

German-Chinese Scientist Symposium

2nd Young

on Structures & Dynamics at Surfaces

28th May - 1st June 2017
Göttingen

Keynote Lectures:

Helmut Zacharias

Westfälische Wilhelms-Universität Münster

Alec Wodtke

MPI für Biophysikalische Chemie/Georg-August Universität

Location:

Max Planck Institute for Biophysical Chemistry, Am Faßberg 11,
37077 Göttingen, Manfred Eigen Hall

Topics:

Among others:

Photoelectron Spectroscopy at Surfaces

Time-resolved Surface Dynamics

Nanostructured Surfaces

Surface Reactions

Molecular Beam Surface Scattering

Surface Science Theory

Sunday night:

Reception with the Showband

"Alec Wodtke and the Heartbreakers"

Organizers:

Tim Schäfer

MPI Biophysical Chemistry/Georg August University Göttingen

Chuanyao Zhou

Dalian Institute of Chemical Physics / Chinese Academy of Science

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biophysikalische Chemie



GEORG-AUGUST-UNIVERSITÄT
GÖTTINGEN

	Sunday	Monday	Tuesday	Wednesday	Thursday		
8:30-8:55			Nagata: Molecular modeling of interfacial water	Excursion Day	Tremblay: Irreversible Tautomerization in Porphycene on Cu(111) Induced by Scanning Tunnelling Microscopy		
8:55-9:20	Arrival	Photoelectrons at Surfaces Zacharias: Photoelectron spectroscopy at surfaces Siefermann: Ultrafast photoemission electron microscopy in materials science	Oberhofer: Simulating photo-electrocatalytic reactions beyond the computational hydrogen electrode		Theory II	Stecher: First-principles free-energy barriers for photo-electrochemical surface reactions	
9:20-9:45			Surface Physics		Tonner: Surface chemistry for organic-inorganic interfaces - a quantum chemical perspective	Molecular Beam Surface Scattering	Li ZY: From Kinetics to Mechanisms via Multiscale Simulations
9:45-10:10			Nanostructures at Surfaces Brida: Sub-cycle Phase Control of Electron Tunneling in an Optical Nanoantenna Jiang H: Dynamics of H Atoms Scattering from Epitaxial Graphene at Zero Surface Coverage Limit Papp: Surface chemistry of nanoclusters Kong XQ: The Applications of Solid State NMR in Porous Materials		Liquid Interfaces Gekle: Dielectric properties of interfacial water Tian CS: Unveiling Microscopic Structure at Charged Water Interface Deng GH: Enhanced Water Structure on Hydrophobic Surfaces in Concentrated Alcohol-Water Solutions Mezger: X-ray reflectivity studies of ionic liquids at interfaces	Meng S: Excited State Quantum Electron-Nuclear Dynamics in Condensed Matter	Harding: Dynamics and kinetics of model catalytic reactions on surfaces
10:10-10:40						Surface Physics	Hagemann: Generation and detection of chemicurrents in gas-surface reactions
10:40-11:05		Time Resolved-Dynamics				Engelhart: Electron induced changes in reflectance and surface morphology of polyimide films	Bünermann: Inelasticity in H atom scattering from surfaces
11:05-11:30		Time Resolved-Dynamics				Wei X: Heterodyne 2D SFG for interfacial molecular structure and charge dynamics at material interfaces	Park: State-to-state scattering of formaldehyde from Au(111)
11:30-11:55		Time Resolved-Dynamics	Gierz: Dynamical band structure engineering of low-dimensional solids				
11:55-12:20		Time Resolved-Dynamics					
12:20-14:00		Time Resolved-Dynamics					
14:00-14:25		Time Resolved-Dynamics					
14:25-14:50		Time Resolved-Dynamics					
14:50-15:15		Time Resolved-Dynamics					
15:15-15:40		Time Resolved-Dynamics					
15:40-16:10		Time Resolved-Dynamics					
16:10-16:35		Time Resolved-Dynamics					
16:35-17:00		Time Resolved-Dynamics					
17:00-17:25		Time Resolved-Dynamics					
17:25-17:50		Time Resolved-Dynamics					
18:00-19:00	Reception				Closing Remarks		
19:00-19:15	Chen Lesheng: Opening Remarks						
19:15-19:45	Auerbach						
19:45-20:15	Wodtke: Future Directions of Surface Dynamics	Dinner	Barbecue	Conference Dinner			

Excursion May 31st

8:45	Departure Hotel Am Papenberg
9:00	Guided Tour in Göttingen: Gauß in Göttingen - Sternstunden der Mathematik
10:00	
11:00	Travel to World Heritage Bergpark Wilhelmshöhe
12:00	Little Hike near Herkules Monument
13:00	Lunch at Kaskadenrestaurant
14:00	
15:00	Little Hike next to the Water Games in Bergpark Wilhelmshöhe
16:00	
17:00	Travel to Castle Berlepsch
18:00	Tour in Castle Berlepsch
19:00	Medieval Style Dinner at Castle Berlepsch
20:00	
21:00	Return to Göttingen

Towards understanding the mechanism of water splitting on TiO₂

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Finding a clean and renewable energy source to replace fossil fuels has attracted much attention, the past few decades, as a requirement for the sustainable development of societies. Direct hydrogen generation on TiO₂ by photocatalytic dissociation of water using sunlight was already proposed more than 40 years ago. However, despite extensive work in this area, the fundamentals of the process remain ill-understood, mainly due to the lack of a proper tool to specifically explore the interface between water and TiO₂. Sum frequency generation spectroscopy (SFG), is an inherently surface sensitive tool, allowing the study of the water-TiO₂ interface. In a sum frequency generation process a visible and an infrared laser beam are combined at the interface and the vibrational spectrum of solely the molecules at the interface can be obtained. In this way we can specifically study the water molecules at the TiO₂ surface. As a first step in understanding the water splitting reaction, we studied the binding of water to the substrate. We present data on water in contact with various types of TiO₂ substrates. From the intensity and frequency of the SFG signal we extract information about the binding of water to the TiO₂. Moreover, we show first time-resolved SFG data after excitation of the TiO₂ with an UV pump pulse which mimics the sun light. Preliminary data show that the surface charge changes on ultrafast timescales upon excitation resulting in reorientation of the water molecules. These UV-pump SFG-probe data illustrate the first steps towards following the photo-induced dissociation of water at the TiO₂ interface in real-time.

Sub-cycle Phase Control of Electron Tunneling in an Optical Nanoantenna

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By accessing the nonperturbative strong-field regime, light-matter interaction is governed by the electric field transient of light as opposed to multiphoton effects. In our experiments, we illuminate a circuit with a nanoscale open junction (Fig. 1(a)) with intense ultrashort pulses at high repetition rate. With this setup, we are able to coherently drive electronic currents at optical frequencies and beyond [1].

In detail, a gold bow-tie nanoantenna with external leads serves as an electronic circuit that exhibits a tunneling-like, antisymmetric and highly nonlinear current-voltage characteristic while providing a strong, local plasmonic field enhancement. By biasing this structure with few-cycle laser pulses, electronic transport across the antenna's feedgap can be achieved: when the electric field transient is cosine-shaped the symmetry break of transport leads to a finite total current. This contribution becomes maximized by approaching the single-cycle regime. With a sine-shaped pulse the effect of the adjacent maxima of precisely opposite polarity cancels out all integral effects. Our Er: fiber femtosecond laser system [2,3] generates 1.4-cycle pulses at a carrier wavelength of 1320 nm and at a repetition rate of 80 MHz. The transients are produced with a passive locking of the carrier-envelope phase (CEP) by a scheme that allows full control of the electric field profile [2]. This broadband radiation is tightly focused onto the nanoantenna in the circuit. A lock-in detection scheme allows to measure the tunneling current induced by the optical field through the gap as a function of CEP, as reported in Fig. 1(b).

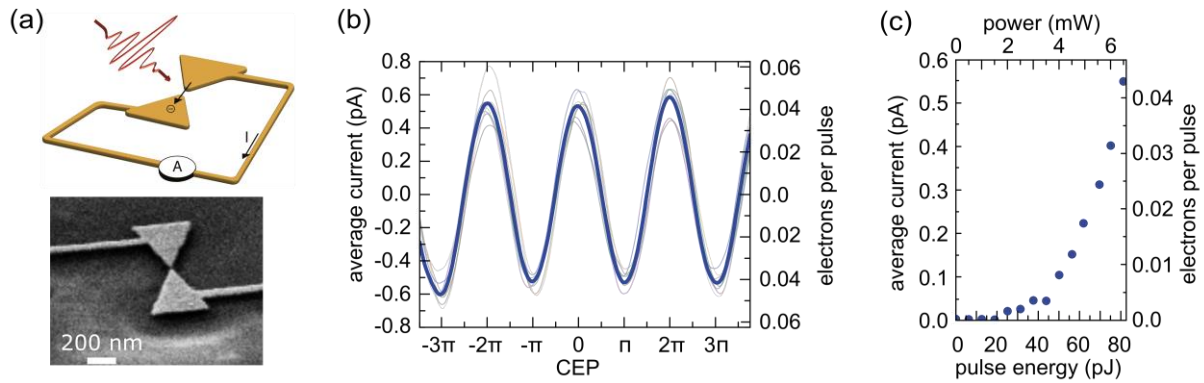


Fig. 1: Carrier-envelope phase optical control of sub-cycle tunneling in nanoantenna. (a) Conceptual sketch of the experiment with a single-cycle light pulse focused on a nanogap of an electronic circuit (upper panel) and a scanning electron micrograph of a nanoantenna with external leads (bottom panel). (b) Tunneling current measured in the circuit as a function of the carrier-envelope phase. The blue line represents an average over 8 subsequent scans (gray lines) acquired at an average optical power of 6.5 mW. (c) Current measured for a cosine-like transient plotted as a function of the optical pulse energy.

