FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

# Report to the Fachbeirat
# Department of Physical Chemistry

# 2015

**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 Remarks

Since the last meeting of the Fachbeirat, the Department of Physical Chemistry has continued to develop its research infrastructure in the existing lab space, while the construction of the new building has made significant progress. The research groups and equipment will move into this new building in summer 2016. Several changes have occurred among the group leaders and senior postdocs of the department:

- *Prof. Leonhard Grill* has moved all activities to the University of Graz after the completion of his EU-funded projects at the FHI.
- With the successful completion of PhD thesis work and two DFG projects the part-time appointment of *Prof. Karsten Horn* will terminate at the end of 2015.
- *Dr. Alexey Melnikov* will also leave the institute with the completion of his DFG Project in December 2015. His activities on spin and magnetization dynamics will be continued in part by *Dr. Ilya Razdolski*.
- Since January 2014, *Dr. Alexander Paarmann* has set up a new research group employing the FHI infrared free electron laser (FEL) for time-resolved optical spectroscopy to study ultrafast dynamics in solids, in particular phonon dynamics. His group contributes significantly to the characterization and future development of the FEL.
- *Dr. Alexander Saywell* has moved from a DFG project ("Eigene Stelle") at the FHI to a position at the University of Nottingham in January 2015.

Two large service groups of the institute, the Electronics and the Mechanical Workshops, are associated with the department. The organization and machine infrastructure of the Mechanical Workshop (headed by *Petrik Bischoff*) has been further improved and the output and support of the workshop for the FHI is well received by the scientists. The Electronics Workshop (headed by *Georg Heyne*) is also 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 focusses on the dynamics of elementary processes at surfaces, interfaces and in solids, aiming at a microscopic understanding of molecular and electronic processes as well as the interactions between various (electronic, spin and lattice) degrees of freedom. Our strategy is to address these problems from several sides using complementary approaches, in particular by the development and application of various time- or spatial-resolved spectroscopic techniques

dedicated to the specific physical questions. The research is performed by small teams with specific expertise, and is structured along two main directions: (I) ultrafast dynamics of elementary processes in solids and at interfaces, and (II) molecular processes at interfaces and in complex systems. Although research topics of the individual groups are quite diverse and their selection is primarily curiosity-driven, our complementary approach creates various synergies between the different groups.

The first line of research investigates the dynamics of elementary processes on their relevant time scales, employing ultrafast laser spectroscopy (with, typically, femtosecond time resolution). Both established and newly developed spectroscopic techniques are used to study the electronic structure and low-energy excitations in solids, dynamics of electron transfer processes, vibrational dynamics at interfaces, as well as optically induced phase transitions in solids. The second line of research addresses elementary molecular processes either at the single molecule level, or by employing various schemes of optical excitations including photoinduced surface reactions. Scanning probe microscopy – in part combined with optical excitation or light scattering – is used for imaging, manipulation and spectroscopy as well as inducing and probing chemical processes of individual molecules. Further activities address problems of molecular biophysics and electrochemistry.

The Department of Physical Chemistry currently has the following research groups:

**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*)
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)
- Time-resolved Second Harmonic Generation Spectroscopy (*Alexey Melnikov*)

**Molecular Processes at Interfaces and in Complex Systems**

- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Complex Chemical and Biological Systems (*Alexander Mikhailov*)
- Spatiotemporal Self-organization (*Markus Eiswirth*)

**Max-Planck-Research Group (MPRG)**

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

A new line of research in the department exploits the potential of the FHI FEL facility for time-resolved optical spectroscopy of solids, in particular of phonons and polaritons. A new research group, headed by *Alexander Paarmann*, has been established, which also develops tools for FEL pulse characterization, sensitive optical detection and non-linear spectroscopy as well as laser synchronization with the FEL.

The MPRG of *Ralph Ernstorfer* is associated with the department and collaborates intensively with regard to the development of high harmonic generation (HHG)-based XUV photoemission. The activity on time-resolved electron diffraction nicely complements the research on ultrafast electronic dynamics of solids in the department.

Promotion and guidance of young scientists in their career development is an important goal of the department, and is implemented by several measures (*e.g.* the IMPRS graduate school, PhD student and department workshops, regular status discussions, nomination for awards and invited talks). In particular, junior group leaders and postdocs are guided to obtain experience in grant applications and to become project leaders in EU or DFG funded projects. Currently, several young group leaders have projects as PIs in three collaborative research centers (Sfb 658, Sfb 951, Sfb 1109), one research unit (FOR 1700) funded by the Deutsche Forschungsgemeinschaft as well as in an EU-funded project (CRONOS). Furthermore, several individual DFG research grants of young scientists exist (see section 3 for a complete list of projects). Very recently, an independent Max Planck Research Group (MPRG) was awarded to *Julia Stähler*, which will start in 2016.

### 1.2 Selected Research Highlights

The following topics are a selection of research achievements as well as instrument developments in the department, obtained since the last report:

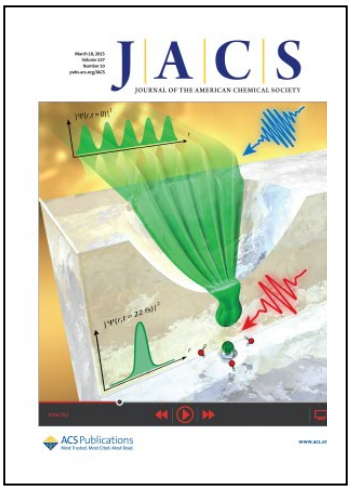
- Femtosecond time-resolved photoemission spectroscopy sheds new light onto the mechanism of the controversial photoinduced phase transition in $VO_2$: An instantaneous band gap collapse is observed upon photoexcitation, i.e. before the structural phase transition takes place. This transition to metallic monoclinic $VO_2$ is caused by photohole doping at the top of the valence band and followed by carrier relaxation on a 200 fs timescale. [Phys. Rev. Lett. **113**, 216401 (2014)].
- Critical phenomena in superconductors are typically observed in or close to equilibrium; however, strong indications for universal behavior in the high-$T_c$ superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ have been found for far out-of-equilibrium conditions induced by

femtosecond laser pulses. Strikingly, the dependence of conductivity vs time delay after laser excitation, probed by THz spectroscopy at multiple sample temperatures, are found to fall onto one curve if the time axis is normalized by a suitable scaling factor. These findings can be explained in part by a model based on the dynamic Ginzburg-Landau equation [Phys. Rev. Lett. **114**, 067003 (2015)].

- The charge density wave (CDW) transition in $TiSe_2$ has been elucidated using time-resolved and angle-resolved photoemission spectroscopy (trARPES), suggesting that the momentum- and energy-resolved relaxation times reveal the material's self-energy, and that the excitonic interaction between valence and conduction bands leads to the CDW instability of $TiSe_2$. Furthermore, a detailed study of the ultrafast photoinduced CDW gap dynamics in tri-tellurides revealed a stabilization of the gap due to increased Fermi surface nesting in the excited state [Faraday Discuss. **171**, 299 (2014)].
- A high repetition rate XUV laser source for time- and angle-resolved photoemission spectroscopy has been developed. The light source is based on high-harmonic generation (HHG) driven with a novel optical parametric laser system, and provides spectrally isolated femtosecond pulses with 21.5 eV photon energy at a repetition rate of 500 kHz [Optics Express **23**, 1491 (2015)].
- Hydrogen adsorption on ZnO(10-10) leads to local and site-specific changes of the surface potential, resulting in the formation of a charge accumulation layer and a global work function reduction of up to 600 meV. These sites host sub-surface bound excitons that form within 200 fs after above band gap photoexcitation of ZnO. The exciton formation is suppressed for excitation densities close to the Mott limit. [Phys. Rev. Lett. **113**, 057602 (2014), Phys. Rev. B **91**, 235313 (2015)].
- Functionalization of graphene with fluorine was used to create fluorographene, which exhibits a transformation between a stable as well as a metastable phase, induced by photon irradiation. The latter phase reverts back to the stable phase under blue luminescence [ACS Nano **8**, 7801(2014)].
- A new experimental setup for mid-infrared second harmonic generation (SHG) spectroscopy of solids employing the FHI infrared free electron laser (FHI FEL) has been developed. The high sensitivity of this technique to optical phonon resonances has been demonstrated for silicon carbide in the Reststrahl band [Appl. Phys. Lett. (in press)].
- To fully exploit the potential of the FHI FEL for time-resolved spectroscopy various techniques for optical characterization of the FEL output have been developed focusing on

nonlinear optics and ultrashort pulse operation of the machine. A synchronization system for a femtosecond near-infrared laser oscillator is currently being implemented for mid/near-infrared two-color experiments.

- THz metamaterials allow control of the effective refractive index by tailoring the shape of periodic metal structures. However, this approach usually requires extensive lithography procedures. To generate flexible THz metamaterials in a much easier and even dynamic and contactless manner, a semiconductor substrate is illuminated using fs laser pulses with a spatially shaped beam profile creating transiently metallic regions. Using such femtosecond lithography, a transient wire-grid polarizer and its ultrafast switch-on to manipulate a picosecond electromagnetic THz pulse with subcycle precision has been demonstrated [Light: Science and Applications **3**, e155 (2014)].
- The first measurement of the vertical binding energy (VBE) of the conduction band of the amorphous solid water phase was achieved using fs time-resolved two-photon photoelectron spectroscopy (2PPE). As all elementary processes "during the birth" of a solvated electron have been monitored in real time, the previous inaccessibility of the conduction band VBE could be attributed to the extremely short population lifetime (22 fs) in these excited states. [J. Am. Chem. Soc. **137**, 3520 (2015), see cover].




- Probing short-lived reaction intermediates at surfaces is extremely challenging due to their extremely low concentrations under steady state conditions. However, femtosecond laser excitation can enable temporal gating of such species: For the CO oxidation reaction on Ru(001) initiated by an ultrashort laser pulse new electronic states – attributed to $CO_2$ reaction intermediates close to the transition state region – have been probed using femtosecond time-resolved x-ray spectroscopy (trRIXS) at the LCLS free electron laser in Stanford. [Science **347**, 978 (2015); Phys. Rev. Lett. **114**, 156101 (2015)].
- The librational mode of interfacial water at the air/liquid water interface has been experimentally probed for the first time and found to be substantially higher in frequency than in bulk liquid water at the same temperature but similar to that in ice. Evidently, from the perspective of water's rotational potential, water at the air/water interface is "ice-like", while viewed from its OH stretch frequency or picosecond structural dynamics water is "liquid-like".

- Tautomerization of individual molecules was studied for porphycene on a Cu(110) surface by using low-temperature scanning tunneling microscopy, revealing a vibrationally mediated excitation mechanism through inelastic electron tunneling. The tautomerization probability can be precisely controlled by placing single adatoms and molecules nearby [Nature Chemistry **6**, 41 (2014)].
- Tip-enhanced Raman spectroscopy (TERS) of graphene nanoribbons grown on Au(111) was applied in an UHV scanning tunneling microscope (STM) setup. The 0.74 nm wide armchair nanoribbons are directly observed by STM and characteristic vibrational modes appear in both the far- and near-field Raman spectra, yielding an enhancement of $4 \cdot 10^5$ in TERS [J. Phys. Chem. C 118, 11806 (2014)].
- Reversible switching of single porphycene molecules on a Cu(111) surface was demonstrated using low-temperature STM. The thermodynamically stable *trans* tautomer can be selectively converted to the metastable *cis* configuration by hot carriers excited by a voltage pulse, whereas *cis* molecules can be switched back to *trans* by thermal activation [ACS Nano **9**, 7287–7295 (2015)].
- A thin-layer electrochemical cell allowing for simultaneously conducting cyclo-voltammetry and interface-specific vibrationally resonant sum frequency generation (SFG) spectroscopy was developed and used to probe the paradigmatic electro-oxidation of formic acid. On Pt(100), weakly adsorbed formic acid was found to play an important role in the so-called *direct* oxidation pathway.
- Hydrodynamic collective effects of active proteins, cyclically changing their shapes, in cytoplasm of a biological cell and in bio-membranes were theoretically investigated. ATP-dependent diffusion enhancement and directed drift-induced by concentration gradients of active proteins were demonstrated, in agreement with experimental data [Proc. Natl. Acad. Sci. (USA) **112**, E3639 -E3644 (2015)].

## 2. Progress Report

### 2.1 Ultrafast Dynamics in Solids and at Interfaces

Elementary processes in solids and at interfaces such as electron transfer, vibrational excitation and relaxation, or coupling between electrons, phonons and spins are the underlying microscopic processes of much more complex phenomena, ranging from surface reactions to phase transitions in complex materials. The study of the non-equilibrium, ultrafast dynamics of such fundamental processes provides mechanistic insights into the coupling and energy exchange between various degrees of freedom. To elucidate these processes, several groups in the department perform real-time studies of solids and interfaces on ultrafast time-scales, complemented by studies of the electronic structure and low-energy excitations.

#### 2.1.1 Ultrafast Electron and Lattice Dynamics in Correlated Materials

Strong correlation effects in solid state materials underlie fundamentally important and potentially useful phenomena such as insulator-metal transitions or unconventional super-conductivity. In such materials, different degrees of freedom (charge, spin, orbital, and lattice) are often strongly coupled and lead to electronic, magnetic, and structural instabilities. Beyond the investigation of ground state properties, studies of the non-equilibrium properties after optical excitation provide insight into the elementary mechanisms responsible for the formation and destruction of the strongly correlated state. Angle-resolved photoemission spectroscopy (ARPES) is a well-established technique to get access to the spectral function and the single-particle band structure of a solid. We use this method in a pump-probe scheme, where a first laser pulse (pump) drives the sample into non-equilibrium conditions and a second laser pulse (probe) monitors the electronic structure after a certain time delay. The variation of the time difference between pump and probe enables the observation of the transient evolution of the electronic structure on femtosecond timescales.

The group of *Julia Stähler* has investigated vanadium dioxide ($VO_2$) as a paradigmatic example for strongly correlated materials. $VO_2$ undergoes an insulator-to-metal transition at 340 K, which is accompanied by a change of the crystal structure from the monoclinic to the rutile phase (see Fig. 1(a)). Despite major scientific efforts over decades, the question whether the monoclinic distortion of the lattice is a sufficient condition for the opening of the gap or if strong electron correlations are responsible to form the insulating state (“Mott gap”) remained unanswered. One approach to tackle this question is to disturb the *electronic* system (i.e. the electron correlation) by optical excitation and to monitor the ultrafast response of the material

in the time domain. If the material instantaneously transforms to a metal, the insulating gap originates purely from electron correlation; if lattice reorganization is needed to precede the electronic transition, a finite time for the gap collapse would be expected.

