the complex, along with the dipole moments for ground and first excited states. The effective moments of inertia/rotational constants of the complexes in the helium droplet environment are determined via the angulon theory[4] and used to generate simulated Stark spectra for each theoretical configuration. This multi-pronged approach is aimed at understanding the workings of the London dispersion forces in molecular complex formation as well as answering questions pertaining to their solvation in the superfluid He environment. Our combined experimental and theoretical approach is applicable to any other types of van der Waals complexes amenable to optical spectroscopy.

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MP 11

Matter-wave diffraction and quantum reflection of atomic and molecular beams

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Optical effects observed with matter-waves represent an analogy to the corresponding phenomena known from classical optics. However, deviations from classical optics can occur, for instance, due to the dispersive (van der Waals) interaction between the atoms or molecules and the optical element, or due to the non-vanishing size of a molecule or cluster. In previous studies we already investigated diffraction efficiencies as well as emerging beam resonances in matter-wave optics with regard to deviations from classical optics. Now, we have made a systematic experimental study to test the validity of the reciprocity principle and Babinet's principle. Reciprocity states that observed signals do not change upon interchanging source and detector in a scattering experiment. It is a basic principle known to hold in various fields including optics and acoustics. Babinet's principle, on the other hand, states that diffracting objects of complementary shape, e.g. a slit and a bar of the same width, cause identical diffraction intensities (except for the non-diffracted or zero-order beam direction).

We have investigated both principles with helium atom beams quantum reflected from a micro-structured diffraction grating. Quantum reflection of atoms or molecules from a solid refers to the reflection of the particle's wave-function at the attractive particle-surface Casimir-van der Waals potential. It can only be observed at extremely low incident kinetic energies (associated with the normal component of the particle's velocity), a condition that we achieve by grazing incidence of a highly collimated molecular beam onto the reflection grating. We observe intense and well resolved diffraction patterns of He or D_2 beams quantum reflected from a commercial grating.

Our experiments indicate that the reciprocity principle holds robustly. It applies even for emerging-beam-resonance conditions when, at a Rayleigh angle of incidence, another diffraction beam emerges from the grating plane. On the other hand, we have found Babinet's principle to hold for conditions where the atom-surface interaction is negligible. However, we have observed a break-down of Babinet's principle under emerging-beam-resonance conditions as well as for very small incidence angles and for diffraction beams scattered at very small angles with respect to the grating surface. We attribute the break-down of Babinet's principle to the effect of the atom-surface interaction potential on the atomic wave-function.

Furthermore, we have investigated quantum reflection and diffraction from gratings made out of different materials and of various grove shapes. Both parameters affect the overall quantum reflection probability and the diffraction efficiencies. For instance, the gratings made out of the photoresist used in the micro-structuring procedure exhibit larger reflection probabilities than gratings formed by gold on a quartz substrate. This behaviour can be explained by the different strengths of the atom-surface interactions. Optimizing the reflection probability and/or the diffraction efficiencies of selected diffraction orders can significantly increase the signal-to-noise ratio, thereby allowing to extend the experimental method to other (heavier) atoms or molecules than He and D_2.

Exploring the spectroscopic properties of diatomic chlorides and fluorides as candidates for a molecular BEC

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Boris G. Sartakov[a], and Gerard Meijer

During the last years, it has been demonstrated that there is a certain sub-class of diatomic molecules for which laser cooling – with still a manageable number of laser frequencies – is possible. Diatomic fluorides like SrF and CaF have been laser-cooled and captured in a magneto optical trap; for CaF cooling below the Doppler limit has recently been demonstrated.[1] Molecules that are both amenable to laser cooling and to manipulation with electric or magnetic fields, form a particularly interesting class of their own. We have started a systematic investigation, exploring the spectroscopic properties of diatomic chlorides and fluorides, to find molecules that can be transversely laser-cooled in a beam, subsequently Stark-decelerated and then optically trapped and laser-cooled below the Doppler limit.

Instead of optical trapping, 3D trapping in electric or magnetic fields might also be possible. A particularly interesting kind of electrostatic trap is the storage ring for neutral polar molecules. This 2D trap is an ideal trap for molecules in low-field seeking states because the centrifugal force ascertains that the trapped molecules never experience a zero-field region, thereby avoiding non-adiabatic transitions to non-trappable states. To fully exploit the possibilities offered by ring structures, it is imperative that the molecules remain in a bunch, i.e. that they stay confined in a moving 3D trap that revolves synchronously with the molecules. The efficiency of the bunching process, and the number of molecular packets that can be stored simultaneously, depends on the number of individual segments of the ring. Several years ago, we have constructed such a *molecular synchrotron*, consisting of 40 straight hexapole segments. In this multi-segment ring, a simplified bunching scheme has been implemented that has resulted in improved stability. Using this scheme, the storage of a single packet of ammonia molecules for over 1000 round trips has been experimentally demonstrated, implying that the molecules have been kept in stable orbit for over a mile. The number of molecules circulating in a bunch decays exponentially with time, with a time constant of about three seconds, determined, about equally, by optical pumping due to blackbody radiation and collisions with background gas.[2] Trapping of the diatomic chlorides or fluorides in this molecular synchrotron, with possibly the opportunity of laser-cooling while they are revolving, offers fascinating prospects, as will be outlined on the poster.

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Photoemission from liquid jets: New developments

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With the prospect of exploring novel and exciting phenomena in liquid solutions and at liquid–gas interfaces we are currently developing research strategies, and building new setups for liquid-jet photoelectron spectroscopy (PES) with increased sophistication in terms of geometrical flexibility, increased temperature control of the liquid jet, and large electron detection efficiency, even at ambient pressures. These improvements allow us to explore phenomena that have previously not been possible to be studied in the liquid phase, like (i) the chiral nature of solvation shells surrounding chiral molecules, (ii) liquid–gas interfacial dynamics, and (iii) the properties of solvated electrons at high density in liquid ammonia.

Photoelectron circular dichroism (PECD) is a recently discovered process with a sensitivity to chirality much larger as compared to traditional (integral) absorption-based techniques. Measurements of the chiral asymmetry parameter are performed by detecting the emitted electrons in (and / or in opposite) propagation direction of circularly polarized light, for left versus right polarization. The realization of such a geometry is technically demanding. While PECD has been demonstrated in the gas phase, it has never been explored in the liquid phase. Thus, the effect of the solvent on the chiral parameter, as well as the chiral nature of solvation shells have never been explored. Such measurements are important for the understanding of chirality in biological systems. In the future, we will also combine liquid-jet PES measurements with Velocity Map Imaging (VMI); this is a highly challenging task. A liquid-jet VMI will offer yet additional experimental opportunities due to an increase of both the collection efficiency and the angular sensitivity.

Another goal is to develop a jet of liquid ammonia suitable for PES experiments. Liquid ammonia can support a high concentration of solvated electrons, leading to metallic ammonia which can be identified by the PE spectra. A proper design of the required liquid-jet temperature control not only allows for experiments on liquid ammonia, but also opens up the possibility of studying other solvents and temperature-dependent processes in solution.

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Molecule – liquid jet scattering with velocity-controlled molecular beams

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The Stark-deceleration technique yields unprecedented control over both the internal and external degrees of freedom of polar molecules in a molecular beam, which holds great promise in molecular beam scattering experiments in general. Several years ago, in the framework of an NSF-DFG supported research project, we have constructed a novel apparatus in which the molecule-surface interaction can be studied using velocity-controlled molecular beams. The apparatus contains a Stark decelerator molecular beam machine, specifically designed to produce pure beams of metastable CO ($a^3\Pi$) molecules. CO molecules are laser-prepared in selected rotational levels of this long-lived electronically excited state, and are then focused with a hexapole on the entrance of the Stark decelerator. To get rid of the carrier gas as well as of the ground-state CO molecules in the beam, the hexapole is placed under a small angle, thereby "bending the CO ($a^3\Pi$) molecules around the corner". After deceleration (acceleration) the metastable molecules are optically pumped back to selected ro-vibrational levels in the $X^1\Sigma^+$ electric ground state. Here, it is exploited that a packet of molecules stays confined throughout the deceleration process, thus enabling efficient transfer in a pump-dump scheme even if the individual optical transfer steps are separated by a long distance. Scattering studies with these beams not only enables an extraordinarily high resolution in the incidence translational energy but also gives access to unusually low incidence translational energies.

Rather than using this machine to scatter the molecules off a temperature-controlled AU(111) surface, as originally planned and successfully executed, we will use this machine to scatter ground-state CO molecules from a liquid jet; the CO molecules will subsequently be state-selectively detected. Alternatively, scattering experiments can be performed with the CO molecules in the metastable state. These experiments aim at understanding energy transfer and chemical reactions at the liquid surface. Initially, we will direct the beam of (metastable) CO molecules towards a conventional, cylindrical liquid jet. But more excitingly, we will also employ a flat liquid jet providing a more suitable scattering surface. The scattering interactions will be characterized by detecting, for instance, the phosphorescence from the metastable CO, and by molecule impact on a position sensitive MCP. A longer-term goal is to also perform PES experiments from the liquid jet at the locus of molecular beam impact which enables to study chemical processes.

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Photoemission from a liquid jet: Intra- and intermolecular processes

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We apply soft-X-ray photo- and Auger-electron spectroscopy from vacuum liquid microjets to study the ground- and excited state electronic structure of aqueous solutions.[1] The experiment reveals lowest ionization energies as well as core-level binding energies of both solute and water solvent. In addition, core-level-induced relaxation processes are uniquely suited to gain insight into hydrogen-bond strengths as well as in ion pairing. Combining the various aspects of photoemission, we can thus address quite different research topics, ranging from very fundamental intra- and intermolecular processes in aqueous solutions (both at the solution surface and in the interior) to the characterization of the nature of the species and their charge state in solution. Three examples of most recent and ongoing projects are presented.

Following up on our earlier discovery of several non-local core-level induced ultrafast relaxation processes (so-called proton-transfer-mediated intermolecular Coulombic decay, PTM-ICD,[2] and energy-transfer-mediated decay, ETMD[3]) in water we demonstrated the formation of a chemical bond, $NH_4^+(aq) + h\nu \rightarrow NH_3^{+*}(aq) + H_3O$ (aq), within less than 7 fs. Using the same techniques, we next explore OH^- and ADP / ATP (in the presence of Mg^{2+} and / or Ca^{2+}) aqueous solutions. Our interest in the former solution is to infer the hydration structure which is related to the fast migration / diffusion mechanism of hydroxide.[4] The second system is studied to fully characterize the electronic structure of the reactant and product states of the ATP hydrolysis in aqueous solution, a key reaction in living cells.

With regard to our research activities within the DFG Collaborative Research Center, CRC 1109, on “Metal Oxide/Water Systems”, we present the very first photoemission studies from hematite (Fe_2O_3) nanoparticles in aqueous solution. These works aim at advancing our understanding of dissociative (liquid) water adsorption at catalytic transition-metal oxide surfaces. Combining non-resonant and resonant (at both the oxygen 1s and the metal 2p edges) photoemission spectroscopy, dissociated H_2O at the nanoparticle surface can be identified. Among others, these works will be extended to TiO_2 and Fe_3O_4 (magnetite) aqueous-phase nanoparticles.

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The FHI-FEL facility: User operation, synchronisation with table-top lasers, planned facility extension & machine upgrade

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The FHI free-electron laser (FHI-FEL) provides intense, widely tunable infrared radiation from 2.9 to 50 micron to currently 6 user stations. Besides user operation the FEL has been continuously improved in terms of power, spectral brightness, reliability and stability. In addition, synchronization of femtosecond pulses from a commercial table-top laser to the FEL pulses at a timing accuracy level of 100 fs rms has been implemented. Furthermore, we will describe our plans to extend the user lab space and we will detail the upgrade plans for the 2-color FHI-FEL.

The FHI-FEL generates macro-pulses (≤ 10 µs long pulse trains at 5 or 10 Hz repetition rate) consisting of several thousand micro-pulses of ~1 ps length at a repetition rate of 1 GHz. The energy per micro-pulse is close to 10 µJ corresponding to 50 - 100 mJ per macro-pulse. The Fourier transform limited relative bandwidth is, typically, about 0.5% FWHM. In this standard mode of operation the FEL radiation has been applied by groups from the departments MP, PC, CP, and AC in experiments ranging from spectroscopy of biomolecules and clusters in the gas phase to nonlinear spectroscopy of solids, surface science, and catalysis. Hence, the experiments performed at the FHI-FEL facility reflect the broad spectrum of experimental research at the FHI.

In the low-repetition-rate mode of operation, the FEL's micro-pulse repetition rate is reduced to 27 or 56 MHz. In these modes the pulses from a Yb-doped fiber laser (100 fs pulse length, 45 nJ pulse energy, 1050 nm central wavelength, 56 MHz repetition rate) have been synchronized to the FEL pulses with a very low timing jitter of only ~100 fs (rms). This paves the way for pump-probe and sum-frequency spectroscopy experiments at the FHI-FEL facility.

In addition, we describe our plans to further develop the FHI-FEL facility by expanding the user beamline and lab space in the basement and the 1st floor of Building D. The plan is to increase the number of user stations from currently 6 to a total of 9 in 2018.

An envisioned machine upgrade was outlined at the last Fachbeirat Meeting: By setting up a second FEL branch the wavelength range can be extended into the far-infrared and Terahertz region beyond 100 µm wavelength. In addition, the proposal included a modification of the existing electron accelerator and beamline system such that simultaneous operation of both FEL branches becomes possible, thereby allowing the generation of inherently synchronized FEL radiation at two independently tunable wavelengths. Such a 2-color FEL will be a unique machine among accelerator-based radiation sources. It can open the door to new 2-color experiments in the mid-infrared regime with possible applications in, e.g., pump-probe studies, 2D IR spectroscopy, or nonlinear spectroscopy of solids. We will describe the technical design which includes a 500 MHz transverse deflecting cavity for electron bunch selection. This new approach, which differs from the previously suggested 500 MHz energy modulation cavity, requires far less RF power, thereby reducing costs and technical complexity.