A moderate energy of 80 pJ results in total tunneling currents up to 0.6 pA, corresponding to the transport of one electron every twenty pulses which is completely reversible with respect to the CEP. The strong nonlinear dependence of the peak current on the optical excitation power is depicted in (Fig. 1(c)). In this case, the free-space bias applied to the antenna gap approaches 40 V and is further enhanced to several hundreds of volts due to the plasmonic resonance. By assuming a Fowler-Nordheim behaviour for the current-voltage

characteristics and by validating it against the experimental power dependence, we could model the instantaneous tunneling current. We evaluated the total current to be resulting from the 3 main half-cycles contained in the driving pulses with the central one dominating the process. The corresponding current spike lasts a few hundred as. After tunneling into the gap, the electrons are ballistically and coherently transported to the other side by the very same optical field within 900 as, i.e. less than the half cycle of the pulse. The maximum current spikes correspond to tens of μA on subcycle timescales, corresponding to current densities that exceed 50 MA/cm^2 . These conditions establish a new regime of coherent charge transport at and beyond optical frequencies.

References

- [1] T. Rybka, M. Ludwig, M. F. Schmalz, V. Knittel, D. Brida und A. Leitenstorfer, "Sub-cycle optical phase control of nanotunnelling in the single-electron regime", *Nature Photon.* 10, 667–670 (2016)
- [2] G. Krauss, S. Lohss, T. Hanke, A. Sell, S. Eggert, R. Huber, and A. Leitenstorfer, "Synthesis of a single cycle of light with compact erbium-doped fibre technology", *Nature Photon.* 4, 33-36 (2010).
- [3] D. Brida, G. Krauss, A. Sell and A. Leitenstorfer, "Ultrabroadband Er: fiber lasers", *Laser Photon Rev.* 8, 409-428 (2014).

H atom scattering from surfaces

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Obtaining an atomic-level understanding of the dynamics of energy conversion at surfaces remains a complex and challenging area of modern research in physical chemistry. A general strategy to this field follows the lessons of gas-phase bimolecular chemical dynamics, where simple model systems are studied experimentally with great care while theoretical simulations are developed. One of the simplest systems to think of is Hydrogen atom scattering from a single crystalline surface. We study this model system experimentally with extraordinary resolution. The experiments give detailed insights about the energy exchange between atom and surface and provide a valuable benchmark for high level theoretical models describing the interaction between atoms or molecules and surfaces.

Recently, we could show that in case of H atom scattering from Au(111) a large amount of the translational energy can be transferred to electronic excitation of the metal, Ref. 1. We expanded our studies to a large parameter space, including incidence H-atom beam, surface and scattering conditions. Furthermore, the isotope effect and a wide set of metals (Cu, Ag, Au, Ni, Pd, Pt) were investigated. The experimentally observed dependencies are presented and their implication for the underlying non-adiabatic process are discussed.

In addition, another example of a very efficient energy transfer between H-atoms and a surface is presented. H-atoms were scattered from a monolayer of graphene deposited on a Pt(111) surface. H atoms can form a covalent bound with Graphene and the adsorption process exhibits a barrier. For normal incidence energies below the adsorption barrier nearly elastic and specular scattering is observed. However, for normal energies larger than the adsorption barrier a large amount of translational energy of the H-atom is transferred to Graphene. Ab initio molecular dynamics (AIMD) simulations qualitatively reproduce the experiment and suggest an adiabatic energy loss mechanism.

Acknowledgements: This work has the support of the SFB1073 under project A04, the Deutsche Forschungsgemeinschaft (DFG), the Agence Nationale de la Recherche (ANR), the Ministerium für Wissenschaft und Kultur (MWK) Niedersachsen, the Volkswagenstiftung, and the Humboldt Foundation.

References

[1] O. Buenermann *et al.*, *Science*, **350** 1346 (2015).

Enhanced Water Structure on Hydrophobic Surfaces in Concentrated Alcohol-Water Solutions

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Abstract

The effects of hydrophobic solutes on the structure of the surrounding water have been the subject of intense study and debate for more than 70 years. However, a molecular insight into the anomalous thermodynamic properties remains elusive. Here we report experimental results that provide unambiguous evidence for the enhancement of water structure around micro-hydrophobic interfaces in alcohol-water solutions, using temperature-dependent linear and femtosecond infrared spectroscopy. Our results further demonstrate that the enhanced ordering of the water structure, which is observed at room temperature, is temperature dependent. As temperature increases, this ordered water structure disappears and a surface topography dependent new disordered water structure arises at concentrated solutions of large alcohols. The water structural transformation is dependent on not only the length of the alkyl chain but also the clustering of the alcohols.

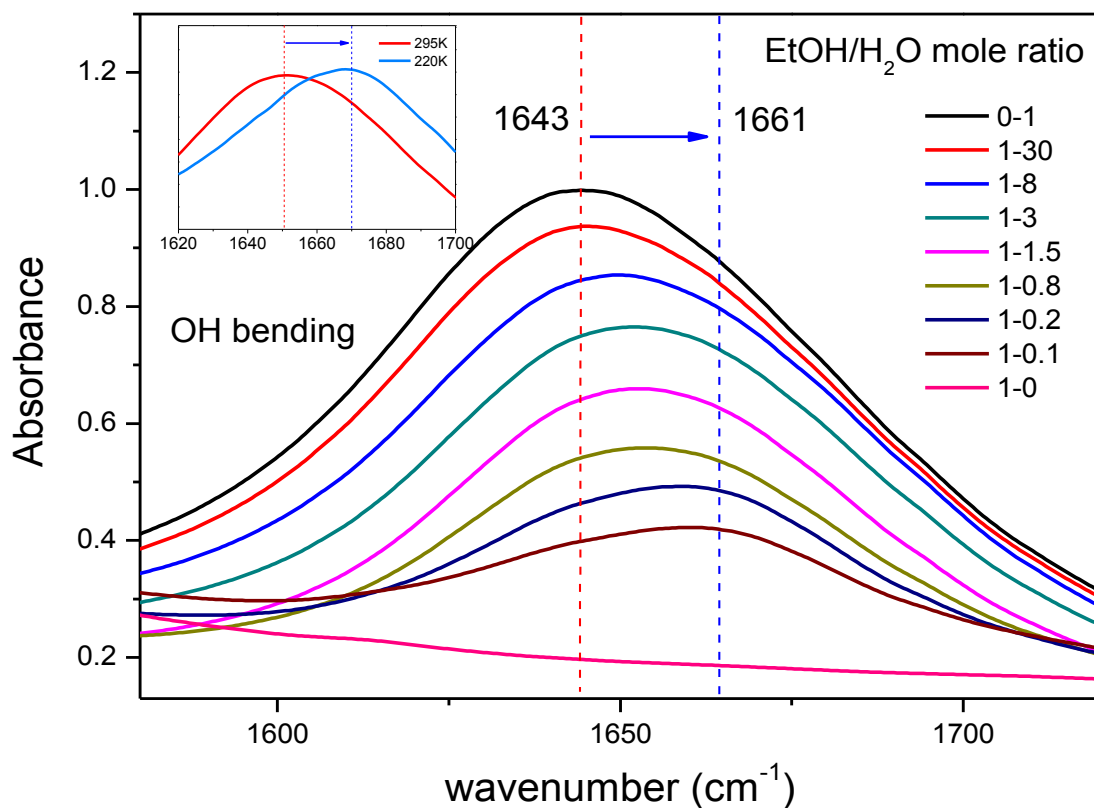


Figure 1. Infrared spectra of the water bending mode region of aqueous ethanol (C_2H_5OH/H_2O) solutions with different ethanol concentrations. The bending peaks show clear blueshifts from 1643 cm^{-1} to 1661 cm^{-1} as the ethanol concentration increases. The inset is the infrared spectra of the water bending mode of ethanol aqueous solutions with a mole ratio of 1:3 at temperature 295K and 220K.