The group recently succeeded to perform the first time-resolved photoemission measurements with sufficient time resolution of the photoinduced phase transition in $VO_2$. [1] Figure 1(b) shows the photoinduced change of the PES intensity in the band gap of insulating $VO_2$ in false colors as a function of energy with respect to the Fermi energy (right axis) and pump-probe time delay (bottom axis). Quasi-instantaneously with the photoexcitation at $t = 0$, spectral weight is observed in the band gap, showing that the gap has collapsed. Analysis of the temporal evolution of the photoemission intensity as a function of time shows that the

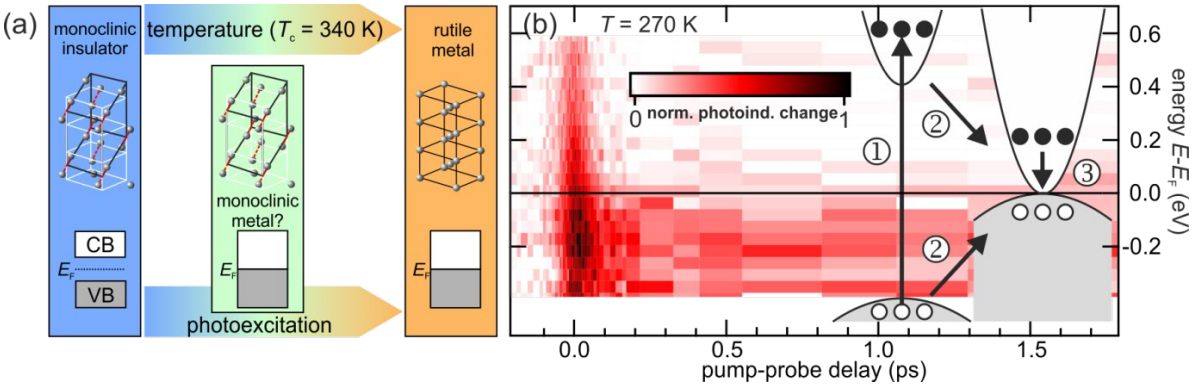



***Figure 1:*** *(a) Thermal and photoinduced transition in $VO_2$ from a monoclinic insulating to a rutile metallic phase. (b) Photoinduced change of the photoemission intensity in the band gap of insulating $VO_2$.* Inset: *Directly after photoexcitation (1), the gap collapses (2) before carriers relax to the Fermi level (3) within 200 fs.*

quasi-instantaneous gap collapse occurs faster than the relaxation of hot carriers occurring in approximately 200 fs. In a close collaboration with Angel Rubio (associated with the Theory Department) it could be shown by first-principles many body perturbation theory that the abrupt change of electronic structure can be explained by the photoinduced depopulation of very localized states at the top of the valence band, leading to pronounced changes in the screening of the Coulomb interaction and strong renormalization of the band gap. The combination of theory and experiment thus shows that the insulating gap of $VO_2$ breaks down instantaneously with the disturbance of electron correlation through photoexcitation, without the necessity of structural rearrangement.

Non-equilibrium conditions may lead to novel properties of photoexcited materials which are not accessible in equilibrium. Such excited states are usually characterized by enhanced fluctuations, leading to a reduced or even vanishing order parameter of a broken symmetry ground state, characterized, e.g., by an electronic energy gap. The group of *Martin Wolf* has

investigated the charge density wave (CDW) material class of rare-earth tri-tellurides, $RTe_3$ ($RTe_3$, R = Te, Ho, Dy) using trARPES and 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 [2]. Furthermore, the electronic structure reveals a persistent energy gap even in highly excited transient states. This is attributed to a competition between fluctuations in the electronically excited state which tend to reduce order, and transiently enhanced Fermi surface nesting that stabilizes the order.

A key quantity describing the physics of correlated materials is the self-energy, which represents the relevant many-body interactions of a system and determines the lineshape of electronic bands probed by ARPES. The group has investigated the mechanism of the charge density wave instability in $TiSe_2$ – a layered transition metal dichalcogenide – using the time-resolved XUV ARPES setup at the Artemis facility, UK. Analysis of the dynamics in the high-temperature fluctuation regime, which precedes the CDW instability, suggests that the momentum- and energy-resolved relaxation times reveal the imaginary part of the material's self-energy. Comparison with theoretical modelling allows the identification of the Coulomb-mediated electron-hole (excitonic) interaction between the valence and conduction bands as the dominant mechanism leading to the CDW instability of $TiSe_2$.

A related compound, $Ta_2NiSe_5$, which undergoes an insulator-semiconductor transition at 328 K accompanied by a structural distortion, was investigated by *Julia Stähler*'*s* group. By combining static Raman spectroscopy (in cooperation with the CP department) with femtosecond time-resolved optical spectroscopy as well as time-resolved ARPES, a very strong coupling of the 4 THz mode, which is characteristic for the low-temperature phase, to the photoexcited carrier density was observed. Most remarkably, the ultrafast dynamics of electrons *and* holes in the conduction and valence band indicate that an intrinsic absorption saturation of $Ta_2NiSe_5$ inhibits a photoinduced phase transition; on the contrary, strong photoexcitation leads to a widening of the band gap, suggesting that photoexcited $Ta_2NiSe_5$ is *more* insulating than in equilibrium.

To provide access to the full electronic structure in the entire Brillouin zone a high harmonic generation (HHG)-based XUV photoemission setup has been developed in close collaboration with the MPRG of *Ralph Ernstorfer*. Our approach relies on a novel high-average power ultrashort laser system [3] with an optical parametric chirped-pulse amplifier (OPCPA) capable of generating spectrally narrow XUV pulses (21.7 eV with 100 meV bandwidth) at 500 kHz repetition rate for trARPES (see MPRG report for more details). This XUV light

source closes a technology gap, which has so far has limited the operation of HHG sources to repetition rates typically below 10 kHz.

[1] D. Wegkamp *et. al*, Phys. Rev. Lett. **113**, 216401 (2014)
[2] L. Rettig *et. al*, Faraday Discuss. **171**, 299 (2014)
[3] M. Puppin *et al.*, Optics Express **23**, 1491 (2015)

### 2.1.2 Electronic Structure of Metal Oxide Surfaces and Low-dimensional Materials

The group of *Takashi Kumagai* has studied the local electronic structure of ultrathin ZnO films by using low-temperature scanning probe microscopy (STM and AFM). The growth and structure of smooth ZnO films on Ag(111) was investigated in collaboration with the CP department [1]. Fig. 2 (a) shows, as an example, the simultaneously recorded STM image and STS mapping for 2 and 3 ML thick ZnO layers, with a characteristic Moiré pattern resulting from the lattice mismatch between ZnO and Ag(111). The atomic arrangement could be further investigated by noncontact AFM with atomic resolution and DFT calculations in collaboration with the Theory department. Furthermore, the local density of states (empty electronic states) was analyzed by STS, whereby local variations caused by the finite size of the films and defects (highlighted by the dashed circle) could be clearly observed. These results provided microscopic insight into the geometric and electronic structure of this system.

The group of *Julia Stähler* has investigated the impact of hydrogen adsorption on the electronic structure and dynamics at the surface of bulk ZnO single crystals using fs time-resolved photoelectron spectroscopy. In collaboration with Patrick Rinke, Theory Department, it was shown that O-H bond formation, which dominates at low-coverages, leads to distinct a local drop of the potential, significantly reducing the sample work function and leading to downward surface band bending (see Fig. 2b). Due to the *n*-type character of ZnO, this results in a partial filling of the conduction band in the surface region, leading to the formation of a charge accumulation layer (CAL) at the surface. Zn-H bonds, on the contrary, lift the potential upwards, thereby reducing the effect of an O-H precoverage. The complex interplay of both adsorption sites strongly influences the CAL density at the surface and causes a saturation of the work function decrease of 0.6 eV [2].

The hydrogen-induced local potential minima host sub-surface-bound excitons (SX) when ZnO(10-10) is optically excited. After ultrafast ($\tau(E)$ = 20-200 fs) relaxation of photoexcited hot carriers through scattering with optical phonons, electron-hole pairs form that exhibit a temperature-dependent decay and nanosecond lifetimes. The formation probability of SX

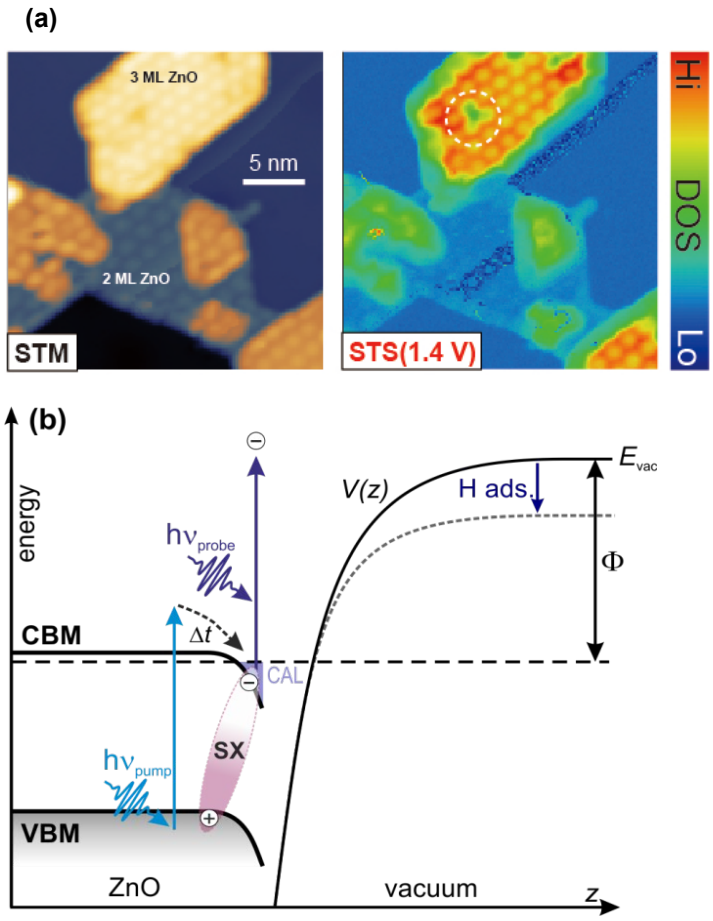



***Figure 2 (a)*** *(Left) STM image of the 2 and 3 ML ZnO films on Ag(111) at 5 K. The characteristic Moiré pattern is observed over the ZnO layers. (Right) STS mapping measured at the resonance state of the 3 ML ZnO layer. (b) Hydrogen adsorption on the ZnO(10-10) surface leads to a reduction of the work function and downward surface band bending. Due to the n-type character of ZnO the conduction band becomes partially filled at the surface, creating a charge accumulation layer (CAL). Above band gap excitation is followed by hot carrier relaxation to the Fermi level and the formation of sub-surface-bound excitons.*

reduces as the excitation density approaches the Mott limit, when the photoexcitation creates an electron-hole plasma that screens the attractive Coulomb interaction [2]. Moreover, hydrogen coverage (and, thus, CAL carrier concentration) dependent experiments unveil that the coupling of excited electrons to the phonons is reduced and thus their lifetime is enhanced. Above a critical density, the screening of the Coulomb attraction even becomes sufficiently large to completely suppress SX formation.

$SrTiO_3$ (STO) is another *n*-type transition metal oxide that exhibits a charge accumulation layer at its surface. Here the CAL is caused by oxygen defects at the surface. The density of the CAL is one order of magnitude larger than the one of hydrogen-terminated ZnO (10-10), thus inhibiting SX formation for this system due to enhanced screening. The response of STO to strong photoexcitation in the near IR was also investigated in *Julia Stähler*'s group: Photons absorbed at in-gap states at the STO surface (at oxygen defects) generate additional charge density in the conduction band. Surprisingly, the highly excited carriers relax on timescales compatible with 2D Fermi liquid theory despite populating energy levels that are degenerate with bulk (3D) conduction band states.

The group of *Karsten Horn* has concentrated on the properties of graphene, both in its pristine form but also modified by adatom functionalization and through contact with metals. A fluorographene modification was found to arise from exposure to fluorine atoms, with a stable as well as metastable phase (induced by photon irradiation), which reverts to the former under emission of blue luminescence. Functionalization of graphene by various adsorbates (NO, $SO_2$) was found to induce massive changes in its electronic structure, and to promote a reversible transformation into graphene oxide [3].

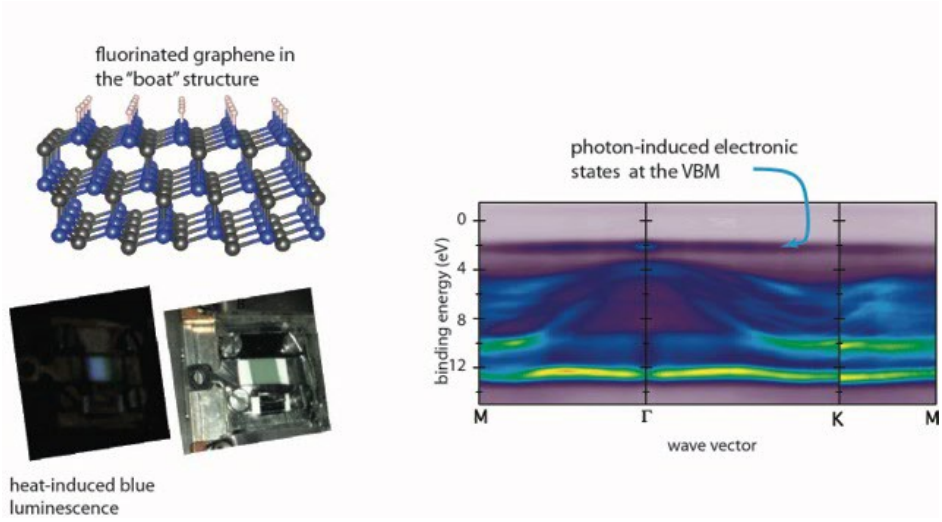



***Figure 3:*** *Single-sided fluorographene exists in the stable „boat" ground state, but can be converted into a metastable state by UV irradiation, upon which new electronic states appear at the valence band maximum as revealed by ARPES. Annealing reverts the metastable state to the ground state under emission of blue luminescence.*

Graphene interaction with metals may lead to symmetry breaking and band gap opening, a process that was elucidated in detail (for copper as a substrate), through comparison with DFT calculations. Emerging ferromagnetism of thin cobalt films underneath graphene was examined through x-ray magnetic circular dichroism (XMCD), and a transfer of magnetic moment onto the carbon atoms of graphene was found, with a reversal of the out-of-plane ordering of magnetic moment in the metal and graphene.

Self-assembled metal nanowires on semiconducting substrates are an important model system for low-dimensional materials providing a versatile and tuneable environment. The electronic structure of the Ag/Si(557) nanowire system exhibits signatures of a quasi-1D electron gas in electron energy loss spectroscopy, but two-dimensional metallic states at the Fermi level with a super-periodicity were observed by ARPES. These seemingly conflicting views of the dimensionality in this and other nanowire systems can be reconciled by considering the electronic coherence length of excitations probed by ARPES or EELS.

[1] A. Shiotari *et al.*, J. Phys. Chem. C **118**, 27428 (2014).

[2] J.-C. Deinert *et.al.*, Phys. Rev. B **91**, 235313 (2015), *Phys. Rev. Lett.* **113**, 057602 (2014)

[3] A.L. Walter *et al*, ACS Nano **8**, 7801(2014)

### 2.1.3 Mid-infrared Nonlinear Spectroscopy of Solids

The possibility of transient control of physical properties of a crystal by means of large amplitude lattice vibrations, excited by intense mid-infrared (mid-IR) laser pulses, provides an attractive alternative route to various electronic excitation schemes. The newly established group of *Alexander Paarmann* develops experimental techniques for studying lattice-driven nonlinear phenomena by employing the FHI infrared free-electron laser. These efforts encompass two major components: the development of novel nonlinear mid-IR spectroscopy approaches using the FEL, and the characterization and optimization of the FEL specifically for these experiments.

Despite much progress in the development of intense, broadband THz and mid-IR light sources based on femtosecond table-top lasers, there is still a lack of intense, narrowband lasers in this frequency region. In that regard, the FHI FEL provides a unique opportunity to study sharp phonon resonances in the nonlinear optical response of a solid. The group has developed second harmonic (SH) phonon spectroscopy as a new even-order nonlinear optical technique, see Fig. 4. For the prototype material silicon carbide (SiC), pronounced resonances in the SH spectrum can be related to phonon-induced enhancements of the nonlinear susceptibility and the local fields through the Fresnel transmission, respectively [1]. Furthermore, the high sensitivity of the SH yield to local fields was exploited in studies of field localization of surface phonon polaritons confined to sub-wavelength nanostructures with SH phonon spectroscopy. By improving the sensitivity of mid-IR SH spectroscopy (e.g. by heterodyne detection), the group aims to establish this method for surface- and interface-sensitive vibrational spectroscopy.

