FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Report to the Fachbeirat
Department of Physical Chemistry

2014

Recent Developments in the Department of Physical Chemistry

Director: Martin Wolf

Max Planck Research Group: Structural and Electronic Surface Dynamics

Head: Ralph Ernstorfer

1. General

Since the last meeting of the Fachbeirat, the Department of Physical Chemistry has developed its experimental and laboratory infrastructure to become fully operational. Currently the research groups of the department are still distributed over several locations on the FHI campus and in rented external lab space. However, the construction of the new building for the department is now on its way and will be completed in early 2016.

Several changes have occurred among the group leaders and senior postdocs of the department:

- *Dr. Zefeng Ren* received an offer for an associate professorship at Peking University and started there in January 2012.
- *Prof. Karsten Horn* (formerly Department of Molecular Physics) joined the department in January 2012. He provides expertise in angle-resolved photoemission spectroscopy and continues his research on electronic structure of grapheme-based materials.
- *Dr. Simon Wall* received an offer for an assistant professorship at ICFO (The Institute of Photonic Science) in Barcelona and left the department in August 2012 to set up an independent research group.
- Also in August 2012 *Dr. Patrick Kirchmann* left for a staff scientist position at SLAC National Accelerator Laboratory in Stanford.
- *Dr. Leonhard Grill* accepted an offer for a full professorship at the University of Graz and started this position in August 2013. He is still affiliated with the department in order to complete a EU funded project (AtMol) until end of 2014.
- Since May 2013 *Dr. Takashi Kumagai* is heading a new research group to study elementary molecular processes at surfaces employing low-temperature atomic force and scanning tunneling microscopy (AFM/STM) as well as tip-enhanced Raman spectroscopy (TERS).
- Starting in January 2014, *Dr. Alexander Paarmann* will set up a new group to employ the new infrared free electron laser (FHI-FEL) for time-resolved optical spectroscopy of ultrafast dynamics of solids, in particular phonon dynamics. He will complement these studies using femtosecond table-top sources.

Furthermore, several postdoc associates and graduate students moved on to new positions in industry or administration.

Two large service groups of the institute, the Electronics Lab and the Mechanical Workshops (since 2013), are currently associated with the department. After the retirement of *Horst*

Schwäricke in April 2013, *Petrik Bischoff*, formerly with the Department of Molecular Physics, was appointed as the new head of the Mechanical Workshops. Currently the services of the Mechanical Workshops are expanded and the machine infrastructure is modernized, a process which will continue over the next few years. The Electronics Lab (headed by *Georg Heyne*) is well organized and continues to provide excellent service for the institute.

1.1 Research of the Department

The research of the Department of Physical Chemistry is focused on the dynamics of elementary processes at surfaces, interfaces and in solids. Our goal is to develop a microscopic understanding of the dynamics of molecular and electronic processes as well as the interactions between various (electronic, spin and lattice) degrees of freedom. The general strategy is to address these problems from several sides using complementary approaches, in particular by the development and application of various spectroscopic techniques dedicated to the specific physical questions. Research is performed by small groups with specific expertise. Although the research of each individual group is mostly curiosity driven our complementary approach creates various synergies between the different groups.

The research of the department is currently structured into two main areas, (I) ultrafast dynamics of elementary processes in solids and at interfaces, and (II) molecular processes at surfaces and is carried out by the research groups listed below.

Ultrafast Dynamics in Solids and at Interfaces

- Dynamics of Correlated Materials (*Martin Wolf*)
- Electron Dynamics at Interfaces (*Julia Stähler*)
- Electronic Structure of Surfaces and Interfaces (*Karsten Horn*)
- Terahertz Physics (*Tobias Kampfrath*)
- Time-resolved Second Harmonic Generation Spectroscopy (*Alexey Melnikov*)

Molecular Processes at Surfaces

- Nanoscale Science (*Leonhard Grill*)
- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- Complex Systems (*Alexander Mikhailov*)
- Spatiotemporal Self-organization (*Markus Eiswirth*)

Max-Planck-Research Group

- Structural and Electronic Surface Dynamics (*Ralph Ernstorfer)*

The Max-Planck-Research Group (MPRG) of *Ralph Ernstorfer* on "Structural and Electronic Surface Dynamics" is closely associated with the department and complements the research on ultrafast dynamics of solids by time-resolved electron diffraction techniques.

The first line of research aims at studying the dynamics of elementary processes on the relevant time scales of the process by ultrafast laser spectroscopy (typically with femto- or picoseconds time resolution). The department applies a broad spectrum of established as well as newly developed techniques; these are used to study the electronic excitations and low energy excitations in solids, dynamics of electron transfer processes, vibrational dynamics at interfaces, as well as optically induced phase transitions. The second line of research is the investigation of elementary molecular processes either at the single molecule level, or by employing various schemes of optical excitations including photo-induced surface reactions. Scanning probe microscopy (in part combined with optical excitation) permits imaging, manipulation and spectroscopy as well as inducing and probing chemical processes of individual molecules. Further activities address problems of molecular biophysics and electrochemistry. Here, theoretical studies of molecular machines are performed, complemented by studies of nonlinear dynamics and pattern formation in electrochemical systems.

The promotion of young scientists is an important goal and several measures are taken to help them developing their career (*e.g.* IMPRS graduate school, PhD student and department workshops, regular status discussions, nomination for awards and invited talks). Recently several prizes have been awarded to junior scientists, namely the Feynman Prize (Foresight Institute) to *Leonhard Grill*, the Carl Ramsauer Award (German Physical Society Berlin) to *Laurenz Rettig* and the Inoue Research Award for Young Scientists to *Takashi Kumagai*.

Furthermore, junior staff scientists and postdocs are guided to gain experience in grant applications and establish their scientific network. Currently, the department cooperates in several EU funded projects, four collaborative research centers (Sfb 658, Sfb 910, Sfb 951, Sfb 1109) and one research unit (FOR 1700) funded by the Deutsche Forschungsgemeinschaft (DFG). These projects are complemented by several individual DFG research grants of young scientist (see section 3 for a complete list of projects).

1.2 Selected Research Highlights

The following research highlights are a selection of results from research projects as well as instrument development in the department obtained during the last two years:

- Progress was achieved in the area of time and angle-resolved resolved photoemission spectroscopy (trARPES, ($h\nu$ = 6 eV)) applied to various correlated materials (high-Tc superconductors, Fe-pnictides and charge density wave (CDW) systems). A systematic study of the tri-telluride CDW system demonstrated direct probing of the transient modulation of the CDW gap as well as vibrational coherent control of the amplitude mode using a three-pulse excitation scheme. Very recently, ultrafast melting of the spin-density-wave phase in Cr was studied with trARPES using XUV light obtained by high harmonics generation. [Phys. Rev. Lett. **108**, 097002 (2012), ibid. **107**, 097002 (2011)].
- The ultrafast evolution of the photoinduced insulator-to-metal transition in VO_2 was probed with a white light supercontinuum. Using the optical phonons of the insulating phase as a marker, an ultrafast change of the lattice potential symmetry (i.e. the restoring forces) was identified on a timescale much faster than the structural phase transition leading to a transient excited state which differs from the equilibrium metallic state of VO_2. [Nature Commun. **3**, 721 (2012), Phys. Rev. B **87**, 115126 (2013)].
- A high repetition rate (500 kHz) laser system for high harmonics generation of XUV laser pulses ($h\nu$ = 20 – 40 eV) in combination with a state-of-the-art ARPES experiment is currently being developed. This system employs multiple stages of fiber lasers, a slab laser amplifier and optical parametric chirped pulse amplification (OPCPA) to generate < 20 fs pulses with more that 20W output power in the visible.
- Bilayer graphene band calculations show a feature that is very desirable but absent in the monolayer – a band gap. Transport experiments, however, have so far failed to detect a clear gap. Using angle-resolved photoemission, this contradiction is explained by showing that small twists in the relative bilayer arrangement lead to the coexistence of massive Dirac particles (expected in the bilayer) with a massless particle band that crosses the ideal bilayer gap. [Nature Materials **12**, 887 (2013)].
- It is still not clear why quasicrystals, which have perfect atomic order yet lack translational periodicity, assume their complex structures. Using bulk-sensitive hard x-ray photoemission evidence for a large pseudogap near the Fermi level is obtained, supporting a Hume-Rothery mechanism for quasicrystal formation. Quasicrystals apparently form a

metallic phase at the surface that masks, when using surface sensitive photoemission, the true bulk electronic structure. [Phys. Rev. Lett. **109**, 216403 (2012)].

- The ultrafast quasiparticle dynamics at the ZnO(10-10) single crystal surface following above-band gap excitation was probed by time-resolved two-photon photoelectron spectroscopy, exhibiting ultrafast electron cooling in the conduction band by electron-phonon scattering and followed by formation of a surface-bound exciton.
- The transport of very short bunches of spin-polarized electrons (spin-current pulses) in magnetic heterostructures has been demonstrated employing THz emission spectroscopy as a probe. Using femtosecond laser excitation, the spin transport was launched from a ferromagnetic Fe thin film into a nonmagnetic cap layer of low (Ru) or high mobility (Au), which results in spin trapping (Ru) or ballistic traversal (Au). The results are potentially useful for future spintronics circuitry operated at highest (THz) frequencies [Nature Nanotech. **8**, 256 (2013)].
- A high-precision optical setup for time-resolved linear and non-linear magneto-optical spectroscopy has been developed, operating in back pump-front probe scheme with 20 fs time resolution. Femtosecond spin current pulses were demonstrated in epitaxial Fe/Au/Fe/MgO(001) multilayers [Phys. Rev. Lett. **107,** 076601 (2011)].
- Manipulation of the spectrum or temporal shape of a light pulse has been achieved by coupling femtosecond laser pulses into waveguides. For example, by suddenly tilting the waveguide's dispersion relation the spectrum can be compressed, a process which is reversible, features high conversion efficiency and could find application as a magnifying lens for optical spectra. Furthermore, the concept for an ultrafast optical delay line could be demonstrated [Phys. Rev. Lett. **108**, 033902 (2012), *ibid.* **108**, 213901 (2012)].
- A breakthrough has been achieved using femtosecond time-resolved x-ray spectroscopy (RIXS) at the LCLS free electron laser in Stanford to probe the electronic structure of CO molecules, as their chemisorption state on Ru(0001) changes upon exciting the substrate by using a femtosecond optical laser pulse. The observed electronic structure changes are consistent with a transient weakening of the CO-metal bond without notable desorption, indicationg the existence of two distinct adsorption wells, a chemisorbed and a precursor state, separated by an entropy barrier [Science **339**, 1302 (2013); Phys. Rev. Lett. **110**, 186101 (2013)].

- Hierarchical “bottom-up” covalent binding of molecular building blocks in a well-defined pattern was demonstrated by sequentially supplying reactive sites on molecular building blocks. Copolymer networks were formed with high spatial selectivity. After dissociation of Br substituents from molecular building blocks on gold surfaces the polymerization to straight chains along the step edges was demonstrated, resulting in a pre-alignment along a given direction over the entire sample. [Nature Chemistry **4**, 215 (2012), Angew. Chem. Int. Ed. **51**, 5096 (2012)].
- The electrical current through a single molecule could be measured at different voltages over a large range. In this way, the conductance properties of an individual polymer could be correlated with its electronic states for the first time. Comparison with calculation reveals that the conductance depends on the precise atomic structure and the bending of the molecule in the STM junction. [Nature Nanotech. **7**, 713 (2012)].
- The intramolecular H-atom transfer reaction (tautomerization) within a single porphycene molecule on Cu(110) was controlled directly by low-temperature STM. The potential landscape of this process can be precisely tuned by putting single Cu adatoms nearby or by changing the orientation of neighboring molecules. Furthermore, the mechanism of thermally and vibrationally-induced tautomerization was deduced from isotope effects and the bias voltage and tunneling current dependence [Phys. Rev. Lett. **111**, 246101 (2013), Nature Chemistry (in press 2013)].
- A new experimental setup for sum frequency generation (SFG) spectroscopy has been developed allowing studies of liquid solid interfaces as well as probing low-frequency vibrations (e.g. surface phonons) down to ~700 cm^{-1}. The dissociative adsorption of water (D_2O) on α-Al_2O_3(0001) has been studied both in UHV and under ambient conditions by (1) characterizing the fragments via the OD stretch vibration and (2) the accompanying surface reconstruction using the Al-O surface phonon SFG spectral response.
- By combined experimental and computational studies of the non-hydrogen bonded (free) OH groups at the air/water interface, it was shown that these are structurally and dynamically heterogeneous on sub-picosecond timescales, and that 2/3 of their vibrational relaxation proceeds via intramolecular energy transfer and 1/3 via reorientation [J Phys. Chem. B, **116**, 9467 (2012), ibid. **117**, 11753 (2013), Proc. Nat. Acad. Sci (in press 2013)].

- Coarse-grained elastic-network numerical investigations of two macromolecules, playing a fundamental role in the cells, have been performed. For the molecular motor myosin, its strain-sensor behavior, previously found in single-molecule experiments, was explained and communication between important functional domains of the protein could be elucidated [Biophys. J. **102**, 542-551 (2012)].
- Many protein machines operate as active inclusions in lipid bilayers forming biological membranes. Fast and efficient methods have been developed for numerical simulations of lipid bilayers in membranes with active protein inclusions indicating the hydrodynamic effects should play a principal role in interactions between active membrane inclusions [J. Chem. Phys. **137**, 055101 (2012) and J. Chem. Phys. **138**, 195101 (2013)].

2. Progress Report

2.1 Ultrafast Dynamics in Solids and at Interfaces

Elementary processes in solids and at interfaces such as transfer of charge and spin, energy dissipation, or electron-phonon coupling are the underlying microscopic basis of much more complex phenomena, ranging from surface reactions to phase transitions in solids. The study of the non-equilibrium, ultrafast dynamics of such fundamental processes provides mechanistic insights into the interplay and energy exchange between electron, spin and lattice degrees of freedom. It is the strategy of the department to elucidate the dynamics of elementary processes from various sides using complementary approaches and techniques. These approaches are implemented by several groups in the department, which perform real-time studies of solids and interfaces on ultrafast time-scales, complemented by studies of the electronic structure.

2.1.1 Transient Electronic Structure of Correlated Materials

Correlated electron materials exhibit exotic electronic and magnetic properties, characterized by broken-symmetry ground states such as metal-to-insulator instabilities, unconventional superconductivity, and various cooperative ordering phenomena. One of the major challenges in this field is to understand the ground and excited state properties on a microscopic level and to disentangle the competing interactions and correlations of charge, spin, orbital and lattice degrees of freedom, which act on multiple length, energy and time scales.

Ultrafast laser spectroscopy provides a tool to access elementary scattering and relaxation processes by optically exciting the electronic system and subsequently probing the evolution of the transient electronic structure by an appropriate spectroscopic technique. For example, in a material undergoing an insulator-to-metal transition, optical excitation can induce a transient melting of the band gap whereby the timescale of the gap closing is characteristic for a mechanism driven by purely electronic correlations (Mott transition) or by ion motions (Peierls instability). The technique of time- and angle-resolved photoemission spectroscopy (trARPES) extends the benefits of momentum-resolved photoelectron spectroscopy into the time domain and provides direct access to the transient evolution of the electronic structure after optical excitation. Furthermore, the collective dynamics of lattice or spin excitations can be studied through their influence on the quasiparticle band structure.

As prototypical charge density wave (CDW) system the group of *Martin Wolf* has investigated the material class of rare-earth tri-tellurides, RTe_3 (RTe_3, R = Te, Ho, Dy) using trARPES with a 6 eV fs laser probe (in collaboration with U. Bovensiepen, Duisburg and

Z.-X. Shen, Stanford). Using a position sensitive detector for two-dimensional imaging of the photoelectron momentum, the transient changes of the Fermi surface and the opening and closing of the CDW gap could be mapped directly on a femtosecond time scale (see Fig. 1). By employing a novel three pulse "pump-reexcite-probe" photoemission scheme, the dynamics of the upper and lower CDW band edges could be resolved in great detail, indicating that the CDW gap modulation (amplitude mode) originates from a complex lattice motion whereby at least two coupled phonon modes are involved. A more detailed analysis of the band collapse reveals a transient reduction of the curvature of the Fermi surface, which is attributed to a transient change of the Te5p orbital overlap in the excited state. This leads to reduced coupling between neighbouring Te chains and thus to a modification in the dimensionality of the 2D band structure. Furthermore, vibrational coherent control has been demonstrated for the amplitude mode using double pulse excitation.

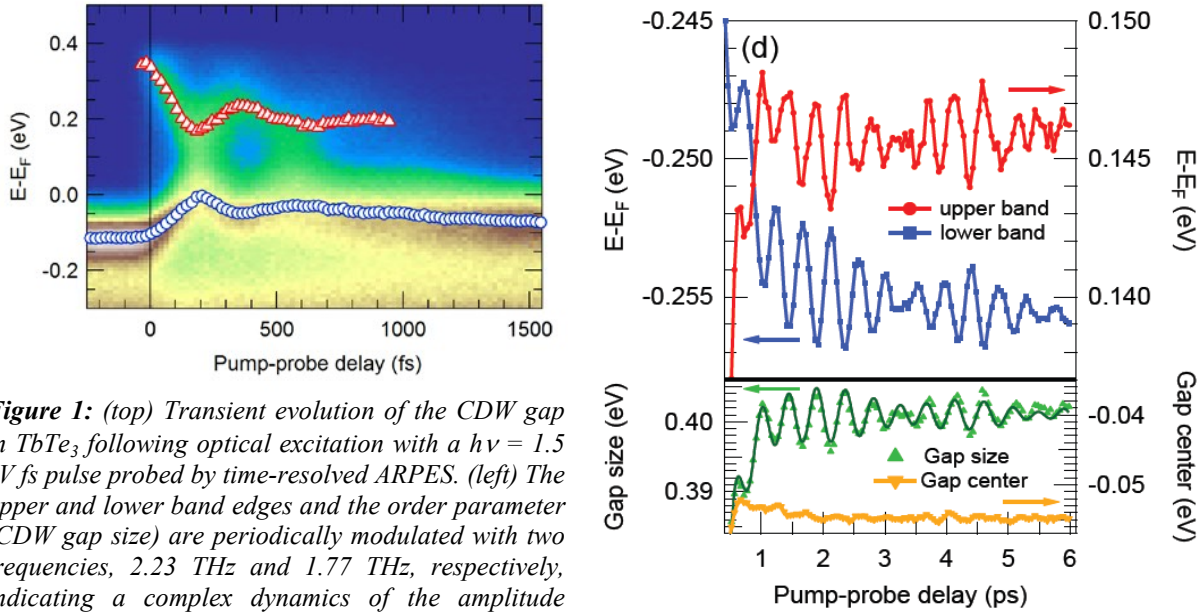

Figure 1: *(top) Transient evolution of the CDW gap in $TbTe_3$ following optical excitation with a hν = 1.5 eV fs pulse probed by time-resolved ARPES. (left) The upper and lower band edges and the order parameter (CDW gap size) are periodically modulated with two frequencies, 2.23 THz and 1.77 THz, respectively, indicating a complex dynamics of the amplitude mode.*

Further studies using trARPES with hν = 6 eV have probed the temperature-dependent relaxation times of photoexcited electrons and holes in antiferromagnetic Fe-pnictide, $EuFe_2As_2$, and have attributed their dynamics with the spin density wave gap and the single-particle band at the zone center, respectively [1]. The recovery of magnetic order after ultrafast excitation occurs four times slower compared to electron-phonon equilibration due to a smaller phase space for spin-dependent relaxation.