Chemical and Optical Characterization of Polyimide in a GEO-like Environment

Daniel Engelhart

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Interaction of high energy electrons with spacecraft materials, such as polyimide (PI, Kapton-H®), is known to cause their physical degradation. A lack of detailed understanding, however, limits predictive spacecraft models (thermal, charging) to only pristine material properties. The chemical and optical changes in PI during and after irradiation with high energy (90 keV) electrons will be presented. Several complimentary characterization techniques were utilized to qualify and quantify radiation induced property changes in the material, including directional-hemispherical reflectance (DHR) coupled with Fourier Transform Infrared (FTIR) spectroscopy, electron paramagnetic resonance (EPR), and the surface potential decay method. It was found that the bulk conductivity of radiation-damaged PI is significantly increased compared to that of the pristine material. This change is accompanied by an increased population of radicals and a smaller effective optical "band gap" in the material.

Low-Energy Electron Microscopy of Inverse Model Catalysts

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Current research efforts in heterogeneous model catalysis aim to provide a deeper understanding of the all components in a real catalytic system, which depending on the conditions typically comprises metals and oxides in nanoparticulate form. While traditional approaches have focused on the role of oxide-supported metal nanoparticles, in the inverse configuration a nanosized metal oxide is supported on a transition metal, thereby allowing us to study the properties of the nanoscale metal oxide and its defect chemistry as well as to gain complementary access to the oxide-metal interface.

Rare-earth oxides are of considerable importance in heterogeneous catalysis owing to their special materials characteristics, which directly originate from their complex structural phase diagram in combination with the peculiar electronic configurations associated with the rare-earth metal cations, namely their partially filled 4f electron shells. In this presentation, we will focus on the growth of rare-earth metal oxide films deposited on transition metals and subsequent monitoring of their structural and chemical modifications in reactive gaseous environments using low-energy electron microscopy and related methods [1]. Using the ceria(111)/Ru(0001) inverse model catalyst [2] as a test case, we will show that we are able to monitor, on the nanometer scale and in real-time, the structural transformations upon thermal or chemical reduction from CeO_2 via the cubic Ce_2O_3 phase [3] to hexagonal Ce_2O_3 . This last step is accompanied by partial dissolution of the cerium oxide particles and considerable mass transport of metallic cerium from the particles to the substrate [4].

References

- [1] J. I. Flege and E. E. Krasovskii, *Phys. Status Solidi RRL* 8 (2014) 463-477.
- [2] D. C. Grinter, S. D. Senanayake, and J. I. Flege, *Appl. Catal., B* 197 (2016) 286-298.
- [3] J. Höcker et al., *Adv. Mater. Interfaces* 2 (2015) 1500314.
- [4] J. Höcker et al., *submitted*.

Dielectric properties of interfacial water

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I will present Molecular Dynamics simulations showing that interfacial water absorbs electromagnetic energy at very different frequencies than bulk water. I will furthermore present a continuum theory which allows to quantitatively predict the spatially dependent dielectric constant of interfacial water from a non-local dielectric theory of *bulk* water. This agreement shows that the observed drastic changes in the dielectric constant at the interface can – to some extent – be understood by properties that are inherent already in bulk water and thus by a completely generic mechanism independent of the interface characteristics themselves.

Femtosecond control of quasiparticle interactions in graphene

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Driven solids are different from matter at equilibrium because the interaction with a periodic driving field results in the formation of new effective Hamiltonians with new eigenstates. We exploit this idea for electronic structure control by shining tailored laser pulses onto various low-dimensional materials.

Recently, two different driving schemes have been developed: Resonant excitation of infrared-active lattice vibrations (“phonon pumping”) has been used to induce superconducting-like states at temperatures far above the equilibrium critical temperature in cuprates [1] and K_3C_{60} [2]. Further, strong circularly polarized mid-infrared fields have been used to generate photon-dressed states resulting in a topological phase transition in Bi_2Se_3 [3].

We combine these driving schemes with time- and angle-resolved photoemission spectroscopy at extreme ultraviolet wavelengths to investigate the electronic properties of driven solids over the whole first Brillouin zone and beyond.

I will show that resonant excitation of the in-plane bond-stretching phonon in bilayer graphene leads to a transient threefold enhancement of the electron-phonon coupling constant [4,5]. Although the microscopic origin of this effect is far from understood our findings have important implications for a possible light-induced superconducting state in graphene and related materials [2]. I will end with a short outlook on other projects we are currently working on, such as one-dimensional Indium wires and C_{60} films.

[1] W. Hu et al., *Nature Materials* 13, 705 (2014)

[2] M. Mitrano et al., *Nature* 530, 461 (2016)

[3] Y. H. Wang et al., *Science* 342, 453 (2013)

[4] I. Gierz et al., *Phys. Rev. Lett.* 114, 125503 (2015)

[5] E. Pomarico et al., *Phys. Rev. B* 95, 024304 (2017)

Generation and detection of chemicurrents in gas-surface reactions

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Hermann Nienhaus, Faculty of Physics, University of Duisburg-Essen

Chemical reactions on metal surfaces transfer energies of a few eV per particle to the metal substrate. Such events can perturb the electronic system during the gas-metal interaction and can cause significant electronic excitations with lifetimes on the femtosecond timescale and energies in the lower eV range [1,2]. Experimental evidence of such non-adiabatic processes is gained by detecting chemiluminescence and hot hole or hot electron generation in the metal using an internal detection scheme. The method uses ultrathin-film electronic devices with internal potential barriers as high-pass energy filters. Metal-semiconductor (Schottky) diodes are the most prominent examples. When hot charge carriers are chemically excited at the surface they can travel ballistically to the interface and may surpass the Schottky barrier inducing a measurable reverse current in the diode, provided that the metal film is in the nm-range. Such chemicurrents are proportional to the reaction rate. Therefore, the current transients reflect the chemical kinetics which are monitored under live conditions. Examples of various reaction systems will be presented which exhibit typical reaction kinetics: spontaneous adsorption and abstraction is observed for interaction of H atoms on Ag; nucleation and growth kinetics with extremely small initial sticking coefficients is characterized with the low-temperature oxidation of Mg and alkali metal surfaces [3]; electric field-assisted bulk reactions (Mott-Cabrera) are detected for the reaction of O₂ with Al and of Cl₂ with K surfaces. The internal detection is a sensitive tool especially for low-power impact. Chemicurrents of less than 100 pA are easily detectable with particle fluxes in the 10¹² per s and cm² range. This corresponds to a reactive energy flow of 100 nW/cm².

References:

- [1] H. Nienhaus, Surf. Sci. Rep. 45 (2002) 3.
- [2] B.I. Lundqvist et al. in : Handbook of Surface Science, Vol. 3, Eds.: E. Hasselbrink and B.I. Lundqvist (North-Holland, Amsterdam, 2008), pp. 430-524.
- [3] U. Hagemann, H. Nienhaus, New Journal of Physics 16 (11), 113035

Dynamics and kinetics of model catalytic reactions on surfaces

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We describe how molecular-beam surface scattering experiments can be combined with 2-dimensional imaging detection techniques, based on gas-phase ion or velocity map imaging, to provide both dynamic and kinetic information about reactions occurring on model catalytic surfaces. By controlling the surface temperature and dosing, detailed information about reaction barriers, reaction order, and the influence of changing surface coverage can be obtained.

We present our first results for CO oxidation on Pt(111), a prototypical surface reaction, and show, by using both the kinetic and dynamical information from our experiment, that two different reaction channels are present over a wide range of surface conditions, reconciling a number of the previously reported results.

Dynamics of H Atoms Scattering from Epitaxial Graphene at Zero Surface Coverage Limit

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H atom adsorption on graphene is highly relevant in many research fields and has been intensively studied for decades. However, two key aspects of the adsorption are still experimentally not known, one which is the adsorption threshold and another which is the energy dissipation characteristics of the newly formed C-H bond. We present experiments on H atom scattering from epitaxial graphene under zero surface coverage. Two separated scattering channels are observed, corresponding to scattered atoms that fail and succeed in crossing the adsorption barrier. Utilizing the dependence of the two scattering channels on the normal incidence energy, the thresholds for initial adsorption are determined: 0.47 ± 0.02 eV for H atom and 0.44 ± 0.06 eV for D atom. Together with *ab initio* molecular dynamics simulations, we show that scattered H atoms that succeed in crossing the barrier lose on average 1 eV energy [half of its incidence energy] in one vibrational period of C-H stretch, pointing to an extremely fast energy dissipation mechanism.