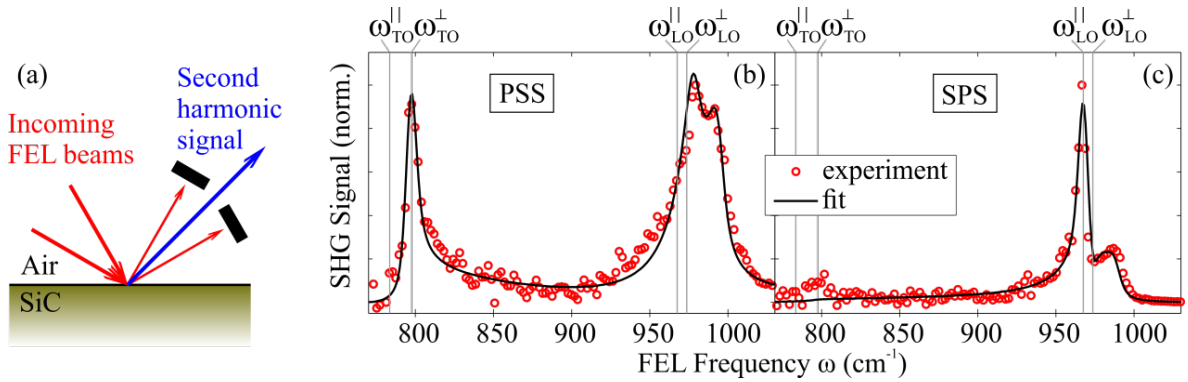



***Figure 4:*** *Second harmonic phonon spectroscopy of SiC. (a) Schematic of the second harmonic experiment employing the FEL in a non-collinear geometry. (b,c) Experimental second harmonic spectra of SiC for two different polarization combinations of incoming and detected beams. For reference, the axial (∥) and planar (⊥) optical phonon frequencies for longitudinal (LO) and transversal (TO) modes in the uniaxial crystal are indicated. From Ref. [1].*

In addition, the group has developed and implemented several experimental approaches to address phonon-driven resonant demagnetization, nonlinear absorption, and second harmonic generation in solids. In part, these frequency-domain studies nicely complement the time-domain experiments in the THz spectroscopy group (*Tobias Kampfrath*): for instance, the role of optical phonon resonances in the ultrafast demagnetization of ferrimagnetic yttrium iron garnet (YIG) has been investigated with both techniques. Similarly, a novel excitation pathway for Raman-active (IR-inactive) phonons by a sum-frequency process at half the phonon frequency was demonstrated with in two complementary approaches: (i) time-domain coherent phonon spectroscopy after excitation with broadband, phase-stable THz pulses and (ii) two-photon absorption spectroscopy employing the tunable FEL radiation.

The characterization of the short pulse and nonlinear operation of the FEL was performed by multiple experimental approaches. The temporal shape of the FEL micropulses was measured using a specifically designed autocorrelator that can operate in the whole tuning range of the FEL [2]. It was demonstrated that the FEL micropulse duration and spectrum, as well as the peak intensities critically depend on the FEL cavity parameters, but also evolve during the FEL macropulse, allowing for precise control of these features for optimal conditions of nonlinear optical experiments. The intrinsic harmonic content of the FEL output (up to the 11th harmonic) has been characterized using a prism-based harmonic separator, and control of the harmonic intensities by variation of the electron beam steering was demonstrated.

A synchronization system for a femtosecond near-infrared (NIR) laser oscillator is currently under construction, and the respective characterization techniques are being developed. The synchronized laser will allow for implementation of time-resolved FEL-pump – NIR-probe experiments, as well as surface specific vibrational sum-frequency spectroscopy.

[1] A. Paarmann *et al.*, Appl. Phys. Lett. **107**, 081101 (2015)

[2] W. Schöllkopf *et al.*, Proc. of SPIE Vol. **9512**, 95121L (2015)

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

The terahertz (THz) frequency range is of key relevance from a fundamental scientific as well as from an applications-related point of view. Many elementary excitations in physical systems have transition energies on the order of 10 meV, for example quasi-free electrons in solids, crystal lattice vibrations, or excitons in semiconductors. As 1 THz corresponds to a photon energy of 4.1 meV, these modes can be probed resonantly and with sub-picosecond time resolution using THz electromagnetic pulses. As today THz pulses with electric-field amplitudes of ~1 MV/cm can be generated in the lab, it has become possible to even drive and control such resonances on sub-picosecond time scales [1]. Furthermore, bit rates in information technology may soon approach the THz range, which requires to manipulate the information carrier (such as the electronic current, spins 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 in order

- To gain insight into the interplay of low-energy excitations in complex materials. Examples are the elusive interaction of lattice and electron spins in magnetically ordered solids or rotational/librational motion of molecules in liquids.
- To gain control over the properties of matter and light at highest frequencies and to explore potential applications. Examples are the ultrafast transport of electron spins and generation of transient metamaterials for THz radiation.
- To develop new and sensitive spectroscopic tools which permit, for example, the detection of ultrafast spin currents ("ultrafast spin amperemeter") and the measurement of high-frequency Hall effects.

Recent examples for these research activities are described in the following.

*Electron dynamics in complex solids:* THz pulses are an excellent and ultrafast probe of the conductivity of transient electrons, in particular following excitation with a femtosecond laser pulse. This strategy allows measuring the mobility of conduction electrons of two intrinsic (insulating) polytypes of the semiconductor SiC in a contact-free manner [2]. These measurements are an important characterization of the electrical transport properties of SiC which is considered a key material in high-voltage and high-temperature electronics.

Using a similar approach, a femtosecond laser pulse is applied to suddenly break Cooper pairs in the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSSCO) and a THz probe is used to monitor the subsequent recovery of the superconducting state. Strikingly, the relaxation to

equilibrium exhibits a power-law dynamics and scaling behavior. In particular, we found that curves of conductivity vs time at multiple sample temperatures fall onto one curve when the time axis is normalized by a suitable scaling factor. Our findings provide strong indication of universality in systems far from equilibrium [3].

*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 to encode bits. 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. Currently, we study the high-frequency (THz) behavior of central spintronic effects in metals: the anomalous and spin Hall effect (AHE and SHE). Both phenomena rely on spin-orbit coupling (SOC) that causes a deflection of spin-up and spin-down conduction electrons in opposite directions. We have developed a method that permits measurement of the AHE (i.e. the full conductivity tensor) of standard magnetic metals such as CoFeB over the broad frequency range from 0.5 to 40 THz in a quasioptical, contact-free manner. As the related photon energies (4 meV at 1 THz) coincide with typical SOC band splittings in 3d metals, we hope to gain direct insight into the energetic structure of SOC of conduction electrons.

*Ultrafast spin-lattice coupling:* The coupling of lattice vibrations and ordered spins in magnetic solids is far from being understood, despite its fundamental and applied relevance for ultrafast spin manipulation (femtomagnetism) and transport of spin angular momentum (spintronics and spin caloritronics). To probe spin-lattice coupling in a direct and highly selective manner and on its natural time scales, we conducted the THz pump-probe experiment shown in Fig. 5(a). As a model ferrimagnetic insulator, yttrium iron garnet (YIG) was chosen because its electronic degrees of freedom are frozen out at room temperature (electronic band gap 2.8 eV). An intense THz pulse exclusively and resonantly excites optical phonons, thereby leaving the electronic subsystem unchanged. Ultrafast demagnetization with a time constant as short as 1 ps is observed [Fig. 5(b)], which is extremely surprising because decoherence of spin precession in YIG is known to occur on much longer time scales of >100 ns. Supported by measurements covering a broad temperature range and time scales from $10^{-13}$ to $10^{-3}$ s as well as analytical modeling and *ab initio* calculations, we found evidence for a new microscopic mechanism of phonon-to-magnon conversion.

*Surface/interface sensitivity:* So far, THz pulses have exclusively addressed the bulk properties of materials (rather than their interfaces). The THz group has recently been able to

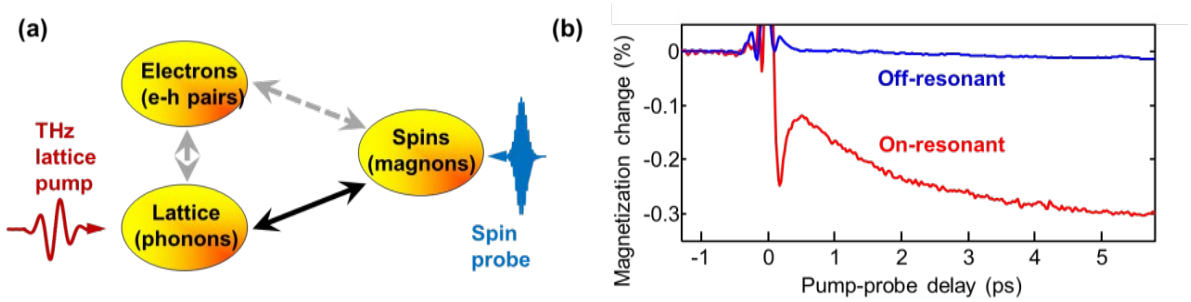



***Figure 5**: (a) Pump-probe scheme for probing spin-lattice coupling in a magnetic solid. A THz pump pulse resonantly excites a zone-center optical phonon, and the impact on the spin system is monitored by a delayed pulse probing the transient magnetization. In the case of a magnetic insulator, the orbital electron degrees of freedom are frozen out (dashed arrows). (b) Observation of ultrafast magnetization quenching of yttrium iron garnet (YIG). While off-resonant pumping in the transparency window of YIG results in a negligible signal, resonant phonon excitation leads to a drop of the magnetization with a time constant as short as ~1 ps.*

optically launch and measure THz currents flowing at the surface of the topological insulator $Bi_2Se_3$. Excitation by a laser pulse (duration 10 fs, photon energy 1.55 eV) shifts electron density from the Se atoms toward the Bi atoms. Our data indicate that this shift current flows predominantly in the first ~2 nm of the surface region. In addition, our results show that previously suggested scenarios based on optically induced changes in the electron group velocity are inoperative or at least result in much less efficient currents than assumed.

*Manipulation of THz radiation:* The THz group also tested new schemes to manipulate THz radiation using optically induced, time-varying structures. More precisely, a laser beam with a spatially modulated cross-section was directed onto a planar semiconductor slab, in which the optical intensity pattern is translated into a spatial modulation of the refractive index. While dark regions remained dielectric, the illuminated regions became metallic at THz frequencies, owing to the generation of an electron-hole plasma. Compared with standard lithography, such "gray-scale transient lithography" offers improved flexibility. This approach has been used to generate a transient wire-grid polarizer, i.e. a pattern of alternating conducting and dielectric stripes. Ultrafast operation was demonstrated by switching the polarizer on when the leading half of an incident THz pulse had traversed the slab. The trailing edge then encountered a polarizer, resulting in a polarization plane by 45° rotated [4]. This approach is a first step toward more complex operations such as frequency shifting and spectral focusing of THz electromagnetic pulses.

[1] T. Kampfrath, K. Tanaka, K.A. Nelson, Nature Photonics **7**, 680 (2013). (Review article)

[2] A. Rubano, M. Wolf, T. Kampfrath, Appl. Phys. Lett. **105**, 032104 (2014)

[3] L. Perfetti *et al.,* Phys. Rev. Lett. **114**, 067003 (2015)

[4] N. Kamaraju, *et al.*, Light: Science and Applications **3**, e155 (2014)

### 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 such as 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 in a back pump-front probe scheme (see Fig. 6) with the help of time-resolved second harmonic generation (SHG) [1, 2] and magneto-optical Kerr effect (MOKE) [2]. In the first experiment, the transport of spin polarized hot carriers through an Au/Fe/MgO(001) stack has been demonstrated [1]. One particular focus of the group is the development of generation, control, and monitoring techniques for ultrashort spin current pulses and the study of their spin transfer torque action on a ferromagnet. The latter is an elegant and promising way to excite magnetization dynamics: when spin-polarized hot carriers reach the ferromagnetic layer, the magnetization experiences a torque and starts moving out of the equilibrium.

In metals, spin currents (SC) can be produced by temperature gradients in a bulk FM or across interfaces to a normal metal, which is known as the spin Seebeck effect. Recently, the group has demonstrated the ultrafast spin Seebeck effect, which is based on the spin-dependent interface transmission for non-equilibrium hot carriers (Fig. 6 (a)): large Fe/Au interface transmission for majority electrons provides a spin flux from Fe to Au forming a pulse of superdiffusive spin current. The SC pulse duration is determined by the hot carrier thermalization time on the order of 200 fs: once the HC relax towards the Fermi level the transmission difference vanishes and the HC emission stops. Experimentally, non-equilibrium carriers are excited in the top Fe layer of a Fe/Au/Fe/MgO(001) structure by a 14 fs, 800 nm laser pulse. Generation of about 300 fs-long spin current pulses has been demonstrated by characterization of their shape with SHG after passing the Au layer (Fig. 6 (c)). Upon reflection at the Fe/Au interface of the bottom Fe layer the SC polarized orthogonally to the Fe magnetization M lose the orthogonal component and become polarized anti-parallel to M. Furthermore, subsequent picosecond precessional dynamics of M excited in the second Fe layer by the spin transfer torque has been monitored with MOKE (Fig. 6 (d)). Owing to a spatially non-uniform spin transfer torque, several lowest standing spin wave modes are excited and spectral analysis of these modes allows an estimate of the spin accumulation depth in Fe $\lambda < 4$ nm (Fig. 6 (e)).

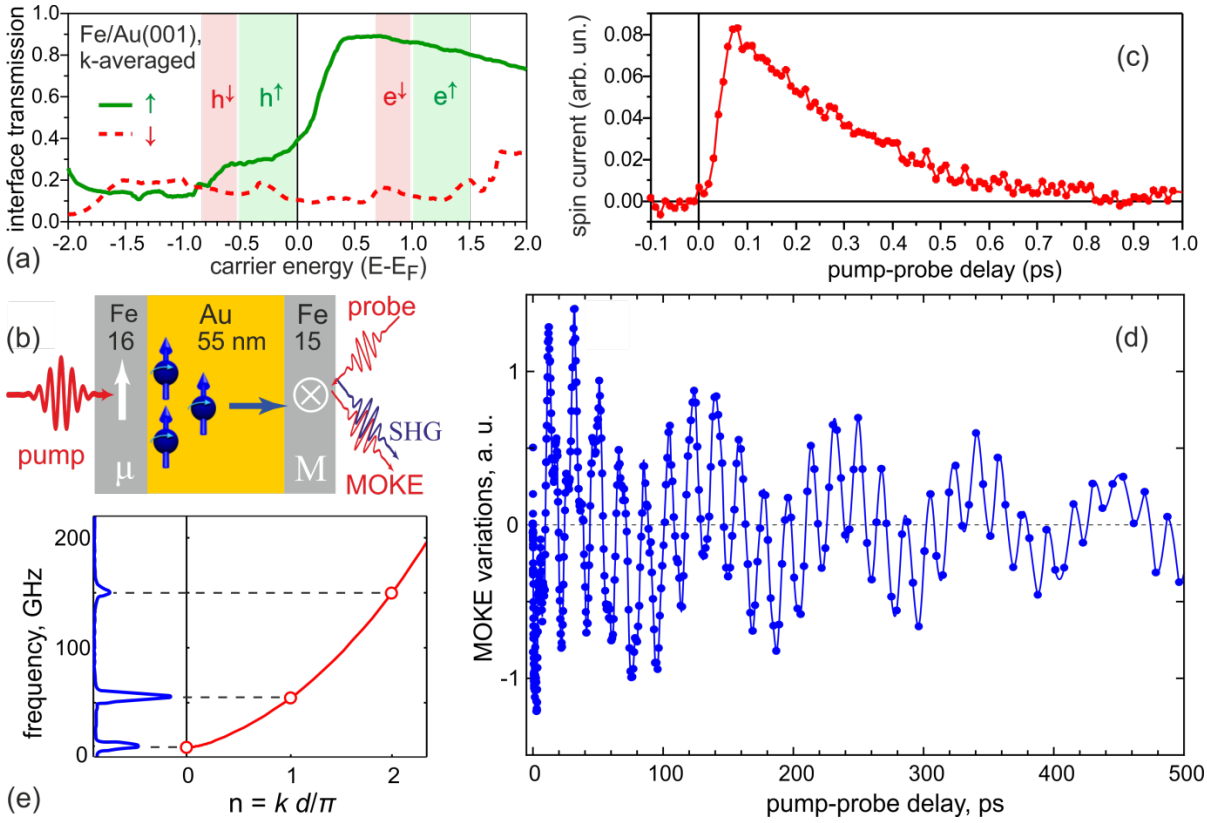



***Figure 6:*** *(a) Ab initio calculated spin-dependent hot carrier transmission of the Fe/Au interface [2]; shadowed areas mark energy ranges where spin-polarized carrier are excited in Fe [1]. (b) Schematic of the experimental geometry. (c) Spin current SC pulse profile given by the SC-induced component of SHG electric field (which is directly proportional to SC in Au in the vicinity of Au/Fe interface) normalized to the magnetization-induced interface contribution. (d) Spin transfer torque -induced MOKE rotation. (e) Fourier spectrum of the MOKE rotation (blue) and the magnon dispersion curve (red solid line) in Fe. Frequencies of the detected modes (open circles) characterized by a wavenumber n are in an excellent agreement with those calculated for the standing waves in a 15-nm-thick Fe film.*

These findings demonstrate the excellent abilities of spin currents for exciting non-uniform spin eigenmodes in thin ferromagnetic films, as compared to other ultrafast mechanisms, such as heat-induced quenching of magnetic anisotropy. Moreover, the obtained results shed light on the properties of ultrafast laser-driven spin currents and its interaction with a non-collinear magnetization.