To overcome the limited accessible *k*-space due to the low kinetic energy of photoelectron using 6 eV laser ARPES, considerable efforts are currently undertaken to set up an advanced trARPES experiment based on a high repetition laser source (100 kHz – 1 MHz) for high

harmonics generation (HHG) of XUV laser pulses ($h\nu$ = 20 – 40 eV) in combination with a state-of-the-art ARPES ultrahigh vacuum system. In addition to the possibility of accessing several Brillouin zones, the HHG-based trARPES will provide much enhanced counting statistics. This experiment employs novel fibre and OPCPA laser technology and is developed in close collaboration with the MPRG group of *Ralph Ernstorfer* (see report MPRG).

On the way to develop HHG-based trARPES experiments, the group has recently performed two studies using the access to exisiting HHG setups, which operate at 1-10 kHz based on established TiSapphire laser technology. In collaboration with M. Weinelt, Freie Universität Berlin, the prototypical spin density wave (SDW) material chromium has been studied. An ultrafast melting of the SDW phase was revealed from the response of the related backfolded band, which can be compared to a transient change in electronic temperature. Very recently, the charge density wave (CDW) material $TiSe_2$ was studied with HHG-based trARPES in a beamtime at the ARTEMIS light source at Rutherford Appleton Lab (UK). The mechanism responsible for the CDW phase transition is still heavily debated. For $TiSe_2$ temperature dependent measurements were conducted as well as long-wavelength excitation to investigate the peculiar physics of this system.

In the group of *Julia Stähler,* the ultrafast electron and lattice dynamics of vanadium dioxide (VO_2) across the insulator-to-metal transition were investigated by means of transient optical spectroscopy using a white light supercontinuum, and by time-resolved two-photon photoelectron spectroscopy. VO_2 undergoes a phase transition from a monoclinic, insulating phase at low temperatures and a rutile, metallic phase above T_{crit} = 340 K. This transition can also be induced by photoexcitation, enabling its investigation on ultrafast time scales. Using Raman-active optical phonons of the monoclinic phase as a sensor, it could be shown that the *symmetry* of the restoring forces is lost within few femtoseconds, even before ionic motion occurs. Re-excitation of the non-equilibrated system, i.e. a pump-probe experiment of the excited state, furthermore unveils that the VO_2 has not reached the metallic phase yet at these early times after excitation. The optical response resembles that of the thermodynamically stable phase only after picoseconds [2].

[1] L. Rettig *et al.,* Phys. Rev. Lett. **108**, 097002 (2012).

[2] S. Wall, D. Wegkamp, L. Foglia, K. Appavoo, J. Nag, R. F. Haglund, J. Stähler, M. Wolf, *Nature Commun.* **3** (2012) 721; S. Wall *et al., Phys. Rev. B* **87**, 115126 (2013).

2.1.2 Ultrafast Carrier and Exciton Dynamics in Inorganic/Organic Hybrid Systems

The combination of inorganic semiconductors with organic molecules to hybrid systems (HIOS) promises superior functionality of the interface compared to a bare linear combination of the single material properties. Applications such as organic LEDs or solar cells would not only benefit from the high charge carrier mobility and stability of the inorganic compound in combination with the tunable optical properties of the organic molecules, but could also make use of interfacial hybrid states that facilitate, for example, charge or energy transfer between the constituents.

A promising candidate for such applications is zinc oxide (ZnO) due to its wide band gap (3.4 eV), n-type conductivity and abundance. Despite several decades of research, a full understanding of the surface properties of ZnO remains elusive. The group of *Julia Stähler* has investigated the electronic structure and ultrafast carrier dynamics of ZnO, its (10-10) surface, and interfaces with organic molecular layers with femtosecond (fs) time-resolved two-photon photoemission (2PPE) and optical spectroscopy. The non-polar ZnO(10-10) surface exhibits a downward surface band bending when terminated with atomic hydrogen, leading to the formation of a charge accumulation layer below the Fermi level E_F with a density on the order of 10^{-13} cm^{-2}, as shown in Fig. 2a. This goes along with a work function decrease of up to $\Delta\Phi$ = -0.6 eV due to charge donation from the hydrogen. Significantly stronger reduction of Φ can be achieved using the dipolar molecule pyridine with negative electron affinity (Fig. 2b). Here, due to the lack of Fermi level pinning, a huge work function decrease of $\Delta\Phi$ = -2.9 eV could be demonstrated in excellent agreement with *ab-initio* calculations by the group of *Patrick Rinke*, Theory Department. [1]

As illustrated in Fig. 2a, above band gap excitation of ZnO leads to the creation of excited electrons in the conduction band (CB). The subsequent ultrafast relaxation dynamics (see processes 1 & 2 in Fig. 2a) are monitored in time-resolved 2PPE by a second, time-delayed fs laser pulse ($h\nu_{probe}$). Fig.2c displays in false colors how the excited electron population relaxes on fs timescales by first electron-phonon scattering towards lower energies, and finally ends up in an excitonic surface state (SX) *below* E_F. The binding energy of more than 200 meV with respect to the bulk CB minimum is responsible for its long lifetime exceeding several 100 ps. Remarkably, such SX is not observed for $SrTiO_3$ (STO), another n-type transparent conducting oxide that exhibits also a 2D electron gas at its surface. Here, however, the charge density is at least one order of magnitude larger than for ZnO, which screens the electron-hole Coulomb attraction.

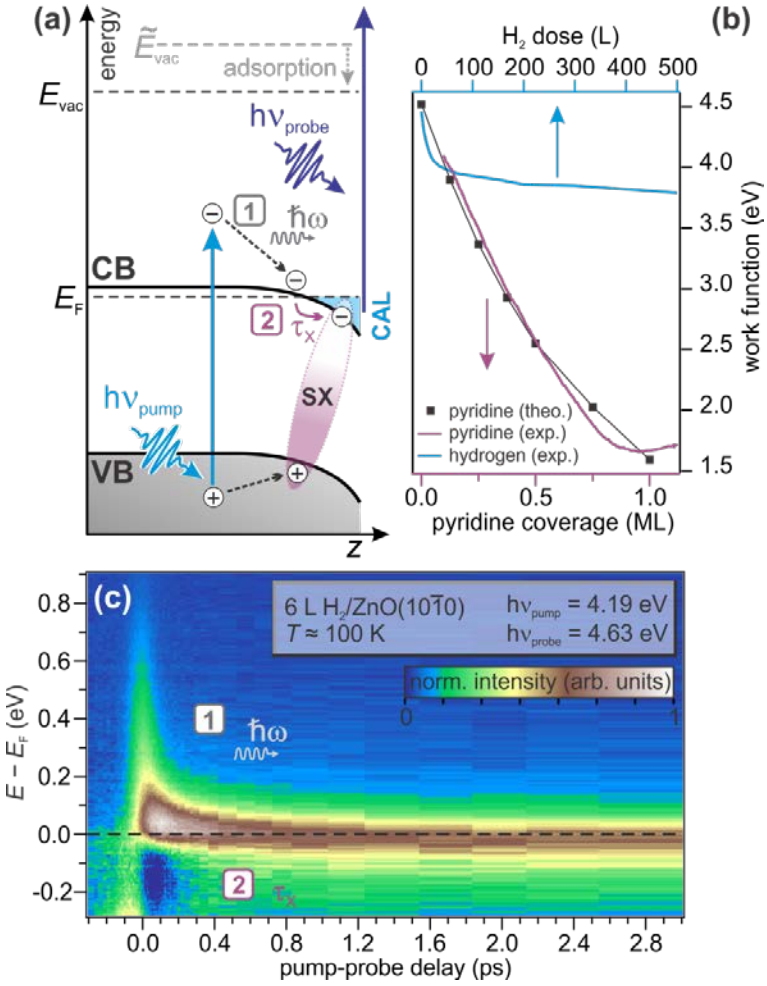

***Figure 2**: (a) Two-photon-photo-emission (2PPE) and scattering processes at the ZnO(10-10) surface. (b) Work function change due to adsorption of hydrogen (blue line) and pyridine (purple line, markers DFT calculation) (c) Ultrafast electron dynamics at the ZnO surface as probed by 2PPE spectroscopy. False colors represent additional electrons excited by the pump pulse. Hot carriers in the CB relax on fs timescales by optical phonon emission. After a few 100 fs, additional electrons are observed below E_F, indicating that a surface exciton has formed.*

The combination of ZnO with organic and optically active molecules is a crucial step towards application. The group has characterized the interface of the organic molecule SP6 (*2,7-bis(biphenyl-4-yl-)2',7'-ditertbutyl-9,9'-spirobifluorene*) with several oxide surfaces by means of non-resonant Raman spectroscopy down to the monolayer level. [2] First optical transient transmission experiments probing the LUMO → LUMO+1 resonance of the molecules point at efficient charge separation at the interface to ZnO. These are complemented by 2PPE studies of the electronic structure of the SP6/ZnO(10-10) interface.

[1] O. T. Hofmann, J.-C. Deinert, Y. Xu, P. Rinke, J. Stähler, M. Wolf, M. Scheffler, *J. Chem. Phys.* **139**, 174701 (2013).

[2] J. Stähler, O. T. Hofmann, P. Rinke, S. Blumstengel, F. Henneberger, Y. Li, T. F. Heinz, *Chem. Phys. Lett.* **584**, 74 (2013).

2.1.3 Electronic Structure of Surfaces and Interfaces

Among the low dimensional materials, graphene has an exceptional status since its electronic structure brings together solid state physics and quantum electrodynamics. Also many real-world applications are envisaged and thus an enormous research effort is under way.

The group of *Karsten Horn* has investigated graphene oxidation, for example using NO_2 and SO_2, and fluorination by interaction with PF_3 and XeF_2. The latter is a particularly interesting process, as "half-fluorinated graphene" has been found, where a fluorine atom is attached to every second carbon atom, is an insulating phase with a large band gap. A metastable phase exists which transitions back to the ground state under emission of blue light. The graphene bilayer has received specific attention since it is supposed to exhibit a small band gap, desirable for electronic switching applications. This has, however, failed to appear in electronic transport measurements. Photoemission data from our collaboration with groups at the Advanced Light Source (Lawrence Berkeley Laboratory), and TU Chemnitz, reveal the reasons for this: they show the coexistence of massive Dirac Fermions with massless ones which bridge the gap predicted from tight binding calculations (see Fig. 3, e.g. features C1 and C2) [1]. An analysis of the data shows that small (~ 0.2°) twists between the two layers, unavoidable even in the highest quality samples, lead to a gradual variation of the relative lateral arrangement of the carbon atoms in the two layers, (A - B and A - A stacking), which induces the above

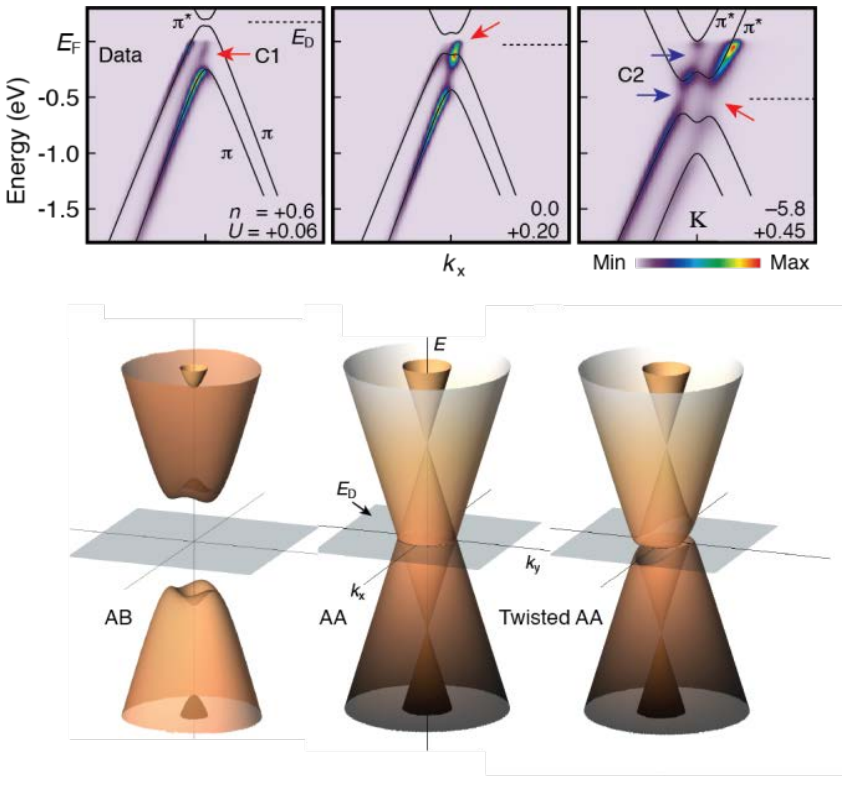

Figure 3: *Top: Experimental band dispersion of hole-doped (left), nearly-neutral (center), and electron-doped (right) bilayer graphene with overlaid lines from tight-binding band structure calculations for AB stacking, doping level n (units 10^{13} cm^{-2}) and Coulomb energy U (units eV). Bottom: Schematic band structure of bilayer graphene with AB, AA, and twisted AA stacking.*

coexistence of massive and massless states in the band structure, as shown schematically in Fig. 3 (bottom).

Furthermore, graphene's interaction with metals has been studied, for intercalation of metals (Cu, Co, Mn) in between graphene on Ir(111). Here, novel phases of these materials could be examined, since the intercalated atoms assume the (larger) lattice constant of the iridium substrate. Graphene deposited on ferromagnetic materials has been predicted to act as spin filter; hence we have studied magnetic interaction in such junctions using x-ray magnetic circular dichroism studies, for example in nickel-grapheme-cobalt "sandwich" layers, where the magnetic coupling between nickel and cobalt across the graphene layer was established. With the aim of graphene functionalization, the adsorption of ammonia and water on graphene has been studied on different substrates (Ni and Ir) showing that the strength of graphene's interaction with its substrate has a marked effect on the nature of the chemisorption interaction.

Further studies on Al-Pd-Mn and Al-Cu-Fe quasicrystals using bulk-sensitive hard x-ray photoemission (HXPES) have provided evidence for the existence of a large pseudogap near the Fermi level (characteristic for a Hume-Rothery mechanism), which is not observed in surface sensitive low energy photoemission, because the spectrum is affected by a metallic phase formed near the surface that masks the true bulk electronic structure [2].

[1] K.S. Kim *et al., Nature Materials* **12**, 887 (2013).

[2] J. Nayak *et al., Phys. Rev. Lett.* **109**, 216403 (2012).

2.1.4 Terahertz Physics: Low-energy Excitations and Control by THz pulses

The terahertz (THz) frequency range is of central relevance from a fundamental-scientific as well as from an application-related point of view. First, many elementary excitations in physical systems have transition energies on the order of 10 meV, for example excitations of quasi-free electrons in solids, crystal lattice vibrations, and excitons in semiconductors. As 1 THz corresponds to a energy of 4.1 meV, these modes can be probed resonantly and with sub-picosecond time resolution using THz electromagnetic field pulses. With recent advances in THz pulse generation providing electric-field amplitudes of ~1 MV cm^{-1} it has become possible to even drive and control such resonances on sub-picosecond time scales [1]. Second, bit rates in current information technology may soon approach the THz frequency range. Therefore, it is important to develop ultrafast techniques to manipulate electric currents or light at THz frequencies, for example with modulators and frequency shifters.

The group of *Tobias Kampfrath* makes use of ultrashort THz and optical laser pulses to investigate the interplay of low-energy excitations in complex materials and to control the properties of matter and light at the highest frequencies. Currently, the group focuses on electron spins in magnetically ordered solids, and studies new schemes to manipulate the dynamics and transport of magnetization. This goal also addresses basic questions of spin-phonon interaction and spin-orbit coupling.

Ultrafast spin transport: Future electronics will potentially not only make use of the electron charge as an information carrier, but also employ the electron spin (up/down) to encode the value of a bit. Successful implementation of such "spintronics" requires the transfer of electron spins through space as well as the manipulation of the spin state. These elementary operations should proceed at a pace exceeding that of today's computers, that is, at THz frequencies. To study and control ultrafast spin transport, a spin-polarized current pulse was launched in a Fe thin film through illumination with a femtosecond laser pulse [Fig. 4(a)].