Photo-induced Carrier Dynamics of Single Defects on TiO₂(110) Surface Probed by Laser-Combined STM/S

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The photoexcitation of oxygen vacancies plays a critical role in the photocatalytic process of TiO₂, but the detailed atomic-scale mechanism is yet to be elucidated. Here we succeeded to probe the photoexcitation of individual oxygen vacancies on rutile TiO₂(110) using a home-made laser-combined scanning tunneling microscope (STM). The surface and subsurface oxygen vacancies induce prominent in-gap states below the Fermi level, which exhibit either redshift or blueshift upon the laser illumination. Ab initio density functional theory calculations revealed that the redshift/blueshift of the gap states arises from the photoexcited charge transfer between the defect levels and valence/conduction bands, respectively. We found that the photoexcitation behaviors of the oxygen vacancies are extremely sensitive to their atomic-scale environment, which dictates the transition probability between the defects states and valence/conduction bands. This work may open up a new avenue for improving the photocatalytic efficiency of TiO₂(110) by proper defect engineering.

Understanding Surface and Interfacial Chemistry in Nanomaterials by Solid-state NMR

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Most functional materials are composites of structurally or functionally distinct moieties with complex interfaces, where critical chemical or physical phenomena take place. Understanding of such interfacial phenomena occurring at the nanometer-scale level is of key importance for today's chemists and materials scientists.

In modern chemistry, nuclear magnetic resonance (NMR) has emerged as an essential tool for identifying and quantifying chemical compounds. Yet the usual NMR analysis requires samples prepared in liquid or solution state which are often incompatible for functional materials. Fortunately, the advancement of solid-state NMR allows materials chemists to investigate their samples in the intact solid phase with molecular precision. The multiplicity of solid-state NMR techniques opens new gateways to explore the nano-world through a multitude of length and time scales¹. It can access detailed information not only about the chemical structures, but also about spatial connectivities, molecular dynamics and reaction processes, thus providing essential guidance for the rapid innovation of functional nanomaterials.

We will use our own works in metal-organic frameworks^{2,3} and quantum dots as illustrative examples to show how various solid-state NMR characterization techniques can be strategically applied to explore the world of nanomaterials.

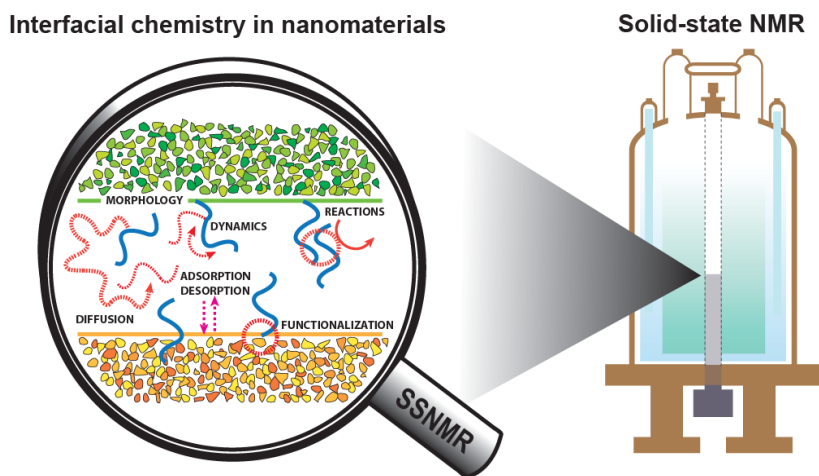


Figure 1: Solid-state NMR Characterization of Interfacial Chemistry in Nanomaterials

References

- [1] A. Marchetti, J. Chen, Z. Pang, S. Li, D. Ling, F. Deng, X. Kong *Adv. Mater.*, (2017), DOI: 10.1002/adma.201605895, in press.
- [2] X. Kong, H. Deng, F. Yan, J. Kim, J. A. Swisher, B. Smit, O., M. Yaghi, J. A. Reimer, *Science* **341**, (2013) 882.
- [3] X. Kong, E. Scott, W. Ding, J. A. Mason, J. R. Long, J. A. Reimer, *J. Am. Chem. Soc.* **134**, (2012) 14341.

Solid-liquid interfaces for electro-chemistry

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In many electro-chemical reactions, it is important that solvated species can diffuse to and adsorb on the electrode surface with low barriers. However, diffusion across water-solid interfaces are not that well understood. Here, I will present computational modeling of a water-Pt(111) interface. This system is used to study the diffusion of O₂ molecules and K⁺ and Cl⁻ ions from the water phase, across the interface, and to the Pt surface. Meta-dynamics is used to obtain potential energy surfaces as a function of the species distance to the Pt surface.

The water molecules situated at the water-Pt(111) interface have increased order. This is manifested in specific orientations of the water molecules and water densities different from bulk liquid water. We find that O₂ molecules have high barriers for passing through the interface region. The high barrier seems to be caused by a change in the water environment surrounding the O₂ molecule situated in the interface region compared to O₂ molecules situated in bulk liquid water. On the other hand, K⁺ ions can diffuse through the interface region with minimum barriers and K⁺ ions are found to retain the water environment that K⁺ ions have in bulk liquid water. The Cl⁻ ions are found to have adsorption barriers in-between O₂ molecules and K⁺ ions.

Time resolved studies of vibrational relaxation dynamics of small physisorbed molecules on noble metal surfaces

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Vibrational relaxation of adsorbate depends upon the properties of the substrate. Vibrational lifetime of excited ($v=1$) state of CO adsorbed on semiconductor is in the order of nanosecond timescale due to interactions of high-energy vibrational modes with low-frequency phonons. Vibrational relaxation of excited ($v=1$) state of chemisorbed CO on metals takes place in the order of few picoseconds due to electron-mediated non-adiabatic vibrational energy transfer processes. In contrast, vibrational lifetime of excited ($v=1$) state of physisorbed CO on NaCl is in millisecond order (~ 4.3 ms). A similar study of vibrational relaxation lifetime of weakly adsorbed/bound molecule on metal surface is unknown in the literature. Therefore the aim of my work is to understand the vibrational energy relaxation pathways in weakly bound adsorbates on noble metal surfaces. Specifically, CO on Au(111) has been chosen for the study.

In the talk, I will present the construction of a new experimental setup to determine the vibrational lifetime of diatomic molecules adsorbed on noble metals using two independently tunable femtosecond IR pulses. A required mechanically vibration-free metal surface at low temperature is also achieved. The transient absorption difference (TAD) spectra of vibrationally excited CO ($v=1$) on Pt(111) and Au(111) are recorded as a function of pump-probe time delay. Small absorption cross section for CO on Au(111) and strong transient surface heating of Au(111) from femtosecond pulses produce more challenges in the study of vibrational lifetime of CO on Au(111). Sum-frequency-generation technique can be an useful procedure to determine the vibrational lifetime of CO on Au(111) as second-order nonlinear optical processes are allowed on the interfaces.

Mid-infrared laser-induced fluorescence with nanosecond time resolution using a superconducting nanowire single-photon detector: New technology for molecular science

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In contrast to UV photomultiplier tubes that are widely used in physical chemistry, mid-infrared detectors are notorious for poor sensitivity and slow time response. This helps explain why, despite the importance of infrared spectroscopy in molecular science, mid-infrared fluorescence is not more widely used. In recent years, several new technologies have been developed that open new experimental possibilities for research in the mid-infrared. We present here one of the more promising technologies - *superconducting nanowire single photon detectors* (SNSPDs) - by sharing our experience with its use in a typical experiment carried out by physical chemists (laser induced fluorescence)¹.

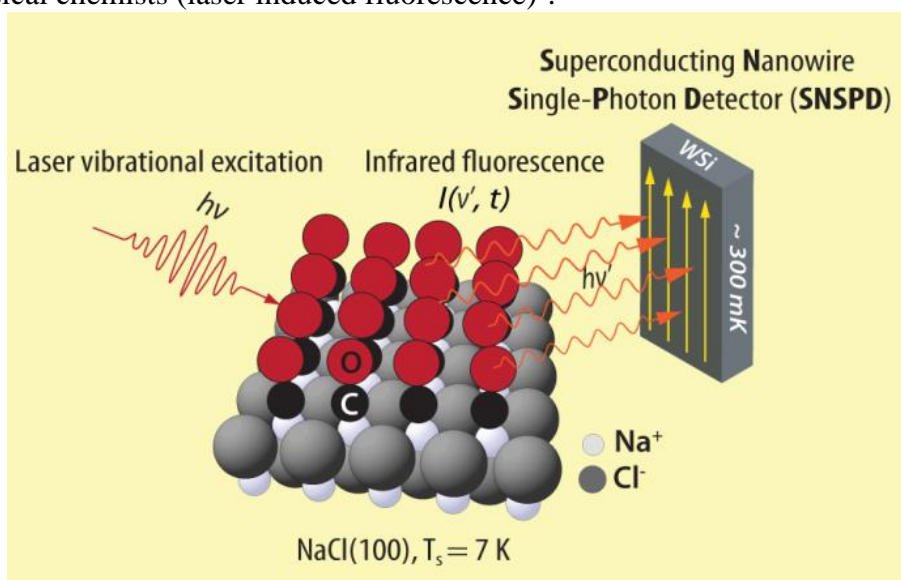


Figure 1 Laser-induced infrared fluorescence spectroscopy with SNSPD.