[1] A. Melnikov *et al.*, Phys. Rev. Lett. **107,** 076601 (2011)

[2] A. Melnikov *et al.*, in Ultrafast Magnetism I, (Eds.) J.-Y. Bigot *et al.*, Springer Proceedings in Physics **159**, p.34 (2015)

## 2.2 Molecular Processes at Interfaces

Understanding interfacial processes on a molecular level provides insights into fundamental aspects of surface reactions. Studies are performed by several groups in the department with complementary techniques, enabling high spatial resolution using scanning probe microscopy as well as chemical sensitivity using vibrational or x-ray spectroscopy. In these studies, surface molecular dynamics and reactions are stimulated by thermal activation, excitation by light, electric fields or charge transfer. This is complemented by computational studies of biomolecular machines and spatiotemporal pattern formation in electrochemical systems.

### 2.2.1 Single Molecule Dynamics at Surfaces

Adsorbate dynamics at interfaces is of fundamental importance for understanding catalytic processes as well as for the development of molecular devices. The group of *Takashi Kumagai* studies single molecule processes using various scanning probe techniques including low-temperature scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM), and tip-enhanced Raman spectroscopy (TERS) under UHV conditions. These methods enable imaging and manipulation of single atoms and molecules and to conduct local spectroscopy.

*Direct observation of H-bond dynamics*: The dynamics hydrogen bonds is relevant for a wide range of chemical and biological processes, but the microscopic understanding often missing. The group has performed detailed studies of H-bond dynamics of molecules on metals surface [1], focusing, in particular, on the intramolecular H-atom transfer reaction (tautomerization) in individual porphycene molecules. Porphycene is a structural isomer of free-base porphyrin and forms a relatively strong H bond in the molecular cavity (in contrast to porphyrin), which offers a unique opportunity to explore H-bond dynamics (see Fig. 7 (a)). It was found that porphycene adsorbs in different tautomeric states depending on surface material and crystal orientation. For example, porphycene exclusively adsorbs as *cis* tautomer on Cu(110) (Fig. 7(b)), while on Cu(111) both *trans* and *cis* tautomers are observed at 5 K (Fig. 7 (c)). The *cis* ↔ *cis* tautomerization can be induced on Cu(110) either by thermal activation, or by excitation in the STM junction. Remarkably, the tautomerization rate can be precisely controlled either by placing a single Cu atom nearby a molecule, or by changing the tautomeric state of neighboring molecules in one-dimensional oligomers [2]. These results highlight the influence of the local environment on the dynamics, which is usually hidden in molecular ensembles probed by spatial averaging spectroscopies. Furthermore, remote control

of tautomer-selective switching has been demonstrated on Cu(111) [3] where the thermodynamically stable *trans* molecules are unidirectionally converted to the meta-stable *cis* tautomer through inelastic scattering with hot carriers generated by the STM and traveling along the surface (the *cis* molecules can be switched back to *trans* by thermal activation).

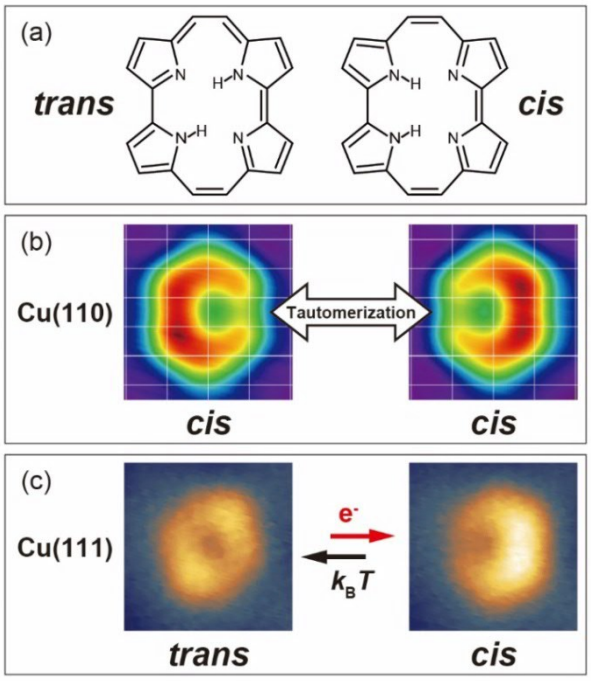



***Figure 7:*** *(a) Chemical structure and tautomers of porphycene. (b) STM image of cis porphycene on Cu(110) at 5 K. The cis ↔ cis tautomerization can be induced either by thermal activation, or by excitation in the STM junction. (c) STM image of trans and cis porphycene on Cu(111) at 5 K. The unidirectional conversion between the tautomers can be controlled by hot carrier injection (STM) or thermal activation.*

*Development of* tip-enhanced Raman spectroscopy: TERS is a powerful method for imaging and chemical characterization at nanoscale and applicable even at the single-molecule level. Recently, the group reported TERS measurement of graphene nanoribbons (GNRs) on Au(111) at room temperature [4]. The 0.74 nm wide armchair GNRs prepared by on-surface polymerization were imaged by STM, and the characteristic vibration modes were observed in both far- and near-field (tip-enhanced) Raman spectra (whereby the signal was enhanced up to $4 \cdot 10^5$ in the near-field). However, it was also found that the instability of the STM junction, such as changes of the tip apex and thermal drift of the relative tip position with respect to the surface, makes it extremely difficult to conduct highly reproducible experiments at room temperature. In order to minimize such instabilities and obtain clear-cut data providing detailed physical insights into the molecular process, a new low-temperature optical SPM system is currently being developed.

[1] T. Kumagai, Prog. Surf. Sci. **90**, 239 (2015)

[2] T. Kumagai *et al.,* Nature Chemistry **6**, 41 (2014)

[3] J. N. Ladenthin *et al*., ACS Nano **9**, 7287–7295 (2015)

[4] A. Shiotari, T. Kumagai, M. Wolf, J. Phys. Chem. **118**, 11806 (2014)

### 2.2.2 Real-time Observation of Photoinduced Surface Reactions

A grand challenge in surface reaction dynamics is the observation of short-lived reaction intermediates and real-time probing of the transition state region. Under steady state conditions, the concentration of such intermediates will be extremely low, in particular if the reaction proceeds at a small number of sites compared to the total surface area. However, if a reaction can be triggered by ultrafast laser excitation temporal gating of such short-lived intermediates may become possible. Such real-time observation of transient species at surfaces requires techniques which are sensitive to the chemical state and simultaneously enable real-time probing of elementary steps with femtosecond time resolution. Using the Stanford x-ray free electron laser, LCLS , the surface science collaboration headed by Anders Nilsson (Stockholm University) has previously applied time-resolved x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) to probe the dynamics of CO desorption from Ru(001) induced by femtosecond laser excitation [1].

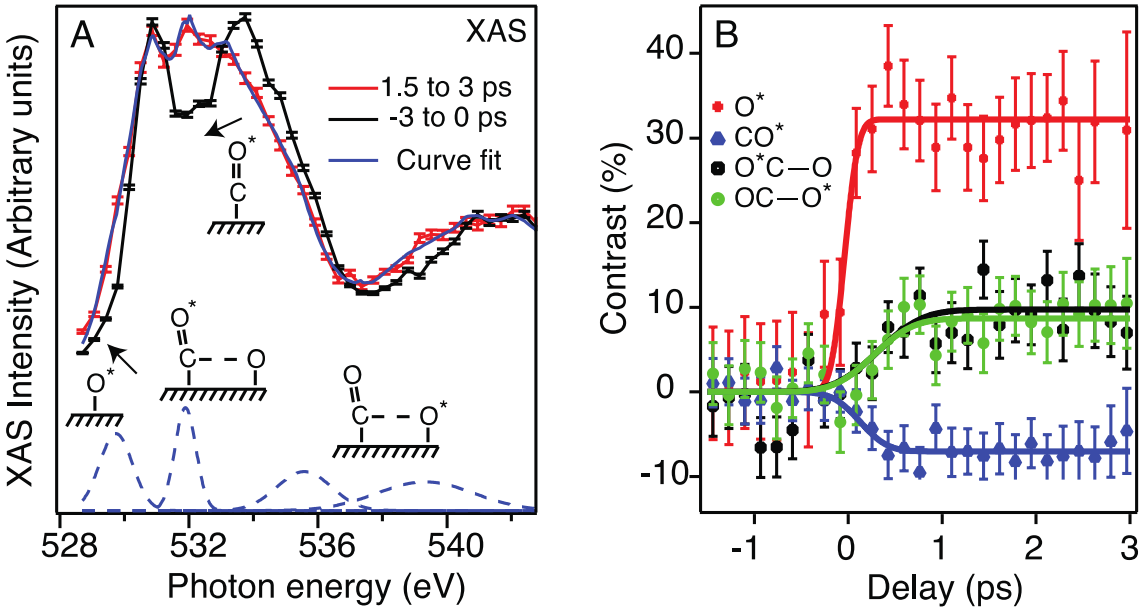



***Figure 8:*** *(A) Pump induced changes of the O 1s x-ray absorption (XAS) spectrum of CO/O/Ru(000). The insets schematically depict the microscopic interpretation of the laser-induced spectral changes as the O and CO species move out from their equilibrium sites (Gaussians plotted with dashed blue lines). (B) Time evolution of the contrast in the four spectral regions (normalized difference between the pumped and unpumped data) [2].*

Recently, this approach has been extended to study chemical bond formation in real time using the example of femtosecond laser induced CO oxidation on Ru(001), a process which has been studied extensively in the past by the group of *Martin Wolf*. In this process non-adiabatic coupling between transiently excited hot metal electrons and adsorbate vibrational degrees of freedom leads to excitation of the reaction coordinate, which mediates $CO_2$ formation on an ultrafast (picosecond) timescale. Fig. 8 (a) depicts x-ray absorption spectra in

the O 1s region of CO and oxygen coadsorbed on Ru(000), before and after excitation with a 400 nm fs laser pulse [2]. Within a few hundred femtoseconds, the laser excitation leads to motions of CO and O on the surface, allowing the reactants to collide, and, with a transient close to a picosecond, new electronic states appear in the O 1s XAS. These transient changes in the electronic structure exhibit a remarkably strong contrast of more than 10% (Fig 8 (b)). Density functional theory calculations indicate that the new electronic states in XAS result from changes in the adsorption sites of CO and O and bond formation between CO and O with a distribution of OC–O bond lengths close to the transition state [2]. After 1 ps, about 10% of the OC–O species populate a region which is close to (but energetically below) the transition state.

These results open the perspective for real time probing of a large number of surface reactions (e.g. water formation or hydrogenation reactions) and to obtain insight into the electronic structure and dynamics of reaction intermediates. However, the extension to other (*e.g.* oxide) surfaces or organic chemistry is still a challenge and requires the development of new photochemical pathways beyond the established femtochemistry at metal surfaces.

[1] M. Dell'Angela *et al.,* Science **339**, 1302 (2013); H.Xin *et al.,* Phys. Rev. Lett. **114**, 156101 (2015)
[2] H. Öström *et al.,* Science **347**, 978 (2015)

### 2.2.3 Interfacial Molecular Spectroscopy

The group of *Kramer Campen* investigates structure, dynamics and chemical reactivity at solid/gas and solid/liquid interfaces using the laser-based, interface-specific technique vibrational sum frequency (VSF) spectroscopy. In a VSF measurement, pulsed infrared (IR) and visible (VIS) lasers overlap spatially and temporally at an interface, and the light emission at the sum of the frequencies is monitored. This VSF emission is a spectroscopy (as the intensity increases by $> 10^4$ when the IR frequency is resonant with an interfacial vibration) and it is interface specific by its symmetry selection rules. Because the interfacial specificity is a result of the symmetry of light/matter interaction, it can be straightforwardly applied to any interface: solid/solid, solid/liquid, solid/gas, liquid/gas, and liquid/liquid. In the last two years three systems have been studied: the electrified metal/water, the air/water, and α-$Al_2O_3$/water interfaces. Depending on the details of the system, conventional, time-averaged VSF spectroscopy has been extended in significant ways.

*Electrochemical Interfaces:* Molecular level insight into reaction mechanisms in electro-chemistry is limited by, at least, two general problems: (i) an inability to experimentally probe

species that exist *both* at the solid/liquid interface *and* in much larger concentrations in the adjoining liquid phase and (ii) and inability to observe molecular species which exist for short times (< nanoseconds) during electron transfer. In the last two years the group has developed experiments that address both these limitations: The first problem has been addressed by construction of a thin layer cell that makes it possible to simultaneously conduct both cyclic voltammetry and VSF spectroscopy (and thus correlate oxidation current and interfacial surface speciation). As a proof-of-principle of this idea, the electrooxiation of formic acid on the Pt(100) surface has been characterized. This work shows both the expected CO oxidation (the so-called *indirect pathway*) and allows characterization of a previously unobserved interfacial species, i.e. weakly adsorbed formic acid, and its possible role in the *direct* pathway of electrooxidation [1]. The second limitation has been addressed by constructing an experiment in which electron transfer from gold across the gold/water interface in driven using an intense UV pulse and the resulting transient radical species characterized with VSF spectroscopy.

In the context of electrochemical interfaces and charge transfer across interfaces, hydrated electrons, i.e. excess electrons surrounded by a cavity of water molecules, play a major role. Despite their relevance also in other fields, the vertical binding energy (VBE) of excess electrons in the conduction band of water or ice remained elusive over decades of scientific efforts. The group of *Julia Stähler* recently succeeded in not only the determination of the VBE of the conduction band of amorphous solid water but, furthermore, resolved the femtosecond evolution of the excess electron's VBE during "the birth" of a solvated electron [2]. Using time-resolved two-photon photoelectron (2PPE) spectroscopy, the group could show that conduction band electrons in ice are trapped at preexisting sites already 22 fs after injection. This extraordinarily short lifetime explains the previous inability to determine the binding energy of the conduction band using techniques without a sufficient time resolution or specificity.