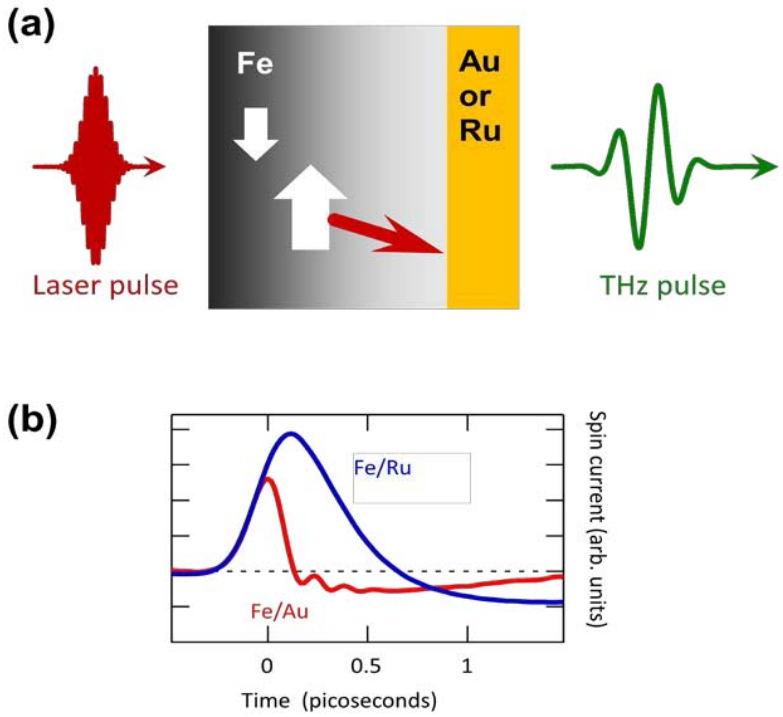

Figure 4: *(a) Schematic of generation, manipulation, and detection of THz spin currents. A femtosecond laser pulse launches a spin current from a Fe thin film (10nm) to a metallic cap layer (2nm) of either Ru or Au. While transport is slowed down in Ru (low electron mobility), it is fast in Au (high electron mobility). The spin current is converted into a charge current (inverse spin Hall effect), resulting in the emission of THz radiation whose detection allows extraction of the spin current dynamics. (b) Spin currents in Fe/Au and Fe/Ru as determined from the THz transients emitted by these heterostructures. The dynamics in Fe/Ru is much slower than in Fe/Au showing that adding layers of different mobility provide a route for manipulation of spin current bursts.*

Such a spin current arises because the laser pulse promotes spin-up electrons from d-type states with low band velocity into sp-like states with high velocity, whereas the minority spin-down electrons remain d-type and, thus, slow. To manipulate these bursts, the Fe film was contacted with another nonmagnetic film of either low (Ru) or high (Au) electron mobility. As a result, the spin transport in the Fe/Au heterostructure should proceed much faster than in

Fe/Ru. To probe the spin flow in a contactless manner, the inverse spin Hall effect is used that (through spin-orbit coupling) converts the longitudinal spin current into a transverse charge current, thereby leading to the emission of a detectable THz electromagnetic transient (see Fig. 4a). The measurements indeed verify the expected behavior: the spin current in Fe/Au exhibits a much faster dynamics than in the low-mobility Fe/Ru structure (see Fig. 4b). These findings are relevant because they show that the inverse spin Hall effect is still operative even at THz frequencies and that ultrafast spin currents can be delayed in a relatively simple manner [2].

Ultrafast spin manipulation: To manipulate the magnetization of a ferromagnetic metal film on ultrafast time scales, the sample is usually illuminated with a femtosecond laser pulse, thereby depositing energy in the electronic subsystem. The resulting reduction of magnetization on a 100-fs time scale is not yet understood, despite considerable experimental and theoretical efforts since the first experiments in 1996. To freeze out the complex electronic degrees of freedom, we recently focused on the ferrimagnetic insulator yttrium iron garnet (YIG, electronic band gap 2.8eV). Energy is brought into the system by exclusively pumping optical phonons with an intense THz pulse, thereby leaving the electronic subsystem unchanged. First results demonstrate a fast demagnetization with a 1.1 ps time constant, which is extremely surprising because spin-lattice relaxation in YIG is known to occur on much slower time scales of 1 ns and more. The results indicate that the coupling of spins with optical phonons is orders of magnitude stronger than with acoustic phonons. Currently a detailed study is under way to understand the microscopic origin of this observation.

Surface/interface sensitivity: So far, THz pulses have exclusively addressed the bulk properties of samples rather than their interfaces. The group of *Tobias Kampfrath* currently investigates the possibility to measure currents flowing at interfaces of topological insulators. Similar to the scheme of Fig. 4a, currents are launched by a circular polarized fs laser pulse in surface states of topological insulators and then measured by detecting the emitted THz electromagnetic transient (THz emission spectroscopy).

Manipulation of light on-the-fly: Besides controlling spins as information carriers, also new schemes for light manipulation have been tested. The basic idea is to couple light into a photonic structure and then vary its photonic mode structure by applying a femtosecond control pulse. The light inside the structure will then adiabatically follow these changes and finally emerge with a modified shape. To test this scheme, a photonic crystal was used and light at the telecommunication band around 200 THz coupled into it. By applying a spatially shaped femtosecond control pulse, free charge carriers were induced in selected regions of the

photonic crystal, thereby (1) shifting and (2) even tilting the dispersion relation (frequency vs wave vector) of the structure. As a result, the probe pulse followed these changes adiabatically, resulting in (1) a blueshift (by up to 0.3 THz) and (2) a compression of the pulse spectrum (by up to 10%) with high efficiency (up to 80%). The frequency shifting is potentially useful for shifting signal trains in optical telecommunication to different frequency channels, whereas the spectral compression may find application as a spectral lens [3].

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2.1.5 Ultrafast Spin Dynamics in Epitaxial Metallic Multilayers

Ultrafast spin dynamics induced by transport of photoexcited spin polarized carriers is of fundamental interest for magnetic applications like spintronics and data storage. To study the underlying elementary processes on femtosecond time scales, the group of *Alexey Melnikov* has developed a time domain approach that probes the spin dynamics induced by hot carriers (HC) in a back-pump-front-probe scheme. In a first experiment the transport of spin polarized HC through a Au/Fe/MgO(001) stack has been demonstrated [1]: Thereby, optical excitation of hot carriers in the Fe film is followed by superdiffusive transport to the Au surface where the carrier density and spin polarization are detected by magneto-induced second harmonic (SH) generation. Later on it has been shown that the ballistic HC fraction can be controlled by the Fe layer thickness and the duration of the ballistic spin current pulse can be as short as 30 fs. The spin dynamics in Fe was studied by a combination of SH and magneto-optical Kerr effect.

To proceed towards a new concept of metal-based elements for femtosecond spintronics, Fe/Au/Fe/MgO(001) stacks with different thickness of Fe layers were used, which allow for parallel or anti-parallel alignment of the magnetizations M_E and M_C in emitter and collector (see Fig. 5). The SH electric field consists of E_{even} and E_{odd} components which are even and odd with respect to magnetization reversal. The relative pump-induced variation $\Delta_{odd}=\Delta E_{odd}/E_{odd}$ characterize variations of the magnetization at the interfaces. Since optical phases are sensitive to interface properties, E_{odd} generated at Fe/Au and Fe/MgO interfaces can interfere constructively or destructively, which leads, respectively, to large or small magnetic contrast $\rho \approx 2\, E_{odd}/E_{even}$. In the first case Δ_{odd} is sensitive to the average (sum) of the

magnetizations at both interfaces (Fig. 5b) while in the second case Δ_{odd} monitors variations of the difference between two interface magnetizations (Fig. 5a).

In Fe/Au/Fe structures with parallel alignment, minority HC which traverse the Au layer within 40 fs [1] are accumulated at the collector Fe/Au interface. This reduces the interface M_C and thus the absolute value of E_{odd}, which results in positive Δ_{odd} (Fig. 5b) due to destructive interference of interface contributions. In the case of antiparallel alignment, ballistic HC (minority HC with respect to M_E) are majority HC with respect to M_C and thus are not accumulated at the interface. The interface demagnetization increasing Δ_{odd} (Fig. 5b) occurs upon the arrival of diffusive HC (now with negative spin) on a timescale of 200 fs [1]. Finally, the HC transport leads to the demagnetization of the Fe/Au interface and occurs on the timescale of ballistic or diffusive HC transport for parallel or antiparallel configurations, respectively.

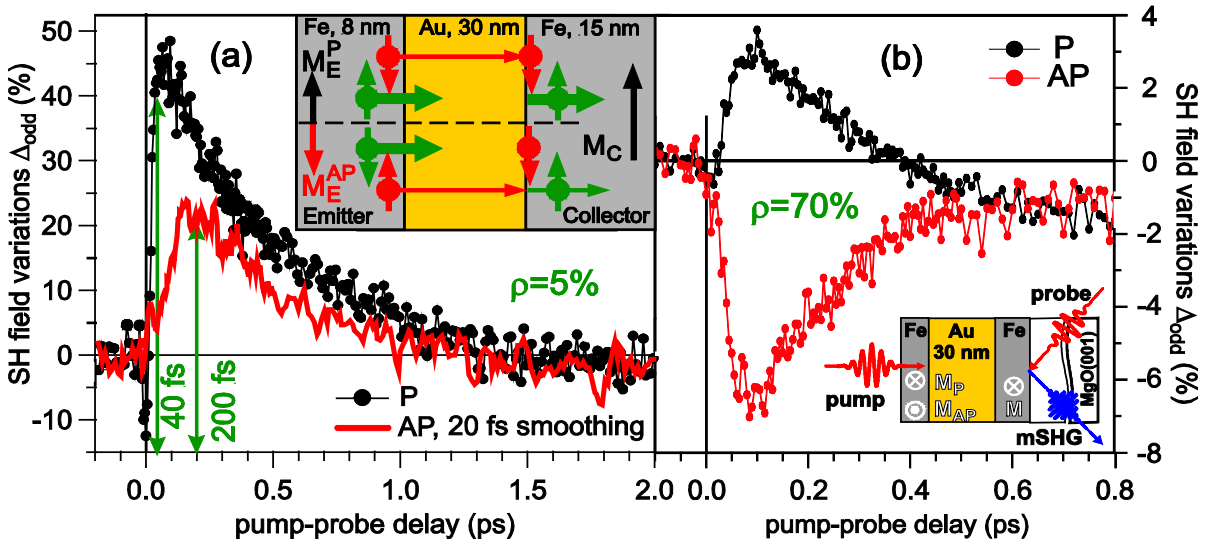

Figure 5: *Pump-induced changes of the odd second harmonic (SH) field Δ_{odd} which probes the spin dynamics in Fe/Au/Fe structures for (a) a 8 nm-thick emitter and small collector magnetic contrast ρ=5% (a) and (b) a 5 nm-thick emitter and large contrast ρ=70%. The parallel (P) and anti-parallel (AP) orientations of magnetizations in the emitter (M_E) and collector (M_C) are shown in the experimental schemes in the insets. Inset (a): The large ballistic propagation length of majority HC in Fe $\lambda^{\uparrow}_{Fe}>>\lambda^{\downarrow}_{Fe}$ leads to more effective emission of majority HC (thick green vs. thin red arrows) and to the accumulation of minority HC at the Fe/Au interface of the collector. However, in Au $\lambda^{\uparrow}_{Au}<<\lambda^{\downarrow}_{Au}$ and hot carrier transport is ballistic (fast) for minority and diffusive (slow) for majority carriers (long red vs. short green arrows).*

In Fe/Au/Fe structures with large magnetic contrast (Fig. 5b), the role of ballistic HC providing small changes of interface M_C due to their small concentration is not significant and we can consider only diffusive (majority with respect to M_E) HC. The reversal of M_E permits to alternate between positive and negative variations of M_C on a femtosecond timescale, which is promising for the future development of spintronics devices.

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2.2 Molecular Processes at Interfaces

Understanding molecular processes at a microscopic level of single molecule reactions, interfacial charge and energy transfer and vibrational dynamics provides fundamental insight into surface reactions. Studies of molecular processes at interfaces are performed by several groups in the department which employ complementary techniques with high spatial resolution as well as chemical sensitivity using vibrational or x-ray spectroscopy. In these studies, surface reactions and molecular rearrangements are stimulated by thermal activation, excitation by light or interfacial charge transfer. These are complemented by computational studies of biomolecular machines and pattern formation in electrochemical systems.

2.2.1 Nanoscience with Functional Molecules

The research activities in the group of *Leonhard Grill* focus on the investigation and manipulation of single functional molecules on surfaces by scanning tunnelling microscopy (STM), preferentially at low temperatures of 5 K. This method makes it possible to image single molecules with very high spatial resolution, and to manipulate them by chemical forces, tunnelling electrons or the electric field in the junction.

An important class of functional molecules are molecular switches that exhibit at least two stable states with characteristic physical and/or chemical properties. The research group has studied various types of molecular switches on metal surfaces. One example follows previous work of the group on azobenzene derivatives with four *tert*-butyl side groups, but here these groups were attached at slightly different positions of the benzene rings (*para* instead of *meta* position). These molecules are found to be prochiral on a Au(111) surface, and enantiomerically pure islands are observed. In manipulation experiments chirality switching is observed, where single molecules change from one enantiomer to the other, probably by a twofold internal rotation. In another study, the group has investigated covalently connected multiple switching systems where the coupling of the different switching units is of particular interest. It could be shown that bisazobenzene molecules with two switching units can be deposited onto a Au(111) surface under clean ultrahigh vacuum conditions, and that they self-organize in large ordered islands of different arrangements depending on their chemical structure. While lateral manipulation can be achieved, no switching processes could be induced by voltage pulses over different parts of the molecules and in different environments. When changing the switching unit and studying imine derivatives on Au(111), it was found that the molecular layer gradually transforms from a nearly complete *trans*- to a nearly complete *cis*-monolayer with increasing molecular coverage [1].

Another focus in the field of functional molecules is on so-called nanomachines, which are objects with dimensions of few nanometers that perform work – a key vision in molecular nanotechnology. Functional molecules are of particular interest in this regard and the research group has studied so-called motorized nano-cars which should move on a surface upon illumination, essentially as a result of an isomerization process of the "motor" unit. After the very difficult synthesis, the intact deposition of such a complex molecule under ultrahigh vacuum conditions represents a central challenge. It could be shown that intact molecules can be sublimed in vacuum onto a Cu(111) surface and that they can be imaged there as individual entities [2]. The molecular appearance in the STM images is in good agreement with the molecular dimensions in the gas phase, and according to their chemical structure, two typical conformations are identified. However, lateral motion on the surface, in particular by activating the molecular motor, has not been achieved so far.

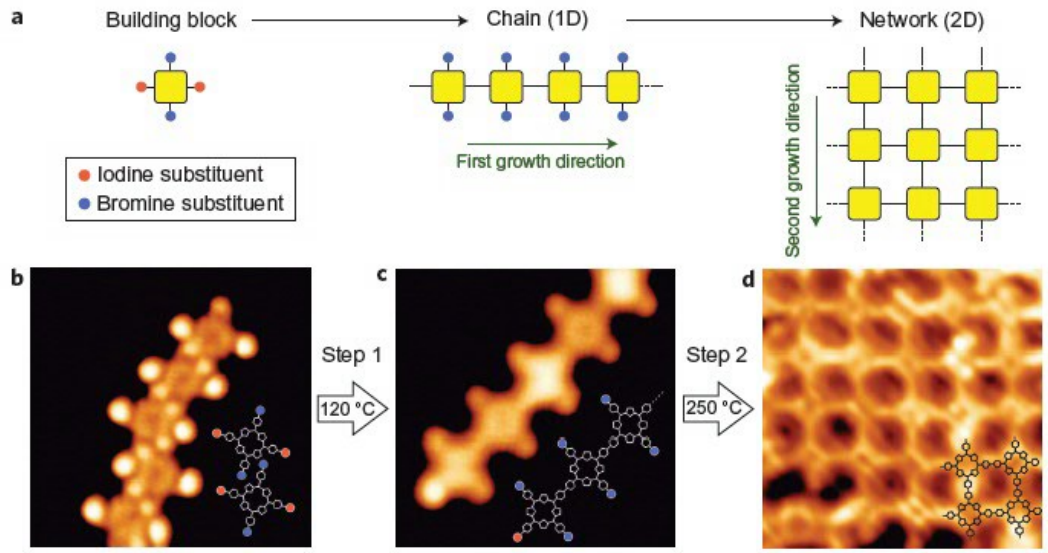

Figure 6: *Hierarchical growth following sequential thermal activation. (a) Scheme of the activation mechanism. Arrows indicate the different growth directions of the two sequential steps. (b–d) STM images (8 × 8 nm^2 in (b,c) and 10 × 10 nm^2 in (d)) of trans-Br_2I_2TPP molecules on Au(111): after deposition (at 80 K, (b)), after heating to 120°C (c) and after further heating to 250°C (d). The corresponding chemical structures are indicated.*

In addition to the fundamental understanding of physical processes and chemical reactions of single molecules on a surface, the research group is interested in the linking of molecular building blocks on surfaces by covalent bonds, i.e. on-surface polymerization that is based on previous work by the group (*Nature Nanotech. 2, 687 (2007)*). An important issue in this regard is the precise location of the molecular activation process, i.e. the dissociation of Br substituents from the molecular building blocks on the surface. By comparing flat and stepped gold surfaces, the research group could precisely identify the kink sites at the step edges as the catalytically active sites because there is a high preference for activation for that side of the

molecules that points towards these sites [3]. After heating the surface, the step edges create polymers that run parallel over the surface, which is of interest for a pre-alignment in future polymerization processes. Another study has focused on the complexity of the molecular structures produced by on-surface polymerization. All approaches so far have relied on a single step process, thus resulting in very simple structures. The research group has extended this method by introducing a hierarchical growth process based on a sequential activation of the molecular building blocks as sketched in Fig.1a [4]. The molecular building blocks (*trans*-Br_2I_2TPP molecules) exhibit two types of halogen substituents (bromine and iodine) that are dissociated from the molecular core at different temperatures, due to their characteristic binding energies. This results in a programmed reactivity in which in the first step, only the iodine atoms and in the second step the bromine atoms are cleaved from the molecule. Starting from the intact molecules (Fig.1b, the two halogen species appear at different height), this leads to polymer chains after the first step (Fig.1c). It is important to note that these polymers were linked exclusively at the former iodine sites, which is visible in the bright lobe, i.e. iodine, at the terminus and darker lobes, i.e. bromine, sideways in Fig.1c. After a second heating process, the polymer chains are connected sideways in a zipping mechanism, resulting in a two-dimensional network (Fig.1d). In addition to these homomolecular polymers, also copolymers could be formed by mixing two different building blocks and the resulting structure could not be formed in a conventional single-step linking process [4].

The research group has used the expertise in on-surface polymerization for the formation of graphene nanoribbons (following a recipe by R. Fasel and co-workers) on a Au(111) surface [5]. The objective was here not the polymerization process itself, but the characterization of charge transport through the molecular wires. By pulling individual graphene nanoribbons off the surface with the STM tip, the current decay along the polymer, which is the key property for the characterization of charge transport, can be determined. In particular, this was done for various electron energies, thus for the first time correlating the conductance of individual molecules with their electronic structure from the HOMO over the gap up to the LUMO. It was found that the charge transport is most efficient if the electron energy matches either the HOMO or the LUMO level, which are both delocalized along the ribbon [6].

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2.2.2 Molecular Manipulation and Spectroscopy at the Nanoscale

Molecular processes and functions are fundamental in nature and also play a key role for molecular devices in future nanotechnology. Low-temperature scanning tunneling microscopy (LT-STM) permits not only to directly observe adsorbate dynamics at the single-molecule level, but also to precisely manipulate adsorbates and to control chemical reactions of single molecules by using chemical forces between the STM tip and adsorbates, the injection of tunneling electrons as well as the electric field in the junction. The research in the group of *Takashi Kumagai* focuses on the investigation of individual molecules and molecular ensembles using LT-STM and tip-enhanced Raman scattering.