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One hundred years of chemical warfare: Research, deployment, consequences

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and Martin Wolf

On April 22, 1915, the German military released 150 tons of chlorine gas at Ypres, Belgium. Carried by a long-awaited wind, the chlorine cloud passed, within a few minutes, through the British and French trenches, leaving behind at least 1,000 dead and 4,000 injured. This chemical attack, which amounted to the first use of a weapon of mass destruction, marks a turning point in world history. The preparation as well as the execution of the gas attack was orchestrated by Fritz Haber, the director of the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in Berlin-Dahlem, the forerunner of today's Fritz Haber Institute of the Max Planck Society. During World War I, Haber transformed his research institute into a center for the development of chemical weapons – and of the means of protection against them.

In order to commemorate the tragic centenary of the infamous chemical attack, we organized an international symposium that examined key aspects of chemical warfare from the first research on and deployment of chemical weapons in WWI to the development and use of chemical warfare during the century hence. The focus was on scientific, ethical, legal, and political issues of chemical weapons research and deployment – including the issue of dual use – as well as the ongoing effort to control the possession of chemical weapons and to ultimately achieve their elimination. The symposium contributions supplemented by additional articles (a total of twenty-three) have been published both as a book and online with open access[1].

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Ultrafast Peierls Transition in In/Si(111) Nanowires Measured by Time- and Angle-Resolved Photoemission

Christopher Nicholson, Andreas Lücke[a], Michele Puppin, Wolf Gero Schmidt[a],
Laurenz Rettig, Ralph Ernstorfer, and Martin Wolf

Quasi-one dimensional (1D) metal wires on semiconducting substrates, of which In/Si(111) is one of the most interesting and intensively studied systems, promise not only novel 1D physics, but also control over electronic properties and dimensionality. In/Si(111) undergoes a structural phase transition from a (4x1) to an (8x2) unit cell at around 120 K, concomitant with a metal-to-insulator transition. A combined DFT and Raman study[1] points strongly to a Peierls-like scenario, whereby a combination of shear and rotary distortions leads to the opening of band gaps and spectral shifts at specific points in the band structure. Furthermore, recent work using time-resolved electron diffraction (trRHEED) demonstrated that the photo induced structural transition occurs ultrafast and proposed a mechanistic scenario based on *ab initio* molecular dynamics (MD) simulations.[2]

Here, we investigate the ultrafast dynamics of the electronic band structure during the ultrafast photo induced transition from the 8x2 to 4x1 phase using XUV time- and angle-resolved photoemission spectroscopy (trARPES) at 500 kHz with sub-50 fs temporal resolution. Starting from the 8x2 phase we follow the gradual evolution of the electronic structure into the 4x1 phase on a femtosecond time scale. Most remarkably, the insulator-to-metal transition associated with the gap closing at the 8x2 Brillouin zone boundary occurs within 200 fs, while states at the zone center shift from above to below the Fermi level within 500 fs. Both processes occur faster than the overall structural transition into the 4x1 phase, as manifested by the splitting of two specific bands, which is completed after 700 fs. The distinct timescales of the insulator-to-metal and structural transitions clearly differ from expectations for a "standard" Peierls-like scenario for a quasi 1D system.[3]

By mapping the momentum space distribution of excited carriers (electron and holes) we derive constrains for *ab initio* MD calculations with realistic initial conditions and obtain a consistent picture for trARPES, trRHEED data and theory. We conclude that the photo induced transition is driven by localized holes in momentum space. Our combined experimental and theoretical approach opens up the possibility of addressing real space electronic distributions and bond breaking and formation dynamics on ultrashort time scales with trARPES.

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Fundamental Couplings in Strongly Correlated Materials Investigated by Complementary Time-Domain Techniques

William Windsor, Christopher Nicholson, Ralph Ernstorfer, Martin Wolf,
and Laurenz Rettig

Correlated materials are characterized by the strong interactions between the elementary degrees of freedom, leading to phase transitions into novel ground states with broken symmetries and often intriguing properties. In the study of such materials, the quantitative determination of those couplings, and their relevance for the formation of broken symmetry ground states and phase transitions remains a major challenge. In particular, in thermal equilibrium the various interactions are present simultaneously, making it difficult to separate them due to their similar energy scale.

These limitations can be overcome by using quantitative and complementary time-resolved spectroscopies, which directly address the dynamics of specific degrees of freedom on their individual time scales, in order to determine the couplings between those degrees of freedom and their relevance for a phase transition from their temporal evolution. In particular, combining femtosecond XUV time- and angle-resolved photoemission spectroscopy (trARPES) and time-resolved x-ray diffraction (trXRD) techniques allows following the ultrafast dynamics of electronic, structural and magnetic degrees of freedom and their orderings individually, yielding direct access to the coupling of the electronic, phononic and spin systems.

We discuss this approach in several strongly correlated model systems: In the Fe-pnictide parent compound $BaFe_2As_2$ trXRD allows us to quantify the fluence dependent structural oscillation amplitude of the coherently excited A_{1g} phonon mode. Comparison of the quantitative coherent modifications of the Fe-As tetrahedra with trARPES data yields the electron-phonon deformation potential and thereby the e-ph coupling strength for this particular mode.[1] Furthermore, the optically driven charge-density wave (CDW) transition in $TbTe_3$ is investigated by trARPES[2] and trXRD, allowing us to extract the quantitative coherent and incoherent dynamics of the electronic and structural CDW order parameters, respectively, and thereby assess their coupling during the ultrafast phase transition. Finally, the coupling of electronic and magnetic degrees of freedom can be investigated in the antiferromagnetic (AFM) intermetallic compound $RERh_2Si_2$ (RE=Gd, Sm) by trARPES and resonant x-ray diffraction.

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Momentum-resolved Exciton Dynamics and Spin-, Valley- and Layer-Polarized Excited States in Inversion-Symmetric WSe_2

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Semiconducting transition metal dichalcogenides (TMDCs) like WSe_2 exhibit fascinating optoelectronic properties due to a combination of anisotropic bonding, pronounced many-body interactions and a peculiar spin texture in the electronic structure. The onset of the optical absorption is governed by excitonic transitions between spin-polarized states at the corners of the Brillouin zone. We directly observe the formation of excitons and their evolution in momentum space by time- and angle-resolved photoemission spectroscopy (trARPES) with XUV probe pulses.

The momentum-, energy- and time-resolved data reveals the formation of an electronic coherence between ground and excited state, its dephasing to an excited state population corresponding to a bright exciton, and the subsequent scattering to a dark exciton state by emission of a phonon with a time constant of ~15 fs. We discuss the signatures of the individual stages in the exciton dynamics and relate the measured bright exciton lifetime to exciton-phonon coupling.

In addition, we utilize the hidden spin texture[1] in inversion-symmetric WSe_2 and demonstrate the generation of spin- and pseudospin-polarized excited states: optical excitation of a bulk crystal with circular polarized light in resonance with the A excitonic transition results in spin-polarized excited states localized in a subset of the K valleys of the Brillouin zone.[2] These excited states have a pronounced 2D character and are localized in real space to specific layers of the crystal. Ultrafast intervalley scattering from the K to the Σ valleys transforms the excited electrons to three-dimensional states with strong interlayer coupling and transport. This suggests the suitability of inversion-symmetric TMDC materials for ultrafast spintronic applications.

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Excited State Mapping with XUV-Based trARPES

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Johannes Feldl, Claude Monney, Martin Wolf, Laurenz Rettig, and Ralph Ernstorfer

Angle-resolved photoemission spectroscopy is the main experimental techniques for determining the electronic structure of solids. We extend this concept of band structure mapping to excited states by recording three-dimensional snapshots of the photoexcited carrier distribution in energy and parallel momentum by photoemission with an ultrashort extreme ultraviolet (XUV) laser pulse. Specifically, we map the excited state structure of bulk WSe_2 approximately 100 fs after optical excitation with 3.1 eV photons and compare the results to different DFT electronic band structure calculations. Furthermore, we investigate the closing of the charge density wave (CDW) energy gap in $TbTe_3$ after excitation with 1.55 eV photons. We discuss the observed unfolding of the band structure and disappearance of CDW shadow bands in terms of Tight Binding band structure calculations. In general, this experimental approach allows the observation of occupied and transiently populated unoccupied states on the same footing, and the determination of direct and indirect band gaps within a single experiment.

This application of time- and angle-resolved photoemission spectroscopy (trARPES) is enabled by the development of a short-pulse XUV laser with 500 kHz repetition rate. The laser frontend is an optical parametric chirped pulse amplifier (OPCPA) based on a hybrid fiber-slab amplifier system.[1] The near-infrared OPCPA output is frequency-upconverted sequentially: frequency-doubling to 3.1 eV photon energy is followed by 7^{th} harmonic generation (21.7 eV) in a dense noble gas jet. After spectral filtering, an XUV pulse with 20 fs pulse duration, a bandwidth of ~100 meV and a photon flux exceeding 10^{11} photons/s is available for trARPES.

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Nonlinear Response and Strong Coupling of Surface Phonon Polaritons

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and Alexander Paarmann

Surface Phonon Polaritons (SPhP) have recently reached considerable attention as an alternative building block for mid-infrared (MIR) nanophotonic applications and promise to possibly solve the intrinsic loss problem of plasmonics.[1] SPhPs arise in polar dielectrics due to IR-active phonon resonances leading to negative permittivity between transverse and longitudinal optical phonon frequencies, a region called the Reststrahlen band. SPhPs exhibit tremendous field enhancements,[2,3] driving the lattice ions into a strongly non-linear regime. Hence, SPhPs might grant a frequency-tunable access to vibrational-driven transient material phases.

In contrast to surface plasmon polaritons in metals, the strong dispersion of the SPhPs in the Reststrahlen region provides a natural way for tailoring SPhP resonances. Multilayers composed of different polar dielectrics with overlapping Reststrahlen bands exhibit a variety of novel phenomena such as mode-splitting, index-sensing, and wave-guiding,[4] thus allowing for the engineering of novel hybrid materials with custom-designed polaritonic response.

Here, we use linear and nonlinear MIR spectroscopy[5] for studying SPhPs in SiC and AlN, employing Otto-type prism coupling. The air gap in the Otto geometry is actively steered, as monitored by the white light interferometry, granting extrinsic control over the critical conditions of the SPhP excitation. Employing intense, tunable and narrow-band MIR pulses from the FHI free-electron laser, our experiments reveal prominent increase of the resonant second harmonic generation (SHG), arising from the optical field enhancement that is associated with propagating SPhPs at the SiC/air interface.[3]

Furthermore, a nanoscale thin (10-100 nm) layer of AlN is grown on SiC, leading to the strong coupling and mode-splitting of the SiC SPhP and the AlN ultrathin film polariton. Specifically, we show that the coupling strength can be tuned both intrinsically (using different AlN layer thicknesses) and extrinsically, by modulation of the SPhP radiative losses through variation of the air gap width. These experimental observations are corroborated by a specifically developed matrix formalism for anisotropic multilayer wave propagation[4], in order to achieve precise understanding and predictability of the linear and non-linear properties of SPhPs in polar dielectric heterostructures.

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A Pathway Towards Engineered Mid-Infrared Nanophotonic Materials: Atomic-Scale Crystalline Hybrids

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The field of nanophotonics focuses on the confinement of light to sub-wavelength dimensions, accompanied by considerable optical field enhancements. Thereby photonic technologies may be realized which are not possible by means of traditional optics. The key building block of nanophotonics are surface polaritons, since these evanescent modes provide sub-diffractional localization of light through their large momenta. While the most-studied species of such surface polaritons are surface plasmon polaritons (SPPs) supported by quasi-free electrons in metals, we focus on polaritons supported by optical phonons in polar dielectric materials, i.e. surface phonon polaritons (SPhP). Due to the relatively long lifetimes of optical phonons, SPhPs are a promising candidate to overcome the intrinsic loss problem of plasmonics.[1] Recently, atomic-scale heterostructures of polar dielectrics, so-called crystalline hybrids (XHs), have been proposed as a novel platform for tunable SPhP materials.[2]

We here take a first step towards engineering of optical phonon frequencies and line-widths and, consequently, of the SPhP dispersion in an atomic-scale heterostructure, here exemplified for AlN/GaN superlattices with atomic-scale layer thicknesses. Using the FHI mid-infrared free-electron laser, we employ second-harmonic phonon spectroscopy[3] to demonstrate phonon polariton hybridization: by varying the thickness of the AlN and GaN layers, respectively, we identify new hybrid phonon modes through their layer-thickness dependent spectral shifts and amplitude variations. The spectroscopic data obtained in the experiment are in an excellent agreement with theoretical predictions.[4]

Additionally, we probe the evanescent modes of the XH using prism coupling in the Otto geometry[5], proving that the XH's effective dielectric function, measured by infrared ellipsometry, is fully predictive for the polaritonic behavior and nanophotonic performance of the hybrid material. Notably, the atomic-scale phonon hybridization truly creates a new material that cannot be described using the dielectric functions of the heterostructure's constituents. These experimental results show that XHs constitute a promising new platform for custom-designed mid-infrared nanophotonic materials.

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Timing and Pulse Shape Characterization at the FHI Free-Electron Laser Using a Synchronized Table-Top Laser

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The Free-Electron Laser (FEL) at the Fritz Haber Institute serves as a mid-infrared coherent light source generating intense, sub-picosecond pulses and narrowband radiation, which is continuously tunable in the wavelength range from 3 to 50 μm. Due to the unique spectral and temporal characteristics, the FHI FEL facility is an ideal platform for high-resolution vibrational spectroscopy of matter. Two-color spectroscopy of low-energy elementary excitations becomes accessible by the combined application of FEL and synchronized table-top laser pulses. In order to perform non-linear and time-resolved solid-state investigations, a low-jitter pulse synchronization system has been implemented. This enables us for the first time to accurately study the short- and long-term timing stability as well as the temporal shape of the FEL pulses by cross-correlation with femtosecond table-top laser pulses.

A table-top fiber oscillator providing 100 fs near-infrared (1030 nm) pulses at a repetition rate of 55.5 MHz is synchronized to the FEL micro-pulses. To this end, a stabilized fiber-optic link was implemented to transfer the 3 GHz reference clock signal driving the accelerators from FEL facility to the experimental user station. Electronic phase-locking of FEL and table-top laser pulses provides a synchronization with a precision < 100 fs. For optical cross-correlation measurements, sum-frequency generation (SFG) in a non-linear crystal was employed. Using a balanced optical cross-correlation scheme[1], the FEL timing jitter was determined to be as low as ~100 fs (rms). Long-term timing drifts of a few picoseconds/hour were found to be clearly correlated to the energy drift of the accelerator electron bunches, accompanied by small shifts in the FEL wavelength.