*Air/Water Interface:* Molecular-level insight into the structure of water and solutes at the air/water interface is important because of this interface's environmental ubiquity, because its physics strongly resemble those of hydrophobic solvation more generally, and because it enhances concentrations of many ions relative to bulk. VSF spectroscopy is a natural tool for such work, but prior efforts have largely focused, for technical reasons, on vibrational modes ranging in frequency from 1550-3800 $cm^{-1}$: C=O, OD (of $D_2O$), CH, and OH stretch modes. This limitation is important: If we could directly probe the modes that describe water's

intermolecular potential, all of which are at IR frequencies < 1500 $cm^{-1}$, we might gain additional insight into interfacial water structure. Similarly, many solutes of interest, *e.g.* all oxyanions, absorb below 1500 $cm^{-1}$, and thus directly probing solute structure is only *possible* at lower IR frequencies. In the last two years group of *Kramer Campen* has extended the IR source for VSF to 700 $cm^{-1}$. This allowed, for the first time, to probe the libration of interfacial water. The resulting resonance is centered at 834 $cm^{-1}$ and is blue-shifted by 160 $cm^{-1}$ from that in liquid water and similar to ice (see Fig. 9).

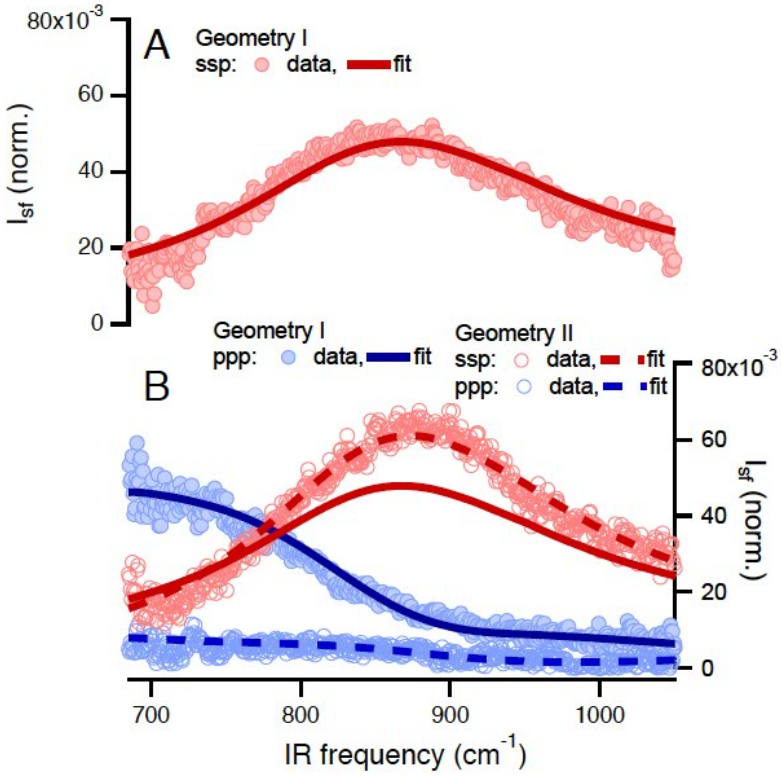



***Figure 9:*** *VSF spectra plotted as a function of incident IR frequency for two different sets of incident angles (i.e. Geometry I and II) and two different polarization conditions (i.e. ssp and ppp). Dashed and solid lines are global fits to the data using a line shape model with a single resonance centered at 834 $cm^{-1}$. The large difference between data collected under the two polarization conditions is the result of linear optical properties of water (i.e. the Fresnel coefficients) that are quantitatively accounted for in the data analysis.*

Evidently, while water at the air/water interface appears *liquid-like* when probing the interfacial OH stretch or picosecond time scale structural dynamics [3], viewed from the perspective of the libration (i.e. rotational potential) it is *ice-like*.

In a related set of experiments the interfacial population and structure of the perchlorate anion has been characterized via its Cl-O modes both at the air/water interface of solutions of perchlorate salts and perchloric acid. These results clearly suggest that interface-induced ion pairing in acid solutions occurs at > 10x lower concentrations than in bulk water. Quantification of this and similar phenomena for other solutes see is a prerequisite to a full understanding of such diverse phenomena as the aggregation of hydrophobic solutes in aqueous solution and the reactivity of ionic solutes at the air/water interface.

*α-$Al_2O_3$ / Water Interaction:* Understanding α-$Al_2O_3$/water interaction is important but challenging for a wide variety of industrial and environmental applications. Much of the challenge lies in the multi-scale nature of the problem: while understanding the thermodynamics and kinetics of single water molecule/*α*-alumina interaction is important, increasing water chemical potential introduces new physics: *e.g.* energetically favorable water adsorption mechanisms may become cooperative, the thermodynamically stable surface termination may change and the surface may donate/accept protons from liquid water. To fully understand water/α-$Al_2O_3$ interaction it is thus clear that we require methods of probing both interfacial water and the α-$Al_2O_3$ surface structure and dynamics over more than $10^{10}$ mbar in water pressure. Additionally, because the surface properties of oxides in general, and of α-$Al_2O_3$ in particular, depend on the degree of under-coordination of surface atoms, we require insight into the manner in which our results depend on crystal face.

This problem has been addressed over the last two years by probing the three most thermodynamically stable surfaces of α-$Al_2O_3$ -- the (0001), $(1\bar{1}02)$, and $(11\bar{2}0)$ -- in three types of experiments. (i) We characterize the unimolecular dissociation pathways at sub-monolayer water coverages on single crystal surfaces in UHV via the time-averaged VSF OD (of $D_2O$) stretch spectral response [4]. We have assigned the resonances we observed based on the dependence of our observed signal on incident beam angles and polarizations, and calculated frequencies and geometries (calculations done in collaboration with group of P. Saalfrank at the University of Potsdam). Given an assignment, the temperature dependent VSF response, and temperature programmed desorption measurements of the same surface, significant experimental constraints on theoretically derived microkinetic models of all surface reactions can be offered. (ii) VSF spectroscopy has been extended to sufficiently low frequency to optically probe surface phonons in ambient air. This capacity allows both quantitative characterization of partially reconstructed surfaces and makes possible probing surface chemistry from the perspective of the solid (via Al-O-H modes) [5]. (iii) We have probed the vibrational relaxation of the OH stretch of surface aluminols via an infrared pump / VSF probe scheme, as a means of probing water structure. Results on the (0001) surface suggest that for this surface, near circumneutral pH, interfacial water is hydrophobic: the first layer of water interacts only weakly with the overlying bulk. Increasing solute concentration (*i.e.* inducing ion adsorption) or changing pH (charging the surface) effectively makes the surface hydrophilic: interfacial water now interacts more strongly with the adjoining bulk liquid.

[1] Y. Tong, K. Cai, M. Wolf, R.K. Campen, Catal. Today (in press)

[2] J. Stähler, J.-C. Deinert, D. Wegkamp, S. Hagen, and M. Wolf, J. Am. Chem. Soc. **137**, 3520 (2015)

[3] M. Sovago, R.K. Campen, H.J. Bakker, M. Bonn, Chem. Phys. Lett., **470**, 7 (2009)

[4] H. Kirsch *et al.*, J. Phys. Chem. C, **118**, 13623 (2014)

[5] Y. Tong *et al.*, J. Chem. Phys., **142**, 054704 (2015)

### 2.2.5 Computational Dynamics of Protein Machines

The group of *Alexander Mikhailov* has continued theoretical investigations of molecular motors and protein machines, employing coarse-grained spring models to describe the dynamics of such macromolecules on millisecond timescales characteristic for their cycles. Such models are built using experimentally known equilibrium structures of proteins, obtained through x-ray diffraction experiments, and are known to approximately reproduce the processes of slow conformational relaxation in them.

To improve the accuracy of spring models, NMR data were used. In contrast to x-ray diffraction measurements with protein crystals, such data provide information on fluctuations of distances between the atomic amino acid groups (*i.e.*, between the protein residues). Through an iterative optimization procedure based on the NMR data for 1500 different kinds of proteins, a set of elastic spring constants, determining the strength of interactions between various pairs of residues, was computed. Fig. 10 (a) graphically displays computed spring constants for 210 possible residue pairs. It was demonstrated that, by using this common set and by calculating fluctuations of distances between the residues in specific proteins, a

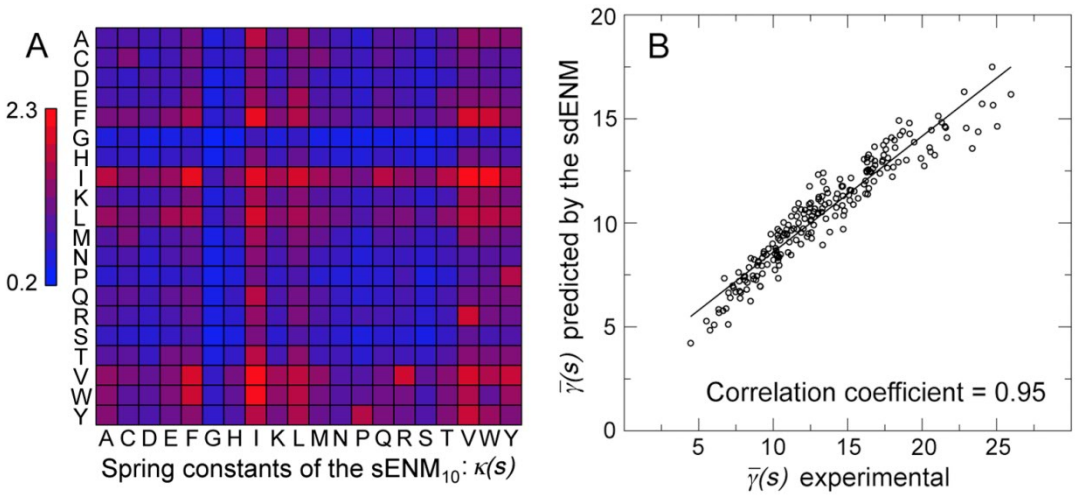



***Figure 10:*** *Improving the accuracy of the spring model for conformational dynamics of proteins. (a) Set of computed spring constants for 210 different pairs of protein residues. (b) Comparison of predictions of the improved spring model with the respective experimental NMR data for 1500 different proteins.*

correlation of 95% with the respective experimental data could be achieved [1]. Fig. 10 (b) illustrates the statistical correlation between theoretical predictions and data extracted from NMR observations for an ensemble of 1500 different proteins, whereby inverse values of predicted and experimental statistical variations of the distance between the residues are displayed.

In this manner accurate and quantitative predictions for protein dynamics can be made. Currently such theoretical descriptions are used in the studies of conformational changes of dynamin, an important membrane protein (cooperation with O. Daumke (MDC for Molecular Medicine, Berlin)). Also hybrid simulation methods for proteins, combining all-atom molecular dynamics (MD) and coarse-grained spring models, are developed together with Y. Togashi and H. Flechsig (Hiroshima University). At the same time, a synthetic molecular motor model is explored in collaboration with J.M. Sancho, University of Barcelona. It intends to reproduce, in a strongly simplified way, the operation of the myosin motor responsible for generation of mechanical forces in muscles. As a model system, a specially designed elastic network with 64 particles connected by elastic springs is used. The system undergoes cyclic conformational changes induced by binding of a ligand, its conversion into a product, and product release. A ratchet mechanism allowing the conversion of cyclic shape changes into steady translational motion of an attached filament is implemented. By varying the temperature, regimes of strong and weak coupling, corresponding to the Brownian ratchet, could be realized, and statistical investigations of the model motor, including estimates of its operation efficiency, have been performed. This approach is seen as providing a road map for subsequent similar investigations of real molecular motors.

Furthermore, collective hydrodynamic effects of active proteins in biological cells are investigated. Diffusion of particles in the interior of biological cells is known to strongly depend on ATP supply. So far, these observations were interpreted as an effect of non-equilibrium fluctuations in active gels formed by actin filaments and myosin motors in the cell. Recent *in vivo* diffusion measurements of microinjected submicron tracers within biological cells in the group of D. Weitz (Harvard University) show however that such explanation is not sufficient. The diffusion coefficient was reduced in these experiments by only about 10% if the activity of myosin motors was chemically inhibited, but ATP supply was maintained. However, the diffusion was dropping down below the measurement limit when ATP supply was stopped. Moreover, substantial diffusion dependence on substrate supply was recently observed *in vitro* in the experiments with water solutions of enzymes, in

absence of any molecular motors characteristic for a living cell. As shown in collaboration with R. Kapral (University of Toronto), an alternative explanation of such experimental data is possible [2]. All active proteins in the cell, including molecular motors and protein machines and also most of the enzymes, are repeatedly changing their shapes within each turnover cycle. Therefore, they are mechanically stirring the fluid cytoplasm in which they are immersed. As a result, non-thermal fluctuating flows develop inside the cell. Diffusion enhancement due to advection of particles in such fluctuating flows has been theoretically determined [2]. Numerical estimates reveal that such diffusion enhancement, persistent only as long as the ATP and other substrates are supplied, can indeed account for the experimentally observed effects. Similar phenomena for of active protein inclusions in biological membranes have been analysed.

Additionally, theoretical investigations on the dynamics of complex chemical networks have been performed in the framework of a research project financed by the Volkswagen Foundation.

[1] Y. Dehouck and A.S. Mikhailov, PLOS Comput. Biol. **9**, e1003209 (2013)
[2] A.S. Mikhailov and R. Kapral, Proc. Natl. Acad. Sci. (USA) **112**, E3639 -E3644 (2015)

### 2.2.6 Spatiotemporal Self-organization

Due to health related issues *Markus Eiswirth* has been on a leave of absence for one year and is now back at the FHI on a part time employment. For that reason no detailed report will be given here.

## 3. Research Projects Funded from Outside Sources

**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 SFB 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)

**Takashi Kumagai and Martin Wolf:**

- 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 and AFM, from 7/2015)

**Karsten Horn:**

- DFG Individual research grant (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, until 5/2014.
- DFG Priority Program SPP 1459 (De 1679/3-1) “Graphene”, project “***Graphene: electronic structure, transport and functionalization”*** (growth and doping of eptaxial graphene 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 2/2013).
- 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. Rostock, from 6/2013).
- DFG priority program SPP 1538 (KA 3305/4-1), "Spin Caloric Transport", project "***Ultrafast spin-dependent and spin Seebeck effect: beyond diffusive spin transport, toward a spin-caloritronic terahertz emitter***" (ultrafast spin and magnon transport in magnetic metals and insulators, THz emission spectroscopy, ultrafast optical spectroscopy, from 7/2014)

**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:**

- Volkswagen Foundation, international project ***"Self-organizing networks of interacting machines"*** (design and analysis of the networks of molecular machines)
- 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, until 3/2014)
- 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, until 3/2014)

**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), until 12/2014)

**Julia Stähler:**

- 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) from 7/2015, from 7/2011 until 6/2015 together with Martin Wolf.

**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 spectroscopy, THz emission, High-harmonic generation, until 5/2015)

## 4. Publications of the Department of Physical Chemistry[1]

### 2013 (late publications)

*Atsumi, Y., S. Hata and H. Nakao:* Phase ordering in coupled noisy bistable systems on scale-free networks. Physical Review E **88** (5), 052806 (2013).

*Bothschafter, E., 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. The European Physical Journal - Web of Conferences **41**, 04021 (2013).

*de Buyl, P., A.S. Mikhailov and R. Kapral:* Self-propulsion through symmetry breaking. Europhysics Letters **103** (6), 60009 (2013).

*Ertl, G.:* A lateral thinker. Nature **502** (7471), S53-S54 (2013).