Direct observation and control of single molecule dynamics: It is known that local environments of individual molecules have a significant impact on chemical processes in condensed phases via the deformation of the potential landscape. However, such local influences have rarely examined at the level of individual molecules in experiments and the effects of nearby single atoms or molecules on chemical reactions have not been studied so far.

Takashi Kumagai and coworkers have achieved precise control of an intramolecular hydrogen transfer reaction (tautomerization) in single porphycene molecules adsorbed on Cu(110) [1]. Single porphycene molecules were imaged at 5 K and found to have a *cis* configuration in which the inner H-atoms are located on one side in the cavity (Fig.7a and b).

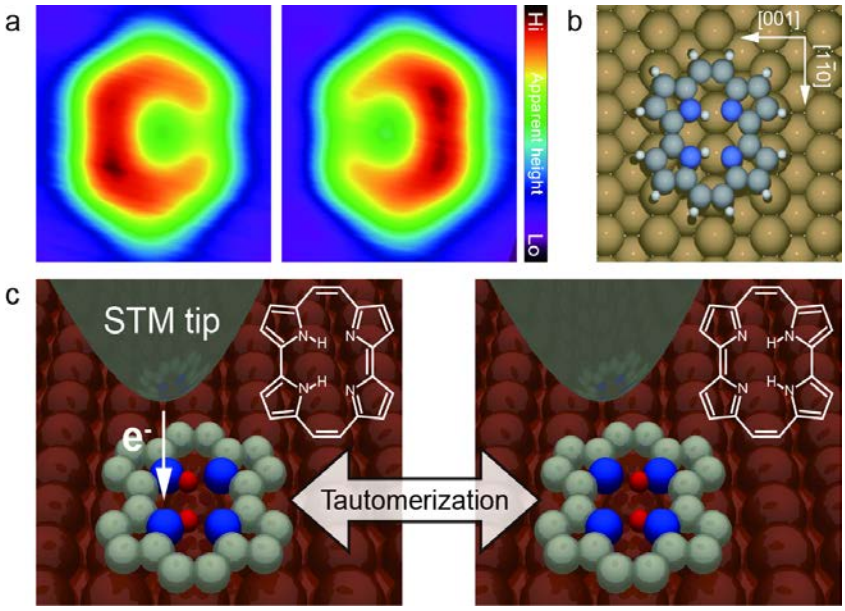

Figure 7: *Porphycene molecules on a Cu(110) surface (a) STM images of a single porphycene molecule. (b) The optimized structure determined by the density functional theory calculations. Porphycene molecule favors cis*

Although the molecule is stationary at low bias voltages, the *cis-cis* tautomerization is induced at higher voltages and the STM image shows a flipping between the two states (Fig.7a and c). The efficiency of tautomerization depends on the lateral STM tip position with respect to a molecule, i.e., atomically precise location of the electron injection into the molecule, and shows maxima when the electron is injected over the position where the inner H-atoms exist. The tautomerization is also thermally induced at elevated temperatures and a barrier of 168±5

meV is determined from an Arrhenius plot. Furthermore, an isotope effect using deuterium-substituted porphycene in which the inner H-atoms are replaced by deuterium revealed that the STM-induced tautomerization is triggered by vibrational excitation via inelastic electron tunneling processes.

Remarkably, the probability for tautomerization can be precisely tuned by placing a single Cu adatom nearby a porphycene molecule. Cu adatoms are controlled by STM manipulation and the rate of tautomerization is significantly affected depending on the relative position between the adatom and molecule. The results demonstrate the high sensitivity of an elementary reaction to the exact position of individual atoms with respect to the molecule, surprisingly also at rather large distances much larger than a van der Waals radius [1].

The group extended this study to molecular assemblies and observed cooperative effects in the tautomerization process. Tautomerization is almost quenched in the dimer, but it becomes active in a specific molecules within larger clusters. It is revealed that even the hydrogen arrangement in the cavity of a neighboring molecule influences the tautomerization, causing positive and negative cooperativity. The results highlight the importance of local environments in the vicinity of individual molecules, and demonstrate the potential to regulate a single-molecule function. It is expected that this control over chemical reactions by subtle changes in the atomic-scale environment can be extended to other systems and will thus improve the understanding of fundamental molecular processes. It might even allow the tuning of molecular processes in functional nanostructures, which would pave the way towards information processing at the single-molecule level.

Tip-enhanced Raman spectroscopy: Tip-enhanced Raman spectroscopy (TERS) is one of the possible techniques to probe both adsorbate geometries and local vibrations, which provides fruitful insight into physical and chemical processes on surfaces. In TERS an STM tip is employed to generate a plasmonic field to enhance the Raman scattering of adsorbates as well as imaging their local structure with sub-molecular resolution. Within the last few years a TERS setup in ultra-high vacuum (UHV) has been developed to achieve a local spectroscopy at the single-molecule level [2]. Current experiments investigate graphene nano-ribbon (GNR) on a Au(111) surface, an attractive material in nano-science and technology. Local defects and alkali doping of GNR are expected to have a significant impact on its properties and the understanding of such influences is of importance for potential device applications.

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2.2.3 Real-time Observation of Photoinduced Surface Reactions

A longstanding dream has been to follow the dynamics of chemical reactions in real time and directly observe each elementary step. While for photoinduced reactions in the gas phase a remarkable level of sophistication has been reached, similar breakthroughs have not be achieved for heterogeneously catalyzed reactions at surfaces. Fundamental questions in surface reaction dynamics address how charge and energy is transferred between the adsorbates and the surface, or how the electronic structure is rearranged within the molecular unit during the elementary reaction steps. The real-time observation of chemical bond formation at surfaces requires techniques which are sensitive to the chemical state and simultaneously enable real-time probing of elementary steps with femtosecond time resolution.

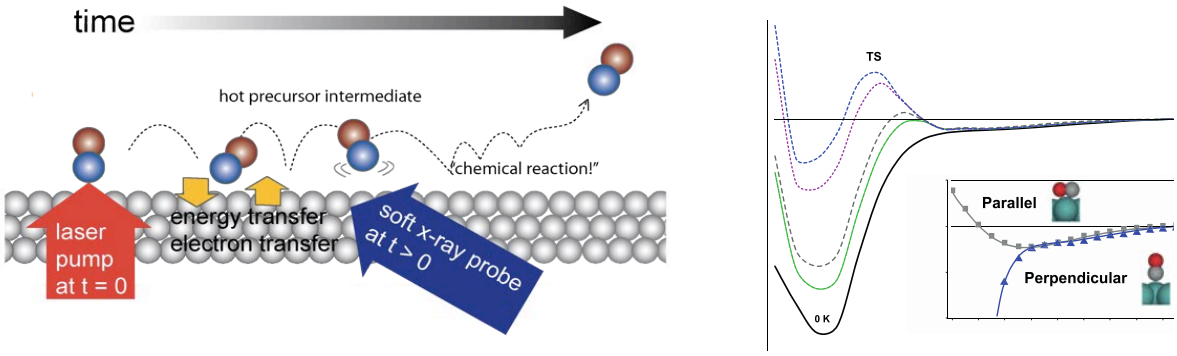

Figure 8: *(left) Schematic illustration of elementary steps in the desorption process of carbon monoxide. The reaction is stimulated by an ultrashort optical laser and probed with soft x-ray spectroscopy using femtosecond x-ray pulses. (right) Free energy diagram along the reaction pathway for CO on Ru(0001) exhibiting a chemisorption well and a shallow precursor which are separated by a temperature dependent barrier[2].*

Both x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) have the unique ability to provide an atom-specific probe of the electronic structure. With the advent of femtosecond x-ray lasers these techniques can now be transformed into time-resolved probes of transient chemical species at surfaces. For real-time probing of surface reactions, the chemical process must be initiated by a time-correlated ultrashort laser pulse, a concept which has been studied previously in the Department by the group of *Martin Wolf*: Femtosecond laser excitation of an adsorbate-covered metal surface can serve as a ultrafast "trigger" of surface reactions, whereby the non-adiabatic coupling between transiently excited metal electrons and adsorbate vibrational degrees of freedom mediates chemical processes such as associate desorption of the reactants [1].

Our collaboration with Anders Nilsson, and groups from Stanford, Stockholm, Hamburg and Berlin has performed a series of surface dynamics experiments, exploiting the unique

capabilities of the Stanford x-ray free electron laser, LCLS, to probe the atom specific electronic structure changes during surface reactions induced by a strong laser pulse. Fig. 8 (left) schematically illustrates the basic principle of these experiments, exemplified for the simple case of desorption. The first experiment addressed desorption of CO from Ru(0001) induced by a 400 nm laser pulse [2]: By combining XAS and XES in the O 1s region both occupied and unoccupied states of the CO-metal bond ($5\sigma/1\pi$, d_π, $2\pi^*$ states) were probed as a function of time delay between the optical and x-ray laser pulses, demonstrating for the first time the feasibility of time-resolved resonant inelastic x-ray scattering (RIXS) in surface chemistry. Remarkably, a substantial transient weakening of the CO-Ru bond was observed, persisting for ~20 ps whereby ~30% of the *adsorbed* CO molecules resembled an electronic structure close to free CO. From DFT calculations including van-der Waals contributions of the free energy along the reaction coordinate (potential of mean force) a consistent picture could be obtained: The desorption dynamics of CO from Ru(0001) is governed by a transient energy landscape with a chemisorption well and a shallow precursor state, which are separated by a transient (entropic) barrier [2]. During desorption, a fraction of the vibrational excited CO molecules are transferred into the precursor state and are stabilized by the barrier prior to desorption (see Fig. 8 right). It should be noted that such insight into the dynamics of an excited (i.e. reacting) adlayer could not be revealed with established techniques like molecular beam scattering.

Further analysis demonstrated that by using resonant XES, selective excitation of different ensembles within the excited CO adlayer becomes possible, which exhibit different dynamical behavior and coupling to substrate electrons and phonons [3].

More recently, the technique of time-resolved RIXS has been successfully applied at LCLS to also study associative surface reactions such as ultrafast photoinduced CO_2 formation and hydrogenation of CO on ruthenium. Future planning includes the development of a dedicated surface science endstation with two XES spectrometers for molecular orientation sensitive detection and optimized sensitivity.

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2.2.4 Interfacial Molecular Spectroscopy

The structure, reactivity and dynamics of molecules at interfaces are addressed by the group of *Kramer Campen* using the interface specific nonlinear optical technique of vibrational sum frequency (VSF) spectroscopy. Furthermore, vibrational and structural dynamics are directly probed by time-resolved infrared pump / VSF probe experiments. Over the last two years three systems have been studied: the air/water interface, CH_4 and C_2H_4 dissociation and reaction at the Ru(0001) surface in UHV, and water dissociation and reaction at the α-Al_2O_3(0001) surface both in UHV and under ambient conditions. For UHV studies a molecular beam source was developed to prepare translational and vibrational non-thermal distributions of impinging molecules, e.g. for dissociative adsorption. Under ambient conditions conventional VSF spectroscopy has been extended either by directly sampling structural dynamics, in the case of the air/water interface, or by probing low-frequency modes (e.g. the surface phonons of α-Al_2O_3) not previously observed.

Air/Water Interface: Prior VSF and simulation studies have shown that, from the H_2O molecule point of view, interfaces between liquid water and hydrophobic surfaces have a large population of water molecules with one non-hydrogen bonded (free) OH groups. Recent theoretical work has made clear that quantitative understanding of hydrophobic solvation requires an understanding of the ultrafast structural dynamics of these free OH groups [1]. We have recently applied both experiment, i.e. time resolved VSF spectroscopy (in collaboration with M. Bonn, MPI for Polymer Science), and simulation (in collaboration with A. Vila Verde, MPI of Colloids and Interfaces), to understand the dynamics of the free OH. Taken together, this work suggests: (1) The free OH rotates 3x faster than hydrogen bonded OH groups either at the air/water interface or in bulk water [2, 3]. (2) The free OH is structurally heterogeneous on picosecond timescales: free OH groups closer to the vapor have a different orientational distribution and persist longer before rotating down towards the liquid than free OH groups closer to bulk water [2-4]. (3) Relaxation of vibrationally excited free OH groups proceeds by a combination of energy transfer between the free and hydrogen bonded OH within a single water molecule (2/3 of relaxation occurs via this pathway) and structural relaxation (1/3) in which the excited free OH rotates towards the liquid and forms a hydrogen bond [5].

Methane and Ethylene at Ru(0001): Interaction of CH_4 and C_2H_4 with metal (oxide) surfaces may lead to their decomposition and the formation of higher hydrocarbons. To study this chemistry we have characterized the interaction of CH_4 and C_2H_4 with the Ru(0001) surface in UHV using temperature programmed desorption (TPD) and VSF spectroscopy as a

function of sample temperature and carbon coverage. To overcome the dissociation barrier of CH_4 a molecular beam source was employed with CH_4. By probing the CH spectral response (2800-3100 cm^{-1}) during the decomposition of both CH_4 and C_2H_4 we have tracked the relative stability of all one and two carbon, CH containing species. We find that both the relative stabilities and rates of interconversion of the various hydrocarbon species present are strongly depending on surface coverage and temperature (Fig. 9 left).

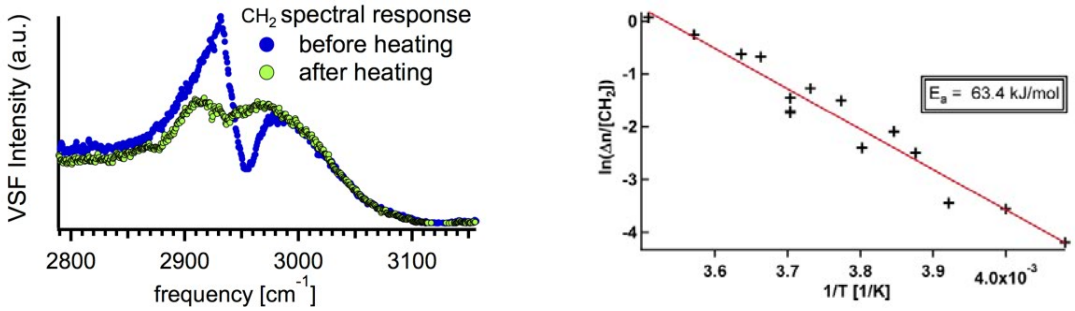

Figure 9: *Left: Measured VSF spectra showing the decrease in CH_2 spectral amplitude on heating above 350 K. Right: Change in CH_2 resonance amplitudes plotted as a function of sample heating temperature on an Arrhenius plot illustrating CH_2 to CH conversion. In the low coverage limit the E_a for CH_2 dehydrogenation is 14 kJ/mol.*

A dramatic change in reactivity was observed above 350 K. Both computation (in collaboration with S. Levchenko, Theory Department) and experiment clarify that below 350 K adsorbed hydrogen blocks energetically favorable surface sites and that above 350 K recombinative desorption of H_2 sets in. This coverage dependence of hydrocarbon reactivity is manifested by the thermal stability of CCH_2/CCH species and the thermal activation for the conversion of CH_2 to CH (Fig. 9 right).

Water Dissociation and Surface Reconstruction at α-Al_2O_3(0001): Most properties of Al_2O_3 surfaces change dramatically on exposure to even submonolayer concentrations of water. To gain insight into the mechanism(s) of such change, we here probe the elementary steps of single molecule water dissociative adsorption on α-Al_2O_3(0001) and the changes in surface structure they induce. Water adsorption was studied by preparing a well defined α-Al_2O_3(0001) surface in UHV and then dosing this surface, using the molecular beam source, with D_2O seeded in He. Next the spectral response of the frequency range corresponding to dissociated water molecules was characterized as a function of sample temperature. This data show five resonances whose relative frequencies, and intensities as a function of experimental geometry, are consistent with computation (collaboration with P. Saalfrank, University of Potsdam). Based on this agreement, these five modes are assigned to fragments resulting from

three different predicted water dissociative adsorption channels. By tracking the thermal stabilities of these fragments, it was demonstrated that models of water surface reactivity must explicitly account for surface coverage effects.

While the water OD stretch is a useful probe of dissociative adsorption, it tells us little about concurrent surface reconstruction. To probe surface reconstruction both within and outside UHV we have extended VSF spectroscopy to infrared frequencies as low as 750 cm^{-1} to probe also α-Al_2O_3 surface phonons. As expected, the amplitudes/line shapes of these modes are dramatically changed by treatments known to dehydrate/rehydrate the surface. Normal mode calculation confirms our assignment and allows a full microscopic description of each mode. This work demonstrates that surface reconstruction outside of UHV can be tracked by optical probing of surface phonons.

Electron solvation at interfaces: The reactivity of excess electrons in aqueous environments is highly relevant in various disciplines ranging from atmospheric chemistry to photosynthesis. The group of *Julia Stähler* has studied excess electrons at ice-vacuum interfaces created by photoexcitation of the metal template and also by low-energy electron impact. Their relaxation and lifetime of several seconds was determined using two-photon photoelectron (2PPE) spectroscopy. In addition to pure charging, permanent changes to the surface dipole and therefore work function (up to 1 eV) were also observed, which may result from a build-up of OH^- induced by the trapped electrons. In combination with simple model calculations, these work function modifications were also used to identify the impact of work function distributions on photoelectron experiments [6].

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2.2.5 Computational Dynamics of Protein Machines

The group of *Alexander Mikhailov* performs computational studies of biomolecular systems. Protein machines play a fundamental role in biological cells. Operating as molecular motors, they transport load over filaments and microtubules or generate mechanical force. They can perform operations with other molecules, such as DNA or RNA, and cut, glue or unwind them. Protein machines can act as enzymes, facilitating reaction events, or as pumps transporting ions across lipid bilayers. In all their functions, the operation of such molecular

devices is based on the ability of proteins to fold into a definite conformation and to perform ordered mechanochemical motions, induced by binding and detachment of ligands or by chemical reactions with them. All machines require energy for their operation and this energy is usually provided through ATP molecules. Understanding the dynamics of protein machines is essential in biophysics of a cell; it can also open a way for engineering of synthetic molecular devices with similar properties.