The temporal shape of the FEL micro-pulse intensity is directly given by the cross-correlation SFG signal. Using a small FEL cavity detuning, sub-picosecond micro-pulses with a Gaussian envelope were generated. Increasing the detuning value, i.e. shortening of the FEL cavity, lengthens the pulse duration to a few picoseconds due to the smeared out temporal overlap of the free-electron gain medium and optical pulses[2], and the FEL micro-pulses develop an asymmetric shape with an exponential rising edge. In addition, the evolution of the micro-pulse shape within the macro-pulse is recorded, where for modest detuning the emergence of multiple pulses is resolved in great detail. These data demonstrate the ability to generate FEL radiation with tunable bandwidth and pulse duration, complementing previous autocorrelation measurements of the FEL pulses.[3]

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Nonlinear Terahertz Phononics: A Novel Route to Controlling Crystal Lattice and Spins

Sebastian Maehrlein, Alexander Paarmann, Martin Wolf, and Tobias Kampfrath

We take advantage of phonons as a novel and specific pathway to drive ultrafast processes in solids. By direct excitation with intense, ultrashort terahertz (THz) electric-field transients, high-frequency phonons in insulating solids are accessed on their intrinsic time- and energy-scales, while avoiding parasitic electronic processes. Here, two examples are considered how nonlinear THz spectroscopy can provide new insights into the coupling of phonons to the electron-spin degrees of freedom and light.

In magnetically ordered solids, fundamental dynamic processes such as magnetization switching and transport of spin angular momentum require an understanding of the way spins interact with oscillations of the crystal lattice. Here, we investigate spin-lattice coupling by resonant excitation of infrared-active phonon modes of the textbook ferrimagnetic insulator yttrium iron garnet (YIG). Remarkably, two distinctive time scales for phonon-magnon equilibration are revealed. A surprisingly rapid change of magnetic order with a time constant of ~1 ps is found to be driven by phonon-induced fluctuations of the exchange coupling, which leads to a sublattice demagnetization under the constraint of conserved total spin angular momentum. The resulting quasi-equilibrium state persists over tens of nanoseconds until the spin angular momentum is released to the lattice via weaker coupling mechanisms. The experimental observations can be reproduced by atomistic spin-dynamics simulations and analytical calculations. These findings have important implications for contemporary research topics such as the spin Seebeck effect, antiferromagnetic spintronics and ultrafast magnetization switching.

In contrast, phonon modes with vanishing electric dipole moments were so far excluded from direct THz excitation. Here, we suggest a novel type of light-matter interaction that enables coherent-phonon excitation via non-resonant two-photon absorption of intense THz fields. This second-order nonlinear process is the so far neglected up-conversion counterpart of stimulated Raman scattering. We here demonstrate this mechanism by exciting the infrared-inactive yet Raman-active 40 THz optical phonon of diamond.[1] Remarkably, the CEP of the driving THz pulse is found to be directly imprinted on the lattice vibration. This study opens up a novel pathway to the phase-sensitive coherent control of phonons that were previously inaccessible by THz radiation. Furthermore, new prospects in action spectroscopy of molecules at free-electron lasers emerge.

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Observation of Ultrafast Spin Accumulation at Terahertz Frequencies by the Anomalous and Spin Hall Effects

Julius Heitz, Lukáš Nádvorník, Tom Seifert, Martin Wolf, and Tobias Kampfrath

Ultrafast spin transport in solid state systems has gained considerable attention as it is the key for understanding and harnessing the appealing functionalities of ultrafast spintronic devices such as the magnetization reversal, spin transfer torque, giant magnetoresistance or emission of terahertz (THz) radiation.[1] One of the established methods to generate such ultrafast spin currents are the anomalous and spin Hall effects (AHE, SHE). It is highly desirable to transfer these effects to the THz frequency range because the bandwidth of digital information processing is gradually approaching this frequency region. However, up to now, there is no observation of ultrafast spin accumulation at sample boundaries or interfaces due to the AHE and SHE.

Here, we demonstrate ultrafast spin separation in thin metallic bilayers such as CoFeB/Pt in the normal (perpendicular-to-plane) direction, resulting in an ultrafast spin accumulation at and/or spin transfer through the interface. In our experiment, the electric field component of an intense incident THz pulse is used to drive THz charge currents in a ferromagnetic metal layer. Through the SHE/AHE, these in-plane currents are transformed into spin-polarized currents in the out-of-plane direction. The ultrafast dynamics of the resulting spin accumulation in the adjacent non-magnetic metallic layer are then measured by means of the magneto-optical Kerr effect (MOKE) using an infrared probe beam.

To provide conclusive evidence of the nature of the measured effects, we performed a systematic study by investigating different stack orders, layer composition and thickness of metallic bilayers (CoFeB/W and CoFeB/Pt). This procedure allowed us to identify the dominant spin flow direction and the dominant underlying effects. Interestingly, we also found that the ultrafast spin accumulation is also observable in much simpler systems such as Fe single layers of sufficient thickness. Finally, comparison of the frequency dependence of the spin accumulation with a spin-diffusion model allowed us to infer the relative size of principal spin transport quantities.

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Spin Orbit Interaction at Terahertz Speeds: Probing and Driving Spins at Highest Frequencies

Tom Seifert, Lukas Braun, Oliver Gückstock, Martin Wolf, and Tobias Kampfrath

Spin-orbit interaction (SOI) will be of central importance for future spin-based electronics (spintronics) as it permits, for example, the conversion of charge into spin currents and vice versa via the spin Hall effect (SHE) and its inverse. With regard to spintronic applications, both the generation and the detection of spin currents need to be as efficient as possible and should eventually operate at the highest speed possible. New classes of spin-orbit materials including topological insulators, heavy-metal-based alloys and heavy-metal oxides hold the promise for a drastically increased charge-to-spin conversion efficiency in the future. On the other hand, the functionality of different spin current generation mechanisms including the SHE and the spin (dependent) Seebeck effect at the picosecond time scale remains to be shown. It is therefore highly interesting to study spin transport at terahertz (THz) frequencies.

In our experiments, we employ femtosecond optical pulses to trigger ultrafast spin transport in magnetic thin-film stacks. Due to SOI, the spin current is partially converted into a transverse charge current which is monitored by detecting the concomitantly emitted THz electromagnetic radiation.[1,2] In particular, we study THz emission from bilayers consisting of a magnetic and a nonmagnetic layer:

First, by studying different nonmagnetic layer materials such as pure heavy metals,[3] heavy-metal alloys (Ta_xAu_{1-x} and Pt_xAu_{1-x}), tungsten oxide and the topological insulator Sb_2Te_3, we aim at testing the functionality of central spintronic effects at terahertz frequencies and eventually identify efficient spin-to-charge conversion materials.

Second, by varying the magnetic layer material from conducting to insulating and from ferromagnetic to antiferromagnetic, we aim at identifying the different mechanisms that can lead to the ultrafast generation of spin currents across those structures. Such mechanisms include super-diffusive spin transport by conduction-band electrons in metal-metal stacks and magnon-mediated transfer of spin angular momentum in insulator-metal stacks.

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Terahertz Spin Dynamics Induced by Femtosecond Spin Current Pulses in Fe/Au/Fe/MgO(001) Spin Valves

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Ultrafast spin dynamics is the key for development of spintronics and fast data storage devices. Of particular interest is the development of generation, control, and detection techniques for ultrashort spin current pulses and action of their subsequent spin transfer torque on a ferromagnet (FM). The latter is a promising and elegant way to excite magnetization dynamics: when spin-polarized hot carriers reach an FM layer, the magnetization experiences a torque and moves out of the equilibrium. The excitation of uniform magnetization precession with frequencies of 10 GHz has been demonstrated in two orthogonally magnetized FM layers separated by a thin normal-metal (NM) spacer.[1] Spin currents can also be produced by (transient) temperature gradients across FM/NM interfaces known as the spin-dependent Seebeck effect, and about 100 ps-long spin currents pulses have been achieved so far.[2]

Here we demonstrate the ultrafast, non-thermal counterpart of this effect governed by the laser-excited hot electron distribution in a FM layer. Thereby, the spin-dependent transmittance at the FM/NM interface for non-thermalized, high-energy hot carriers leads to generation of an ultrashort spin current pulse with a duration defined by the hot carrier thermalization time.[3] Upon excitation of hot carriers in the top 16 nm-thick Fe layer (emitter) of a Fe/Au/Fe/MgO(001) structure by 14 fs laser pulses we demonstrate the generation of ~250 fs-short spin current pulses. After passing a 55 nm-thick Au spacer layer the spin current pulse is reflected from the Au/Fe interface to the 15 nm-thick bottom Fe layer (collector). We show that upon interaction with the interface the spin current component orthogonal to the Fe magnetization **M** is absorbed by the collector. With the magneto-optical Kerr effect, we monitor subsequent picosecond pre–cessional dynamics of **M** excited in the Fe collector by this spin transfer torque. Owing to the spatially non-uniform distribution of the spin transfer torque several lowest perpendicular standing spin wave modes can be excited on top of the uniform precession.[4] Reducing the collector thickness, we achieve the generation of single intense standing spin waves with variable frequency up to 0.6 THz.

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Development of Ultrafast THz-Gated Scanning Tunneling Microscopy Combined with Optically Excited Plasmonic Nanofocusing

Melanie Müller, Markus Raschke[a], Ralph Ernstorfer and Martin Wolf

Understanding the spatio-temporal dynamics of nanostructures and molecules at surfaces on their natural length and time scales is a key goal in surface dynamics. Recently, it has been demonstrated that combining THz-pulses with scanning tunneling microscopy (THz-STM) enables atomic spatial resolution together with femtosecond temporal resolution in a THz-pump THz-probe excitation scheme.[1] However, excitation with optical light pulses would provide a much broader access to a variety of spatio-temporal phenomena. To study the local, atomically resolved response of such systems after photoexcitation and the subsequent dynamics of photogenerated charge carriers, we aim to combine the Angstrom spatial and femtosecond temporal resolution of a THz-pulse gated STM with femtosecond optical excitation.

We report on first steps in the development of a room-temperature THz-STM combined with optical photoexcitation employing the nanofocused plasmonic near-field of nanostructured gold tips. Plasmonic nanofocusing of few-cycle optical fields can be used to trigger nonlinear photoemission from the tip apex with higher efficiency compared to direct apex illumination as shown recently in the MPRG of Ralph Ernstorfer.[2] The combination of a nano-confined mode volume of the femtosecond excitation pulse together with the non-local excitation scheme, without direct illumination of the tip apex, promises an increased photoexcitation efficiency of the sample at reduced thermal load on the STM junction. In order to explore the optical near-field pump - THz-probe STM scheme, a home-built room-temperature STM was constructed, which provides easy and flexible optical access to the tip-sample junction. First experiments will focus on the local dynamics of charge carriers in low-dimensional materials, such as 2D transition metal dichalcogenides (TMDCs), TMDC heterostructures and graphene nanoribbons employing few-cycle optical pump pulses and a broadband spintronic THz-emitter.[3]

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Fabricating Specially Designed Scanning Probe Microscopy Samples for Controlled *in-situ* Charge Transport Measurements

Matthias Koch, Takashi Kumagai, and Martin Wolf

Studying charge transport on a single molecular level is a key challenge in molecular electronics.[1,2] Molecular break junctions[1] and STM pulling experiments[3] are common techniques to measure the conductance through single molecules. However, these techniques have the disadvantage that the details of the junction i.e. the molecule-electrode contact, the molecular configuration, orientation and bending are experimentally not directly accessible although they strongly affect the charge transport.[4,5] For a better understanding of charge transport through molecular systems, a detailed characterization, control as well as gating of the junction is essential.

We will address this problem by developing a new silicon sample for STM/AFM that hosts an integrated circuit. The integrated circuit is made of highly doped regions embedded in an insulating silicon crystal. With scanning tunneling hydrogen resist lithography[6] we want to extend the highly doped regions to nanoscopic contact patches which act either as a gate, source or drain electrode in single-molecule transport measurements. This setup bears the advantage that the SPM tip can image the molecular junction, manipulate individual molecules inside the junction and, most importantly, the SPM tip can act as an additional electrode which can be positioned with Angstrom precision.

We introduce the new project and present experimental ideas. In particular, we plan to test our experimental setup with molecular rotors that exhibit a permanent dipole moment.[7] The applied gate voltage should align the dipole moment with respect to the electrodes. Furthermore we want to tunnel-couple a single molecule to one nanoscopic contact patch and to the SPM tip. The tunnel-coupled molecule should behave similar to a single electron transistor that is gated by the second nanoscopic contact patch.[8]

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Single-Molecule Mechanochemistry Studied by Non-Contact Atomic Force Microscopy

Janina N. Ladenthin, Matthias Koch, and Takashi Kumagai

Single-molecule mechanochemistry is an important, emerging field. With low-temperature non-contact atomic force microscopy (AFM) one can directly study force-induced reactions at the single atom/molecule level. In the poster, we will discuss our recent two topics.

Force-induced tautomerization in a single porphycene molecule: We showed force-induced tautomerization in a single porphycene molecule on a Cu(110) surface at 5 K by a combination of non-contact AFM experiments and density functional theory calculations[1]. Force spectroscopy quantifies the force needed to trigger tautomerization with sub-molecular spatial resolution. The calculations show how the reaction pathway and barrier of tautomerization is modified in the presence of a copper tip and reveal the atomistic origin of the process. Moreover, we demonstrate that a chemically inert tip whose apex is terminated by xenon atom cannot induce the reaction because of a weak interaction with porphycene and a strong relaxation of xenon on the tip as contact to the molecule is formed.

The Role of defects on the mechanical and electronic properties of individual molecular chains: Atomically precise Graphene Nanoribbons[2] are an ideal system to study the influence of defects on the charge transport for multiple reasons. First, the charge transport of defect free graphene nanoribbons has been studied in advance and is well understood[3]. Second, it has been reported that well-defined and chemical precise defects can be fabricated when the cyclodehydrogenation temperature is reduced[4]. We will present here a combination of scanning tunneling microscopy (STM) and AFM pulling experiments where single molecules are lifted from the surface while the current and the frequency shift are observed simultaneously. The combination of conductance, force measurements and theoretical modelling gives us a detailed understanding of the configuration of the molecule during the pulling process and we can isolate the contribution of the chemical defects on the charge transport.