*Ge, A., Q. Peng, H. Wu, H. Liu, Y. Tong, T. Nishida, N. Yoshida, K. Suzuki, T. Sakai, M. Osawa and S. Ye:* Effect of Functional Group on the Monolayer Structures of Biodegradable Quaternary Ammonium Surfactants. Langmuir **29** (47), 14411-14420 (2013).

*Hsieh, C.-S., R.K. Campen, M. Okuno, E.H.G. Backusa, Y. Nagata and M. Bonn:* Mechanism of vibrational energy dissipation of free OH groups at the air-water interface. Proceedings of the National Academy of Sciences of the USA **110** (47), 18780-18785 (2013).

*Kumagai, T., F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill:* Thermally and Vibrationally Induced Tautomerization of Single Porphycene Molecules on a Cu(110) Surface. Physical Review Letters **111** (24), 246101 (2013).

*Lüneburg, S., M. Müller, A. Paarmann and R. Ernstorfer:* Microelectrode for energy and current control of nanotip field electron emitters. Applied Physics Letters **103** (21), 213506 (2013).

*Neppl, S., 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. In: Proceedings of Ultrafast Phenomena and Nanophotonics XVII. (Eds.) M. *Betz, A.Y. Elezzabi, J.-J. Song and K.-T. Tsen:* (Proceedings of the SPIE, Vol. 8623). SPIE, Bellingham, WA, 862312 (2013). ISBN 978-0-8194-9392-7.

*Paasch-Colberg, T., A. Schiffrin, 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. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, QTh4D.5 (2013). ISBN 978-1-55752-972-5.

*Schubert, O., M. Porer, A. Sell, F. Junginger, B. Mayer, C. Schmidt, S. Maehrlein, A. Pashkin, T. Kampfrath, M. Wolf, K. Kim, A. Leitenstorfer and R. Huber:* Multi-THz Nonlinear Optics and Sub-cycle Control of Charge and Spin. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, JF1K.6 (2013). ISBN 978-1-55752-972-5.

*Zhang, Z., H. Stark and A.S. Mikhailov:* Hydrodynamic ratchet: Controlled motion of a polymer in an alternating microchannel flow. Europhysics Letters **104** (1), 14002 (2013).

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[1] = Gold open access publication

**Master's Thesis**

*Cataldi, P.*: Exciton formation and electron transfer at SP6/oxide interfaces in transient transmission spectroscopy. Università degli Studi di Genova Italy 2013.

**2014**

*Arion, T., O. Takahashi, R. Püttner, V. Ulrich, S. Barth, T. Lischke, A.M. Bradshaw, M. Förstel and U. Hergenhahn:* Conformational and nuclear dynamics effects in molecular Auger spectra: fluorine core-hole decay in $CF_4$. Journal of Physics B **47** (12), 124033 (2014).

*Barbiellini, B., J.N. Hancock, C. Monney, Y. Joly, G. Ghiringhelli, L. Braicovich and T. Schmitt:* Inelastic x-ray scattering from valence electrons near absorption edges of FeTe and $TiSe_2$. Physical Review B **89** (23), 235138 (2014).

*Bi, W., Y. He, M.F. Cabral, H. Varela, J. Yang, R. Jiang and Q. Gao:* Oscillatory electro-oxidation of thiosulfate on gold. Electrochimica Acta **133**, 308-315 (2014).

*Bisogni, V., S. Kourtis, C. Monney, K. Zhou, R. Kraus, C. Sekar, V. Strocov, B. Büchner, J. Brink, van den, L. Braicovich, T. Schmitt, M. Daghofer and J. Geck:* Femtosecond Dynamics of Momentum-Dependent Magnetic Excitations from Resonant Inelastic X-Ray Scattering in $CaCu_2O_3$. Physical Review Letters **112** (14), 147401 (2014).

*Böttcher, S., H. Vita and K. Horn:* Reversible photon-induced oxidation of graphene by $NO_2$ adsorption. Surface Science **621**, 117-122 (2014).

*Čechal, J., C.S. Kley, T. Kumagai, F. Schramm, M. Ruben, S. Stepanow and K. Kern:* Convergent and divergent two-dimensional coordination networks formed through substrate-activated or quenched alkynyl ligation. Chemical Communications **50** (69), 9973-9976 (2014).

*Che, M. and G. Ertl:* Helmut Knözinger (1935-2014). Angewandte Chemie International Edition **53** (40), 10579-10580 (2014).

*Che, M. and G. Ertl:* Helmut Knözinger (1935-2014). Angewandte Chemie **126** (40), 10751-10752 (2014).

*Deinert, J.-C., D. Wegkamp, M. Meyer, C. Richter, M. Wolf and J. Stähler:* Ultrafast Exciton Formation at the ZnO(10$\bar{1}$0) Surface. Physical Review Letters **113** (5), 057602 (2014).

*Delmonde, M.V.F., M.A. Nascimento, R. Nagao, D.A. Cantane, F.H.B. Lima and H. Varela:* Production of Volatile Species during the Oscillatory Electro-oxidation of Small Organic Molecules. The Journal of Physical Chemistry C **118** (31), 17699-17709 (2014).

*Eschenlohr, A., M. Sultan, A. Melnikov, N. Bergeard, J. Wieczorek, T. Kachel, C. Stamm and U. Bovensiepen:* Role of spin-lattice coupling in the ultrafast demagnetization of $Gd_{1-x}Tb_x$ alloys. Physical Review B **89** (21), 214423 (2014).

*Flechsig, H.:* Computational biology approach to uncover hepatitis C virus helicase operation. World Journal of Gastroenterology **20** (13), 3401-3409 (2014).

*Hata, S., H. Nakao and A.S. Mikhailov:* Advection of passive particles over flow networks. Physical Review E **89** (2), 020801(R) (2014).

*Hata, S., H. Nakao and A.S. Mikhailov:* Dispersal-induced destabilization of metapopulations and oscillatory Turing patterns in ecological networks. Scientific Reports **4**, 3585 (2014).

*Hata, S., H. Nakao and A.S. Mikhailov:* Sufficient conditions for wave instability in three-component reaction-diffusion systems. Progress of Theoretical and Experimental Physics **2014** (1), 013A01 (2014).

*Ilchen, M., L. Glaser, F. Scholz, P. Walter, S. Deinert, A. Rothkirch, J. Seltmann, J. Viefhaus, P. Decleva, B. Langer, A. Knie, A. Ehresmann, O.M. Al-Dossary, M. Braune, G. Hartmann, A. Meißner, L.C. Tribedi, M. AlKhaldi and U. Becker:* Angular Momentum Sensitive Two-Center Interference. Physical Review Letters **112** (2), 023001 (2014).

*Jia, Z., Z. Zeng, R. Li, Z. Xu and Y. Deng:* Extremely asymmetric electron localization in $H_2^+$ controlled with a THz field. Physical Review A **89** (2), 023419 (2014).

*Kaluza, P. and A.S. Mikhailov:* Autonomous learning by simple dynamical systems with delayed feedback. Physical Review E **90** (3), 090901(R) (2014).

*Kamaraju, N., A. Rubano, L. Jian, S. Saha, T. Venkatesan, J. Nötzold, R.K. Campen, M. Wolf and T. Kampfrath:* Subcycle control of terahertz waveform polarization using all-optically induced transient metamaterials. Light: Science & Applications **3**, e155 (2014).

*Kampfrath, T.:* Intense terahertz pulses: probing and controlling fundamental motions of electrons, spins and ions. In: Proceedings of the Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SW3F.1 (2014). ISBN 978-1-55752-999-2.

*Kampfrath, T., M. Battiato, A. Sell, F. Freimuth, A. Leitenstorfer, M. Wolf, R. Huber, P.M. Oppeneer and M. Münzenberg:* Ultrafast spin precession and transport controlled and probed with terahertz radiation. In: Proceedings of the Ultrafast Phenomena and Nanophotonics XVIII. (Eds.) M. Betz, A.Y. Elezzabi, J.-J. Song and K.-T. Tsen. (Proceedings of the SPIE, Vol. 8984). SPIE, Bellingham, WA, 898415 (2014). ISBN 978-0-8194-9897-7.

*Kawai, S., M. Koch, E. Gnecco, A. Sadeghi, R. Pawlak, T. Glatzel, J. Schwarz, S. Goedecker, S. Hecht, A. Baratoff, L. Grill and E. Meyer:* Quantifying the atomic-level mechanics of single long physisorbed molecular chains. Proceedings of the National Academy of Sciences of the USA **111** (11), 3968-3972 (2014).

*Kirsch, H., J. Wirth, Y. Tong, M. Wolf, P. Saalfrank and R.K. Campen:* Experimental Characterization of Unimolecular Water Dissociative Adsorption on α-Alumina. The Journal of Physical Chemistry C **118** (25), 13623-13630 (2014).

*Kirsch, H., X. Zhao, Z. Ren, S.V. Levchenko, M. Wolf and R.K. Campen:* Controlling $CH_2$ dissociation on Ru(0001) through surface site blocking by adsorbed hydrogen. Journal of Catalysis **320**, 89-96 (2014).

*Koch, M., M. Gille, A. Viertel, S. Hecht and L. Grill:* Substrate-controlled linking of molecular building blocks: Au(111) vs. Cu(111). Surface Science **627**, 70-74 (2014).

*Kouvaris, N.E., T. Isele, A.S. Mikhailov and E. Schöll:* Propagation failure of excitation waves on trees and random networks. Europhysics Letters **106** (6), 68001 (2014).

*Kübel, M., K. Betsch, N.G. Kling, A.S. Alnaser, J. Schmidt, U. Kleineberg, Y. Deng, I. Ben-Itzhak, G.G. Paulus, T. Pfeifer, J.H. Ullrich, R. Moshammer, M.F. Kling and B. Bergues:* Non-sequential double ionization of Ar: from the single- to the many-cycle regime. New Journal of Physics **16** (3), 033008 (2014).

*Kumagai, T., F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill:* Controlling intramolecular hydrogen transfer in a porphycene molecule with single atoms or molecules located nearby. Nature Chemistry **6** (1), 41-46 (2014).

*Lee, J.J., B. Moritz, W.S. Lee, M. Yi, C.J. Jia, A.P. Sorini, K. Kudo, Y. Koike, K.J. Zhou, C. Monney, V. Strocov, L. Patthey, T. Schmitt, T.P. Devereaux and Z.X. Shen:* Charge-orbital-lattice coupling effects in the dd excitation profile of one-dimensional cuprates. Physical Review B **89** (4), 041104(R) (2014).

*Leicht, P., L. Zielke, S. Bouvron, R. Moroni, E. Voloshina, L. Hammerschmidt, Y. Dedkov and M. Fonin:* In Situ Fabrication of Quasi-Free-Standing Epitaxial Graphene Nanoflakes on Gold. ACS Nano **8** (4), 3735-3742 (2014).

*Machado, E.G. and H. Varela:* Oscillatory Instabilities in the Electrooxidation of Borohydride on Platinum. Journal of the Brazilian Chemical Society **25** (3), 442-447 (2014).

*Maniraj, M., A. Rai, S.R. Barman, M. Krajčí, D.L. Schlagel, T.A. Lograsso and K. Horn:* Unoccupied electronic states of icosahedral Al-Pd-Mn quasicrystals: Evidence of image potential resonance and pseudogap. Physical Review B **90** (11), 115407 (2014).

*Martínez-Blanco, J., B. Walter, A. Mascaraque and K. Horn:* Long-Range Order in an Organic Overlayer Induced by Surface Reconstruction: Coronene on Ge(111). The Journal of Physical Chemistry C **118** (22), 11699-11703 (2014).

*Mikhailov, A.S. and G. Ertl:* Engineering of Chemical Complexity II. (World Scientific Lecture Notes in Complex Systems, Vol. 12). World Scientific, New Jersey (2014). ISBN 978-981-4616-12-6.

*Mitrano, M., G. Cotugno, S.R. Clark, R. Singla, S. Kaiser, J. Stähler, R. Beyer, M. Dressel, L. Baldassarre, D. Nicoletti, A. Perucchi, T. Hasegawa, H. Okamoto, D. Jaksch and A. Cavalleri:* Pressure-Dependent Relaxation in the Photoexcited Mott Insulator ET-$F_2$TCNQ: Influence of Hopping and Correlations on Quasiparticle Recombination Rates. Physical Review Letters **112** (11), 117801 (2014).

*Moreschini, L., P.-H. Lin, C.-H. Lin, W. Ku, D. Innocenti, Y.J. Chang, A.L. Walter, K.S. Kim, V. Brouet, K.-W. Yeh, M.-K. Wu, E. Rotenberg, A. Bostwick and M. Grioni:* Consequences of Broken Translational Symmetry in $FeSe_xTe_{1-x}$. Physical Review Letters **112** (8), 087602 (2014).

*Moser, S., L. Moreschini, H.-Y. Yang, D. Innocenti, F. Fuchs, N.H. Hansen, Y.J. Chang, K.S. Kim, A.L. Walter, A. Bostwick, E. Rotenberg, F. Mila and M. Grioni:* Angle-Resolved Photoemission Spectroscopy of Tetragonal CuO: Evidence for Intralayer Coupling Between Cupratelike Sublattices. Physical Review Letters **113** (18), 187001 (2014).

*Mota Lima, A.B., E.R. Gonzalez and M. Eiswirth:* Complex Electrooxidation of Formic Acid on Palladium. Journal of the Brazilian Chemical Society **25** (7), 1208-1217 (2014).

*Müller, M., A. Paarmann and R. Ernstorfer:* Femtosecond electrons probing currents and atomic structure in nanomaterials. Nature Communications **5** (10), 5292 (2014).

*Nascimento, M., R. Nagao, M. Eiswirth and H. Varela:* Coupled slow and fast surface dynamics in an electrocatalytic oscillator: Model and simulations. The Journal of Chemical Physics **141** (23), 234701 (2014).

*Nepijko, S.A., A. Chernenkaya, K. Medjanik, S.V. Chernov, D.V. Shapko, I.Y. Protsenko, W. Schulze and G. Schönhense:* Investigation of a Ge nanoparticle film by means of electron stimulated photon emission spectroscopy. Journal of Electron Spectroscopy and Related Phenomena **193**, 54-57 (2014).

*Nogueira, P.A., B.C. Batista, R.B. Faria and H. Varela:* The effect of temperature on the dynamics of a homogeneous oscillatory system operated in batch and under flow. RSC Advances **4** (57), 30412-30421 (2014).

*Ostler, M., F. Fromm, R.J. Koch, P. Wehrfritz, F. Speck, H. Vita, S. Böttcher, K. Horn and T. Seyller:* Buffer layer free graphene on SiC(0 0 0 1) via interface oxidation in water vapor. Carbon **70**, 258-265 (2014).

Paasch-Colberg, T., 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 **8** (3), 214-218 (2014).

*Perini, N., B.C. Batista, A.C.D. Angelo, I.R. Epstein and H. Varela:* Long-Lasting Oscillations in the Electro-Oxidation of Formic Acid on PtSn Intermetallic Surfaces. ChemPhysChem **15** (9), 1753-1760 (2014).

*Previdello, B.A.F., E.G. Machado and H. Varela:* The effect of the alkali metal cation on the electrocatalytic oxidation of formate on platinum. RSC Advances **4** (29), 15271-15275 (2014).

*Rettig, L., J.-H. Chu, I.R. Fisher, U. Bovensiepen and M. Wolf:* Coherent dynamics of the charge density wave gap in tritellurides. Faraday Discussions **171**, 299-310 (2014).

*Rubano, A., M. Wolf and T. Kampfrath:* Terahertz conductivity and ultrafast dynamics of photoinduced charge carriers in intrinsic 3C and 6H silicon carbide. Applied Physics Letters **105** (3), 032104 (2014).