SNSPDs^{2,3} are fabricated from a thin film of superconducting metal, patterned into a meandering nanowire. The nanowire is cooled below its superconducting temperature, T_c , and held in a constant current circuit below the critical current necessary to destroy superconductivity, I_c . Upon absorption of a photon, the resulting heat is sufficient to destroy superconductivity across the entire width of the nanowire, an event that can be detected as a voltage pulse. In contrast to semiconductor-based detectors, which have a long wavelength cut-off determined by the band gap, the SNSPD exhibits single-photon sensitivity across the entire mid-IR spectrum.

In this talk, I demonstrate the advantages of these detectors in a frequency- and time-resolved laser-induced infrared fluorescence experiment (as shown in Figure 1) on the vibrational energy pooling^{4,5} in a multilayer CO on a NaCl (100) surface. For example, the fluorescence detection in a broad mid-IR wavelength range of $1.9\text{--}7.0\ \mu\text{m}$ obtained by single-photon counting; the high sensitivity of this WSi-based detection system- the system's Noise Equivalent Power (NEP) value at $3\ \mu\text{m}$ is $\sim 10^{-3}$ of a conventional InSb photovoltaic device. Straightforward modifications are expected to provide at least 100-fold improvement. Furthermore, the temporal resolution of the experiment is limited only by the pulse duration of the laser used in this work (FWHM = 3.7 ns).

References

- (1) Li Chen, D. S., Varun B. Verma, Martin J. Stevens, Francesco Marsili, Richard P. Mirin, Sae Woo Nam and Alec M. Wodtke. Mid-infrared laser-induced fluorescence with nanosecond time resolution using a superconducting nanowire single-photon detector: New technology for molecular science. *Accounts Chem Res* **2017**. (Accepted for publication)
- (2) Baek, B.; Lita, A. E.; Verma, V.; Nam, S. W. Superconducting a-W_xSi_{1-x} nanowire single-photon detector with saturated internal quantum efficiency from visible to 1850 nm. *Appl Phys Lett* **2011**, *98*, 251105-251103.
- (3) Natarajan, C. M.; Tanner, M. G.; Hadfield, R. H. Superconducting nanowire single-photon detectors: physics and applications. *Supercond Sci Tech* **2012**, *25*.
- (4) Corcelli, S. A.; Tully, J. C. Vibrational energy pooling in CO on NaCl(100): Methods. *J Chem Phys* **2002**, *116*, 8079-8092.
- (5) Chang, H. C.; Ewing, G. E. Vibrational-Energy Transfer and Population-Inversion in Co Overlayers on NaCl(100). *J Phys Chem* **1990**, *94*, 7635-7641.

Investigation of the electronic structure of UPd₂Al₃ using ARPES and tr-ARPES

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We use time- and angle-resolved photoemission spectroscopy to measure the equilibrium and nonequilibrium electronic states in heavy Fermion UPd₂Al₃. In this talk, we will present our observation and analysis of dynamics of quasiparticle states in UPd₂Al₃ as a function of momentum and photon energy. Time-resolved work was performed with temporal resolution of 35fs.

Excited State Quantum Electron-Nuclear Dynamics in Condensed Matter: An Example on Charge Density Wave

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Photoexcitation induced ultrafast phase dynamics in 1T-TaS₂, a well-known charge density wave (CDW) material, has been investigated using time-dependent density functional theory molecular dynamics. We discover a new metallic phase induced by photodoping, which is significantly different from thermally-induced undistorted 1T phase of TaS₂. This observation, together with the fact that the amplitude mode of CDW is induced at low light intensities, supports that conventional hot electron model is inadequate to explain the photoinduced phase transition. Our results imply that not only electron-phonon coupling but also electron-electron correlation plays a vital role in the formation and excitation of CDW in 1T-TaS₂.

X-Ray Reflectivity Studies of Ionic Liquid Interfaces

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Ionic Liquids (ILs) are promising candidates in a variety of applications such as heterogeneous catalysis. In the SILP (Supported Ionic Liquid Phase) catalysis the chemical reaction takes place in a thin IL film, wetting a solid support material with high surface area. Recently, it has been proposed that the observed performance degradation is related to aggregation of side products at the IL/gas inter-face, forming diffusion barriers for educts and products. However, for an in-depth understanding of the processes influencing the transport properties of reactants and products across the liquid/gas interface, knowledge of the interfacial structure of ILs on a molecular length scale is essential.

Density profiles across the IL/vapor interface with sub-nanometer resolution are determined by X-ray reflectivity (XRR). Depending on the molecular architecture of the ILs containing long aliphatic side chains, we observe pinning of bulk correlations at the surface and surface induced smectic order. As model systems for complex multi component mixtures, we studied the near surface structure of an alkane containing IL. Analysis of the experimental data revealed surface segregation of the alkanes that induce ordered structures, affecting the interfacial ion profiles over a length scale up to 30 nm.

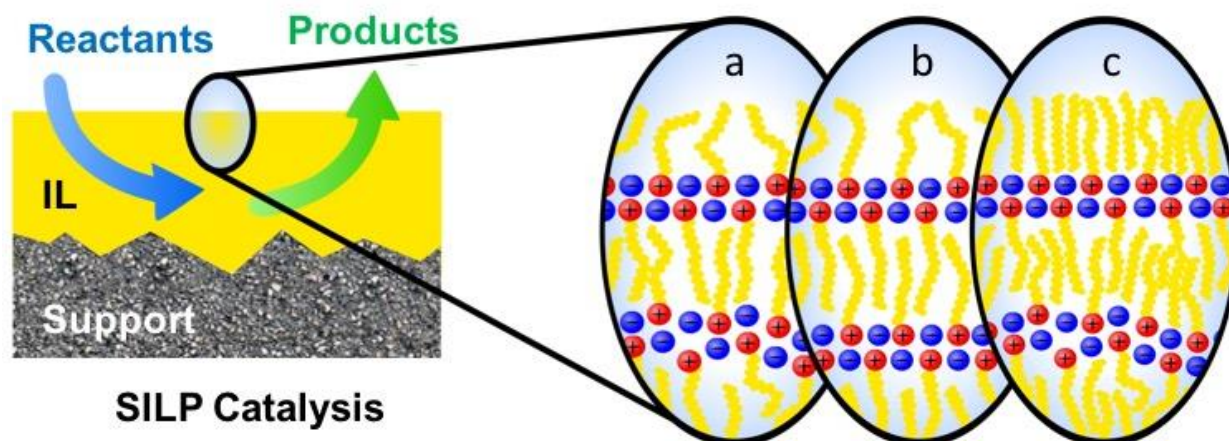


Figure: Sketch of the molecular scale structure of IL surfaces. The transport properties of reactants and products across the liquid/gas interface can be affected by the near surface structure that is governed by (a) the pinning of bulk correlations, (b) surface induced smectic order, and (c) surface segregation of impurities and side products.

Molecular modeling of interfacial water

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We study the variation of the topmost layer of water molecules at the basal facet in the temperature range between 150 K and 245 K by combining molecular dynamics simulations with vibrational sum-frequency generation measurements. The frequency of the dangling O-H peak is constant up to ~185 K, shifting to higher frequency above ~185 K. This frequency shift reflects the interconversion of different hydrogen-bond-accepting and -donating water molecules at the ice surface. At temperatures above 185 K, thermal fluctuations cause breaking of hydrogen-bonds; at temperatures < 185 K, the formation of crystalline interfacial structures of the topmost water layer also causes hydrogen-bond breaking. As a result, the topmost layer of ice has a minimum in free O-H groups and a maximum in hydrogen-bonds around 185 K.

Simulating photo-electrocatalytic reactions beyond the computational hydrogen electrode

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The role computer modelling plays today in understanding and optimising catalysts for photo-electrochemical reactions is undisputed. Yet, state of the art simulation approaches tend to rely on a number of assumptions and simplifications which according to newest results may not be fully justified. For example, simulation of the all-important electro-catalytic water oxidation reaction is mainly based on idealised surfaces and the computational hydrogen electrode (CHE) approach, which evaluates the thermodynamic feasibility of a catalyst looking at pathways where each hydrogen abstraction is coupled to the removal of one electron (PCET). The precise reactive site of the catalyst is thereby viewed as irrelevant, based on the premise of idealised surfaces. Yet, especially on semi-conducting catalysts both the assumption of PCET and of pristine, defect-free catalyst surfaces are not necessarily fulfilled.

The great success of the CHE approach is in part due to its low computational cost allowing a computational screening of suitable catalyst materials. Any other scheme going beyond PCET and pristine surfaces should therefore match this advantage, ideally avoiding costly numerical sampling of solvent degrees of freedom. Yet, recent developments in thermodynamic modelling as well as embedding techniques, both liquid and solid-state, especially considering the interface between catalyst and solvent, point the way towards photo-electrochemistry modelling beyond the computational hydrogen electrode.