The cycles of protein machines involve slow conformational motions on the scales of milliseconds or longer. Therefore, they cannot be reproduced in current full molecular dynamics simulations and coarse-grained descriptions are required. One such description consists in modeling a protein as an elastic networks (EN) formed by particles (amino acids) with effective elastic interactions between them. EN models are popular and often used in the context of normal-mode analysis. A special feature of the investigations in the group of *Alexander Mikhailov* is that complex nonlinear dynamics is considered in the EN models of various real protein machines through numerical simulations. The research is undertaken in cooperation with partners in Japan, Canada, Belgium and Taiwan.

Myosin is the molecular motor responsible for muscle contraction and for transport along actin filaments in biological cells. It has been extensively investigated in the group of T. Yanagida, Osaka University, and at RIKEN Quantitative Biology Center in Japan. Their recent single-molecule experiments have shown that this protein acts as a "strain sensor", so that its affinity towards the actin filament is strongly modulated by the applied external forces; this behavior is of principal importance for the motor function. Numerical analysis of responses of myosin molecules to external forces could not only confirm the experimental results, but also disclose the nature of the strain-sensor behavior in this macromolecule [1].

Actin is a structural protein able to form, through polymerization, long filaments which build the skeleton of a cell and are also used for intracellular transport by myosin motors. The filaments are permanently growing at one end and dissolving at the other end through the process of "treadmilling". While it was known that ATP is needed for filament growth, its role in the polymerization process remained unclear. The EN simulations have revealed that, when ATP binds to an actin monomer, this stabilizes its closed conformation already present as a metastable conformational state in the ATP-free molecules. Such closed conformation much better fits the growing filament end and thus the polymerization rate is greatly enhanced. The metastable conformational states of actin were previously detected in single-molecule FRET experiments by T. Yanagida with coworkers.

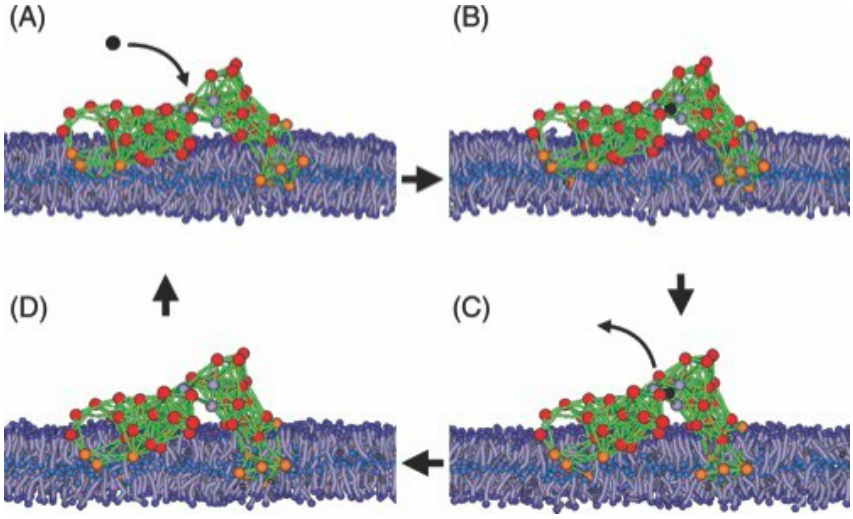

Figure 10: *The cycle of a membrane machine. (A) The ligand binds to the machine; (B) the machine conformation changes from the open state to the closed state; (C) the reaction takes place and the ligand is released; (D) the machine returns to its open state.*

Many protein machines operate as active inclusions in lipid bilayers forming *biological membranes*. In such cases, additional complications arise because of the necessity to incorporate lipids and the solvent into a model. Together with R. Kapral, Toronto University, and researchers from the National Central University in Taiwan, fast and efficient methods for such simulations, combining the EN description for proteins with a coarse-grained description for lipids and the multiparticle collision dynamics for the solvent, were developed [2,3]. Fig.10 shows a cycle of a model protein machine attached to a lipid bilayer. An important result is that strong hydrodynamic flows in the lipid bilayer, induced by operating machines, were found, indicating that hydrodynamic effects should play a principal role in interactions between active membrane inclusions. The swimming behavior of active machines in biomembranes has been further discussed [4].

Furthermore, a statistical analysis based on the NMR data for conformational ensembles in a set of 1500 different proteins was analyzed and used improvement of the accuracy of the EN method (with Y. Dehouck, ULB in Belgium). In addition to the work on biomolecular systems the group has also investigated complex dynamics in networks.

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2.2.6 Electrochemical Dynamics

The co-existence of distinct timescales is an important feature in most natural and man-made systems exhibiting kinetic instabilities and oscillatory behavior. The group of *Markus Eiswirth* has concentrated on different aspects of non-linear dynamics in electrochemical systems from both experimental and theoretical points of view. For electrochemical reactions taking place at the solid/liquid interface, experimentally recorded time-series are often subjected to a long-term surface deactivation process that acts as a slowly evolving bifurcation parameter. Recently, mechanistic aspects associated to this process during the catalytic electro-oxidation of small organic molecules have been investigated. Experiments and numerical simulations were carried out in cooperation with Hamilton Varela, University of Sao Paulo at Sao Carlos, Brazil, and Jaeyoung Lee, Ertl Center for Electrochemistry and Catalysis, Gwangju, Korea).

Fig. 11 shows results for the electro-oxidation of formaldehyde on platinum in terms of the time-trace of the electrode potential, *U*, obtained under a slow galvanodynamic sweep [1]. The deliberate increase of the applied current mimics the spontaneous and slow poisoning process, also observed in many other systems. Therefore, the oscillatory patterns depicted in (c - h) and monitored at different applied currents appear spontaneously after setting a given fixed current. For a certain kind of oscillation or waveform, the mean electrode potential increases in time (Fig. 11 a). The system thus consists of two parts: the core oscillator, associated to the main dynamics or the oscillations themselves, and a slowly evolving drift.

The coupled system is characterized by the co-existence of two disparate time-scales. After each cycle, the surface would ideally return to its original state and, under those conditions, oscillations would persist as long as the reaction proceeds. Conversely, the slowly evolving parameter may arise from the fact that the surface is not completely restored to its initial conditions after one oscillatory cycle. Since the drift in acidic media is always accompanied by an increase in the mean electrode potential, it is likely that the surface is slowly getting oxidized after each cycle.

Based on the above conjectures and also on *in situ* infrared and *online* mass spectrometry, one can describe the interplay between slow and fast processes in terms of the surface coverage of adsorbates. The main aspects are summarized in the reaction scheme in Fig. 11 (bottom). Generally speaking, the electro-oxidation of organic molecules on platinum proceeds via parallel pathways: the direct pathway, with an active intermediate (adsorbed formate in this scheme) transforming to carbon dioxide relatively fast, and the indirect route, where adsorbed carbon monoxide is oxidized at comparatively high overpotentials in a Langmuir-

Hinshelwood step with adsorbed oxygenated species. Steps 1 to 6 in this scheme are associated to oscillations and thus belong to the core subsystem

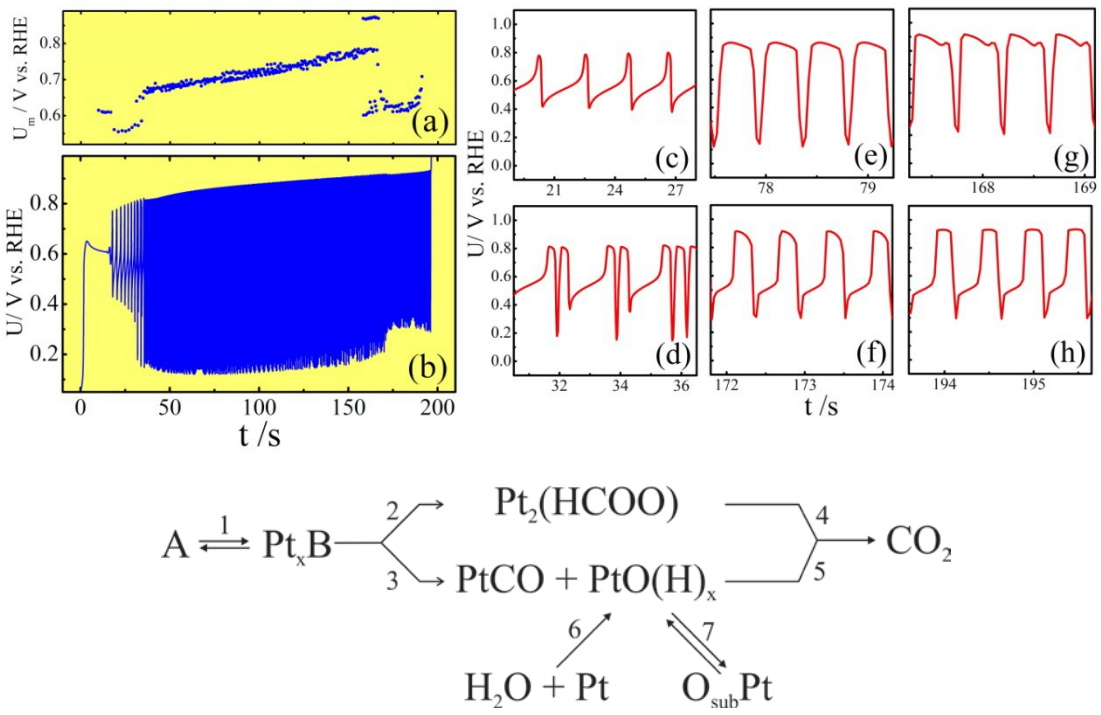

Figure 11: *(top) Time-traces of (a) the mean electrode potential, and of (b) the electrode potential, during the galvanodynamic (10.42 μA cm^{-2} s^{-1}) electro-oxidation of formaldehyde on platinum (c-h expanded time axis). Electrolyte: 0.5 M H_2SO_4 aqueous solution with 0.1 mol L^{-1} of HCHO. (Bottom): Reaction scheme of electro-oxidation of methanol and formaldehyde on platinum [1].*

The adsorbed species $PtO(H)_x$ represents a generic oxygenated adsorbate that participates in the oxidation of species such as adsorbed carbon monoxide. Further oxidation of the platinum surface leads to the so-called place-exchange process, in which surface oxygen atoms are inserted in the platinum lattice in order to allow further surface oxidation to take place. Sub-surface oxygen is in principle unavailable for Langmuir-Hinshelwood steps such as the illustrated electro-oxidation of adsorbed carbon monoxide. As a consequence, the increase in the amount of O_{sub}-Pt accompanying the increase in the electrode potential is equivalent to a decrease in the overall number of surface sites, which in turn, causes an increase in the actual current density (in contrast to the applied current, which is strictly constant). Therefore, coupled to the core oscillator, the spontaneous drift that slowly evolves in time is suggested to result from the increase of sub-surface oxygen.

After assigning the slowly evolving parameter as the coverage of a surface-blocking species, incorporated this process has been incorporated in a generic model for this family of oscillators. The resulting model consists of four ordinary differential equations, and it was investigated over a wide parameter range. Besides the bifurcation analysis, the system was

studied by means of high-resolution period and Lyapunov diagrams. It was observed that the system's dynamics becomes simpler as the irreversible poisoning evolves, as evidenced by the changes in the structure of the bifurcation diagram. Nevertheless, periodic cascades are preserved in a confined region of the resistance *vs.* potential diagram.

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3. Research Projects Funded from Outside Resources

Kramer Campen and Martin Wolf:

- DFG Collaborative Research Center SFB 658 "Elementary processes of molecular switches at surfaces", project B9 ***"Molecular switching in self-assembled monolayers at liquid-solid interfaces"*** (selfassembled monolayers, liquid-solid interfaces, static and time-resolved vibrational SFG spectroscopy, from 7/2013)

Kramer Campen:

- DFG Collaborative Research Center 1109 "Understanding of Metal Oxide/Water Systems at the Molecular Scale: Structural Evolution, Interfaces and Dissolution", Project B1, **"*Understanding water structure and reactivity at aluminum oxide surfaces using nonlinear vibrational spectroscopy and theory*"** (oxide/water interfaces, time resolved vibrational SFG spectroscopy, *ab initio* dynamics and thermodynamics, together with P. Saalfrank, Univ. Potsdam, from 4/2014)

Ralph Ernstorfer and Martin Wolf:

- DFG Reseach Unit FOR1700 (Wo 653/8-1) "Metallic nanowires on the atomic scale: Electronic and vibrational coupling in real world systems", Project E5 ***"Time-resolved spectroscopy of photoinduced transitions and electronic excitations in quasi-1D metal wires on semiconductors"*** (electronic structure and dynamics in quasi 1D systems, time-resolved ARPES, from 11/2012)

Leonhard Grill:

- European research project (ICT FET) ***"Alternative routes towards information storage and transport at the atomic and molecular scale (ARTIST)"*** (single molecule manipulation and spectroscopy with low-temperature STM, until 7/2013)
- European research project (ICT FET) ***"Atomic scale and single molecule logic gate technologies (AtMol)"*** (formation and characterization of molecular wires with low-temperature STM, until 12/2014)
- Marie Curie Initial Training Networks (multipartner ITN) of the European Union "Actuation and characterization at the single bond limit" (ACRITAS) (Jan – July 2013, now transferred to University of Graz)
- DFG Collaborative Research Center SFB 951 "Hybrid Inorganic/Organic Systems for Opto-Electronics", project A2 ***"Assembly and local probing of single molecules on ultrathin ZnO films on metals"*** (deposition and imaging of single molecules on utrathin

oxide films with STM, until 6/2015, project will be continued by Takashi Kumagai and Martin Wolf)

Leonhard Grill and Martin Wolf:

- Collaborative Research Center SFB 658 "Elementary Processes of Molecular Switches at Surfaces", project A5 ***"Complex switching units and molecular architectures, studied by scanning tunneling microscopy"*** (nanostructuring, single molecule spectroscopy and manipulation with low-temperature STM, until 6/2013)

Karsten Horn:

- Individual project (Ho 797/18-1) ***"Graphene-based systems for spintronics: Magnetic interactions at the graphene/3d metal interface (SpinGraph)"*** within the program "EuroGRAPHENE" of the European Science Foundation
- DFG Priority Program SPP 1459 (De 1679/3-1) "Graphene", project ***"Graphene: electronic structure, transport and functionalization"*** (growth and doping of eptaxial grapheme layers, angle-resolved photoemission spectroscopy)

Tobias Kampfrath:

- DFG individual research grant (KA 3305/2-1), ***"Femtosecond coherent control of terahertz radiation by transient nanophotonic structures"***, (ultrafast optical spectroscopy, THz photonics, from 02/2013)
- DFG priority program SPP 1666 (KA 3305/3-1), "Topological Insulators", project ***"Investigation of directional THz spin currents in topological surface states"*** (ultrafast spin dynamics in topological insulators, THz emission spectroscopy, together with C. Heiliger, Univ. Gießen and M. Münzenberg, Univ. Göttingen, from 06/2013)

Alexey Melnikov:

- DFG individual research grant (ME 3570/1-3), ***"Ballistic electron-driven magnetization dynamics induced by femtosecond laser excitation"*** (ultrafast spin dynamics and transport, epitaxial metallic multilayer films, non-linear optical SHG spectroscopy, from 10/2013)

Alexander Mikhailov:

- DFG Collaborative Research Center SFB 910 "Control of Self-Organizing Nonlinear Systems", project A6 ***"Control of self-organization in dynamical networks"*** (control of nonlinear dynamics in chemical and biological networks)

- Volkswagen Foundation, international project ***"Self-organizing networks of interacting machines"*** (design and analysis of the networks of molecular machines)
- DFG Research Training Group GRK 1558 "Nonequilibrium Collective Dynamics in Condensed Matter and Biological Systems", project ***"Active microfluidics based on floating molecular machines"*** (molecular machines at liquid interfaces)

Alexander Saywell:

- DFG individual research grant "eigene Stelle" (Sa 2625/1-1), ***"Force induced dissociation of individual molecules"*** (Single molecule spectroscopy and manipulation, low-temperature atomic force microscopy (AFM), from 1/2014)

Julia Stähler and Martin Wolf:

- Collaborative Research Center SFB 951 "Hybrid Inorganic/Organic Systems for Opto-Electronics", project B9 ***"Electronic structure and ultrafast carrier dynamics at hybrid inorganic/organic interfaces"*** (time-resolved 2PPE and non-linear optical spectroscopy, organic/inorganic semiconductor interfaces)

Julia Stähler, Tobias Kampfrath, Ralph Ernstorfer and Martin Wolf:

- European Research Project (*NMP-2011-SMALL*): ***"Time dynamics and Control in nanostructures for magnetic recording and energy applications (CRONOS)"***, project FHIB, (time-resolved 2PPE and non-linear optical spectroscopy, magneto-optical Kerr spectroscopy, THz emission, high-harmonic generation, from 6/2012)

Martin Wolf:

- German-Israel Foundation (GIF), cooperation with Prof. Micha Asscher, Hebrew University of Jerusalem, project ***"Photochemistry and electron dynamics of oriented molecules within a nano-capacitor"*** (photochemistry and charge transfer processes in thin molecular films, until 3/2013)

4. Publications of the Department of Physical Chemistry

2011 (late publications)

Cortes Rodriguez, R., L. Rettig, Y. Yoshida, H. Eisaki, M. Wolf and U. Bovensiepen: Momentum-Resolved Ultrafast Electron Dynamics in Superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$. Physical Review Letters **107** (9), 097002 (2011).

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Doctoral Thesis

Duettmann, M.: Elastic Network Models of Proteins: Uncovering the Internal Mechanics of Actin and Myosin. Technische Universität Berlin 2012.

Giese, P.: Photoinduced N_2O dissociation and CO oxidation on thin MgO films. Freie Universität Berlin 2012.

Rettig, L.: Ultrafast Dynamics of Correlated Electrons. Freie Universität Berlin 2012.

Scheuch, M.: Strong Modulation of THz Optical Properties of Layered Materials by Thermal and Ultrafast Heating. Freie Universität Berlin 2012.

Diploma Theses

Kogler, F.: Interactions of artificial Molecular Machines. Freie Universität Berlin 2012.

Plottke, H.: Präparation und Charakterisierung von Wolfram-Nanospitzen als Feldemissions-Elektronenquelle. Freie Universität Berlin 2012.

Pronobis, W.: Ultrafast Optical Spectroscopy of Lattice Vibrations in Solids. Freie Universität Berlin 2012.

Master's Thesis

Popp, D.: Elastic networks: Study of large-scale conformational motions of membrane proteins. TU Bergakademie Freiberg 2012.