*Sajadi, M., M. Wolf and T. Kampfrath:* Terahertz field enhancement via coherent superposition of the pulse sequences after a single optical-rectification crystal. Applied Physics Letters **104** (9), 091118 (2014).

*Saywell, A., W. Greń, G. Franc, A. Gourdon, X. Bouju and L. Grill:* Manipulating the Conformation of Single Organometallic Chains on Au(111). The Journal of Physical Chemistry C **118** (3), 1719-1728 (2014).

*Schick, D., A. Bojahr, M. Herzog, R. Shayduk, C. von Korff Schmising and M. Bargheer:* UDKM1DSIM - A simulation toolkit for 1D ultrafast dynamics in condensed matter. Computer Physics Communications **185** (2), 651-660 (2014).

*Schick, D., M. Herzog, A. Bojahr, W. Leitenberger, A. Hertwig, R. Shayduk and M. Bargheer:* Ultrafast lattice response of photoexcited thin films studied by X-ray diffraction. Structural Dynamics **1** (6), 064501 (2014).

*Schick, D., M. Herzog, H. Wen, P. Chen, C. Adamo, P. Gaal, D.G. Schlom, P.G. Evans, Y. Li and M. Bargheer:* Localized Excited Charge Carriers Generate Ultrafast Inhomogeneous Strain in the Multiferroic $BiFeO_3$. Physical Review Letters **112** (9), 097602 (2014).

*Schiffrin, A., 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:* Addendum: Optical-field-induced current in dielectrics. Nature **507** (7492), 386-387 (2014).

*Schöllkopf, W., S. Gewinner, W. Erlebach, G. Heyne, H. Junkes, A. Liedke, G. Meijer, A. Paarmann, G. von Helden, H. Bluem, D. Dowell, R. Lange, J. Rathke, A.M.M. Todd, L.M. Young, U. Lehnert, P. Michel, W. Seidel, R. Wünsch and S.C. Gottschalk:* The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. In: Proceedings of the 36th International Free Electron Laser Conference. (Eds.) J. Chrin, S. Reiche and V. Schaa. JACoW.org, WEB04 (2014). ISBN 978-3-95450-133-5.

*Shimada, T., N. Kamaraju, C. Frischkorn, M. Wolf and T. Kampfrath:* Indication of Te segregation in laser-irradiated ZnTe observed by *in situ* coherent-phonon spectroscopy. Applied Physics Letters **105** (11), 111908 (2014).

*Shiotari, A., T. Kumagai and M. Wolf:* Tip-Enhanced Raman Spectroscopy of Graphene Nanoribbons on Au(111). The Journal of Physical Chemistry C **118** (22), 11806-11812 (2014).

*Shiotari, A., B.H. Liu, S. Jaekel, L. Grill, S.K. Shaikhutdinov, H.-J. Freund, M. Wolf and T. Kumagai:* Local Characterization of Ultrathin ZnO Layers on Ag(111) by Scanning Tunneling Microscopy and Atomic Force Microscopy. The Journal of Physical Chemistry C **118** (47), 27428-27435 (2014).

*Tang, H., A.S.M. Sutherland, L.M. Osusky, Y. Li, J.F. Holzwarth and C. Bohne:* Chiral recognition for the complexation dynamics of β-cyclodextrin with the enantiomers of 2-naphthyl-1-ethanol. Photochemical & Photobiological Sciences **13** (2), 358-369 (2014).

*Vita, H., S. Böttcher, K. Horn, E.N. Voloshina, R.E. Ovcharenko, T. Kampen, A. Thissen and Y.S. Dedkov:* Understanding the origin of band gap formation in graphene on metals: graphene on Cu/Ir(111). Scientific Reports **4**, 5704 (2014).

*Vita, H., S. Böttcher, P. Leicht, K. Horn, A.B. Shick and F. Máca:* Electronic structure and magnetic properties of cobalt intercalated in graphene on Ir(111). Physical Review B **90** (16), 164532 (2014).

*Walter, A.L., H. Sahin, K.-J. Jeon, A. Bostwick, S. Horzum, R. Koch, F. Speck, M. Ostler, P. Nagel, M. Merz, S. Schupler, L. Moreschini, Y.J. Chang, T. Seyller, F.M. Peeters, K. Horn and E. Rotenberg:* Luminescence, Patterned Metallic Regions, and Photon-Mediated Electronic Changes in Single-Sided Fluorinated Graphene Sheets. ACS Nano **8** (8), 7801-7808 (2014).

*Wegkamp, D., M. Herzog, L. Xian, M. Gatti, P. Cudazzo, C.L. McGahan, R.E. Marvel, R.F. Haglund, A. Rubio, M. Wolf and J. Stähler:* Instantaneous Band Gap Collapse in Photoexcited Monoclinic $VO_2$ due to Photocarrier Doping. Physical Review Letters **113** (21), 216401 (2014).

*Ye, S., Y. Tong, A. Ge, L. Qiao and P.B. Davies:* Interfacial Structure of Soft Matter Probed by SFG Spectroscopy. The Chemical Record **14** (5), 791-805 (2014).

**Doctoral Thesis**

*Böttcher, S.*: Adsorption und Funktionalisierung von Graphen auf Metalloberflächen. Freie Universität Berlin 2014.

*Kirsch, H.*: Chemical reactions on surfaces - a SFG study. Freie Universität Berlin 2014.

**Master's Thesis**

*Richter, C.*: Electron and Exciton Dynamics at ZnO surfaces. Freie Universität Berlin 2014.

*Wlosczyk, S.: Probing α-$Al_2O_3$ (1102) Role of Surface Structure. Freie Universität Berlin 2014.*

**Bachelor Thesis**

*Linde, J.*: Understanding the oxidation mechanism of formic acid on transition metal electrodes. Freie Universität Berlin 2014.

## 2015

*Alekhin, A., D. Bürstel, A. Melnikov, D. Diesing and U. Bovensiepen:* Ultrafast Laser-Excited Spin Transport in Au/Fe/MgO(001): Relevance of the Fe Layer Thickness. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 241-243 (2015). ISBN 978-3-319-07742-0.

*Bisti, F., G. Profeta, H. Vita, M. Donarelli, F. Perrozzi, P.M. Sheverdyaeva, P. Moras, K. Horn and L. Ottaviano:* Electronic and geometric structure of graphene/SiC(0001) decoupled by lithium intercalation. Physical Review B **91** (24), 245411 (2015).

*Böttcher, S., H. Vita and K. Horn:* Photon-Induced Oxidation of Graphene/Ir(111) by $SO_2$ Adsorption. Surface Science 641, 305-309 (2015).

*Braune, M., G. Hartmann, M. Ilchen, A. Knie, T. Lischke, A. Reinköster, A. Meißner, S. Deinert, L. Glaser, O. Al-Dossary, A. Ehresmann, A.S. Kheifets and J. Viefhaus:* Electron angular distributions of noble gases in sequential two-photon double ionization. Journal of Modern Optics, in press.

*Deinert, J.-C., O.T. Hofmann, M. Meyer, P. Rinke and J. Stähler:* Local aspects of hydrogen-induced metallization of the ZnO(10T0) surface. Physical Review B **91** (23), 235313 (2015).

Dell'Angela, M., T. Anniyev, M. Beye, R. Coffee, A. Föhlisch, J. Gladh, S. Kaya, T. Katayama, O. Krupin, A. Nilsson, D. Nordlund, W.F. Schlotter, J.A. Sellberg, F. Sorgenfrei, J.J. Turner, H. Öström, H. Ogasawara, M. Wolf and W. Wurth: Vacuum space charge effects in sub-picosecond soft X-ray photoemission on a molecular adsorbate layer. Structural Dynamics **2** (2), 025101 (2015).

*Deng, Y. and X. Xie:* Real-time probing of the electron dynamics of an atom in a strong infrared laser field. Physical Review A **91** (4), 043414 (2015).

*Ernstorfer, R.:* Im Fokus ultrakurzer Laser: das Wechselspiel von Elektronen und Kristallstruktur. Jahrbuch 2015, Max-Planck-Gesellschaft, (2015).

*Errami, H., M. Eiswirth, D. Grigoriev, W.M. Seiler, T. Sturm and A. Weber:* Detection of Hopf bifurcations in chemical reaction networks using convex coordinates. Journal of Computational Physics **291**, 279-302 (2015).

*Ertl, G.:* Walther Nernst and the Development of Physical Chemistry. Angewandte Chemie International Edition **54** (20), 5828-5835 (2015).

*Ertl, G.:* Walther Nernst und die Entwicklung der Physikalischen Chemie. Angewandte Chemie **127** (20), 5922-5930 (2015).

*Jeon, H., B. Jeong, J. Joo and J. Lee:* Electrocatalytic Oxidation of Formic Acid: Closing the Gap Between Fundamental Study and Technical Applications. Electrocatalysis **6** (1), 20-32 (2015).

*Jia, Z.-M., Z.-N. Zeng, R.-X. Li, Z.-Z. Xu and Y. Deng:* Control of electron localization in the dissociation of $H_2^+$ and its isotopes with a THz pulse. Chinese Physics B **24** (1), 013204 (2015).

*Jin, Z., A. Tkach, F. Casper, V. Spetter, H. Grimm, A. Thomas, T. Kampfrath, M. Bonn, M. Kläui and D. Turchinovich:* Accessing the fundamentals of magnetotransport in metals with terahertz probes. Nature Physics **11** (9), 761-766 (2015).

*Kampfrath, T., M. Battiato, A. Sell, F. Freimuth, A. Leitenstorfer, M. Wolf, R. Huber, P.M. Oppeneer and M. Münzenberg:* Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 324-326 (2015). ISBN 978-3-319-07742-0.

*Kim, K.W., M. Porer, A. Pashkin, A. Sell, T. Kampfrath, A. Leitenstorfer and R. Huber:* THz Spin Dynamics: Phonon-Induced Spin Order. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 327-330 (2015). ISBN 978-3-319-07742-0.

*Kumagai, T.:* Direct observation and control of hydrogen-bond dynamics using low-temperature scanning tunneling microscopy. Progress in Surface Science **90** (3), 239-291 (2015).

*Ladenthin, J., L. Grill, S. Gawinkowski, S. Liu, J. Waluk and T. Kumagai:* Hot Carrier-Induced Tautomerization within a Single Porphycene Molecule on Cu(111). ACS Nano **9** (7), 7287-7295 (2015).

*Lemell, C., S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger and J. Burgdörfer:* Real-time observation of collective excitations in photoemission. Physical Review B **91** (24), 241101 (2015).

*Massimi, L., O. Ourdjini, L. Lafferentz, M. Koch, L. Grill, E. Cavaliere, L. Gavioli, C. Cardoso, D. Prezzi, E. Molinari, A. Ferretti, C. Mariani and M.G. Betti:* Surface-Assisted Reactions toward Formation of Graphene Nanoribbons on Au(110) Surface. The Journal of Physical Chemistry C **119** (5), 2427-2437 (2015).

*Melnikov, A., A. Alekhin, D. Bürstel, D. Diesing, T.O. Wehling, I. Rungger, M. Stamenova, S. Sanvito and U. Bovensiepen:* Ultrafast Non-local Spin Dynamics in Metallic Bi-Layers by Linear and Non-linear Magneto-Optics. In: Ultrafast Magnetism I. (Eds.) J.-Y. Bigot, W. Hübner, T. Rasing and R. Chantrell. (Springer Proceedings in Physics, Vol. 159). Springer, Cham, 34-36 (2015). ISBN 978-3-319-07742-0.

*Meyer, M., I. Agarwal, M. Wolf and U. Bovensiepen:* Ultrafast electron dynamics at water covered alkali adatoms adsorbed on Cu(111). Physical Chemistry Chemical Physics **17** (13), 8441-8448 (2015).

*Mielke, J., F. Hanke, M.V. Peters, S. Hecht, M. Persson and L. Grill:* Adatoms underneath Single Porphyrin Molecules on Au(111). Journal of the American Chemical Society **137** (5), 1844-1849 (2015).

*Mikhailov, A.S. and R. Kapral:* Hydrodynamic collective effects of active protein machines in solution and lipid bilayers. Proceedings of the National Academy of Sciences of the USA **112** (28), E3639-E3644 (2015).

*Müller, M., A. Paarmann and R. Ernstorfer:* Visualization of Photocurrents in Nanoobjects by Ultrafast Low-Energy Electron Point-Projection Imaging. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 667-670 (2015). ISBN 978-3-319-13241-9.

*Nacci, C., F. Ample, D. Bleger, S. Hecht, C. Joachim and L. Grill:* Conductance of a single flexible molecular wire composed of alternating donor and acceptor units. Nature Communications **9** (7), 7397 (2015).

*Nayak, J., M. Maniraj, A. Gloskovskii, M. Krajčí, S. Sebastian, I.R. Fisher, K. Horn and S.R. Barman:* Bulk electronic structure of Zn-Mg-Y and Zn-Mg-Dy icosahedral quasicrystals. Physical Review B **91** (23), 235116 (2015).

*Neppl, S., R. Ernstorfer, A.L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E.M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J.V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz and R. Kienberger:* Direct observation of electron propagation and dielectric screening on the atomic length scale. Nature **517** (7534), 342-346 (2015).

*Nicholson, C., C. Monney, U. Krieg, C. Tegenkamp, H. Pfnuer, K. Horn and M. Wolf:* Electronic Structure of Self-Assembled Ag Nanowires on Si(557): Spectroscopic Evidence for Dimensionality. New Journal of Physics, in press.

*Öberg, H., J. Gladh, M. Dell'Angela, T. Anniyev, M. Beye, R. Coffee, A. Föhlisch, T. Katayama, S. Kaya, J. LaRue, A. Møgelhøj, D. Nordlund, H. Ogasawara, W.F. Schlotter, J.A. Sellberg, F. Sorgenfrei, J.J. Turner, M. Wolf, W. Wurth, H. Öström, A. Nilsson, J.K. Nørskov and L.G.M. Pettersson:* Optical laser-induced CO desorption from Ru(0001) monitored with a free-electron X-ray laser: DFT prediction and X-ray confirmation of a precursor state. Surface Science, **640**, 80-88 (2015).

*Öström, H., H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell'Angela, J. Gladh, M.L. Ng, J.A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W.F. Schlotter, G.L. Dakovski, J.J. Turner, M.P. Minitti, A. Mitra, S.P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J.K. Nørskov, F. Abild-Pedersen, H. Ogasawara, L.G.M. Pettersson and A. Nilsson:* Probing the transition state region in catalytic CO oxidation on Ru. Science **347** (6225), 978-982 (2015).

*Paarmann, A., I. Razdolski, A. Melnikov, S. Gewinner, W. Schöllkopf and M. Wolf:* Second harmonic generation spectroscopy in the Reststrahl band of SiC using an infrared free-electron laser. Applied Physics Letters **107** (8), 081101 (2015).

*Perfetti, L., B. Sciolla, G. Biroli, C.J. van der Beek, C. Piovera, M. Wolf and T. Kampfrath:* Ultrafast Dynamics of Fluctuations in High-Temperature Superconductors Far from Equilibrium. Physical Review Letters **114** (6), 067003 (2015).

*Punckt, C., P.S. Bodega, P. Kaira and H.H. Rotermund:* Wildfires in the Lab: Simple Experiment and Models for the Exploration of Excitable Dynamics. Journal of Chemical Education **92** (8), 1330-1337 (2015).

*Puppin, M., Y. Deng, C. Nicholson, C. Monney, M. Krenz, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer:* 500 kHz OPCPA-Based UV-XUV Light Source For Time-Resolved Photoemission Spectroscopy. In: Proceedings of Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SF2M.4 (2015). ISBN 978-1-55752-968-8.

*Puppin, M., Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf and R. Ernstorfer:* 500 kHz OPCPA delivering tunable sub-20 fs pulses with 15 W average power based on an all-ytterbium laser. Optics Express **23** (2), 1491-1497 (2015).