In-situ Studies of the Reactivity of Model Catalysts: Surface Chemistry from flat surfaces to nanoparticles

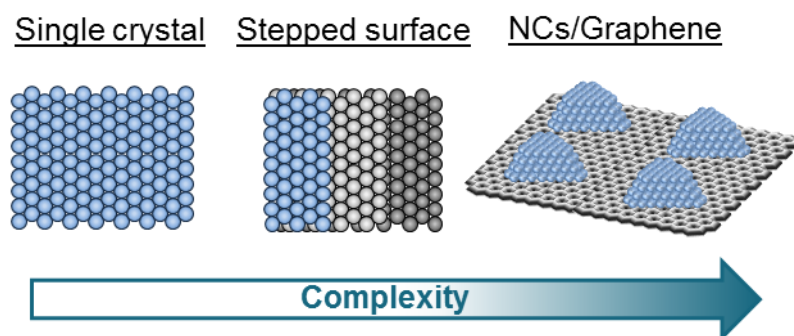
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The increasing complexity from surface science to real catalysis leads to the “materials gap”. To close this gap, studies of adsorption and reaction experiments on graphene-supported nanoparticles under *in situ* conditions were conducted with the particular aim to point out similarities and differences of results from “traditional” single crystal studies and the more complex, more realistic nanoparticles. It is shown that the use of a quantitative spectroscopy allows for gaining a detailed insight even to these complex systems, thereby facilitating a further step into bridging the materials gap from fundamental science to applied sciences. The use of graphene as a substrate gives intriguing new possibilities, as the template effect of graphene can lead to a very narrow size distribution, while graphene itself is chemically innocent, thereby making side processes such as spill over and reverse spill over less likely.

The systems discussed range from extremely well studied systems such as the adsorption and reaction of CO on a Pt(111) surface, going to stepped surfaces and finally to nanocluster arrays supported on a graphene support. Also the important chemistry of sulphur, being a strong catalyst poison, on such systems will be discussed. While the adsorption behavior on nanoclusters is strongly reminiscent of the adsorption on stepped surfaces, a strong increase in the reactivity of nanoparticles systems is found.

1. K. Gotterbarm, F. Späth, U. Bauer, C. Bronnbauer, H.-P. Steinrück, C. Papp, ACS Catalysis, 5 (2015) 2397.
2. C. Papp, Catalysis Letters, 147 (2016) 2.



The figure illustrates the increasing complexity of different model systems.

Rotationally-resolved scattering of formaldehyde from the Au(111) surface

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The conversion of translational to rotational motion often plays a major role in the trapping of small molecules at surfaces, a crucial first step for a wide variety of chemical processes that occur at gas-surface interfaces. However, to date most quantum-state resolved surface scattering experiments have been performed on diatomic molecules, and very little detailed information is available about how the structure of non-linear polyatomic molecules influences the mechanisms for energy exchange with surfaces. In the current work, we employ a new rotationally-resolved $1+1'$ resonance-enhanced multiphoton ionization (REMPI) scheme to measure the rotational state distribution in formaldehyde molecules directly scattered from the Au(111) surface at incident kinetic energies in the range 0.3–1.2 eV.

The results indicate a pronounced propensity to excite rotation about the molecular a -axis (twirling) rather than the b - or c -axes (tumbling or cartwheeling), and are consistent with a rotational rainbow scattering model. Classical trajectory calculations suggest that the effect arises—to zeroth order—from the three-dimensional shape of the molecule (steric effects). Our results suggest that facile excitation of a -axis rotation is likely to characterize a wide variety of prolate top molecule-surface scattering systems and may play a key role in the enhanced trapping probabilities of these molecules when they impinge upon surfaces at high kinetic energy.

A New Type of Tunable THz Emitters Based on the Ferromagnet/Non-Ferromagnet Heterostructures

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Terahertz (THz) wave, which lies in the frequency gap between infrared and microwave, has an electromagnetic spectrum conventionally defined in the range from 0.1 to 30 THz, which has a great potential in fundamental scientific research and other applications. Very recently, it was reported that the THz wave can be generated in heterostructure composed of ferromagnetic (FM) and non-FM metal films upon excitation of ultrafast laser pulses, which could open a new direction of ultrafast spintronics.

In this contribution, we report our study on the THz emission in the Ferromagnet/Non-Ferromagnet heterostructures, such as Fe/Pt and Co/Pt. We carried out a comprehensive investigation of THz emission from these magnetic heterostructures, employing time-domain THz spectroscopy. We revealed that by properly tuning the thickness of ferromagnetic or non-magnetic layer, THz emission can be greatly improved in this type of heterostructure. We further demonstrate that the THz field strength emitted from a newly designed multilayer can be strongly increased. Polarization of the emitted THz wave has been shown to follow the rotation of the applied magnetic field. In addition, the intensity and spectrum of THz wave is demonstrated to be tunable by the magnetic field applied on the patterned magnetic heterostructures. These findings thus promise novel approaches to fabricate powerful and tunable THz emitters based on magnetic heterostructure.

Probing Adsorption Structures of Methanol on TiO₂(110) under both Ultrahigh Vacuum and Near Ambient Pressure Conditions

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The photocatalytic reaction on TiO₂ material has attracted more and more attention since the photosplitting of water on TiO₂ was discovered in 1972. Here, we will present our recent studies of the adsorption structures of methanol and its photocatalytic reaction on TiO₂(110) by sum frequency generation (SFG) vibrational spectroscopy. SFG is an intrinsic surface-specific method, which enables us to probe the vibrational spectra under both ultrahigh vacuum (UHV) and near ambient pressure conditions.[1] We found that the adsorption structure of methanol on TiO₂(110) is not only dependent on the coverage of methanol under the vacuum condition,[2, 3] but also on the methanol pressure in the gas phase. Under the UHV condition, the methanol at not more than one monolayer coverage adsorbs on the five coordinated titanium site as both molecular and dissociated forms with comparable quantities. While as the coverage increases to more than one monolayer, the dissociated methanol decreases, and even disappears at the multilayer coverage as shown in Figure 1. Due to pressure gap in catalysis, the issue of the surface structure and the catalytic reaction under near ambient pressure turns to a hot topic in the last decade. Our results shows that the dissociated methanol percentage on TiO₂(110) decreases due to the methanol in the gas phase, and the TiO₂(110) surface might reconstruct under the condition. The methanol in the gas phase can also induce methanol dissociation to form more methoxy as the pressure increases. Our results not only provide a detailed insight into the adsorption structure of methanol on TiO₂(110), but also shed light on the photochemistry on this surface under real reaction condition.

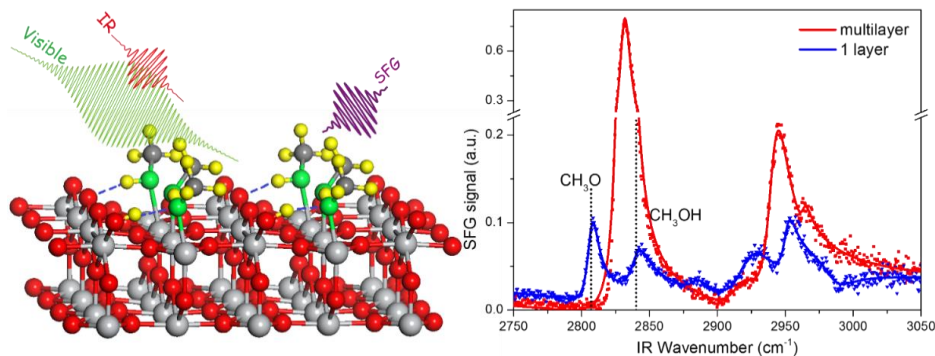


Figure 1. The SFG vibrational spectra of one layer and multilayer methanol on TiO₂(110).

[1] Liu S, Liu A-a, Zhang R, Ren Z. *Rev. Sci. Instrum.* **2016**, 87, 044101

[2] Liu A-a, Liu S, Zhang R, Ren Z. *J. Phys. Chem. C* **2015**, 119, 23486-23494

[3] Liu S, Liu A-a, Wen B, Zhang R, Zhou C, Liu L-M, Ren Z. *J. Phys. Chem. L* **2015**, 6, 3327-3334

Ultrafast nanoscale dynamics probed by time-resolved electron microscopy

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Ultrafast transmission electron microscopy (UTEM) is a promising technique which provides access to ultrafast dynamics on nanometer length scales [1]. In UTEM, a pulsed electron beam with sub-picosecond bunch duration is utilized to stroboscopically probe optically triggered processes. Dynamics in structural, electronic and spin degrees of freedom are generally accessible in UTEM by utilizing the versatile imaging and diffraction capabilities of state-of-the-art electron microscopes. However, up to now, the broad applicability of UTEM was limited by the coherence properties of available pulsed electron sources.