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Avigo, I., R. Cortés Rodriguez, L. Rettig, S. Thirupathaiah, H.S. Jeevan, P. Gegenwart, T. Wolf, M. Ligges, M. Wolf, J. Fink and U. Bovensiepen: Coherent excitations and electron–phonon coupling in $Ba/EuFe_2As_2$ compounds investigated by femtosecond time- and angle-resolved photoemission spectroscopy. Journal of Physics: Condensed Matter **25** (9), 094003 (2013).

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Doctoral Thesis

Koch, M.: Growth and Characterization of Single Molecular Wires on Metal Surfaces. Freie Universität Berlin 2013.

Lafferentz, L.: Covalent Molecular Architectures and Dithienylethene Switches on Metal Surfaces. Freie Universität Berlin 2013.

Mielke, J.: Investigation of Single Functional Molecules on Metal Surfaces by Scanning Tunneling Microscopy. Freie Universität Berlin 2013.

Schambach, P.: Tip-enhanced Raman spectroscopy in ultra-high vacuum. Freie Universität Berlin 2013.

Weser, M.: Electronic and magnetic properties of graphene-based systems. Freie Universität Berlin 2013.

Diploma Theses

Loutchko, D.: Tryptophas Synthase: Single Enzyme Kinetic Modeling and Numerical Simulations. Humboldt-Universität zu Berlin 2013.

Lüneburg, S.: Novel electrostatic microlens for collimation of femtosecond electron pulses photoemitted from a nano-sized tip. Humboldt-Universität zu Berlin 2013.

5. Invited Talks of the Members of the Department of Physical Chemistry

Lea Bogner

Feb 2013	Seminar, Department of Physics (Prof. Katharina Franke/ Prof. Petra Tegeder), Freie Universität Berlin, Berlin, Germany *Poly(3-Hexylthiophene) Thin Films and Dicyanovinyl-Sexithiophene on Au(111) Investigated with Two-Photon Photoemission*
Apr 2013	Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Electronic Structure and Excited States Dynamics in Polythiophene and an Acceptor-Subtituted Oligothiophene*

Kramer Campen

Jun 2012	Workshop on Nonlinear Optics at Interfaces, Telluride Science Research Center, Telluride, CO, USA *Understanding Methane Decomposition at the Ru(0001) Interface*
Aug 2012	244th ACS National Meeting and Exposition: Materials for Health and Medicine, Philadelphia, PA, USA *Understanding Methane Decomposition at the Ru(0001) Interface*
Sep 2012	CRC-FHI Joint Meeting on Complex Surfaces in Material Science, Berlin, Germany *Methane Decomposition at the Ru(0001) Interface*
Dec 2012	Group Seminar, Theoretical Chemistry, Institute of Chemistry, University of Potsdam, Potsdam, Germany *Structure and Dynamics of the Free OH at the Air/Water Interface*
Mar 2013	Integrated Research Training Group Seminar on Elementary Processes in Molecular Switches: Collaborative Research Center 658, Technische Universität Berlin, Berlin, Germany *Interfacial Spectroscopy: A Tool for Characterization of Semiconductor Surface Structures and Surface Solvation*
Jun 2013	CECAM Workshop on Liquid/Solid Interfaces: Structure and Dynamics from Spectroscopy and Simulations, Lausanne, Switzerland *Understanding Water Dissociation and Surface Reconstruction on the α-Al_2O_3(0001) Surface*
Sep 2013	20th International Conference on Horizons in Hydrogen Bond Research, Antwerp, Belgium *Structure and Dynamics of the Non-Hydrogen Bonded (Free) OH at the Air/Water Interface*
Oct 2013	Block Course on Dynamic Processes at Interfaces and Surfaces, International Max Planck Research School Complex Surfaces in Materials Sciences, Berlin, Germany *How to Probe Interfaces with Optical Sum Frequency Spectroscopy*

Jan-Christoph Deinert

May 2013 Seminar, Institute of Solid State Physics (Prof. Mario Dähne), Technische Universität Berlin, Berlin, Germany
Electronic Structure and Dynamics at the ZnO (10-10) Surface

Yunpei Deng

Oct 2012 Meeting on the Frontiers in Optics/Laser Science XXVIII (FiO/LS), Rochester, NY, USA
Few Cycle Infrared OPCPA System and Applications

Dec 2013 Conference on high intensity laser and attosecond science, Tel-Aviv, Israel
High Power OPCPA system for XUV sources at 500 kHz

Markus Eiswirth

Sep 2011 Institute of Computer Science, University of Bonn, Bonn, Germany
Stoichiometric Network Analysis

Jan 2012 B-IT Lecture Series in Life Science Informatics, University of Bonn, Bonn, Germany
Nonautocatalytic Oscillators and Olfactory Response

Jun 2012 2nd Ertl Symposium on Surface and Interface Chemistry, Stuttgart, Germany
Chemical Kinetics and Algebraic Geometry

Oct 2012 GIST, School of Environmental Science and Engineering, Gwangju, Korea
Dissipative Structures

Oct 2012 ADeKo Conference Basic Science for the 21st Century, Seoul, Korea
Frozen Dynamical Patterns

Oct 2012 GIST, Ertl Center for Electrochemistry and Catalysis, Gwangju, Korea
Stoichiometric Network Analysis

Nov 2012 Dagstuhl-Seminar Symbolic Methods for Chemical Reaction Networks, Schloss Dagstuhl, Germany
Stoichiometric Networks and Dynamic Instabilities

Ralph Ernstorfer

Aug 2012 MPS 2012 International Conference on Many Particle Spectroscopy of Atoms, Clusters and Surfaces, Berlin, Germany
Attosecond Photoelectron Spectroscopy of Solids

Sep 2012 KTH Stockholm, School of Information and Communication Technology, Stockholm, Sweden
Attosecond Photoelectron Spectroscopy of Solids

Sep 2012	Department Seminar, Department of Chemical Physics, Lund University, Lund, Sweden *Attosecond Photoelectron Spectroscopy of Solids and Optical-Field-Induced Current in Dielectrics*
Nov 2012	Institutskolloquium, Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany *Non-Equilibrium Structural Dynamics in Solids and Optical-Field-Induced Current in Dielectrics*
Mar 2013	APS March Meeting, Baltimore, MD, USA *Attosecond View of the Photoelectric Effect*
Mar 2013	Seminar, Department of Chemistry, Columbia University, New York, NY, USA *Attosecond View of the Photoelectric Effect and Nonthermal Phase Transitions in Solids*
Mar 2013	Seminar, University of Delaware, Department of Physics and Astronomy, Newark, DE, USA *Optical-Field-Induced Current in Dielectrics*
Apr 2013	Seminar, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany *Attosecond View of the Photoelectric Effect and Optical-Field-Induced Current in Dielectrics*
Sep 2013	Seminar, Ultrafast X-Ray Science Laboratory, Lawrence Berkeley National Laboratory, Berkeley, CA, USA *Non-Equilibrium Structural Dynamics and Phase Transitions in Solids*
Sep 2013	246th ACS National Meeting and Exposition, Indianapolis, IN, USA *Chemical Control of Heterogeneous Electron Transfer Dynamics and Strong Electron-Lattice Coupling in TiO_2*
Sep 2013	Physics Colloquium, University of Nebraska-Lincoln, Kearney, NE, USA *Non-Equilibrium Structural Dynamics and Phase Transitions in Solids*

Gerhard Ertl

Oct 2011	Lecture, 100 Jahre Fritz-Haber-Institut, Berlin, Germany *Molecules at Surfaces*
Nov 2011	Clemens Winkler Lecture, Freiberg, Germany *Katalyse an Oberflächen: Vom Atomaren zum Komplexen*
Nov 2011	Marie Sklodowska-Curie Symposium, Warsaw, Poland *Catalysis by Surfaces: From Atoms to Complexity*
Jun 2012	2nd Ertl Symposium on Surface and Interface Chemistry, Stuttgart, Germany *Reactions at Surfaces*
Aug 2012	4th EuCheMS Congress, Prague, Czech Republic *Catalysis at Surfaces*

Oct 2012	Lecture, Opening Ertl Center, Technische Universität Berlin, Berlin, Germany *Catalysis and Surface Science*
Nov 2012	Lecture, Ponteficia Accademia delle Scienze, Rom, Italy *Complexity in Chemistry: From Disorder to Order*
Jan 2013	Lecture, Romain-Rolland-Gymnasium, Berlin, Germany *Katalyse an Oberflächen*
Jan 2013	Lecture, Technische Universität Darmstadt, Darmstadt, Germany *Moleküle an Oberflächen*
May 2013	Otto-Stern-Symposium, Hamburg, Germany *Moleküle an Oberflächen*
May 2013	Lecture, Technische Universität München, Munich, Germany *Reaktionen an Oberflächen: Vom Atomaren zum Komplexen*
Jul 2013	Nobel Laureate Meeting, Lindau, Germany *Moleküle an Oberflächen*

Leonhard Grill

Sep 2011	FUNMOLS Workshop, Barcelona, Spain *Characterization and Manipulation of Single Functional Molecules by STM: From Switches to Wires*
Sep 2011	11th European Conference of Molecular Electronics (ECME 2011), Barcelona, Spain *Model Systems for Molecular Electronics Studied by Scanning Probe Microscopy*
Oct 2011	Symposium on Transport Through Molecules, Berlin, Germany *Conductance Measurements of Single Polymers as a Continuous Function of Their Length*
Jan 2012	Seminar, Chemistry Department, University of Graz, Graz, Austria *Single Functional Molecules at the Atomic Scale: Imaging, Manipulation and Assembly*
Feb 2012	Supramolecular Chemistry Conference, Lanzarote, Spain *Bottom-Up Assembly and Manipulation of Covalent Molecular Nanostructures*
Mar 2012	Seminar, Physics and Astronomy Department, University of Nottingham, Nottingham, UK *Functional Molecules Studied by STM: From Switches to Wires*
Apr 2012	Seminar, Institute of Science and Technology, Klosterneuburg, Austria *Single Functional Molecules at the Atomic Scale: Imaging, Manipulation and Assembly*
Jun 2012	CNR Workshop on Organic Molecules on Surfaces, Parma, Italy *Covalent Linking of Functional Molecules on Surfaces: Wires and Networks*

Jul 2012	Seminar, Physics Department, University of Graz, Graz, Austria *Single-Molecules Manipulation and Molecular Assembly on Surfaces*
Sep 2012	29th European Conference on Surface Science (ECOSS-29), Edinburgh, UK *Functional Molecules on Surfaces: Assembly and STM Manipulation*
Sep 2012	38th Micro and Nano Engineering Conference (MNE2012), Toulouse, France *Assembly and Manipulation of Functional Molecules at the Atomic Scale: From Switches to Wires*
Sep 2012	CRC-FHI Joint Meeting on Complex Surfaces in Material Science, Berlin, Germany *On-Surface Chemistry by Covalent Linking of Molecules on Metals*
Nov 2012	Lorentz-Center Workshop on Dynamical Phenomena at Surfaces, Leiden, The Netherlands *Manipulating Single Molecules with Mechanical, Optical or Electrical Functions*
Dec 2012	Conference on Molecular Electronics (ElecMol12), Grenoble, France *Assembly and Manipulation of Single Functional Molecules: Switches and Wires*
Jan 2013	Foresight Technical Conference: Illuminating Atomic Precision, Palo Alto, CA, USA *Assembly and Manipulation of Molecules at the Atomic Scale: Stitching and Switching*
Mar 2013	Interdisciplinary Surface Science Conference (ISSC-19), Nottingham, UK *Manipulation of Single Functional Molecules on Surfaces: Wires and Switches*
Jun 2013	Nanopack, Workshop, Grenoble, France *Bottom-Up Assembly of Functional Molecular Nanostructures*
Jun 2013	4th European Workshop on Nanomanipulation, Krakow, Poland *Manipulating Single Molecules and Nanostructures by STM*
Jul 2013	Seminar, Swiss Federal Laboratories for Materials Science and Technology (EMPA), Dübendorf, Switzerland *Assembly and Manipulation of Molecules at the Atomic Scale: "Stitching and Switching"*
Sep 2013	Trends in Nanotechnology Conference (TNT2013), Sevilla, Spain *Assembly and Manipulation of Single Functional Molecules*
Oct 2013	Workshop on Modeling Single-Molecule Junctions: Novel Spectroscopies and Control, Berlin, Germany *Combined Imaging, Spectroscopy and Conductance Measurements of Single Molecules: Towards Molecular Wires*
Oct 2013	543th Wilhelm-und-Else-Heraeus-Seminar on Electron Transport through Atoms, Molecules and Nanowires: Advances in Theory and Experiments, Bad Honnef, Germany *STM Manipulation of Single Functional Molecules: Towards Molecular Wires*

Karsten Horn

Mar 2012	VIIIth Prague Workshop on Photoinduced Molecular Processes, Prague, Czech Republic *Electronic Structures Studies of Surfaces and Solids Using Photoelectron Spectroscopy*
May 2012	Physikalisch-Chemisches Seminar, University of Göttingen, Göttingen, Germany *Quantum Well States in Thin Metallic Films: From Textbook Physics to Spin-Resolved Photoemission*
May 2012	Statistical Physics and Low Dimensional Systems, Abbaye des Prémontrés, Pont-à-Mousson, Frankreich *Electronic Structure and Fermi Surface of Decagonal Al-Cu-Co Quasicrystals*
Sep 2012	29th European Conference on Surface Science (ECOSS-29), Edinburgh, UK *Graphene - Electronic Structure of a 2D Model Solid*
Jan 2013	European Workshop on Epitaxial Graphene, Aussois, France *Electronic Structure and Many-Body Effects in Graphene Studied by Angle-Resolved Photoemission*
Jan 2013	International Workshop on Nanoscience on Surfaces - Present Stand and Future Challenges, Schladming, Austria *Graphene - Surface Science and Solid State Physics of a 2D Model Solid*
Mar 2013	Graphene Workshop: From Fundamental Properties to Applications, Ajdovscina, Slovenia *Electronic Structure of Epitaxial Graphene on Metals and Silicon Carbide*
Apr 2013	Seminar, Department of Physics and Astrononmy, Uppsala University, Uppsala, Sweden *Graphene - What Do We Learn about Its Electronic Structure from Angle-Resolved Photoemission?*
Jun 2013	Graphene Week, Chemnitz, Germany *Graphene Based Systems for Spintronics: Magnetic Interactions - Magnetic Interactions at the Graphene/3D Metal Interface*
Oct 2013	Seminar, Paul-Scherrer-Institut, Villigen, Switzerland *Aperiodic „Quasi"-Crystals and their Electronic Structure*
Oct 2013	Seminar, Swiss Federal Laboratories for Materials Science and Technology (EMPA), Dübendorf, Switzerland *Epitaxial Graphene and its Electronic Structure*

Tobias Kampfrath

Nov 2011	User Meeting at BESSY II (Berlin Electron Synchrotron), Berlin, Germany *Intense Terahertz Pulses as Driving Force of Electronic and Spin Excitations*

Dec 2011	Center of Excellence Colloquium, University of Göttingen, Göttingen, Germany *How to Enhance Magnetic Light-Matter Interaction at Highest Frequencies*
Apr 2012	Seminar, Department of Physics, Freie Universität Berlin, Berlin, Germany *Spectroscopy and Control of Spin Dynamics Using Terahertz Pulses*
May 2012	Seminar, Department of Physics, Freie Universität Berlin, Berlin, Germany *Spectroscopy and Control of Spin Dynamics Using Terahertz Pulses*
Jun 2012	Physikalisches Kolloquium, Chemnitz University of Technology, Chemnitz, Germany *Beyond Body Scanners: How to Use Terahertz Pulses to Observe and Control Spin Dynamics in Solids*
Jan 2013	Seminar, Department of Physics, University of Duisburg-Essen, Duisburg, Germany *Beyond Body Scanners: How to Use Terahertz Pulses to Observe and Control Spin Dynamics in Solids*
Jan 2013	12th Joint MMM/Intermag Conference (MMM/Intermag 2013), Chicago, IL, USA *Engineering Ultrafast Spin Currents and Terahertz Transients by Magnetic Heterostructures*
Mar 2013	DPG-Frühjahrstagung, Ratisbon, Germany *Manipulating Terahertz Spin Currents*
Mar 2013	Workshop on Terahertz/Carbon, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany *THz Transport of Charges and Spins*
Apr 2013	Colloquium, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany *Beyond Body Scanners: How to Use Terahertz Pulses to Observe and Control Spin Dynamics in Solids*
Jun 2013	Department colloquium, MPI for Polymer Research, Mainz, Germany *Spintronics with Terahertz Radiation*
Okt 2013	UMC 2013 (Ultrafast Magnetism Conference), Strasbourg, France *Spintronics with Terahertz Radiation*

Patrick S. Kirchmann

Jan 2012	Donostia International Physics Center, San Sebastián, Spain *Femtosecond Time- and Angle-Resolved Photoemission Spectroscopy*
Apr 2012	Department Workshop, Department of Physical Chemistry, FHI, Zeuthen, Germany *The Ultrafast Dynamics of Correlated Materials - Combining Time-Resolved Photoemission and Diffraction*
Jun 2012	Faculty of Physics, University of Duisburg-Essen, Duisburg, Germany *New Light on Charge Density Waves: Electron-Phonon Coupling in the CDW Material $TbTe_3$ Seen by Femtosecond Time-Resolved ARPES and Resonant Soft X-Ray Diffraction*

Jun 2012	Chair for Ultrafast Phenomena and Photonics at the University of Konstanz, Konstanz, Germany *New Light on Charge Density Waves: Electron-Phonon Coupling in the CDW Material $TbTe_3$ Seen by Femtosecond Time-Resolved ARPES and Resonant Soft X-Ray Diffraction*
Jun 2012	Chair of Solid State Physics at the Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany *Ultrafast Electron Dynamics in the Topological Insulator Material Bi_2Se_3*
Aug 2012	Virtual Institute Dynamic pathways in multidimensional landscapes, Scientific Kick-Off and Summer School, Helmholtz-Centre Potsdam - GFZ German Research Centre for Geosciences, Potsdam, Germany *Ultrafast Dynamics of Amplitude and Phase Excitations in Charge- and Spin-Ordered Materials*

Harald Kirsch

Apr 2013	Gordon Research Conference on Chemical Reactions at Surfaces: Surfaces in Energy and the Environment: Selected talk from submitted poster, Les Diablerets, Switzerland *CH_4 and C_2H_4 Decomposition and Higher Hydrocarbon Formation on Ru(0001)*