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Optical Near-Field Induced Tautomerization of Single Porphycene Molecules

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and Takashi Kumagai

In the vicinity of metallic nanostructures, photochemical reactions in molecules can be significantly enhanced through near-field excitation.[1,2,3] The enhancement effect under visible light irradiation is of particular interest since it facilitates the use of sunlight to promote material and energy conversion.[4] In near-field coupled reactions, (sub)nanometer gaps between nanoparticles, so-called "hot spots" where the local electromagnetic field is dramatically enhanced, are expected to play a crucial role. However, chemical processes in the hot spot remain poorly understood at the molecular level.

In the poster we show the direct observation of near-field-coupled tautomerization in single porphycene molecules on a Cu(111) and Cu(110) surface by using a low-temperature scanning tunneling microscope combined with a wavelength tunable laser. It is revealed that the tautomerization cross-section increases considerably in the red and near-infrared region when the surface is illuminated in the presence of a metallic tip. The reaction cross section is directly compared between near- and far-field excitation (in the absence of the tip), to extract the wavelength dependent enhancement factor of $10^{2\text{-}3}$. We also elucidate the plasmonic nature of the generated field enhancement by investigating the material, polarization and tip geometry dependence of the measured cross section. It is further revealed that the plasmonic excitation dephases into hot carriers which subsequently attach to the molecule to induce the reaction by comparing the spectral variation of the cross section of the porphycene tautomerization with the photochemically excited flip motion of a hydroxyl dimer. These results shed light on the mechanism of photochemical reactions in the vicinity of metallic nanostructures as employed in plasmon enhanced photocatalysis.

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Single-Molecule Spectroscopy of Naphthalocyanine Molecules on Ultrathin ZnO Layers

Shuyi Liu, Martin Wolf, and Takashi Kumagai

In order to attain the precise control of the optoelectronic properties of hybrid inorganic/organic systems (HIOS), it is of fundamental importance to understand geometric and electronic structure of an inorganic/organic interface at the atomic/molecular level. Ultrathin dielectric layers expitaxially grown on a metal surface can serve as a basic model to study chemical interactions with adsorbed molecules and physical properties of the formed HIOS interface[1]. ZnO is an important material for optoelectronic applications such as photovoltaics, light-emitting devices, laser diodes, and photodetectors[2, 3] and combination with organic molecules will open up a possibility for highly efficient coupling with light. However, it is necessary to understand microscopic mechanisms of the structure and the energy level alignment at the interface.

We have investigated the adsorption and electronic structure of single naphthalocyanine (NPc) molecules on ultrathin ZnO layers epitaxially grown over a Ag(111) surface by using low-temperature scanning tunneling microscopy (STM). The molecular orbitals are directly visualized in the STM images and the adsorption geometry of a NPc molecule is determined by atomic-resolution imaging. Single-molecule spectroscopy reveals the electronic structure and a different energy level alignment for the NPc molecules adsorbed on 2 or 3 monolayer ZnO layer as well as an influence from possible impurities. It is also found that the interaction between NPc and the ZnO layer results in the emergence of an additional state in the HOMO–LUMO gap, which could be attributed to the bonding interaction of the amine N atoms in the molecular cavity with the surface Zn atoms underneath. Furthermore, the gap state can be switched on/off by removing an electron from the NPc molecule.

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Towards High-Precision, Phase-Resolved, Sensitive, Sum Frequency Spectroscopy

Martin Thämer, Tobias Garling, Yujin Tong, R. Kramer Campen, and Martin Wolf

Sum Frequency Generation (SFG) is a coherent nonlinear optical process in which two incident fields with frequency ω_1 and ω_2 are mixed at an interface and the emitted field at frequency $\omega_{sf} = \omega_1 + \omega_2$ is detected. This sum frequency emission is interface specific by its symmetry selection rules and provides spectroscopic information arising from resonances of either incident field to optically accessible transition at an interface By choosing the incident field frequencies in the infrared or visible it is thus possible to create the interfacial analog of UV/Vis absorption, infrared absorption, or spontaneous Raman in bulk. While the technique has been used with great success to gain molecular-scale information in a variety of interfacial systems inaccessible to conventional surface science, its current application has two limitations:

i) Detecting the emitted sum frequency intensity as a function of frequency of one of the incident fields creates a signal arising from interference between contributions from other resonances and non-resonant contributions. This challenge can be overcome by detecting both the intensity and phase of the emitted SF field by interfering the emission from the sample with that from a well-defined reference. Currently such heterodyne detection approaches suffer from significant phase drifts on hour time-scales, primarily because of different optical paths of the sample and reference, and thus strongly distorting measured spectra.

ii) Because the emitted sum frequency field is weak (10^7 less intense than linear scattered light) pulsed laser sources with high peak powers and sensitive detection are required.

We have addressed this challenge in two ways. Firstly, by detecting the intensity spectrum of the emitted SF field as a function of delay of the two incident fields with respect to each other, and employing a phase retrieval algorithm developed for femtosecond pulse characterization, we achieved high precision relative phase retrieval. Secondly, a collinear, time-domain, heterodyne, phase-referenced, balance-detected SFG spectrometer has been constructed. The collinear, heterodyned, shot-to-shot phase referenced aspects of the design allow accurate detection of phase resolved SF signals with essentially no drift on time scales of hours to days. Simultaneously, the balance-detected, heterodyned aspects increase signal to noise vs., conventional, homodyne set-ups by > 15x thus also allowing us to overcome the second challenge. The application of this spectrometer will allow the detection of previously inaccessible weakly resonant interfacial species, e.g. interfacial Eigen or Zundel cations, with artifact-free line shapes, or the use of weak, extremely spectrally broad incident fields, e.g. continuum sources that would allow detecting a vibrational spectrum from 500-4000 cm^{-1} in each laser shot. Either prospect promises significant new frontiers for SFG spectroscopy.

Probing Structure and Chemistry at Au and Pt Electrodes in Aqueous Electrolyte

Yujin Tong, Gregor Zwaschka, Tobias Garling, Julius Plescher, Martin Wolf,
and R. Kramer Campen

Gaining molecular-level insight into chemistry at electrochemical interfaces is important in the design and optimization of a wide variety of energy storage and generation applications. Achieving such insight, however, is challenging for two reasons: (i) it often requires probing interfacial species, with the interface under bias, in the presence of much larger amounts of similar moieties in the electrolyte (ii) reaction intermediates often exist in small concentrations and have ultrashort lifetimes. In this period we have addressed the first question by performing, interface-specific, vibrational and electronically resonant sum frequency (VSF or ESF) spectroscopy in thin-film and meniscus spectro-electrochemical cells. We have addressed the second challenge by using an ultrafast perturbation of electrode potential, driven by femtosecond laser pulses, to initiate electron transfer and tracked the resulting products both optically, using VSF/ESF spectroscopy, and electrically, using laser-induced photovoltage.

Within the double-layer region at the Au electrode/liquid water interface we have shown, using VSF spectroscopy of the interfacial OH stretch spectral response, the existence of a previously unobserved *structural type* of interfacial water (with one OH group points towards the Au electrode)[1]. This non-H-Bonded structure suggests it is likely to play a particular role in the solvation of interfacial solutes. Curiously, contrary to simple electrostatic arguments, this population of interfacial water appears to *increase* as the electrode surface becomes more positive. Moving to oxidizing potentials and characterizing the spectral response of interfacial Au-O modes we have shown that as gold is oxidized the surface is dominated by interfacial hydroxide. Purely thermodynamic considerations (on idealized crystal surfaces) suggest hydroxide should not appear during Au oxidation. Our results thus suggest that, at least on polycrystalline Au, kinetics may control interfacial structure during gold oxidation.

The hydrogen evolution reaction (HER) on Pt proceeds in a two-step process: proton adsorption followed either by recombinative desorption or combination of one surface bound Pt-H with a neighboring hydronium to generate H_2. In contrast neither protons nor water strongly adsorb on Au so HER must here proceed either via tunneling or formation of an interfacial solvated electron. In this period we show that, following adiabatic e^- transfer into a, relatively low energy, Pt-H surface state, interfacial Pt-H population increases on sub-picosecond time scales but decreases on >2 ps timescales in a manner that is potential dependent and implies H_2 formation is rate limiting. In contrast, on Au following adiabatic e^- transfer into water's conduction band, we have generated an interfacial delocalized electron that lives for hundreds of femtoseconds followed by formation of an interfacial, localized, solvated electron. Some fraction of these localized electrons relax back into the electrode, on, potential dependent timescales ranging from 1.5-15 picoseconds, while the remainder diffuse away and, presumably, induce the HER.

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Characterizing Water/α-Alumina Interaction: From Sub-Monolayer to Liquid

Harald Kirsch, Yanhua Yue, Sophia Heiden[a], Giacomo Melani[a], Peter Saalfrank[a],
and R. Kramer Campen

α-Alumina surfaces are omnipresent in optics and catalysis and a useful model for more complicated, environmentally abundant aluminosilicate surfaces. Decades of work have made clear that essentially all their properties – *e.g.* stable termination, reactivity, charge – change dramatically, and continuously, with increasing amounts of water and the particular crystal face examined. To deconvolute these effects we work on the three most stable surfaces of α-Al_2O_3, *i.e.* the (0001), $(1\bar{1}02)$ and $(11\bar{2}0)$ consider water coverages ranging from the sub-monolayer to liquid of varying pH and solute composition.

In this period we considered sub-monolayer coverages of water on the α-$Al_2O_3(1\bar{1}02)$ and $(11\bar{2}0)$ both experimentally (using interface-specific, vibrationally resonant sum frequency (VSF) spectroscopy of the OD stretch (from D_2O), low energy electron diffraction and temperature programmed desorption) and theoretically (principally using *ab-initio* molecular dynamics). For the $(1\bar{1}02)$ surface it is apparent that surface structure creates a population of surface OD groups with sufficient anharmonicity to delocalize the deuteron.[1] In contrast, on the $(11\bar{2}0)$ surface the arrangement of surface metal atoms allows strong bidentate adsorption of surface OD fragments and explains the greater reactivity of this surface towards water. To probe this effect we have extended our previous demonstration of optical characterization of surface phonons (*i.e.* Al-O spectral response)[2] as a function of water coverage on the $(11\bar{2}0)$ surface.

By contact angle measurements the α-$Al_2O_3(0001)$ surface is hydrophilic. Intriguingly prior work on this surface in contact with liquid water has shown that a significant population of surface aluminols exists that are not hydrogen-bond donors. Such *free OH* groups at aqueous interfaces are characteristic of macroscopically *hydrophobic* surfaces. In this period we have characterized the local water structure that enables this microscopic amphiphilicity by investigating the vibrational relaxation dynamics of this population of surface aluminols. We find that, in contact with pure water their population relaxation time (T_1) is 3.5 ps, 3.5 times slower than the T_1 of non-H-bonded OH groups at the air/water interface but >50x faster than relaxation of isolated surface hydroxyls on other oxides or aluminosilicates. Changing solution chemistry, either by changing pH or changing salt concentration, modulates this T_1 by 3x. *Ab-initio* simulation suggests that these non-H-bonded aluminols exist because of a templating effect of surface structure and that the relaxation mechanism proceeds via neighboring H-bonded aluminols and then to interfacial molecular water. Both the existence and orientation of H-bonded aluminols should be strongly sensitive to bulk aqueous phase composition. Such local interfacial structure, effectively local dewetting, has not previously been observed at solid/water interfaces and is expected to have dramatic consequences for surface chemistry.

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Characterizing Hydrogen Bonding, Anion Polarizability and Ion Structure at the Air/Water Interface

Yujin Tong and R. Kramer Campen

Interfaces between aqueous solutions and air are ubiquitous in the environment and are perhaps the paradigmatic hydrophobic/water interface. Elucidating their molecular-scale structure and structural fluctuations is thus a prerequisite to understanding the flow of matter in the environment and more generally how aqueous solutions meet hydrophobic surfaces in biological, environmental and engineered systems. Clearly any full picture of such an interface must clarify *both* interfacial water structure *and* solute structure.

Viewed from the perspective of water structure, perhaps the most important characteristic of the aqueous solution/air interface is the necessity to terminate bulk water's hydrogen bonding network. Spurred by IR absorption and spontaneous Raman studies in bulk water, over the last 25 years a variety of groups have applied the interface-specific, laser-based technique, vibrational sum frequency spectroscopy, to extract the OH stretch spectral response of the monolayer of water at the air/aqueous solution interface. While the OH stretch response is known to report on a water molecule's local environment it is an indirect probe of hydrogen bonding: one is trying to gain insight into liquid water's intermolecular potential by its modulation of an intramolecular vibration. In this period we report the first experimental study of a mode of interfacial water's intermolecular potential: the libration of interfacial water.[1] We find the frequency of this mode is 130 cm^{-1} blue shifted from its value in bulk liquid water: the presence of the interface stiffens water's rotational potential in a manner similar to the formation of ice. Interestingly, in contrast to ice, while the rotational potential of interfacial water is stiffened relative to bulk, most other structural metrics, e.g. hydrogen bond distance, hydrogen bond angle, etc., are quite similar.

From the perspective of solute structure, the classical, Debye-Hückel inspired, description of water/air interfaces suggests that ions should be excluded. Within the last 25 years, however, this view has been substantially revised. It is now clear, based on simulation, theory, reaction rate measurements and surface sensitive spectroscopies that large, polarizable anions tend to partition preferentially to the air/water interface. However understanding the mechanism of adsorption, and particularly the importance of anion polarizability and the possibility of interface induced ion/ion correlation, has proven challenging. The anion perchlorate is known to be strongly interface-active. Here, by probing two of its four fundamental Cl-O modes with interfacial specificity we show (a) that from 0-1 M bulk concentration of $HClO_4$ the polarizability anisotropy of interfacial perchlorate increases by 2.5x and that this change is consistent with the a change in dipole moment from 0-0.75 D (b) above bulk concentrations of 1 M there is interface induced ion pairing. Such ion pairing occurs at the interface at concentrations 10x lower than in the adjoining bulk phase. This is the first direct experimental evidence for either phenomenon and offers important quantitative constraints on the thermo–dynamics of anions at the air/water interface.