In the Göttingen UTEM project, we developed nanoscale laser-driven photocathodes, which allow for the generation of electron pulses with largely improved coherence properties. With this approach, we achieve, at the sample position, electron focal spot sizes down to below one nanometer and pulse durations of about 200 fs [2].

High-coherence ultrafast electron probes now enable the investigation of fast processes in nanostructured systems and at interfaces. I will present first applications, including the coherent phase modulation of electron pulses in optical near-fields [3] and its use in plasmon imaging and Ramsey-type electron-light interferometry [4], the nanoscale mapping of optically induced ultrafast structural dynamics [5], and our current progress towards ultrafast magnetic imaging using electron holography and phase sensitive imaging.

- [1] A. H. Zewail, Four-dimensional electron microscopy. *Science* 328, 187–93 (2010).
- [2] A. Feist, N. Bach, N. Rubiano, Th. Danz, M. Möller, K. E. Priebe, T. Domröse, J. Gatzmann, S. Rost, J. Schauss, S. Strauch, R. Bormann, M. Siviş, S. Schäfer, C. Ropers, Ultrafast transmission electron microscopy using a laser-driven field emitter: femtosecond resolution with a high coherence electron beam, submitted, arXiv:1611.05022.
- [3] A. Feist, K. E. Echternkamp, J. Schauss, S. V. Yalunin, S. Schäfer, C. Ropers. Quantum coherent optical phase modulation in an ultrafast transmission electron microscope. *Nature* 521, 200–203 (2015).
- [4] K. E. Echternkamp, A. Feist, S. Schäfer, C. Ropers, Ramsey-type phase control of free electron beams, *Nature Phys.* 12, 1000-1004 (2016).
- [5] A. Feist, N. Rubiano da Silva, W. Liang, C. Ropers, S. Schäfer, in preparation.

State-to-state molecular beam surface scattering of diatomic molecules

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The fate of molecular vibrational energy after surface collisions provides insights into the underlying nature of the interaction. In particular, electronically non-adiabatic dynamics are characterized by a strong coupling between vibrational degrees of freedom and electron-hole-pair (EHP) excitation. Such dynamics have been observed for several molecule-surface systems. Specifically, multi-quantum relaxation of NO molecules scattered from metal surfaces has become one of the most thoroughly studied examples of non-adiabatic dynamics at surfaces. However, it remains unclear how unique the NO/metal system is and which molecular and surface properties promote non-adiabatic dynamics.

In the talk, I will present recent work on the interaction of different highly vibrationally excited molecules scattered from various surfaces. In particular, we recently scattered CO($v = 17$) from Au(111) in a molecular beam surface scattering experiment. In contrast to NO, CO exhibits significantly less vibrational relaxation when scattered from Au(111). We explain this observation in terms of the lower electron affinity of the CO molecule, which leads to weaker electronically non-adiabatic interactions with the metal surface.

Imaging Nanoscale Morphology of Semiconducting Polymer Films with Photoemission Electron Microscopy

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In my talk I will present a new method to image the structure of organic semiconducting films. These films consist of electrically conducting (macro-) molecules and form the basis for organic electronics. In the near future, organic electronics may revolutionize our world with extremely lightweight, mechanically flexible and semitransparent electronic devices.

Prerequisite for a steep take-off of organic electronics is a further systematic improvement of material performance. Clear images of the nanoscale morphology of organic semiconducting films, i.e. the arrangement of the (macro-) molecular building blocks in the films, are key to these improvements. Until today, a major bottleneck was the lack of a convenient method to visualize this nanoscale morphology.

We have recently developed such a method. In our setup, we combine a photoemission electron microscope (PEEM) with a pulsed laser system. This method directly delivers images of the nanoscale morphology of organic semiconducting films with a lateral resolution of 50 nanometers. Striking advantages are non-destructive and fast measurements, straightforward data analysis, low complexity of sample preparation, as well as the possibility to perform measurements on a broad variety of technologically relevant substrates and even on devices.

Using this technique, we further identified remarkable structural motifs in a semicrystalline polymer film - gradual and abrupt change of polymer chain orientation - which may largely govern the material's performance.

In future, PEEM based nanoscale imaging may provide a valuable platform for new research efforts with the following goals:

- a) Evaluating and improving our understanding of the correlation between nanoscale morphology and material performance.
- b) Developing and optimizing techniques to process organic semiconducting polymers.
- c) Expanding the technique into an analytical tool for quality control of semiconducting polymer films for organic electronic devices.

First-principles free-energy barriers for photo-electrochemical surface reactions: Proton abstraction at TiO₂(110)

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First-principles modelling of electrocatalytic surface reactions is still largely defined by the computational hydrogen approach. This approach evaluates free energy differences between consecutive reaction steps and thereby accounts only for thermodynamic barriers. In order to access additional kinetic barriers in the photocatalytic oxidation of water, we present an approach based on ab initio molecular dynamics (AIMD) simulations and umbrella sampling. [1] We showcase the method by explicitly calculating the free-energy barrier for the initial proton abstraction in the water splitting reaction at rutile TiO₂(110), which was previously studied within the computational hydrogen electrode approach. [2] Combining electrostatic QM/MM embedding, an energy based reaction co-ordinate and state-of-the-art free-energy reconstruction techniques render the calculation tractable at the hybrid density-functional theory level, which is required for a realistic description particularly of the transition state. The obtained free-energy barrier of approximately 0.2 eV, depending slightly on the orientation of the first acceptor water-molecule, suggests a hindered reaction on the pristine rutile surface.

- [1] T. Stecher, K. Reuter and H. Oberhofer, *Phys. Rev. Lett.*, 117, 276001 (2016).
[2] H. Oberhofer and K. Reuter, *J. Chem. Phys.* 139, 044710 (2013).

Unveiling Microscopic Structures of Charged Water Interfaces by Surface-Specific Vibrational Spectroscopy

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Charged water interfaces are ubiquitous and responsible for many important processes in nature and modern technologies, such as protein folding, electrochemistry, and photocatalysis. They appear in the form of an electric double layer that can be divided into two sub-layers. One is the so-called Stern layer composed of one to two hardly mobile, hydrogen-bonded, water monolayers next to the charged plane. The other is the diffuse layer, in which ions assuming the Poisson-Boltzmann distribution set up a dc field distribution. Being directly associated with the charged surface, the Stern layer directly controls the microscopic energy transfer and chemical reaction pathway at the interface. However, despite extensive studies on charged water interfaces, current knowledge on the microscopic structure of the Stern layer is still extremely limited. The difficulty lies in the inability of existing techniques to selectively extract structural information about the Stern layer in the presence of the diffuse layer. We now have developed a sum-frequency spectroscopy method that allows us to obtain the vibrational spectrum, and hence the microscopic structural information, of a Stern layer. Application of the method to a prototype lipid (fatty acid)–water interface reveals significant variation of its Stern layer structure upon deprotonation of the lipid headgroup. The measurement also yields a spectrum that characterizes the dc-field-induced sum-frequency generation from bulk water in general, and can help to deduce vibrational spectra of the Stern layer of other charged water interfaces. This unique ability of our method provides opportunities to gain better microscopic understanding of properties and functionality of charged water interfaces.

Surface chemistry for organic-inorganic interfaces – a quantum chemical perspective

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The interface between a solid inorganic substrate and an ordered adsorbate layer of organic molecules is of continued interest for the experimental and theoretical physics and chemistry community due to their promised application range, e.g. for building chemical sensors. Many fundamental aspects of these interfaces are still under investigation and concerted efforts of the aforementioned communities are currently being undertaken.

Among the most challenging aspects in this context is the controlled formation of a highly ordered layer of organic molecules covalently bound to the semiconductor surface.[1] The high reactivity of the surface, the need for at best barrier-less adsorption of the organic molecule in the orientation required for further functionalization and the understanding of non-Langmuir behavior of multiple adsorption are some examples here.

Experimental endeavors can help to rationalize some of these aspects but some key quantities, for example reaction barriers and transition state structures, are available only to first principles methods. The talk will highlight aspects of surface chemistry for organic-inorganic interfaces that can be approached by theoretical methods. Special emphasis will be on the successful transfer of concepts from molecular chemistry to surface reactions that can lead to surprising insights in this field.[2]

Examples from our work on surface adsorption, reactivity and chemical bonding[3] of organic molecules with the silicon(001) surface will be used to highlight the strength of the approach.

[1] a) G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* 556, 70 (2013); b) B. Shong, T. E. Sandoval, A. M. Crow, S. F. Bent, *J. Phys. Chem. Lett.* 6, 1037 (2015); c) G. Mette, M. Reutzel, R. Bartholomäus, S. Laref, R. Tonner, M. Dürr, U. Koert, U. Höfer, *ChemPhysChem* 15, 3725 (2014); d) M. Reutzel, N. Münster, M. A. Lipponer, C. Langer, U. Höfer, U. Koert, M. Dürr, *J. Phys. Chem. C* 120, 26284 (2016).