Alexey Melnikov

Mar 2012	APS March Meeting, Boston, MA, USA *Ultrafast Transport of Laser-Excited Spin-Polarized Carriers in Metallic Multilayers*
May 2012	Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Ultrafast Spin Dynamics Induced by Superdiffusive Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multilayers*
Mar 2013	DPG-Frühjahrstagung, Ratisbon, Germany *Ultrafast Spin Dynamics Induced by Laser-Generated Spin Currents in Metallic Multilayers Probed by Non-Linear Magneto-Optics*
Apr 2013	Seminar, Department of Physics (AG Martin Aeschlimann), Technische Universität Kaiserslautern, Kaiserslautern, Germany *Ultrafast Spin Dynamics Induced by Laser-Generated Spin Currents in Metallic Multilayers and Probed by Non-Linear Magneto-Optics*
Jun 2013	Seminar, Department of Physics (AG Markus Münzenberg), University of Göttingen, Göttingen, Germany *Ultrafast Non-Local Spin Dynamics Induced by Hot Carrier Transport in Metallic Multilayers and Probed by (Non-Linear) Magneto-Optics*

Sep 2013 Advanced Laser Technologies 2013, Budva, Montenegro
Time-Resolved Non-Linear Magneto-Optics as a Tool to Study Spatially Non-Uniform Non-Local Ultrafast Spin Dynamics in Metallic Multilayers

Alexander S. Mikhailov

Nov 2011 Lecture, Department of Physics, Central National University, Johngli, Taiwan
Elastic-Network Models of Molecular Machines

Dec 2011 Seminar, Center for Theoretical Biology, Peking University, Peking, China
Evolutionary Design of Genetic Networks

Mar 2012 Conference on Statistical Mechanics and Nonlinear Dynamics, National S. N. Bose Center for Basic Sciences, Calcutta, India
Elastic-Network Models of Molecular Machines

Mar 2012 Seminar, Department of Physics, National Science University, Hefei, China
Turing Patterns in Network-Organized Activator-Inhibitor Systems

Sep 2012 Workshop on Active Dynamics on Micro Scales: Molecular Motors and Self-Propelled Particles, Leiden University, The Netherlands
Elastic-Network Models of Molecular Machines

Oct 2012 Symposium on Complex Network Analysis: From Graph Theory to Systems Biology, Hall in Tirol, Austria
Evolutionary Design of Robust Functional Networks

Feb 2013 Conference on Self-Organization and Emergent Dynamics in Active Matter, Yukawa Institute of Theoretical Physics, Kyoto University, Kyoto, Japan
Elastic-Network Models of Protein Machines

Claude Monney

May 2013 Colloquium, University of Greifswald, Greifswald, Germany
Possible Exciton Condensation in $TiSe_2$: Experimental and Theoretical Evidences

May 2013 V. V. Nemoshkalenko Memorial Conference and Workshop, Electronic Structure and Electron Spectroscopies, Kiev, Ukraine
Electron-Hole Fluctuations Driving the Charge Density Wave Phase Transition in $TiSe_2$

Jul 2013 CCP9/CECAM Workshop on Electronic Excitations and Photoelectron Spectroscopy: Bridging Theory and Experiment, Oxford, UK
Charge Density Wave Phase in $TiSe_2$: Calculating the Spectral Function Within the Exciton Condensate Model

Jul 2013 CORPES 13 - International Workshop on Strong Correlations and Angle-Resolved Photoemission Spectroscopy, Hamburg, Germany
Complementary Momentum-Resolved Spectroscopies on a Charge Density Wave Material: ARPES and RIXS

Aug 2013 — 8th International Conference on Inelastic X-Ray Scattering (IXS 2013), Stanford, CA, USA
Determining the Short-Range Spin Correlations in Edge-Shared Chain Cuprates with RIXS

Melanie Müller

Oct 2013 — Workshop on New Trends and Faces in Ultrafast Structural Dynamics, Stellenbosch, Südafrika
Femtosecond Low-Energy Electron Diffraction and Imaging: A Compact Approach

Bruno Pettinger

Jun 2012 — Il Congresso Nazionale di Spettroscopic Raman and Effetti Ottici Non Lineari, Bologna, Italy
Recent Progress in Tip-Enhanced Raman Spectroscopy

Andrea Rubano

Mar 2012 — MAMA-Protheo Workshop, Vietri, Italy
Optical Second Harmonic Generation as a Tool for the Characterization of Buried Interfaces

Mar 2012 — Seminar, Department of Physics, University of Naples, Naples, Italy
High Frequency THz-Ellipsometry on Perovskite Oxides

Sep 2012 — XCVIIIth National Congress of the Italian Physics Society (SIF), Naples, Italy
Optical Second-Harmonic Generation: A Powerful Tool for Buried Interfaces Investigation

Sep 2012 — Seminar, Department of Physics, University of Naples, Naples, Italy
Setup of a Versatile High-Field THz Spectrometer

Nov 2012 — Seminar, Department of Materials, ETH Zurich, Zurich, Switzerland
High Frequency THz-Ellipsometry on Perovskite Oxides

Julia Stähler

Sep 2011 — 16th Workshop on Electronic Excitations, European Theoretical Spectroscopy Facility (ETSF), Turin, Italy
Two Sides of the Same Coin: Ultrafast Dynamics and Interactions of Electrons and Lattices

Nov 2011 — Seminar, Nanoscale Science Department, MPI for Solid State Research, Stuttgart, Germany
Ultrafast Electron Dynamics at Organic/Inorganic Interfaces Probed by 2PPE Spectroscopy

Jan 2012	SFB 616 Colloquium, Faculty of Physics, University of Duisburg-Essen, Duisburg, Germany *Energy Level Alignment and Ultrafast Electron Dynamics at the Pyridine/ZnO(10-10) Interface*
Feb 2012	Department Seminar, Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse (CSNSM), Orsay cedex, France *Energy Level Alignment and Ultrafast Electron Dynamics at the Pyridine/ZnO(10-10) Interface*
May 2013	8th International Symposium on Ultrafast Surface Dynamics, Estes Park, CO, USA *Ultrafast Surface Dynamics of ZnO(10-10): Photons, Electrons, and Excitons*
Oct 2013	GDNÄ Tageskongress: Karrierewege - Frauen in Naturwissenschaft, Medizin und Technik, Berlin, Germany *Was ist eine Männerdomäne?*

Lutz Waldecker

Oct 2013	Workshop on New Trends and Faces in Ultrafast Structural Dynamics, Stellenbosch, Südafrika *Ultrafast Dynamics of Phase Transitions in $Ge_2Sb_2Te_5$*

Daniel Wegkamp

Apr 2013	Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany *Long-Lived Electrons Trapped in Amorphous Ice Adsorbed on Cu(111) + Hot Electrons in the 2DEG at the STO/Vacuum Interface*

Martin Wolf

Oct 2011	Conference on X-Ray Spectroscopy on Magnetic Solids (XRMS 2011), Stanford, CA, USA *Dynamics of Correlated Materials Probed by trARPES*
Nov 2011	Distinguished Lectureship, APCTP-POSTECH-MPK, Pohang, Korea *Ultrafast Photoinduced Dynamics in Correlated Materials*
Nov 2011	Physikalisches Kolloquium, University of Göttingen, Göttingen, Germany *Ultrafast Photoinduced Dynamics in Solids*
Dec 2011	Conference on Ultrafast Chemical Physics and Physical Chemistry (UCP 2011), Glasgow, UK *Transient Electronic Structure Probed by trAPRES: From Electron Solvation in Ice to Phase Transitions in Solids*

Jan 2012	RIXS/REXS Workshop, SLAC National Accelerator Laboratory, Stanford, CA, USA *Time- and Angle-Resolved Photoemission Spectroscopy of Correlated Materials*
Jan 2012	Institutskolloquium, Ilmenau University of Technology, Ilmenau, Germany *Ultraschnelle Dynamik in komplexen Festkörpersystemen*
Feb 2012	Gordon Research Conference on Photonions, Photoionization and Photo-detachment, Galveston, TX, USA *Dynamics of Photo-Excited Electrons at Ice/Metal Interfaces: Electron Transfer and Solvation*
Feb 2012	Gordon Research Conference on Ultrafast Phenomena in Cooperative Systems, Galveston, TX, USA *Introductory Talk: Exploring Complex Quantum Systems of Condensed Matter*
Mar 2012	LCLS-II New Instruments Workshop, SLAC National Accelerator Laboratory, Stanford, CA, USA *Challenges in Catalysis and Dynamics of Surface Chemistry at LCLS II*
Apr 2012	Workshop on Exploiting Free Electron Lasers in Chemistry, University of Nottingham, Nottingham, UK *Surface Femtochemistry and Low Energy Excitations in Solids: Experiments in the Lab and at LCLS*
May 2012	SFB 951 Kolloquium, Humboldt-Universität zu Berlin, Berlin, Germany *Electron Dynamics and Energy Level Alignment at ZnO(10-10) Probed with 2PPE: Effect of Hydrogen and Pyridine Adsorption*
Jun 2012	TYC Energy Materials Workshop, King's College, London, UK *Ultrafast Dynamics of Interfacial Electron Transfer*
Jun 2012	Julius Springer Forum on Applied Physics, Berlin, Germany *Transient Electronic Structure of Photoexcited Solids Probed by Time-Resolved ARPES*
Jun 2012	2nd Ertl Symposium on Surface and Interface Chemistry, Stuttgart, Germany *Dynamics of Electron Transfer and Solvation Processes at Water Ice/Metal Interfaces*
Aug 2012	Plenary Lecture, JMC 13 Conference, Montpellier, France *Transient Electronic Structure of Complex Materials Probed by Time-Resolved ARPES*
Sep 2012	Plenary Lecture, International Conference CMD-24 and European Conference on Surface Science (ECOSS-29), Edinburgh, UK *Transient Electronic Structure and Ultrafast Dynamics of Solids*
Sep 2012	IMPACT Conference, Orsay, France *Transient Electronic Structure of Complex Materials Probed by Time-Resolved ARPES*

Oct 2012	CECAM Workshop on Surface Dynamics, Zaragoza, Spain *From Surface Femtochemistry to Ultrafast Phase Transitions in CDW Systems*
Nov 2012	Lorentz-Center Workshop, Leiden, The Netherlands *Probing the Transient Electronic Structure in Surface Femtochemistry and Ultrafast Phase Transitions in Solids*
Nov 2012	Photon Science Colloquium, DESY, Hamburg, Germany *Transient Electronic Structure and Ultrafast Dynamics of Solids*
Feb 2013	International Workshop on Physics at the Borderline between 1D and 2D, Bad Honnef, Germany *Ultrafast Dynamics of CDW Systems Probed by Time-Resolved ARPES*
Feb 2013	Workshop on Short-Time Dynamics in Strongly Correlated Systems, Bochum, Germany *Transient Electronic Structure and Lattice Dynamics of Photo-Excited Solids*
Feb 2013	SFB 616 Seminar, University of Duisburg-Essen, Duisburg, Germany *Transient Electronic Structure and Ultrafast Dynamics of Solids*
Feb 2013	WUPCOM Winterschool, Winklmoosalm, Germany *Ultrafast Changes in the Structural Properties of VO_2 During the Photoinduced Insulator-to-Metal Transition*
Mar 2013	Winterschool on Chemical Reaction Dynamics at Surfaces, Ringberg Castle, Germany *Probing the Transient Electronic Structure in Surface Femtochemistry*
May 2013	GDCh Kolloquium, Julius Maximilian University of Würzburg, Würzburg, Germany *Interfacial Charge Transfer Dynamics and Femtochemistry of Molecular Adsorbates*
May 2013	Plenary Lecture, 112. Bunsentagung, Karlsruhe, Germany *Interfacial Charge Transfer Dynamics and Femtochemistry of Molecular Adsorbates*
May 2013	International Workshop on Controlled Atomic Dynamics at Solid Surfaces, San Sebastián, Spain *Probing Transient Electronic Structure in Femtochemistry and Charge Transfer Processes at Surface*
May 2013	Plenary Lecture, Conference on Ultrafast Surface Dynamics, USD-8, Estes Park, CO, USA *Transient Electronic Structure and Lattice Dynamics of Photo-Excited Solids*
Jun 2013	International Workshop on Energy Dissipation at Surfaces, Bad Honnef, Germany *Dynamics of Electron Transfer and Exciton Formation at Interfaces*
Jun 2013	CNR-MPG Workshop on Quantum Science and Technology, Villa Vigoni, Italy *Dynamics of Solids: Insights from Ultrafast Spectroscopy*

Sep 2013	246th ACS National Meeting and Exposition, Indianapolis, IN, USA *Dynamics of Electron Transfer and Exciton Formation at Interfaces*
Sep 2013	International Conference on Dynamic Pathways in Mulitdimensional Landscapes, Berlin, Germany *Dynamics of Electron Transfer and Exciton Formation at Interfaces*
Oct 2013	Conference on Ultrafast Dynamics of Correlated Materials, ITCP, Trieste, Italy *Ultrafast Dynamics of Complex Materials Probed by Time-Resolved Photoemission*
Oct 2013	60th International Symposium, American Vacuum Society (AVS), Long Beach, NY, USA *Dynamics of Electron Transfer and Exciton Formation at Interfaces*

Max Planck Research Group for **Head: Ralph Ernstorfer**

Structural and Electronic Surface Dynamics

Group members

Scientists:

Roman Bertoni (from 10.2013)
Alexander Paarmann (until 12.2013)

Doctoral students:

Melanie Müller
Michele Puppin
Lutz Waldecker

Diploma and master's students:

Sebastian Lüneburg
Henry Plottke
Niels Schröter

Research projects funded from outside resources

- European Research Project (*NMP-2011-SMALL*): *"Time dynamics and Control in nanostructures for magnetic recording and energy applications (CRONOS)"*, project within work package FHIB (*Optimal control schemes of high-harmonic generation*), together with Martin Wolf.
  Project scientist: Yunpei Deng.

- DFG Research Unit FOR1700 *"Metallic nanowires on the atomic scale: Electronic and vibrational coupling in real world systems"*, Project E5 *"Time-resolved spectroscopy of photoinduced transitions and electronic excitations in quasi-1D metal wires on semiconductors"*, together with Martin Wolf.
  Project graduate student: Christopher Nicholson.

Max Planck Research Group for Structural and Electronic Surface Dynamics **Head: Ralph Ernstorfer**

General

The Max Planck Research Group *Structural and Electronic Surface Dynamics*, established in September 2010 and hosted by the Department of Physical Chemistry, performs experimental research investigating ultrafast phenomena in condensed matter. Part of the group's research, in particular in its initial phase, has focused on the development of new experimental instrumentation and methodology. The work has been carried out by two postdoctoral researchers, three graduate students and three diploma or master's students.

Dr. Alexander Paarmann left the group at the end of 2013 for a group leader position in the Department of Physical Chemistry and the graduate students entered the final stage of their respective doctoral research studies. The transition to the 2nd generation of postdoctoral and doctoral researchers is initiated.

Scientific scope

The ground state properties of complex materials as well as the reaction pathways of photo-excited states are governed by many-body phenomena and the mutual dependence of electron, spin and lattice subsystems. Ultrafast techniques provide access to these fundamental correlations as femtosecond light pulses allow for subsystem-specific excitations and time-resolved observation of the same or another subsystem's response. In the limit of weak optical excitation, this concept may be seen as an experimental perturbative approach where correlations governing ground state properties are revealed by the system's response to modest, but specific excitations. Employing intense ultrashort laser pulses, on the other hand, allows for the preparation of transient states of matter exhibiting strong non-equilibrium, in particular between electrons and lattice. The coupling of the subsystems of such states can be significantly different compared to the ground state and the induced photo-physical or photo-chemical reaction may follow a non-thermal reaction pathway not available in thermal equilibrium.

These concepts require the application of different, complementary probes revealing the temporal evolution of the different subsystems: femtosecond electron diffraction (FED) unfolds the structural dynamics, femtosecond time- and angle-resolved photoelectron spectroscopy (trARPES) reveals the evolution of the electronic structure, and femtosecond

optical spectroscopy provides the optical response. We investigate correlations and photo-induced reactions by employing, and partially developing, these ultrafast techniques. As these phenomena inherently depend on the symmetry of the system, specifically on the dimensionality of the translational symmetry, we put a particular emphasis on the development of ultrafast probes highly sensitive to structural and electronic dynamics in two- and one-dimensional systems.

Research fields

Non-equilibrium structural dynamics of crystals

Transition metal oxides like TiO_2 exhibit a pronounced coupling of electronic and lattice degrees of freedom. As valence and conduction bands are formed from different atomic orbitals, namely O *2p* and Ti *3d*, respectively, interband excitation effectively causes a charge re-distribution within the unit cell modifying the potential energy surface of the lattice. We investigate the effect of electron temperature and carrier relaxation on the excited-state potential energy surface prepared by a few-fs ultraviolet laser pulse (Fig.1). The analysis of the phase of the induced coherent Ti-O stretch vibration reveals a dynamic evolution of the lattice potential synced to the extremely fast cooling of charge carriers. This correlation between electron temperature and the lattice potential is in agreement with non-equilibrium density functional theory calculations performed by the group of Martin Garcia, Universität Kassel.

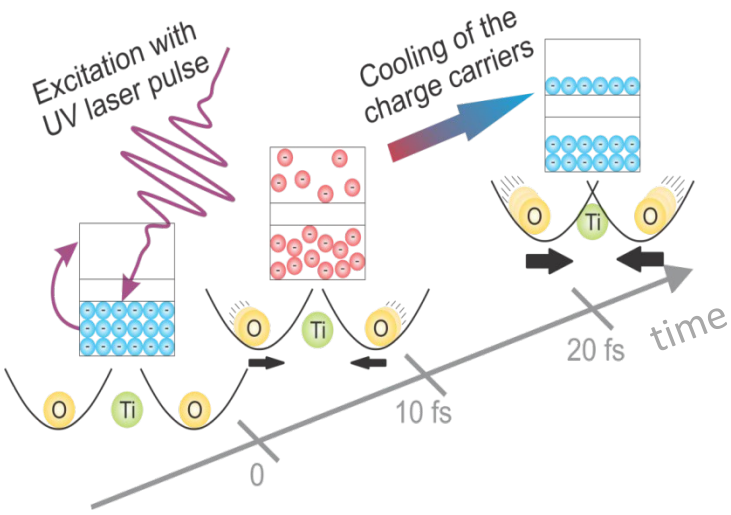

Figure 1: *Schematic representation of the effect of carrier relaxation on the lattice potential energy surface in TiO_2. E.M. Bothschafter et al., Phys. Rev. Lett., **110**, 067402 (2013). Poster PC 21.*

Photo-induced phase transitions in solids

A limiting case of non-equilibrium electron-lattice interaction is the situation of electronic excitation inducing a structural phase transition. Such phase transitions may occur in a

thermal fashion, i.e. after thermal equilibration between electrons and lattice, or nonthermally as a direct consequence of electronic excitation-induced changes to the lattice potential. The latter scenario occurs predominantly in covalently bound crystals as optical excitation transfers population from bonding to antibonding states. Currently, the ultrafast optical and structural response to photoexcitation of the phase change material $Ge_2Sb_2Te_5$ (GST) is investigated in collaboration with the group of Simon Wall, ICFO Barcelona. GST is commonly used as optical storage medium as it exhibits two meta-stable states with a large contrast in optical, electrical and crystalline properties. We aim to clarify the relation between the photo-induced ultrafast optical response and the structural response of the lattice by single-shot femtosecond optical spectroscopy and femtosecond electron diffraction in transmission mode employing a newly developed fs electron diffractometer providing a temporal resolution of 100 fs (Fig. 2).