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Intermolecular Mode Coupling in Liquids: Insights from THz Kerr Effect

Tobias Kampfrath, Martin Wolf, and Mohsen Sajadi

Low-frequency structural dynamics in liquids occurring at frequencies below ~10 THz (~330 cm^{-1}) are believed to strongly contribute to the outcome of chemical and biological processes.[1,2] The underlying dynamics are complex and include reorientational, vibrational and translational motions of single molecules and/or molecular clusters. These collective motions are directly influenced and even controlled by the intermolecular interactions. To interrogate the dynamics associated with the structural relaxation and reveal the intermolecular mode coupling in liquids, often non-linear optical spectroscopy is applied to study the multidimensional response of liquids upon excitation with a train of ultrashort visible laser pulses. However, in this process the collected signal originates from the light induced polarization in the medium, which for many liquids - such as water - is very weak and thus challenging to measure.

Here, we use intense THz pulses to drive orientational molecular dynamics in polar liquids such as dimethyl sulfoxide and acetonitrile by coupling directly to their low-frequency resonances. We show that resonant excitation of the rotational degrees of freedom leads to a transient optical anisotropy induced by the torque of the THz electric field exerted on the permanent dipole moments of the solvent molecules.[3] We observe a hallmark of this effect as a transient optical birefringence with an amplitude up to one order of magnitude higher than obtained with optical excitation. In light of a simple but quite general model and excitation at different THz frequencies, we show that the observed enhancement arises from the coupling between two intermolecular modes in the liquids, namely the resonantly excited librational (hindered rotational) motions and the optically resolved reorientational relaxation in the liquids. Our approach provides insights into the character of THz absorption resonances, the coupling between low-frequency modes, namely librational and reorientational motions and the sign of the polarizability anisotropy of the solvent molecules.

Our approach in comparing the transient optical anisotropy induced by THz and optical excitation can also be implemented in liquid water. As water is highly polar, we expect a strong coupling of the THz electric field and the permanent dipole moment of the liquid, thus resolving the coupling between the intermolecular modes associated with the hydrogen bonding network of water.

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Stochastic Thermodynamics of a Chemical Nanomachine: The Channeling Enzyme Tryptophan Synthase

Dimitri Loutchko, Maximilian Eisbach, and Alexander S. Mikhailov

The enzyme tryptophan synthase is characterized in review articles as an allosteric molecular factory[1] and a channeling nanomachine.[2] It consists of two subunits, each with its own active center, and catalyzes as a single molecule 13 different reaction steps. It possesses a complex pattern of allosteric interactions that regulate the catalytic activity of the two subunits and opening or closing of their ligand gates. Moreover, one intermediate product is directly channeled within the protein from one subunit to another, so that it is never released into the solution around it. The enzyme is important because it is used by all bacteria, yeast, and plants to synthesize one of the essential amino acids, tryptophan.

Based on experimental data, a stochastic model for the operation of tryptophan synthase has been constructed.[3] Now this model is used to consider stochastic thermodynamics of such a chemical nanomachine.[4] In particular, the Gibbs energy landscape of the internal molecular states is determined, the production of entropy and its flow within the enzyme are analyzed, and the information exchange between the subunits resulting from allosteric cross-regulation and channeling is discussed.

We find that the cycle of this enzyme is driven by the Gibbs energy gradient of 19.56 k_BT between its substrates and the products. The amount of 27.79 bits of entropy is produced and exported to the environment within a single cycle. The distribution of entropy production over the transition network is largely non-uniform. Mutual information is generated in both subunits at the rates of 3.09 and 1.49 bits per second. Contributions from individual allosterically regulated transitions in each of the subunits to the total mutual information change were determined too.

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Accessing Electron-Phonon Interactions Beyond the Two-Temperature Approximation

Lutz Waldecker, Roman Bertoni, Thomas Vasileiadis, Daniela Zahn, Jan Vorberger[a],
Tobias Zier[b], Felipe H. Valencia[b], Martin E. Garcia[b], Hannes Hübener[c],
Thomas Brumme[c], Angel Rubio[c], and Ralph Ernstorfer

The evolution of non-equilibrium states in condensed matter is governed by electron-electron, electron-phonon and phonon-phonon interactions, eventually restoring thermal equilibrium. We quantitatively access these microscopic coupling phenomena by preparing non-equilibrium states through impulsive photo-excitation and the observation of the ultrafast structural response with femtosecond electron diffraction.[1] Up to now, the microscopic energy flow between electrons and lattice has been extracted from time-resolved experiments based on the two-temperature approximation, i.e., the assumption of thermal distribution for both electrons and phonons at all stages of the equilibration process. We challenge this approximation and show that transient non-thermal phonon distributions need to be considered in prototypical materials: the simple metal aluminum[2], the semimetal antimony[3], and the semiconductor WSe_2.[4]

In the case of Al, we propose a refinement of the two-temperature model which treats the coupling between electrons and the three acoustic phonon branches as well as phonon-phonon coupling. This *non-thermal lattice model* appears to be the minimal model capable of predicting the microscopic energy flow in quantitative agreement with DFT calculations.[2] For Sb, we find perfect agreement between experiment and first principle calculations if the coupling of electrons to optical and acoustic phonons is treated independently.[3]

A momentum-resolved view of the strength of electron-phonon interactions was demonstrated for the layered semiconductor WSe_2 by *q*-resolved analysis of the inelastic scattering background. Again, these results are compared to ab initio calculations and allows us to differentiate the contributions of intravalley and intervalley scattering processes.

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Ultrafast Microscopy of Charge Carrier Motion in Nanoscale Systems

Faruk Krecinic, Melanie Müller, Jannik Malter, Alexander Paarmann,
Vasily Kravtsov[a], Markus Raschke[a], and Ralph Ernstorfer

The ultrafast motion of charge carriers in nanostructured systems is a crucial aspect of their functionality in optoelectronic applications. We recently developed femtosecond point projection microscopy (fs-PPM) as a new technique for visualization of ultrafast charge motion in real space.[1] This methodology is based on the visualization of transient ultrafast changes of the electric field distribution near nanoscale objects. The temporal derivative of the spatially resolved field dynamics reveals the underlying net carrier motion, as demonstrated for semiconducting InP nanowires.[1] The temporal resolution of this microscopic technique is below 40 fs, as experimentally verified by the visualization of the photoelectrons emerging from metallic Ag nanowires.

The sensitivity of the fs-PPM technique to local electromagnetic fields will be further enhanced by taking advantage of the phase information of the electron wave packet used for imaging. This approach corresponds to a femtosecond version of the first in-line holographic experiment performed by Gabor[2] and modern implementations by Fink and co-workers.[3] A key requirement for performing femtosecond low-energy electron holography is an ultrafast point-like source of coherent electron wave packets, without the presence of an intense laser pulse. We developed such a source based on nonlinear electron emission from a sharp Au tip driven by a nanofocused sub-10 fs surface plasmon polariton (SPP).[4] The SPPs are generated nonlocally by optical excitation of a grating 20 µm away from the apex. Employing this novel electron source, we expect a significant improvement in spatio-temporal resolution to a few nanometers and few femtoseconds, as well as an increased sensitivity to electric field changes to the extent that it may become possible to image the motion of a single moving elementary charge.[5]

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Nanoscale Energy Flow in 0D-2D and 2D-2D Heterostructures Studied with Femtosecond Electron Diffraction

Thomas Vasileiadis, Daniela Zahn, Lutz Waldecker, Dawn Wells[a],
Richard Palmer[b], and Ralph Ernstorfer

The ability to construct heterostructures of different low-dimensional materials offers vast perspectives in the design of novel nanodevices.[1] Such future devices will be controlled by external stimuli like pulses of light, current or heat and hence, short-living, non-equilibrium phenomena will play a major role in the heterostructure's functionalities. Therefore, it is necessary to develop methods for investigating ultrafast energy flow in nanoscale heterogeneous systems. We apply femtosecond electron diffraction (FED) - a technique in which the lattice response to electronic excitations is probed by ultrashort electron bunches – to two different kinds of heterostructures: size-selected gold nanoclusters on various thin film substrates (0D-2D heterostructures) and heterostructures composed of two different transition metal dichalchogenide (TMDC) thin films (2D-2D heterostructures). After optical excitation, the energy content of the lattice motion is quantified by means of the time-dependence of the Debye-Waller effect. The various energy transfer rates can then be extracted using a model in which the thermal equilibration proceeds through intrinsic heat flow, between the electrons and the corresponding lattice, and extrinsic heat flow, among the different components of the heterostructure.

The 0D-2D heterostructures are composed of size-selected Au_{923} nanoclusters soft-landed on light-transparent silicon nitride and light-absorbing amorphous carbon (a-C) films. We perform comparative studies with both substrates where the same increase of lattice heating is reached in the equilibrated excited state. In the case of transparent substrates, the clusters are heated through direct photo-excitation of the electrons, whereas lattice heating occurs primarily by injection of hot phonons from the light-absorbing substrate in case of a-C. We investigate transient structural and morphological changes for both regimes. Only in the case of transient hot electron distributions in the Au clusters, we observe reversible disordering of the surface atoms, which we discuss in terms of a modified potential energy surface at high electronic temperatures that facilitates diffusion of surface atoms.

Semiconducting WS_2-WSe_2 heterostructures were produced by exfoliation and manual stacking. These heterostructures exhibit a type-II band alignment, which leads to charge separation across the interface after photoexcitation. Our FED results indicate efficient sub-100 fs carrier transfer after optical excitation of WSe_2 with 400 nm light and suggest that the equilibration between the two materials is carried out entirely by electronic coupling. In contrast, preliminary results on energy transfer induced by excitation of an excitonic state in WSe_2 point towards the existence of an interfacial energy barrier.

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Ultrafast Dynamics in Low-Dimensional Materials

Selene Mor, Marc Herzog[a], Denis Golež[b], Philipp Werner[b], Martin Eckstein[c],
Hagen W. Klemm[d], Mauricio Prieto[d], Claude Monney[e], and Julia Stähler

The coupling of electronic and structural degrees of freedom determines many material properties. Such interplay tightens in low-dimensional systems and is manifested in rich phase diagrams and dynamics. Here we study (1) a quasi-1D system whose electronic band structure and photoinduced dynamics are affected by strong electron-hole interaction; (2) quantum well and image potential states and their impact on interfacial electronic coupling.

(1) Ta_2NiSe_5 is proposed to support an excitonic insulator phase below $T_C \approx 328$ K combined with a structural change. The former occurs in small gap semiconductors with strong electron-hole interaction where excitons form spontaneously and condense into a new insulating ground state. We study the ultrafast electron and lattice dynamics of Ta_2NiSe_5 by means of time- and angle-resolved photoemission spectroscopy[1] (trARPES) and time-resolved coherent optical phonon spectroscopy. We find that the low-temperature structural phase persists even for high excitation densities and the photoinduced structural phase transition is hindered by absorption saturation of excitation pulses at a fluence of $F_C = 0.2$ mJ cm^{-2}. We also show that the electronic band gap can be optically controlled by tuning the excitation density. Below F_C, the band gap shrinks transiently due to photoenhanced screening of the Coulomb interaction. However, above F_C, the band gap transiently widens at Γ and recovers to its equilibrium value after ≈ 1.5 ps. Hartree-Fock calculations reveal that the band gap widening is due to photoenhancement of the exciton condensate density, persisting until interband carrier relaxation occurs. These results demonstrate the possibility to manipulate exciton condensates with light and gain ultrafast band gap control.

(2) Oxide films are widely applied in technology and their properties are crucially determined by the electronic coupling of unoccupied states at the interface. We use thin SiO_2 films on a Ru(0001) substrate as a model system to study this interplay. By means of time-resolved two-photon photoelectron spectroscopy, we identify two states at 3.7 and 4.5 eV above the Fermi level. These states are populated after photoexcitation of the Ru substrate and exhibit lifetimes shorter than 100 fs. We assign those states to quantum well states originating from the SiO_2 conduction band that are electronically coupled to the metal. Their energy separation is successfully reproduced by a triangular quantum well potential. We rationalize this by a combination of electron confinement in the oxide layer and image potential of the metal surface.

Acknowledgment:
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Dynamics of Interfacial Electronic States of Polar Solvents: Water and Dimethylsulfoxide

Sarah B. King, Katharina Broch, Angelika Demling, Daniel Wegkamp,
and Julia Stähler

The properties of polar solvents at, and near, vacuum or metal interfaces have broad implications, including surface chemical reactivity in the atmosphere or the effect of interfacial solvent electronic states on battery reactions. We have investigated the interface reactivity and electronic state dynamics of two different polar solvents, (1) water and (2) dimethylsulfoxide, using time-resolved two-photon photoemission (2PPE) spectroscopy.

(1) Amorphous solid water (ASW) is the most prevalent form of water in space, and surface reactions of ASW are believed to play a role in the formation of reactive molecular species. We show that a surface-bound electronic state is formed at the ASW/vacuum interface via the bulk conduction band of ASW, located at 2.1 eV above the Fermi level (E_F). This electronic state is extremely long-lived with a decay time of 15-18 seconds. The energy released in the trapping process and the long lifetime of the trapped electrons allows for chemical reactivity, such as the reaction between two trapped electrons and two water molecules, producing hydroxide anions on the ASW/vacuum interface.[1] Such a reaction has implications for the importance of ASW surfaces in producing reactive hydroxide anions in space.

(2) Dimethylsulfoxide (DMSO) is a common battery electrolyte and reactivity of sulfur compounds in the atmosphere with oxygen compounds influence cloud albedo and acid rain. Using time- and angle-resolved 2PPE we observe the conversion from delocalized DMSO electronic states, influenced by the image potential of the Cu(111) substrate, to localized small polaron and DMSO/vacuum electronic states. A delocalized electronic state 2.81 eV above E_F is formed in DMSO immediately upon photon excitation from the occupied Cu(111) electronic band structure. This initially delocalized electronic state increases in binding energy and becomes localized, forming a small polaron at 2.64 eV above E_F on a 200 fs timescale before becoming further solvated on a 600 fs timescale. The small polaron is also involved in forming a long-lived DMSO/vacuum interfacial electronic state that exhibits a transient increase in the photoemission intensity 2.35 eV above E_F on the same 200 fs timescale as the small polaron formation. This surface-bound electronic state is highly sensitive to oxygen exposure, indicating possible reactivity of the surface electronic state with oxygen. This could be of relevance to the reactivity of DMSO bound to dust grains in the atmosphere.