[2] a) J. Pecher, G. Mette, M. Dürr, R. Tonner, *ChemPhysChem* 18, 357 (2017).; b) J. Pecher, R. Tonner, *ChemPhysChem* 18, 34 (2017); c) J. Pecher, C. Schober, R. Tonner, *Chem.– Eur. J.* (2017), DOI: 10.1002/chem.201605952.

[3] M. Raupach, R. Tonner, *J. Chem. Phys.*, 142, 194105 (2015).

Irreversible Tautomerization in Porphycene on Cu(111) Induced by Scanning Tunnelling Microscopy

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Scanning tunnelling microscopy (STM) is a widely appreciated characterization technique in surface science. The applications range from imagery to catalysis and nanoelectronics, to name but a few. In recent experiments, STM was further used to selectively induce reactions in the vicinity of metallic surfaces. It is well-known that non-adiabatic coupling to hot electrons impinging from the STM tip can play an important role in such phenomena (see Refs. [1,2] and references therein). To demonstrate their dynamical effect, we will investigate the irreversible tautomerization in porphycene on a Cu(111) surface induced by hot electrons injected by a neighbouring STM tip [3]. We demonstrate that the reaction can be understood as a quasi-thermal hydrogen migration mechanism and rationalized in terms of non-adiabatic coupling and intramolecular vibrational energy redistribution: hot electrons from the STM-tip excite a large number of skeletal vibrations of the molecule, which distorts the potential energy landscape along the hydrogen transfer coordinate [4].

References

- [1] M. Blanco-Rey, M. Alducin, J. I. Juaristi, and P. de Andres “Diffusion of Hydrogen in Pd Assisted by Inelastic Ballistic Hot Electrons” *Phys. Rev. Lett.* 108 115902 (2012).
- [2] J.C. Tremblay “A unifying model for non-adiabatic coupling at metallic surfaces beyond the local harmonic approximation: from vibrational relaxation to STM-driven transitions” *J. Chem. Phys.* 138 244106 (2013).
- [3] J. N. Ladenthin, L. Grill, S. Gawinkowski, S. Liu, J. Waluk, T. Kumagai “Hot Carrier-Induced Tautomerization within a Single Porphycene Molecule on Cu(111)” *ACS Nano* 9 7287 (2015).
- [4] D. Novko, M. Blanco-Rey, and J.C. Tremblay “Intermode Coupling Drives the Irreversible Tautomerization in Porphycene on Copper(111) Induced by Scanning Tunnelling Microscopy” *J. Phys. Chem. Lett.* 8 1053 (2017).

Quantification of Single Molecular Interactions at Solid/Liquid Interfaces

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Unraveling the complexity of the macroscopic world relies on understanding single molecule interactions and their scaling towards integral interactions at the meso- and macroscopic scale. Here, I will discuss how one can measure the interaction free energy of single interacting functional groups at various solid/liquid interfaces. Also, I will show how these interactions scale with the number density towards the macroscopic level [1, 2], where a large number of these bonds interact simultaneously. In particular, we developed a synergistic experimental approach combining Surface Forces Apparatus (SFA) experiments and single molecule force spectroscopy (SMFS) in an Atomic Force Microscope.

First, equilibrium SFA measurements scale linearly with the number density of a model gold-amine bond at an interface, providing acid-amine interaction energies of $\sim 35 \pm 2$ kT. Using Bell-Evans theory together with Jarzynski's equality, we can demonstrate how a set of single molecule interaction forces measured by SMFS similarly converges to an interaction energy of 36 ± 3 kT. This demonstrates excellent predictive power of our newly developed scaling approach.

Second, and in addition to gold-amine interactions, we tested a number of other bonds including hydrophobic, electro-active mussel-peptide/surface [3] and other metal/polymer [2] bonds with our model and find that our model is widely applicable, in particular also to electrified interfaces. In this context, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions. As such, our experimental strategy provides a unique framework for the molecular design of novel functional coatings through predicting of large-scale properties such as adhesion and molecular interactions in various systems based on experimentally determined single molecule energy landscapes.

[1] S. Raman et al. in *Nature Communications*, 5 (2014), 5539.

[2] T. Utzig et al. in *Langmuir*, 31(9) (2015), 2722.

[3] T. Utzig et al. in *Angewandte Intl.* (2016).

Direct Charge Transfer across Organic Semiconductor and Metal Interfaces.

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Direct charge transfer across molecular interfaces promotes charges from donors to acceptors in one step and can enable new mechanisms for molecular electronics, light harvesting and photocatalysis. Despite its potential, its experimental demonstration and understanding are limited, which has constrained applications of direct interfacial charge transfer in energy materials. To probe hidden interfaces, we implement transient vibrational sum frequency generation (VSFG) spectroscopy. We observe transient electric-field-induced VSFG signal, which indicates a charge transfer process at spin-coated prepared organic semiconductor-metal interfaces. The photon-energy and polarization dependence of pump pulses further indicates that electrons are directly transferred across interfaces. Frequency-resolved transient spectra reveal that, even though the interfaces are prepared without deliberate orientation control, a sub-ensemble of surface molecules can adopt orientations for direct charge transfer. Experimental observations are supported by density functional theory calculations, which show that although many orientations can exist at interfaces, at parallel orientation, electronic orbitals are delocalized across interfaces. The observation of direct charge transfer at complex interfaces paves the way for a new foundation of implementing direct charge transfer in energy materials.

Nonlinear Optical Studies of Oxide Surfaces

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Low-coordinated lattice sites play key roles in oxide surface reactions; however, it remains challenging to probe such sites in situ under surface reactions, especially outside the ultrahigh vacuum. Using optical sum-frequency generation, we investigated such sites on titanium dioxides (TiO₂) by probing the stemming surface phonon modes. With those newly identified modes, we can characterize not only the low-coordinated surface titanium sites, but related oxygen vacancies as well, at the ambient pressure and temperature upon surface reactions. By monitoring the mode evolution in situ under the uv irradiation, we found ambient gas molecules to strongly affect the surface stability of oxygen vacancies, and the response differs drastically between different single crystal surfaces, which may help to further our understanding in the fundamental of surface catalysis on titanium oxides [1].

[1] Y. Cao et al., Science Advances, 2, e1601162 (2016).

Photoelectron Spectroscopy at Surfaces

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In this talk I will present basic concepts of photoelectron spectroscopy at surfaces, discussing both standard surface characterization techniques as well as modern tools for the investigation of ultrafast dynamic electron processes in surfaces and adsorbates. At the beginning Auger electron and x-ray photoelectron spectroscopy for elemental characterization will be touched. A larger part is devoted to ultraviolet photoelectron spectroscopy for the characterization of the valence band structure, a spectral range which can be accessed by the new free-electron laser in Dalian. These techniques yield information about the occupied states of the sample.

Unoccupied states can be investigated by inverse photoelectron spectroscopy and by two-photon photoemission. Advantages and limitations of both methods will be discussed. The latter methods allows two color and temporally delayed spectroscopy, which enables the investigation of ultrafast electron dynamics. These techniques will be illustrated for the electron dynamics in organic 2D systems and graphene nanoribbons.

An additional degree of freedom is available through the spin of the photoelectrons. Their spin polarization can be measured by Mott scattering. This will be discussed for the electron transmission through organized chiral and helical molecules adsorbed on various surfaces.

Electronic Structure at TiO₂ Interface

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In reduced TiO₂, electronic transitions originating from the Ti³⁺- induced states in the band gap are known to contribute to the photoabsorption, being in fact responsible for the material's blue color and visible light photocatalysis, but the excited states accessed by these transitions have not been characterized in detail. In this work, the ground and excited states near Fermi level (E_F) at rutile TiO₂(110) and anatase TiO₂(101) interface have been investigated by ultraviolet photoelectron spectroscopy (UPS) and two-photon photoemission spectroscopy (2PPE) respectively in combination with density functional theory (DFT) calculations. The band gap states and the excited states located at 2.5 eV above (E_F) originate from the Jahn-Teller induced splitting of the 3d-t_{2g} orbitals of Ti³⁺ ions in reduced TiO₂. Localized excitation of Ti³⁺ ions via 3d→3d transitions from the gap state to this empty resonant state increases significantly the TiO₂ photo-absorption and extends the absorbance to the visible region, consistent with the observed enhancement of the visible light induced photocatalytic activity of TiO₂ through Ti³⁺ self-doping. Our work reveals the physical origin of the Ti³⁺ related photoabsorption and visible light photocatalytic activity in prototypical TiO₂, and also paves the way for the investigation of the electronic structure and photoabsorption of other metal oxides.

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