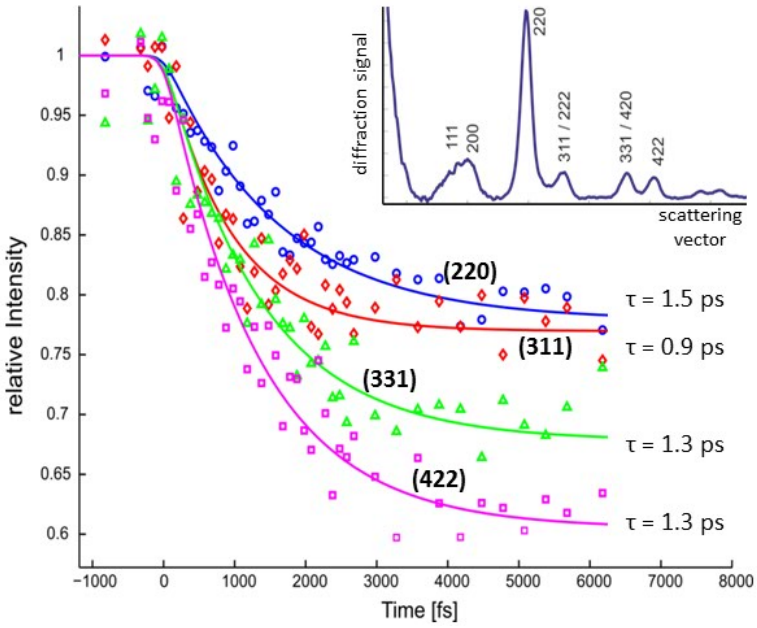

Figure 2: *Time-resolved electron diffraction data of poly-crystalline GST after reversible optical excitation with 800 nm light. The drop in diffraction intensity, the time-resolved Debye-Waller effect, reveals the rate of energy transfer from electrons to lattice through electron-phonon scattering. While the optical properties of GST exhibit a pronounced and persistent change within 100 fs after optical excitation, the lattice heats with a time constant of approximately 1 ps. This indicates that electronic effects, e.g. a transition from resonant to non-resonant bonding, dominate the ultrafast optical response. Poster PC 21.*

Femtosecond low-energy electron diffraction and imaging

As motivated above, there is strong interest in ultrafast experimental techniques that provide direct structural information, e.g. the structural evolution of a crystal or a molecule on the time scale of the fundamental vibrational modes. There has been tremendous progress in the development of femtosecond electron and x-ray diffraction and imaging techniques optimally suited for three-dimensional systems. The highest scattering cross-section, hence the highest sensitivity to structural dynamics in low-dimensional materials, however, is obtained with sub-keV electrons. We are developing a femtosecond low-energy electron diffraction and imaging apparatus based on a laser-triggered field emission electron source. The current operation modes include diffraction in transmission and point projection microscopy, see Fig.

3. Electron diffraction in reflection mode for the investigation of surface-specific structural dynamics will be added in the future.

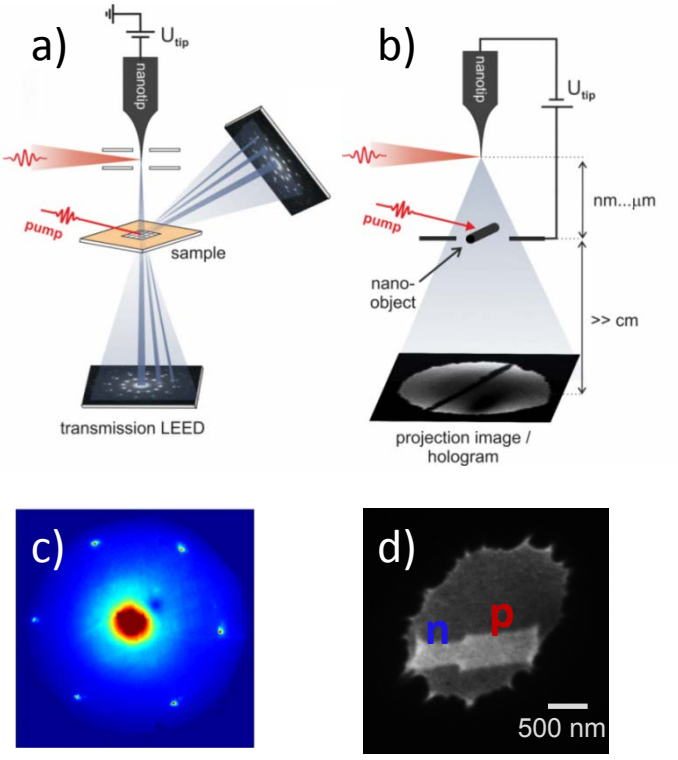

Figure 3: *Scheme of the time-resolved low-energy electron diffraction (a) and point projection microscopy (b). Coherent fs low-energy electron wave packets are generated from a laser-triggered nanotip. Employing an integrated micro-electrode for collimation, 2-D materials like free-standing graphene can be investigated in transmission mode (c). Taking advantage of the high sensitivity of low-energy electrons to electric fields, the electrostatic potential in the vicinity of a nanoobject can be investigated. Panel (d) shows the point-projection image of a spatially homogeneous InP nanowire with 30 nm diameter with integrated p-n junction. The p-n junction causes a local variation of the vacuum level visible in the projection image. In a time-resolved experiment, this approach will make it possible to visualize photo-induced currents in nanoobjects with high temporal and spatial resolution. Paarmann et al., J. Appl. Phys. 112, 113109 (2012); Lüneburg et al., Appl. Phys. Lett. 103, 213506 (2013). Poster PC 20.*

High-repetition rate extreme ultraviolet laser for time- and angle-resolved photoelectron spectroscopy (trARPES)

Complementary to the structural probes introduced above, time-resolved ARPES provides a view on a material's electronic structure with potentially high temporal resolution such that movies of the electronic response to optical excitation may be obtained (see section 2.1.1 of the PC report and poster PC 18 for the material classes under investigation). In practice, there are two branches in the implementation of trARPES, one based on high repetition rate laser systems providing high counting statistics but limited probe photon energies, which limits the accessible range in the Brillouin zone, and another based on probing with extreme ultraviolet (XUV) light generated by high harmonic generation employing high power laser systems of limited repetition rate. In close cooperation with the research group *Dynamics of Correlated Materials* headed by Martin Wolf, we aim at bridging this technology gap by developing a high power laser system providing sufficiently short and intense laser pulses allowing for XUV generation at 500 kHz repetition rate. This approach is based on a two-stage optical

parametric chirped-pulse amplifier (OPCPA) pumped with a hybrid fiber-slab laser system as front end. This laser provides spectrally tunable, both in terms of central wavelength and bandwidth, femtosecond laser pulses with average output power exceeding 20 W, see Fig. 4. As this laser system deviates from established approaches to laser-based XUV generation, a computer program for numerical simulations of high harmonic generation has been developed and employed in order to identify the optimal phase matching conditions for the given laser parameters. Next, this will be investigated experimentally.

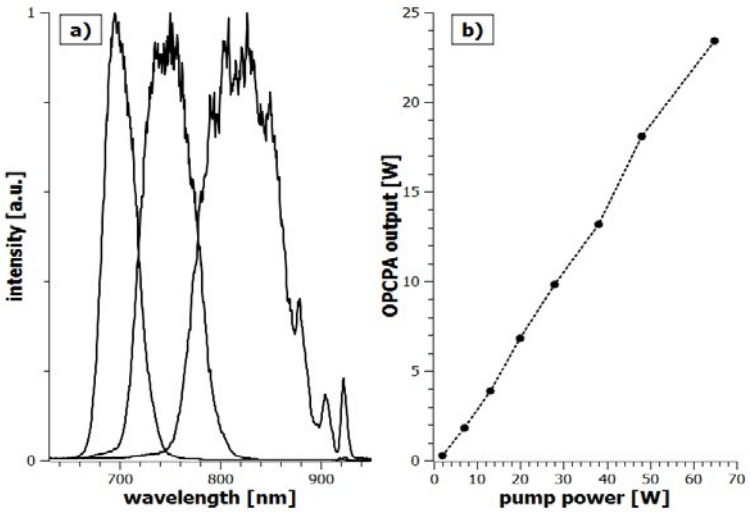

Figure 4: *Exemplary output spectra of the developed OPCPA laser system providing tunable visible and near-infrared pulses with adjustable time-bandwidth product (a). Power scaling of the second OPCPA stage output versus pump power revealing an almost constant conversion efficiency exceeding 30%.*
Poster PC 19.

Observation and control of electron motion in solids on the attosecond time scale

Propagating electrons in crystals are described as coherent superposition of Bloch states around a central wave vector. Free propagation of Bloch wave packets in crystals, however, is very limited in space and time as elastic and inelastic scattering processes destroy the wave packet's coherence. Ultrashort laser pulses with few femtosecond or attosecond duration allow for the investigation and even control of Bloch wave packet propagation in conventional crystals. For instance, attosecond photoelectron spectroscopy performed on metals covered with a variable number of adsorbate layers provides a time-resolved view on the propagation of Bloch wave packets from the substrate through the adsorbate. In an independent set of experiments, collective electron motion, which might be described as highly non-linear polarization, is induced and controlled by the shape of a laser pulse's electric field (see Fig. 5). These experiments demonstrate the feasibility of controlling macroscopic currents at optical frequencies.

These research projects had been initiated while being as scientist in the groups of R. Kienberger and F. Krausz (TU München and MPQ, Garching) and continued in collaboration since the start of the MPRG at the FHI.

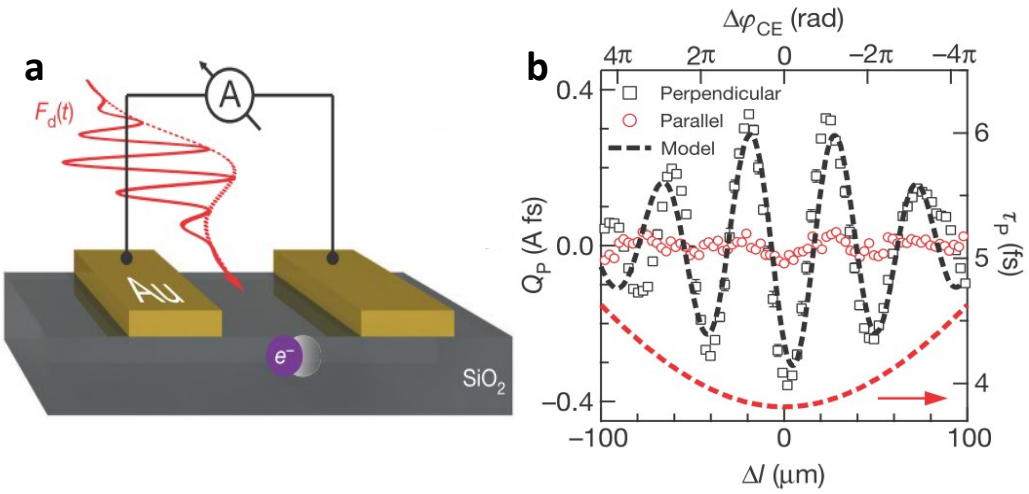

Figure 5: *Optical-field-induced current in dielectrics. A sub-two cycle laser pulse with controlled shape of its electric field is exposed to an unbiased metal-dielectric-metal nanojunction (a). Depending on the shape of the laser field, described in terms of the carrier-envelope phase φ_{CE}, a current is induced in the external circuit whose direction and amplitude critically depends on the symmetry of the pulse (charge flow per laser pulse: Q_P) (b).*
Schiffrin et al. Nature 493, 70 (2013). Paasch-Colberg et al., Nature Photonics, in print. Poster PC 22.

Publications (2012-2013)

A. Paarmann, M. Gulde, M. Müller, S. Schäfer, S. Schweda, M. Maiti, C. Xu, T. Hohage, F. Schenk, C. Ropers, and R. Ernstorfer: Coherent femtosecond low-energy single-electron pulses for time-resolved diffraction and imaging: A numerical study. J. Appl. Phys. **112**, 113109 (2012).

S. Neppl, R. Ernstorfer, E.M. Bothschafter, A.L. Cavalieri, D. Menzel, J.V. Barth, F. Krausz, R. Kienberger, and P. Feulner: Attosecond Time-Resolved Photoemission from Core and Valence States of Magnesium. Phys. Rev. Lett. **109**, 087401 (2012).

S.Kahra, G. Leschhorn, M. Kowalewski, A. Schiffrin, E. Bothschafter, W. Fuß, R. de Vivie-Riedle, R. Ernstorfer, F. Krausz, R. Kienberger,T. Schaetz: A molecular conveyor belt by controlled delivery of single molecules into ultrashort laser pulses. Nature Physics **8**, 238 (2012).

E.M. Bothschafter, A. Paarmann, E.S. Zijlstra, N. Karpowicz, M.E. Garcia, R. Kienberger, and R. Ernstorfer: Ultrafast Evolution of the Excited-State Potential Energy Surface of TiO_2 Single Crystals Induced by Carrier Cooling. Phys. Rev. Lett. **110**, 067402 (2013).

A. Schiffrin, T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J.V. Barth, R. Kienberger, R. Ernstorfer, V.S. Yakovlev, M.I. Stockman, and F. Krausz: Optical-field-induced current in dielectrics. Nature **493**, 70 (2013).

S. Lüneburg, M. Müller, A. Paarmann, and R. Ernstorfer: Microelectrode for energy and current control of nanotip field electron emitters. Appl. Phys. Lett. **103**, 213506 (2013).

T. Paasch-Colberg, A. Schiffrin, N. Karpowicz, S. Kruchinin, Ö. Sağlam, S. Keiber, O. Razskazovskaya, S. Mühlbrandt, A. Alnaser, M. Kübel, V. Apalkov, D. Gerster, J. Reichert, T. Wittmann, J.V. Barth, M.I. Stockman, R. Ernstorfer, V.S. Yakovlev, R. Kienberger, and F. Krausz: Solid-state light-phase detector. Nature Photonics, in print.

Proceedings (2012-2013)

S. Neppl, R. Ernstorfer, A.L. Cavalieri, J.V. Barth, D. Menzel, F. Krausz, P. Feulner, and R. Kienberger: Probing ultrafast electron dynamics in condensed matter with attosecond photoemission. Proc. SPIE 8623, Ultrafast Phenomena and Nanophotonics XVII, 862312 (2013).

M. Müller, A. Paarmann, C. Xu, and R. Ernstorfer: Coherent Electron Source for Ultrafast Electron Diffraction and Imaging. EPJ Web of Conferences **41**, 10007 (2013).

E.M. Bothschafter, A. Paarmann, N. Karpowicz, E.S. Zijlstra, M.E. Garcia, F. Krausz, R. Kienberger, and R. Ernstorfer: Interband excitation and carrier relaxation as displacive driving force for coherent phonons. EPJ Web of Conferences **41**, 04021 (2013).

Diploma and master's theses

S. Lüneburg: Novel electrostatic microlens for collimation of femtosecond electron pulses photo-emitted from a nanosized tip, Humboldt-Universität zu Berlin, 2013.

N. Schröter: Numerical study of high harmonic generation as a light source for time- and angle-resolved photoelectron spectroscopy, Freie Universität Berlin, 2013.

H. Plottke: Präparation und Charakterisierung von Wolfram-Nanospitzen als Feldemissions-Elektronenquelle, Freie Universität Berlin, 2012.

Invited Talks (2012-2013)

Ralph Ernstorfer

Aug 2012	MPS 2012 International Conference on Many Particle Spectroscopy of Atoms, Clusters and Surfaces, Berlin, Germany *Attosecond Photoelectron Spectroscopy of Solids*
Sep 2012	KTH Stockholm, School of Information and Communication Technology, Stockholm, Sweden *Attosecond Photoelectron Spectroscopy of Solids*
Sep 2012	Department Seminar, Department of Chemical Physics, Lund University, Lund, Sweden *Attosecond Photoelectron Spectroscopy of Solids and Optical-Field-Induced Current in Dielectrics*
Nov 2012	Institutskolloquium, Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany *Non-Equilibrium Structural Dynamics in Solids and Optical-Field-Induced Current in Dielectrics*
Mar 2013	APS March Meeting, Baltimore, MD, USA *Attosecond View of the Photoelectric Effect*
Mar 2013	Seminar, Department of Chemistry, Columbia University, New York, NY, USA *Attosecond View of the Photoelectric Effect and Nonthermal Phase Transitions in Solids*
Mar 2013	Seminar, University of Delaware, Department of Physics and Astronomy, Newark, DE, USA *Optical-Field-Induced Current in Dielectrics*
Apr 2013	Seminar, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany *Attosecond View of the Photoelectric Effect and Optical-Field-Induced Current in Dielectrics*
Sep 2013	Seminar, Ultrafast X-Ray Science Laboratory, Lawrence Berkeley National Laboratory, Berkeley, CA, USA *Non-Equilibrium Structural Dynamics and Phase Transitions in Solids*
Sep 2013	246th ACS National Meeting and Exposition, Indianapolis, IN, USA *Chemical Control of Heterogeneous Electron Transfer Dynamics and Strong Electron-Lattice Coupling in TiO_2*
Sep 2013	Physics Colloquium, University of Nebraska-Lincoln, Kearney, NE, USA *Non-Equilibrium Structural Dynamics and Phase Transitions in Solids*

Melanie Müller

Oct 2013	Workshop on New Trends and Faces in Ultrafast Structural Dynamics, Stellenbosch, Südafrika *Femtosecond Low-Energy Electron Diffraction and Imaging: A Compact Approach*

Lutz Waldecker

Oct 2013 Workshop on New Trends and Faces in Ultrafast Structural Dynamics, Stellenbosch, Südafrika
Ultrafast Dynamics of Phase Transitions in $Ge_2Sb_2Te_5$