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Ultrafast Electron Dynamics at ZnO-Molecule Interfaces

Lukas Gierster, Sesha Vempati, Jan-Christoph Deinert, and Julia Stähler

ZnO is a semiconducting material with versatile application areas ranging from hybrid inorganic-organic systems (HIOS) to heterogeneous catalysis. To exploit its full capabilities a fundamental understanding of the interaction of ZnO with molecular adsorbates is required. This is challenging, in part, due to the complex and ultrafast nature of the involved dynamical electronic processes.[1] Here we exploit the potential of time-resolved two-photon photoelectron spectroscopy (TR-2PPE) in a controlled UHV environment to resolve the energetics and population dynamics of molecular frontier orbitals for two ZnO-based molecular interfaces.

(1) In heterogeneous catalysis, ZnO is used to activate CO_2 for methanol synthesis. The activation requires the transfer of an electron from ZnO to CO_2.[2] Indeed, we observe that the adsorption of a monolayer CO_2 on ZnO (10-10) leads to a substantial work function increase of ~1 eV, which we explain by a (partial) reduction of CO_2 and the associated dipole moment. Time-resolved pump-probe experiments strongly suggest that electrons can be injected transiently from the ZnO substrate into the LUMO of CO_2 following above band gap photoexcitation of ZnO. After electron transfer, the LUMO shifts down within 1-2 picoseconds resulting in a long-living state below the Fermi level which we assign to activated CO_2 molecules. In complementary work the role of ZnO in an industrially relevant catalyst consisting of Cu and ZnO nanoparticles on Al_2O_3 is investigated by the AC department (see poster AC 5.3).

(2) For hybrid inorganic-organic systems (HIOS), ZnO is a promising inorganic ingredient due to its wide band gap of 3.4 eV and the ability to form stable surface excitons.[3] Here we study the energy level alignment of 5P-Pyridine (provided by Yves Garmshausen, Stefan Hecht, HU Berlin) on ZnO (10-10). Upon adsorption of 5P-Pyridine multilayers the work function reduces drastically by 1.8 eV. The buildup of an in-gap state is observed, possibly arising from a down shift of the LUMO and pinning at the Fermi level. Resonant optical excitation with 2.5 eV from this state creates an ultrashort-lived (90 fs) population in the LUMO+n states, suggesting either very fast electron-hole recombination or resonant coupling to the ZnO conduction band. On the contrary, excitation with 3.9 eV creates an electron population at the same energy, albeit with a lifetime of several 10 picoseconds, which we interpret as exciton formation. These results will be discussed in the context of film thickness and morphology as well as bulk versus interface effects.

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Theory Department

Theory Department

Poster List

Recent work of the *Theory Department* is displayed on 24 posters. Below we give a selection of what may be called “the top 15”. However, we emphasize that this differentiation is marginal and the breadth of the topics addressed in the *Department* played a role in the selection as well.

All posters are displayed in building T, and we kept the numbering, i.e. the poster-site index, of all 24 posters.

The superscript $^{\text{OHG}}$ marks work by or done in collaboration with Mariana Rossi and her Otto Hahn Group. And the superscript $^{\text{ERC}}$ marks the work of Alexandre Tkatchenko’s ERC Group.

Poster Site	*Poster Title and Authors*

New Concepts, Methods, and Techniques

TH 1	**The Novel Materials Discovery Laboratory (NOMAD)** Luca M. Ghiringhelli, Fawzi R. Mohamed, Angelo Ziletti, Ankit Kariryaa, Benjamin Regler, Alfonso Sastre, Christian Carbogno, Sergey V. Levchenko, Georg Huhs, Rubén Jesús García Hernández, Atte Sillanpää, Stefan Heinzel, Kimmo Koski, Dieter Kranzlmüller, Jose Maria Cela, Alessandro De Vita, Daan Frenkel, Francesc Illas, Risto Nieminen, Angel Rubio, Kristian Sommer Thygesen, Claudia Draxl, and Matthias Scheffler
TH 2	**The FHI-aims Project** Volker Blum, Danilo S. Brambila, Björn Bieniek, Christian Carbogno, Luca M. Ghiringhelli, Dorothea Golze, Jan Hermann, Oliver T. Hofmann, Johannes Hoja, William P. Huhn, Yosuke Kanai, Matthias Kick, Jan Kloppenburg, Raul Laasner, Björn Lange, Marvin Lechner, Chi Liu, Andrew Logsdail, Andreas Marek, Florian Merz, Reinhard Maurer, Lydia Nemec, Harald Oberhofer, Nathaniel Raimbault, Xinguo Ren, Karsten Reuter, Stefan Ringe, Patrick Rinke, Mariana Rossi, Christoph Schober, Honghui Shang, Markus Sinstein, Christopher Sutton, Alexandre Tkatchenko, Alvaro Vazquez-Mayagoitia, Mina Yoon, Victor W. Yu, Igor Y. Zhang, Tong Zhu, and Matthias Scheffler
TH 4	**Towards Efficient Orbital-Dependent Density Functionals for Weak and Strong Correlation** Igor Y. Zhang, Patrick Rinke, John P. Perdew, and Matthias Scheffler
TH 7$^{\text{ERC}}$	**Bridging Scales from van der Waals to Casimir Interactions** Jan Hermann, Andrii Kleshchonok, Majid Mortazavi, and Alexandre Tkatchenko

TH 9 **Replica-Exchange Grand-Canonical Algorithm for Determining Phase Diagrams of Surfaces in Reactive Atmospheres**

Yuanyuan Zhou, Matthias Scheffler, and Luca M. Ghiringhelli

Bulk Materials

TH 10^{OHG} **Adiabatic Vibronic Coupling in Molecules and Solids: Physical Insight from Density-Functional Perturbation Theory and Machine Learning**

Honghui Shang, Nathaniel Raimbault, Carlos Mera Acosta, Patrick Rinke, Matthias Scheffler, Mariana Rossi, and Christian Carbogno

TH 11 **Massively Parallel Compressed-Sensing Optimizer for Identifying Materials-Property Descriptors: Application to the Classification of Materials as Metals**

Runhai Ouyang, Emre Ahmetcik, Stefano Curtarolo, Matthias Scheffler, and Luca M. Ghiringhelli

TH 12 **Structure Dependence of Small Polarons in Transparent Oxides: *Ab Initio* Study of Polymorphs of TiO_2 and Ga_2O_3**

Sebastian Kokott, Sergey V. Levchenko, Patrick Rinke, and Matthias Scheffler

TH 13 **Predicting and Understanding Quantum Spin-Hall Insulators with the Help of Machine Learning**

Carlos Mera Acosta, Runhai Ouyang, Adalberto Fazzio, Matthias Scheffler, Luca M. Ghiringhelli, and Christian Carbogno

TH 14 **The Face of Crystals: Insightful Classification Using Deep Learning**

Angelo Ziletti, Devinder Kumar, Matthias Scheffler, and Luca M. Ghiringhelli

TH 16 **Unified Representation of Molecules and Crystals for Machine Learning**

Haoyan Huo and Matthias Rupp

Surfaces, Adsorption, and Heterogeneous Catalysis

TH 19^{OHG} **Impact of Nuclear Quantum Effects on Surface Mediated Water Dissociation at Finite Temperatures**

Yair Litman and Mariana Rossi

TH 20 **New Insights into the Catalytic Activity of Solid Solutions: Carbon Dioxide Activation at Ni_xMg_yO**

Aliaksei Mazheika, Marie M. Millet, Sabine Wrabetz, Andrey Tarasov, Elias Frei, Robert Schlögl, Matthias Scheffler, and Sergey V. Levchenko

Organic Materials, Interfaces, and Biophysics

TH 23^{OHG} **Structure and Electronic Properties of Diverse (Bio)organic Molecules in Hybrid Inorganic/Organic Systems**

Carsten Baldauf, Volker Blum, Svenja Janke, Sergey V. Levchenko, Dmitrii Maksimov, Haiyuan Wang, Matthias Scheffler, and Mariana Rossi

TH 24 **Peptide-Cation Systems: Observing Kinetically Trapped Liquid-State Conformers in the Gas Phase and How to Improve the Force Field Description with Machine Learning**

Markus Schneider and Carsten Baldauf

The Novel Materials Discovery Laboratory (NOMAD)

Luca M. Ghiringhelli, Fawzi R. Mohamed, Angelo Ziletti, Ankit Kariryaa,
Benjamin Regler, Alfonso Sastre, Christian Carbogno, Sergey V. Levchenko,
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Since its launch in November 2015, the *NOMAD European Centre of Excellence (CoE)*, https://nomad-coe.eu, has been working to unify and improve the usefulness of computational materials science data. Orthogonally to other databases in this field that typically focus on a single computer code and are restricted to a closed research group or consortium, the *NOMAD CoE* serves ***all important computer codes*** and develops open Big-Data tools and services that benefit the whole materials-science community.

NOMAD creates, collects, cleanses, refines, and stores data from computational materials science, and develops tools to mine this Big-Data to find patterns, structure, and novel information that could not be discovered from studying smaller data sets. The large volume of data and innovative tools already available from *NOMAD* will enable researchers to advance materials science, identify new physical phenomena, and help industry to improve existing and develop novel products and technologies.

A recent Nature Editorial: “Empty rhetoric over data sharing slows science (Not-so-open data)”[1], notes that many fields are resistant to openly sharing data. In materials science, there has been a cultural shift in attitude towards open data, fostered by *NOMAD*.[2] The ***NOMAD Repository*** provides open access to input and output files of computational materials science from all[3] major data collections in the field, together with those of many individual researchers and groups. In this role, the *NOMAD Repository* is also listed among the recommended repositories of Nature Scientific Data, where it is the only one for materials science. The *Repository* currently contains, more than 44 million total-energy calculations, corresponding to billions of CPU-core hours used at high-performance computers worldwide. *NOMAD* hosts the data for at least 10 years (for free), and it offers DOIs to make the data citable.

The *NOMAD Repository* serves all important computer codes used in computational materials science (more than 30 very different codes). As repository this is extremely useful. However, the files created by the many different codes are very heterogeneous. Thus, they are not directly suitable for Big-Data analytics and extensive comparisons. *NOMAD* therefore converts the code-dependent, heterogeneous data of the *Repository* into code-independent, homogeneous data that are stored in the ***NOMAD Archive***. This is achieved via *NOMAD Meta Info*, a flexible and extensible metadata infrastructure.

Building on the *Repository & Archive*, the *NOMAD* team has developed various tools and services: ***Encyclopedia***, ***Advanced Graphics***, and ***Big-Data Analytics Toolkit***.

The ***NOMAD Encyclopedia*** is a web-based public infrastructure that provides a materials-oriented view of the *Archive* data. Its purpose is to provide access to whatever property of a given material has been computed, through a user-friendly graphical user interface (GUI). Properties available span from structural features to mechanical behavior, thermal properties, electronic structure, transport characteristics, and the materials response to light and other excitations.

Advanced graphics aims at offering a visual and interactive data analysis for a large and geographically dispersed user base in an accessible and interactive way. As a proof of concept 3D videos and virtual-reality applications have been created for the visualization of crystal structures, molecular dynamics, Fermi surfaces, and electron densities for a selection of systems.

With the ***Analytics Toolkit***, we present a general, flexible framework to perform analyses on materials-science data. On the one hand, the *Analytics Toolkit* empowers users to perform complex analyses, even if they have only a basic understanding of data analytics techniques, and no prior knowledge on how the data are stored in the *NOMAD Archive*. On the other hand, the toolkit is also flexible, allowing more advanced users to explore different settings, add new functionalities, and even to further develop the example tools to answer their own scientific and engineering questions.

The central entity of the *Analytics Toolkit* is a *notebook,* i.e., an interactive web page for writing and executing code. From these notebooks, the user has immediate access to all the libraries needed for advanced data analyses and the whole *NOMAD Archive*. Users do not need to install any software on their local machines, as everything they need to perform analytics on *NOMAD Archive* data is available via their web browser.

In order to demonstrate the functionality of the *Toolkit*, we developed tools and associated tutorials for various specific, but complementary, materials-science topics, which cover different aspects of Big-Data analytics and showcase different relevant materials-science applications. Behind these tools, there are methodologies developed at FHI and presented separately in the following posters: TH 11, 13, 14, 16, 17, 18, 21, and 22.

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The FHI-aims Project

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The FHI-aims all-electron electronic structure code, which begun at FHI almost 13 years ago, continues to be a flagship project for computational molecular and materials science, with a global community of users and developers. The core strength of the code is high numerical accuracy of the underlying basis sets and other numerical algorithms [now validated in several high-profile, community-wide cross-comparisons for density-functional theory[1,2] (DFT) and many-body perturbation theory[3] (MBPT)] while enabling scalability to very large problem sizes with support for current and next-generation high-performance computers. This poster highlights key recent enhancements: *(i)* DFT-based ground state electronic structure (meta-generalized gradient approximations, DFT+U, advanced methods for van der Waals interactions, efficient inclusion and broad validation of spin-orbit coupling across the periodic table), *(ii)* MBPT (more general approaches to the GW self-energy, the Bethe-Salpeter equation, periodic implementations of the random-phase approximation, second-order Møller-Plesset theory, and GW), *(iii)* Access to efficient, massively parallel Kohn-Sham solvers scaling as $O(N^3)$ or lower through the ELPA project and a new electronic structure infrastructure "ELSI", *(iv)* A density-functional perturbation theory framework for phonons, electronic friction, and spectroscopic observables (hyperpolarizabilities, Raman, and magnetic resonance), *(v)* Embedding in effective environments (polarizable continuum solvation, a modified Poisson-Boltzmann environment for solvation effects including ionic effects, fragment-orbital density-functional theory to estimate matrix elements for molecular electronic transport), *(vi)* Enhancements for high-throughput screening and embedding into statistical-physics tools, dedicated to structure prediction, cluster expansion (including Wang-Landau and nested sampling), molecular dynamics and thermal conductivity calculations, *(vii)* First steps on GPUs and Intel many-core architectures. Beyond the scientific functionality, future directions will include increasing exchange with and creation of software for community libraries, e.g., with ELPA, ELSI, libxc, SPGlib (symmetry), the CECAM Electronic Structure Library, and other projects.

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Towards Efficient Orbital-Dependent Density Functionals for Weak and Strong Correlation

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The popularity of density-functional theory (DFT) in physics, chemistry, and materials science stems from the favorable balance between accuracy and computational efficiency offered by semilocal or hybrid approximations to the exchange-correlation (XC) functional. However, certain well-documented failures, in particular the inability to correctly describe strongly interacting scenarios with pronounced multi-reference character, such as bond dissociation, limit the predictive power of these functionals in certain cases[1]. On this poster, we present a new concept for the design of exchange-correlation functionals in density-functional theory.

We started from the Bethe-Goldstone equation (BGE) to derive a simple orbital-dependent correlation functional, namely BGE2, which terminates the BGE expansion at the second-order, but retains the self-consistent coupling of electron-pair correlations[2]. This electron-pair coupling effect can be efficiently improved by a simple screened variant (sBGE2). We demonstrated that sBGE2 is size consistent and one-electron 'self-correlation' free. The screened electron-pair correlation coupling ensures the correct H_2 dissociation limit and gives a finite correlation energy for any system even if it has no energy gap. sBGE2 correctly dissociates H_2 and H_2^+ dimers, which is regarded as a big challenge in DFT.[1]

We then took the sBGE2 functional as a building block for an orbital-dependent functional, termed ZRPS, which is a natural extension of the PBE0 hybrid functional[3]. ZRPS delivers an overall mean absolute deviation of less than 70 meV in our collection of benchmarks that includes 55 atomization energies, 76 reaction barriers, 34 isomerization energies and 22 weak interactions. Taking N_2 and C_2 dissociations and 2 ozone-involved chemical reactions with pronounced many-body multi-reference character as examples, we demonstrate that ZRPS yields a remarkable and consistent improvement over other density functionals across various chemical environments from weak to strong correlation.

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Bridging Scales from van der Waals to Casimir Interactions

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Quantum fluctuations of electrons in matter are manifested in observable phenomena ranging from van der Waals (vdW) interactions between neutral atoms and molecules (0.1–1 nm) to Casimir interactions between macroscopic metal plates (1–10 μm). Although vdW and Casimir effects share the same underlying mechanism, the respective quantitative theories are disconnected and often narrowly applicable. Increasingly, however, a single experimental process can probe the target systems at multiple length scales, exposing gaps between existing calculations. Here, we present several advances in bridging these gaps, all based on a common many-body dispersion (MBD) framework[1,2], forming a coherent multiscale approach to vdW interactions.

First, we show that the MBD framework provides a straightforward access to the microscopic electronic fluctuations in nanoscale materials[3], while its combination with DFT achieves accuracy in binding energies comparable to high-level *ab initio* methods. Our analysis demonstrates that π–π stacking in supramolecular complexes is characterized by unusually delocalized, collective charge fluctuations.

Next, we extend the MBD model beyond the dipole approximation to include the effects of electric fields, and find that these can contribute up to 35% of the vdW stabilization of amino acid dimers in potassium channels. Although our model is efficient and applicable to mesoscopic environments, it is in a remarkable agreement with much more expensive electronic-structure methods such as RPA or the coupled-cluster method.

We further combine the MBD model with density-functional tight-binding (DFTB) calculations, extending its potential applicability to nanosecond-scale molecular dynamics, which is inaccessible to standard density-functional calculations. In particular, we demonstrate that DFTB+MBD predicts structures of molecular crystals that give a 5% accuracy of the subsequent lattice energy calculations.

At mesoscale, retarded vdW (Casimir) interactions are usually modelled by electrodynamic continuum techniques using bulk material properties, thus lacking any microscopic information. We demonstrate that this approximation is unnecessary by using the MBD response properties as an input for the continuum calculations. We find that the largest deviations from approximate models occur for elongated semi-metallic systems[4].

Taken together, our developments unite modelling of vdW and Casimir interactions from atomistic to mesoscopic ranges into a single homogeneous framework. This will enable seamless treatment of multiscale systems, and could bring rapid development of more accurate and general models for complex composite materials.

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Replica-Exchange Grand-Canonical Algorithm for Determining Phase Diagrams of Surfaces in Reactive Atmospheres

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For the advancement and refinement of modern technology, a large range of time and length scales need to be described, from the electronic (microscopic/atomistic) to the macroscopic regime. This calls for multi-scale modeling. Moreover, catalytic processes take place at finite temperature and pressure. In this project, we aim at developing a multi-scale modeling approach, applicable to a wide range of realistic conditions.

A temperature-pressure phase diagram describes the composition and structure of a system at thermal equilibrium and is an essential tool for understanding material properties. The *ab initio* atomistic thermodynamics (aiAT)[1,2] approach has been very successful in predicting phase diagrams for surfaces and gas-phase clusters[3] at realistic T, p conditions. However, its limitation is the lack of an unbiased sampling of the configurational space.

Here, we introduce a novel Replica-Exchange (RE) Grand-Canonical (GC) Monte-Carlo (MC)/Molecular-Dynamics (MD) algorithm that enables the efficient calculation of complete pressure-temperature phase diagrams. We specifically target open systems in the GC ensemble, aiming at describing (nano)structured surfaces in a reactive atmosphere at realistic T, p. RE allows for an efficient sampling by shuttling configurations from regions of low T or high chemical potential (μ) to regions of high T or low μ. This massively parallel algorithm requires no prior knowledge of the phase diagram and takes only the potential-energy function together with the desired μ and T ranges as inputs. From the partition function of the system it is then straightforward to calculate all desired thermodynamic variables.

We demonstrate REGC-MC by exploring a two-component Lennard-Jones system (a model for purely dispersion-forces interacting systems) with a surface in contact with a gas phase. From the estimated partition function, we construct the phase diagram in a range of temperatures T and pressures p and compare the results with phase diagrams constructed via AT. The two phase diagrams are very similar at low coverage (up to the formation of the first adlayer), but at higher coverages our phase diagram contains more phases, including (off-lattice) disordered ones.

Furthermore, we implement the REGC algorithm in the framework of density-functional theory. *Ab initio* REGC-MD is applied to Si_2 and Si_4 clusters in contact with a H_2 reactive atmosphere. We identify the thermodynamically most stable phases, including dissociated and non-dissociated H_2 molecules, at realistic T, $p(H_2)$ conditions, as a first step for the understanding of chemical vapor deposition of amorphous hydrogenated silicon.

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Adiabatic Vibronic Coupling in Molecules and Solids: Physical Insight from Density-Functional Perturbation Theory and Machine Learning

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First-principles calculations of the coupling of vibrational and electronic degrees of freedom have become possible only in recent years[1], and still little is known about the underlying qualitative mechanisms, the limits of the current methodologies, and the trends across chemical and structural space. In this work, we combine our recent density-functional perturbation theory (DFPT) implementation[2] with machine-learning techniques to shed light on these issues for two examples: anharmonic vibrational Raman spectra and temperature-dependent electronic band structures.

Vibrational Raman spectroscopy is frequently used for characterizing different molecular-crystal polymorphs and their phase transitions. Using the DFPT framework for electric field responses, we obtain polarizability tensors for isolated and periodic systems, and calculate fully anharmonic Raman spectra from the Fourier transform of the polarizability autocorrelation functions. We focus on polymorphs of Paracetamol and Aspirin containing hundreds of atoms, and use the PBE functional augmented by many body van der Waals interactions[2]. Thermal lattice expansion is taken into account. Comparison with published experimental studies shows good quantitative agreement on low and mid-frequency ranges. We observe strong anharmonic effects on NH bending modes and on low-frequency modes corresponding to collective vibrations of the lattice. In order to move towards a high-throughput framework and to bypass the cost of these DFPT calculations, we employ Kernel Ridge Regression to obtain DFPT-level polarizability tensors by exploiting geometrical data and polarizabilities obtained from cheaper semi-empirical models.

We have also investigated the influence of nuclear motion on the electronic band structure of solids at 0K (zero-point renormalization: ZPR) and as a function of temperature for 82 octet binaries in both the zincblende and the rocksalt structure. After validating our approach and the employed exchange-correlation functional for polar and non-polar systems, we discuss the observed trends in chemical and structural space, especially the several exceptions to generally accepted rule-of-thumbs, e.g., to the so-called mass rule (ZPR should decrease with atomic mass)[3]. To explain these deviations, a machine-learning techniques (SISSO) is used to identify reliable, physically meaningful descriptors[4]. In turn, this analysis reveals *(i)* that the descriptors are crystal-structure dependent and *(ii)* that the investigated effects cannot be explained solely in terms of atomic descriptors, but require explicit information on the bonding, e.g., by including features of dimers in the descriptor identification.

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Massively Parallel Compressed-Sensing Optimizer for Identifying Materials-Property Descriptors: Application to the Classification of Materials as Metals

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Luca M. Ghiringhelli

Discovering the relationship between a property of a material and its chemical composition and structure is of great importance for understanding the underlying mechanisms. In recent years, there has been a rapid growth of research interest in developing machine-learning approaches for finding the relationship between a set of descriptive parameters (termed descriptor) of a material and the property of interest. For this task, Ghiringhelli *et al.*[1,2] recently proposed the LASSO+ℓ_0 approach, a compressed-sensing (CS) method for descriptor identification from a pool of candidates (feature space) based on minimizing the ℓ_1 and ℓ_0 norms. The last two years have shown that this approach has severe limitations as it requires modest pool size and low mutual correlation between the offered descriptor candidates.

We have recently developed a new CS[3] scheme that combines Sure Independence Screening (SIS)[4] with a sparsifying operator (SO). SISSO overcomes the above-mentioned problems and enables us to find a proxy to the optimal descriptor in huge-sized feature spaces (billions of descriptor candidates or more). The approach starts with feature construction by building analytical functions of the input physical parameters (primary features), via the application of various algebraic operators. The SIS iteratively prunes the feature space by discarding features that have low correlation with the target property, and subsequent residuals. SIS is followed by the application of a SO method for finding the optimal solution inside the pruned feature space. Here, we apply the ℓ_0-norm regularization that in practice finds the optimal solution by full enumeration.

The approach was applied to the metal/nonmetal classification of binary A_xB_y materials belonging to several structure prototypes. Several hundreds of materials as listed in the Springer Materials database[5] were used to train the model. A simple descriptor, which classifies all the training metal/nonmetal, was identified. It is a function of atomic radius, ionization energy, electronegativity, and cell volume. The found descriptor provides insights into the relationships between the metallic/nonmetallic character and the structure of a material.

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Structure Dependence of Small Polarons in Transparent Oxides: *Ab Initio* Study of Polymorphs of TiO_2 and Ga_2O_3

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Thin films of transparent oxides are an important component for the fabrication of solar cells, photocatalysts, and more. Since the applications are extremely diverse, conductivity in the films is either required or should be suppressed for certain types of charge carriers. For both scenarios a detailed theoretical understanding is necessary in order to predict new functional materials. One important factor limiting the conductivity is the interaction of the charge carrier with phonon modes, i.e. the formation of polarons. The strength of the electron-phonon (el-ph) interaction determines the localization of the polaron, which in turn defines its characteristic temperature dependence for the charge-carrier mobility and ensuing properties. The present study focusses on materials with strong el-ph coupling, where the localization of the polaron has a length of the order of the interatomic distance (a so-called small polaron).

Though density-functional theory (DFT) has been often used for calculating properties of polarons, there are two challenges that were not addressed properly, so far: sensitivity to errors in the exchange-correlation approximation and finite-size effects in supercell calculations. In this work, we developed an approach that addresses these challenges. The polaron properties are obtained using a modified neutral potential-energy surface (PES)[1]. Using the hybrid HSE functional and considering the whole range $0 \leq \alpha \leq 1$ of exact exchange, we show that the modified PES model significantly reduces the dependence of the polaron level and binding energy on the functional. Based on Pekar's model[2], we derive the proper elastic long-range behavior of the polaron and a finite-size correction that allows to obtain the polaron properties in the dilute limit.

Specifically, we investigated the influence of the crystal structure on the polaron properties for rutile and anatase polymorphs of TiO_2 and for the monoclinic β- and orthorhombic ε-polymorphs of Ga_2O_3. The existence of small polarons in TiO_2 is a matter of a continuing discussion[3-5], and our study points out issues not considered thus far. We find that small-polaron formation in TiO_2 is sensitive to the crystal structure: While in rutile TiO_2 only small *electron* polarons are stable, only small *hole* polarons are found in anatase. On the contrary, small hole polarons exist in both Ga_2O_3 polymorphs but have significantly different binding energies.

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Predicting and Understanding Quantum Spin-Hall Insulators with the Help of Machine Learning

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Quantum spin-hall insulators (QSHIs) are two-dimensional topological insulators (TIs) with a spin-orbit coupling (SOC) driven band inversion[1]. They have attracted considerable interest in recent years for spintronic applications[2], since backscattering is forbidden in their edge states that are protected by time-reversal symmetry[1]. Accordingly, QSHIs can be characterized by a non-zero topological Z_2 invariant[2]. So far, the computational search for new QSHIs has been a costly trial-and-error process guided by empirical rule-of-thumbs, e.g., focusing on heavy elements with a strong SOC.

In this work, we investigated the topological character of 220 two-dimensional, *C*-functionalized honeycomb lattice materials ABC_2 (*AB* are IV-IV, III-V, II-VI materials, and *C* is from group VII). Starting from DFT-PBE calculations that account for van-der-Waals interactions[3] and spin-orbit coupling[4], we computed the Z_2 invariant using our recent local atomic orbitals based implementation of the Wannier centers of charge evolution formalism[5]. Besides confirming the QSHI character of known materials, e.g., functionalized stanene, our study found 15 other yet unreported QSHIs, as for example $AlNBr_2$ and $GaAsBr_2$. Quite surprisingly, these TIs consist of relatively light elements and thus defy the widespread reasoning that heavy elements with strong SOC are required to induce a topological transition. To understand these trends, we use a recently developed machine-learning approach[6] to classify these compounds by means of a physically meaningful two-dimensional *descriptor* that only depends on the properties of the material's atoms, but not on the properties of the material itself. This analysis reveals that the actual topological transition is not only triggered by the strength of the SOC, but by the relative position and mixture of hybridized atomic orbitals in the valence and conduction band. As a consequence, strongly electronegative functionalization with fluorine or chlorine typically suppresses the QSHI state, whereas functionalization with bromine or iodine can trigger it. Besides correctly capturing this behavior, the found descriptors also correlate with the computed bond-lengths and lattice constants. Eventually, we show that the identified descriptors can predict over 50 additional QSHIs out of a different set of 140 2D honeycomb compounds that consist of elements not included in our original machine-learning procedure.

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The Face of Crystals: Insightful Classification Using Deep Learning

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The crystal structure - how atoms are periodically arranged in space - is an essential ingredient for predicting properties from a material's chemical composition. It has also a large impact on real-world materials applications. For example, in iron, carbon solubility (important for steel formation) increases nearly forty times going from body-centered-cubic α-ferrite to face-centered-cubic γ-austenite.

With the advent of high-throughput materials-science computations, millions of calculated crystals structures are now available to the scientific community[1]. A reliable identification of the lattice symmetry is a critical first step for their characterization and analysis. Current methods require a user-specified threshold, and are unable to detect "average" symmetries for defective structures. Clearly, there is no threshold which performs optimally (or even sub-optimally) for such a large amount of data, nor a well-defined procedure to test the soundness of a chosen threshold.

Here, we propose a new machine-learning based approach to automatically classify crystals based on their symmetry. Unlike other representations (e.g. Voronoi tessellation[2], which is real-space based) we represent crystals in reciprocal space, and in particular by diffraction images. From these, we construct a deep neural network model[3] for classification. Using this procedure, we are able to correctly classify a dataset comprising more than 80,000 heavily defective cubic structures, without using any tolerance threshold. Unfolding the model's internal operations, we show that the neural network uses the same landmarks a materials scientist would use, although it was never explicitly instructed to do so.

Thanks to its robustness to defects, our method could also be used to determine local microstructures in atomic probe tomography experiments[4] (arguably the most important source of atomic structural information) where, however, more than 20% of the atoms escape detection.

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Unified Representation of Molecules and Crystals for Machine Learning

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Accurate simulations of polyatomic systems require first-principles approaches whose high computational cost limits number and size of studied systems. In high-throughput settings, machine learning can reduce these costs significantly by interpolating between reference calculations[1]. This requires a numerical representation for arbitrary atomistic systems that supports interpolation. For this purpose we introduce[2] a *many-body tensor representation* (MBTR) enabling sub-kcal/mol prediction errors for molecular energies and single-digit meV/atom errors for materials (bulk crystal) in benchmark settings. For molecules, MBTR outperforms published results we are aware of; for materials, it is the first competitive approach not requiring locality assumptions.

The key idea of MBTR is to represent an atomistic system via distributions of *k*-body terms, such as (inverse) distances or angles, stratified by chemical elements (Fig. 1). Its value at *x* for a combination of elements $\boldsymbol{Z} = Z_1, \dots, Z_k$ is

$$MBTR_k(x, \boldsymbol{Z}) = \sum_{i_1,\dots,i_k=1}^{N_a} w_k(i_1, \dots, i_k) D(x, g_k(i_1, \dots, i_k)) \prod_{j=1}^{k} \boldsymbol{C}_{Z_j Z_{i_j}} ,$$

where x and $\boldsymbol{Z}$ correspond to the *x*-axes and lines in Fig. 1, respectively, N_a is the number of atoms, g_k computes *k*-body terms, *D* is a normal distribution broadening g_k, and w_k is a weighting function decaying with distance between atoms. The product term allows for correlations between chemical elements.

We present atomization energy prediction errors below 1 kcal/mol for 7000 organic molecules and 6 meV/atom for 11000 elpasolite crystals. Applicability is demonstrated for phase diagrams of Pt-group/transition-metal binary systems, where convex hulls are correctly identified for AgPt, IrZn, CdPt, AgPt, and IrPt.

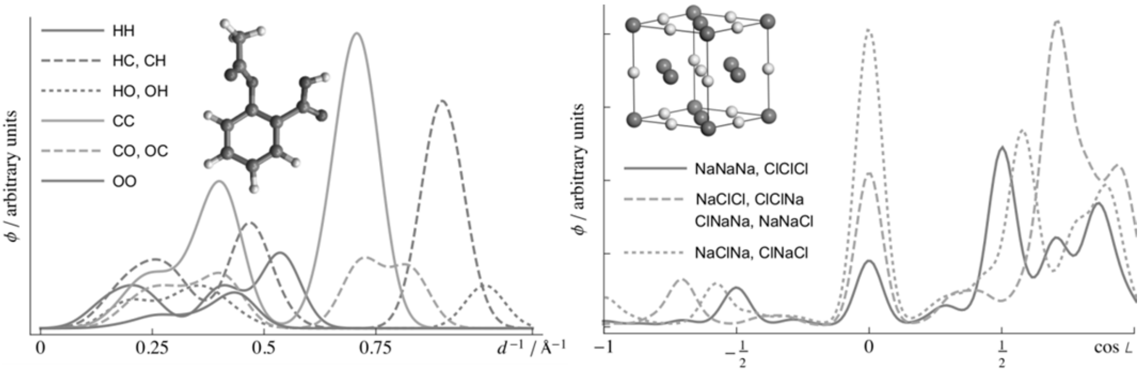

Figure 1: Visualization of many-body tensor representation for aspirin (left, *k*=2, inverse *distances*, quadratic weighting) and fcc salt (right, *k*=3, *angles*, exponential weighting).

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Impact of Nuclear Quantum Effects on Surface Mediated Water Dissociation at Finite Temperatures

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The interface of molecules with inorganic substrates has received great attention in the scientific community in search of new technological devices. The presence of light atoms in these adsorbates can greatly enhance the importance of nuclear quantum effects in the structural stability and dynamical properties (e.g. reactions rates) of these systems, as highlighted by several studies that find non-trivial isotope effects in different properties of these systems[1].

In this work, we explore the impact of nuclear quantum effects (NQE) on the dissociation of water wires on stepped Pt(221) surfaces, where NQE have been previously identified as necessary to stabilize dissociated structures[2]. By performing *ab initio* molecular dynamics simulations with density-functional theory and van der Waals dispersion[3], we note that there are several competing minima for both the intact and dissociated structures, making the usually reported harmonic estimates of the contributions of NQE to their free energies a questionable approximation. We thus performed *ab initio* path integral molecular dynamics (PIMD) in order to calculate these contributions and their interplay with the electronic structure in an accurate fully anharmonic fashion. We propose a scheme based on a spatial partition of the system to accelerate PIMD simulations when adsorption is weak and NQE on the substrate are negligible, which we implement in the i-PI code[4]. We treat NQE on the adsorbate in full but in isolation, while the surface-adsorbate system is evaluated contracted to a few beads. This represents a considerable speed up of the simulations. This scheme allowed us to calculate the contribution of NQE to the free energies in an all-electron framework, summing up to an equivalent of 1.1 ns of simulations. We find that anharmonicities result in an increase of up to 20% per dissociated dimer of the quantum contribution to the dissociation free energy, compared to harmonic estimates.

We also show how both temperature and NQE indirectly impact dipoles and the redistribution of electron density, causing work function changes of up to 0.4 eV with respect to static estimates. This quantitative assessment provides a possible approach to determine experimentally the most stable configurations of water oligomers on the stepped surfaces. Finally, we find that zero point energy can increase the dissociation rate by a factor of ~1000 in the harmonic approximation. To go beyond this picture, we present an implementation of ring polymer instanton theory[5] that can be used to calculate tunneling contributions in these (and other) multidimensional atomistic simulations of proton transfer reactions.

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New Insights into the Catalytic Activity of Solid Solutions: Carbon Dioxide Activation at Ni_xMg_yO

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NiO/MgO solid solutions are stable and active catalysts for dry reforming of CH_4 and CO_2 hydrogenation. Despite numerous experimental investigations, the structure of Ni_xMg_yO surfaces as well as the nature of the catalytically active centers remained unclear. We present a combined hybrid DFT/microcalorimetry study of CO_2 adsorption at Ni_xMg_yO surfaces. For the first time, poly-crystalline samples with low concentrations (3-10%) of Ni in MgO were successfully synthesized and experimentally studied. The homogeneous distribution of Ni in MgO allowed a clear comparison of theory and experiment, and clarified the effects of Ni on MgO surface structure. Periodic DFT calculations with the hybrid HSE(α) functional[1] augmented with a many-body dispersion correction[2] are performed, where the fraction of exact exchange α is set to 0.3 based on a comparison of the HSE(α) and CCSD(T) embedded-cluster calculations of energies of CO, CO_2, and H_2 adsorption at Ni_xMg_yO flat and stepped (100) surfaces, and Ni_{Mg} point defect formation energies in MgO[3].

The calculations reveal that Ni_{Mg} defects prefer to occupy low-coordinated sites (corners and steps) at the MgO (100) surface. Thus, Ni doping promotes formation of such sites during synthesis of the solid solution. Indeed, diffuse reflectance infrared spectroscopy (DRIFTS) showed that the number of undercoordinated O sites at NiMgO surfaces is significantly increased compared to pure MgO samples. Calculated CO_2 adsorption energy at the MgO (100) terrace (0.64 eV) at low coverage is much lower than the experimental one (1.15-1.25 eV for 3 at.-% of Ni), while at the steps it is much higher, about 2.2 eV. Increasing coverage of CO_2 at steps reduces the adsorption energy to 1.6 eV, and increasing the concentration of Ni_{Mg} at the steps decreases it further to values very close to the experimental ones. We also find that the calculated adsorption energy of CO_2 at the MgO (110) and at the O-terminated octopolar reconstruction of the polar MgO (111) surface are close to the experimental results, strongly evidencing the presence of Ni_{Mg} at the surfaces. Thus, Ni doping and CO_2 adsorption promote the formation of stepped (110) and reconstructed (111) MgO surfaces. After a dedicated sample pre-treatment, the adsorbed CO_2 capacity measured by microcalorimetry strongly correlates with the amount of Ni in MgO. The experimental differential heat of adsorption values of these samples are perfectly explained by the occupation of CO_2 vacancies in this surface carbonate as well as adsorption at the reconstructed (111) surface. The significance of carbonates as surface species and reaction intermediates are experimentally confirmed by *in situ* IR studies.

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Structure and Electronic Properties of Diverse (Bio)organic Molecules in Hybrid Inorganic/Organic Systems*

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Hybrid inorganic-organic materials are desirable for the use in technological and medicinal applications, in particular since organic and bio-inspired systems present a large range of functionalities, are abundant, cheap, and comparably environment friendly. Theoretical modeling of the electronic structure of these systems is challenging, because the results can be very sensitive to the choice of the exchange-correlation approximation and the high number of possible adsorbate geometries. We here present first-principles structure searches and electronic properties of organic systems ranging from rigid aromatic molecules to flexible bio-organic peptides adsorbed on both semiconductor [H-Si(111)] and metallic [Cu(111)] surfaces.

We consider F4-TCNQ, F6-TCNNQ, which are interesting for electronic doping, and tetracene (Tc) and pentacene (Pc) which are interesting for singlet exciton fission, adsorbed on H-Si(111). Internal degrees of freedom do not play a significant role in these systems and we explore adsorption under different coverage conditions with random structure searches. Generalized gradient approximation functionals yield the same qualitative level alignment compared to hybrid functionals, even if they differ quantitatively. F4-TCNQ and F6-TCNNQ prefer to lie flat on the surface for low coverages and the LUMO of the molecules lies slightly below valence band maximum (VBM) of H-Si(111) in our level of theory, causing a work function increase and a charge transfer from the surface to the molecule. In Tc and Pc the LUMO lies above the VBM, allowing, at best, little charge transfer to occur. We disentangle contributions to work-function changes by calculating core level shifts, the space charge layer, and charge transfer, also taking level-broadening due to temperature effects into account.

For the highly-flexible peptides HisProPheH$^+$ and ArgH$^+$, which are known from experiment to self-assemble into dimers or hexamers on Cu(111), we tackle the structure-search problem by extending the Fafoom first-principles genetic algorithm package that works on internal degrees of freedom in order to include the position and orientation of molecules with respect to the surface. By comparing two protonation states (Arg and ArgH$^+$) of an amino acid in the gas phase, we conclude that the charge reduces the size of the accessible conformational space: while Arg presents several isoenergetic alternative conformations, ArgH$^+$ presents a single energetically-privileged minimum structure. However, when ArgH$^+$ gets in contact with the Cu(111) surface, the positive charge is efficiently screened by concentration of electrons from the surface close to the charged group and the conformational space is expanded with respect to the gas-phase picture, even though it still retains one well defined minimum. This efficient screening of a peptide's charge is likely to play a role in the experimentally-observed self-assembly.

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Peptide-Cation Systems: Observing Kinetically Trapped Liquid-State Conformers in the Gas Phase and How to Improve the Force Field Description with Machine Learning[*]

Markus Schneider and Carsten Baldauf

Metal cations are essential to life, *e.g.* by shaping the three-dimensional structure of proteins. One-third of the proteins in the human body require a metal cofactor for biological function[1]. Peptides in complex with cations undergo significant conformational changes that may alter important properties. As an example, we investigate the peptide $AcPheAla_5LysH^+$, a model system for studying helix formation in the gas phase. To address the question of whether the local fixation of the positive charge at the peptide's C-terminus is a prerequisite for forming helices, we replace the protonated C-terminal Lys residue by Ala and a sodium cation. The combination of molecular simulations based on DFT with experimentally observed conformer-selective vibrational spectra in the gas phase at 10 K allows for detailed structure elucidation[2]. For sodiated $AcPheAla_6$, we find globular rather than helical structures, as the mobile positive charge strongly interacts with the peptide backbone and disrupts secondary-structure formation. Interestingly, the global minimum structure from simulation is not present in the experiment. Following a rigorous experiment-theory comparison, we interpret that this is due to high barriers involved in re-arranging the peptide-cation interaction in isolation that ultimately result in kinetically trapped structures being observed in the experiment.

In order to yield accurate conformational energies and vibrational spectra of peptide-cation systems, one needs to rely on computational costly hybrid density-functional approximations. On the other hand, the accuracy of computationally cheaper empirical simulation frameworks, i.e. force fields (FFs), is anything but clear and, in fact, can be grossly misleading. An intent for a solution could be the machine learning approach presented here. In essence, torsional parameters and van-der-Waals parameters in the potential-energy function E_{pot} of a particular FF, here OPLS-AA[3], are "tuned" by fitting E_{pot} using ridge regression[4,5] and/or LASSO regression[6] against higher-level energies from DFT calculations for a set of conformers. For the system of $AcAla_2NMe$, this approach reduces the mean absolute error between FF and DFT energies from 2.5 to 0.9 kcal/mol, hence resulting in an energetic description within *chemical accuracy*.

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