*Puppin, M., Y. Deng, O. Prochnow, J. Matyschok, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer:* Fiber-Slab-Pumped OPCPA for XUV-Based Time-Resolved Photoelectron Spectroscopy at 500 kHz Repetition Rate. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 766-769 (2015). ISBN 978-3-319-13241-9.

*Schöllkopf, W., S. Gewinner, H. Junkes, A. Paarmann, G. von Helden, H. Bluem and A.M.M. Todd:* The new IR and THz FEL facility at the Fritz Haber Institute in Berlin. In: Proceedings of Advances in X-ray Free-Electron Lasers Instrumentation III. (Ed.) S.G. Biedron. (Proceedings of the SPIE, Vol. 9512). SPIE, Bellingham, WA, 95121L (2015).

*Stähler, J., J.-C. Deinert, D. Wegkamp, S. Hagen and M. Wolf:* Real-Time Measurement of the Vertical Binding Energy during the Birth of a Solvated Electron. Journal of the American Chemical Society **137** (10), 3520-3524 (2015).

*Tong, Y., Q. Peng, T. Ma, T. Nishida and S. Ye:* Photocatalytic oxidation of the organic monolayers on $TiO_2$ surface investigated by *in-situ* sum frequency generation spectroscopy. APL Materials **3** (10), 104402 (2015).

*Tong, Y., J. Wirth, H. Kirsch, M. Wolf, P. Saalfrank and R.K. Campen:* Optically probing Al—O and O—H vibrations to characterize water adsorption and surface reconstruction on α-alumina: An experimental and theoretical study. The Journal of Chemical Physics **142** (5), 054704 (2015).

*Tong, Y., K. Cai, M. Wolf, and R.K. Campen:* Probing the Electrooxidation of Weakly Adsorbed Formic Acid on Pt(100). Catalysis Today, in press.

*Waldecker, L., R. Bertoni and R. Ernstorfer:* Compact femtosecond electron diffractometer with 100 keV electron bunches approaching the single-electron pulse duration limit. Journal of Applied Physics **117** (4), 044903 (2015).

*Waldecker, L., T.A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer and S. Wall:* Time-domain separation of optical properties from structural transitions in resonantly bonded materials. Nature Materials, in press.

*Xin, H., J. LaRue, H. Öberg, M. Beye, M. Dell'Angela, J.J. Turner, J. Gladh, M.L. Ng, J.A. Sellberg, S. Kaya, G. Mercurio, F. Hieke, D. Nordlund, W.F. Schlotter, G.L. Dakovski, M.P. Minitti, A. Föhlisch, M. Wolf, W. Wurth, H. Ogasawara, J.K. Nørskov, H. Öström, L.G.M. Pettersson, A. Nilsson and F. Abild-Pedersen:* Strong Influence of Coadsorbate Interaction on CO Desorption Dynamics on Ru(0001) Probed by Ultrafast X-Ray Spectroscopy and Ab Initio Simulations. Physical Review Letters **114** (15), 156101 (2015).

**Doctoral Thesis**

*Vita, H.*: Interaction of magnetic and non-magnetic metals with graphene. Humboldt Universität zu Berlin 2015.

*Wegkamp, D.*: Ultrafast electron dynamics and the role of screening. Freie Universität Berlin 2015.

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

### Alexandr Alekhin

Nov 2013 — Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
*Ultrafast Non-Local Spin Dynamics in Epitaxial Metallic Multilayers*

### Lea Bogner

Jun 2015 — Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
*Dynamics of Exciton Formation and Decay in SP6/ZnO(10T0) and DCV5T-$Me_2$/Au(111)*

### Lukas Braun

Jul 2014 — New Trends in Topological Insulators (NTTI) 2014, Helmholtz-Zentrum Berlin, Berlin, Germany
*Ultrafast Photocurrents in the Topological Insulator $Bi_2Se_3$ Probed with Terahertz Emission Spectroscopy*

Jan 2015 — Group Seminar, Department of Physics (AG Sergey Ganichev), Universität Regensburg, Regensburg, Germany
*Ultrafast Currents at the Surface of the Topological Insulator $Bi_2Se_3$*

Feb 2015 — Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
*Ultrafast Currents at the Surface of the Topological Insulator $Bi_2Se_3$*

### Kramer Campen

Jun 2014 — Workshop, Nonlinear Optics at Interfaces, Telluride Science Research Center, Telluride, CO, USA
*Understanding How Water Interacts with α-$Al_2O_3$*

Aug 2014 — Vibrational Spectroscopy, Gordon Research Conference (GRC), Biddeford, ME, USA
*Understanding How Water Interacts with α-$Al_2O_3$(0001): Structure and Dynamics*

Nov 2014 — Workshop, Water – the Most Anomalous Liquid, Working Group 4: Quantum Effects, Nordita, Stockholm, Sweden
*$ClO_4^-$ at the Air/Water Interface: Population, Desolvation, Aggregation and the Role of $H_3O^+$*

May 2015 — 114th General Assembly of the German Bunsen Society for Physical Chemistry, Bochum, Germany
*From UHV to the Solid/Liquid Interface: Probing Water Adsorption, Surface Reconstruction and Dynamics on α-$Al_2O_3$*

May 2015 — FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
*From UHV to Solid/Liquid Interface: Probing α-Alumina/Water Interaction over 10 Orders of Magnitude in Water Pressure*

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| Jun 2015 | 15th International Conference on Vibrations at Surfaces, Donostia-San Sebastian, Spain<br>*From UHV to the Solid/Liquid Interface: Probing Water Adsorption, Surface Reconstruction and Dynamics on α-$Al_2O_3$* |
| Sep 2015 | Workshop, Surface Potentials – Facts, Findings and Fantasies, École polytechnique fédérale de Lausanne, Lausanne, Switzerland<br>*Looking for Solvent Polarization in Nonlinear Optical Signals at Charged Solid/Liquid Interfaces* |

**Yunpei Deng**

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| Oct 2013 | The 97th OSA Annual Meeting and Exhibit/Laser Science XXIX, Frontiers in Optics, Orlando, FL, USA<br>*Few Cycle Infrared OPCPA System and Applications* |
| Dec 2013 | Conference on High Intensity Laser and Attosecond Science in Israel (CHILI 2013), Tel Aviv, Israel<br>*High Power OPCPA System for XUV Sources at 500 kHz* |

**Ralph Ernstorfer**

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| May 2014 | FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany<br>*Ultrafast Structural and Electronic Dynamics in Low Dimensional Materials* |
| May 2014 | Physikalisches-Kolloquium, RWTH Aachen University, Aachen, Germany<br>*Photo-Induced Structural Dynamics in Solids* |
| Aug 2014 | SPIE Optics and Photonics, Ultrafast Nonlinear Imaging and Spectroscopy II, San Diego, CA, USA<br>*Femtosecond Low-Energy Electron Diffraction and Imaging* |
| Sep 2014 | ELI-ALPS 2nd User Workshop, Extreme Light Infrastructure - Attosecond Light Pulse Source, Szeged, Hungary<br>*Towards Mapping Excited Electronic States in Molecules and Correlated Materials with tr-ARPES* |
| Oct 2014 | Workshop, DIET 14, Dynamics, Interactions and Electronic Transitions at Surfaces, Pacific Grove, CA, USA<br>*Femtosecond Low-Energy Electrons Probing Currents and Atomic Structure in Nanomaterials* |
| Feb 2015 | 4th Banff Meeting on Structural Dynamics: Ultrafast Dynamics with X-Rays and Electrons, Banff, AB, Canada<br>*Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials* |
| Mar 2015 | 79. Jahrestagung der DPG und DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses, Berlin, Germany<br>*Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials* |
| Mar 2015 | Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany<br>*Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents* |

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| Apr 2015 | Seminar in Solid State Physics, Physik-Institut, University of Zurich, Zurich, Switzerland<br>*Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents* |

**Gerhard Ertl**

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| Oct 2013 | 8th Lorenz Kramer Memorial Lecture, University of Bayreuth, Bayreuth, Germany<br>*Katalyse an Oberflächen* |
| Nov 2013 | 100 Years of Ammonia Synthesis, BASF, Ludwigshafen, Germany<br>*The Development of the Haber-Bosch Process* |
| Nov 2013 | Schwarz-Zahradnik Symposium, Berlin-Brandenburg Academy of Sciences and Humanities, Berlin, Germany<br>*From Atoms to Complexity* |
| Jun 2014 | Symposium zum 150. Geburtstag von Walther Nernst, Magnus-Haus Berlin, Berlin, Germany<br>*Walther Nernst und die Entwicklung der Physikalischen Chemie* |

**Laura Foglia**

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|---|---|
| Jul 2015 | Group Seminar, Department of Physics (AG Fulvio Parmigiani), Università degli Studi di Trieste, Trieste, Italy<br>*Exciton Dynamics in Hybrid Organic-Inorganic Semiconducting Systems* |
| Jul 2015 | Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany<br>*Charge Relaxation Pathways and Exciton Dynamics at an Hybrid Inorganic Organic Interface* |

**Leonhard Grill**

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| Dec 2013 | Seminar, Institute of Applied Physics, Vienna University of Technology, Vienna, Austria<br>*Controlling Chemical Processes in Single Molecules on Surfaces* |
| Mar 2014 | 247th ACS National Meeting and Exposition, American Chemical Society, Dallas, TX, USA<br>*Controlling Chemical Processes at the Level of Single Molecules* |
| Apr 2014 | DPG-Frühjahrstagung, Symposium Molecular Switches and Motors at Surfaces (SYMS), Dresden, Germany<br>*Imaging and Manipulation of Single Functional* |
| Apr 2014 | Sino-German Symposium on π-Conjugated Nanomaterials for Catalysis and Clean Energy Applications, Berlin, Germany<br>*Controlling Chemical Processes at the Level of Single Molecules* |
| May 2014 | Keynote Lecture, International Workshop "On-Surface Synthesis", Ecole de physique des Houches, Les Houches, France<br>*Covalent Molecular Assembly on Metal Surfaces: Towards Functional Nanostructures* |

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| Sep 2014 | 64th Annual Meeting of the Austrian Physicsal Society (ÖPG), Pöllau, Austria<br>*Functional Molecules on Surfaces: From Conducting Wires to the Role of Single Atoms* |
| Sep 2014 | Beilstein Nanotechnology Meeting 2014 "Molecular Machines and Devices", Potsdam, Germany<br>*Manipulating Single Functional Molecules by Scanning Tunnelling Microscopy* |
| Sep 2014 | European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland<br>*Assembly and Manipulation of Single Functional Molecules* |
| Oct 2014 | 5th Vacuum Symposium, Institute of Physics, Coventry, UK<br>*Every Atom Counts: Manipulation of Single Functional Molecules on Surfaces* |
| Nov 2014 | Seminar, Institute of Physical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany<br>*Single-Molecule Chemistry: From Fundamental Understanding to Functional Systems* |

**Karsten Horn**

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| Dec 2013 | 8th International Conference on Advanced Materials and Devices, Jeju, South Korea<br>*Electronic Structure of Epitaxial Graphene and its Interaction with Semiconductor and Metal Substrates* |
| Dec 2013 | Korea Research Institute of Standards and Science (KRISS), Daejeon, South Korea<br>*Epitaxial Graphene and its Electronic Structure* |
| Jun 2014 | Lecture, Department of Physics, Tohoku University, Sendai, Japan<br>*A Short Walk through the Photoemission Technique and Some of its Applications* |
| Jun 2014 | Seminar, Research Institute of Electrical Communication, Tohoku University, Sendai, Japan<br>*Electronic Structure of Graphene and Related Materials* |
| Dec 2014 | Conference, German Scientists Interactions in Physics with UNamur, Namur, Belgium<br>*Electronic Structure of Graphene and Some of its Interfaces* |

**Tobias Kampfrath**

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|---|---|
| Nov 2013 | Department Seminar, Institute of Solid State Physics, Technische Universität Berlin, Berlin, Germany<br>*Ultrafast Adiabatic Manipulation of Slow Light* |
| Jan 2014 | Center-of-Excellence Colloquium, Fachbereich Physik, University of Marburg, Marburg, Germany<br>*Beyond Body Scanners: How to Use Terahertz Pulses to Observe and Control Spin Dynamics in Solids* |

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| Feb 2014 | Department Seminar, Stanford Institute for Materials and Energy Sciences (SIMES), Stanford University, Stanford, CA, USA<br>*How to Use Terahertz Pulses to Probe and Control Spin Dynamics in Solids* |
| Feb 2014 | Photonics West (SPIE OPTO), San Francisco, CA, USA<br>*Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation* |
| Mar 2014 | Joint Symposium, SFB IR-ON and SFB Next-Lite, Vienna University of Technology, Vienna, Austria<br>*Ultrafast Spin Precession and Transport Controlled and Probed with Terahertz Radiation* |
| Apr 2014 | Department Seminar, Department of Materials, ETH Zurich, Zurich, Switzerland<br>*Ultrafast Spin Dynamics and Transport Controlled and Probed with Terahertz Radiation* |
| May 2014 | 4th EOS Topical Meeting on Terahertz Science and Technology (TST2014), Camogli, Italy<br>*Spintronics with Terahertz Radiation* |
| May 2014 | FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany<br>*Probing and Controlling the Dynamics of Charges and Spins Using THz Radiation* |
| May 2014 | Group Seminar, Institute of Physics (AG Georg Woltersdorf), Martin Luther University Halle-Wittenberg, Halle, Germany<br>*THz Spectroscopy and THz Spintronics* |
| Jun 2014 | Conference, CLEO: 2014 - Laser Science to Photonic Applications, San José, CA, USA<br>*Tutorial: Intense Terahertz Pulses: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions* |
| Jan 2015 | Department Seminar at BESSY, Department of Photovoltaics, Berlin, Germany<br>*THz Spectroscopy and THz Spintronics* |
| Jan 2015 | Workshop, Von Pico zu Femto - Time-Resolved Studies at BESSY II, Helmholtz-Zentrum Berlin, Berlin, Germany<br>*Ultrafast Spin-Lattice Interactions: New Route to Magnetization Control* |
| Mar 2015 | Institute Seminar, Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany<br>*Terahertz Spectroscopy: From Ultrafast Probing toward Control of Electron and Spin Dynamics* |
| Mar 2015 | Optical Terahertz Science & Technology Conference (OTST 2015), San Diego, CA, USA<br>*Tutorial: Material Control with THz Transients* |
| Apr 2015 | Seminar, Department of Inorganic Chemistry, Fritz-Haber-Institut, Berlin, Germany<br>*Terahertz Spectroscopy: From Ultrafast Probing toward Control of the Motion of Electrons, Ions and Spins* |

May 2015 Workshop, Ultrafast Dynamics in Condensed Matter, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
*Terahertz Spectroscopy: From Ultrafast Probing toward Controlling the Motion of Electrons, Phonons and Spins*

Aug 2015 Department Seminar, Institute for Advanced Simulation, Forschungszentrum Jülich, Jülich, Germany
*Probing and Controlling Spin Dynamics with Terahertz Pulses*

Sep 2015 CECAM Workshop, Exploration of ultra-fast timescales using time dependent density functional theory and quantum optimal control theory, Lausanne, Switzerland
*Probing and Controlling Spin Dynamics with Terahertz Pulses*

**Takashi Kumagai**

Feb 2014 17th Meeting of the Fachbeirat of the Fritz-Haber-Institut, Berlin, Germany
*Direct Observation of Molecular Dynamics Using Scanning Tunneling Microscopy*

May 2014 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
*Direct Observation of Molecular Dynamics Using Scanning Probe Microscopy*

Jun 2014 SFB 658 Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany
*Control of Intramolecular H Atom Transfer Reaction Using Scanning Tunneling Microscopy*

Apr 2015 Colloquium of the Collaborative Research Centre 951 "Hybrid Inorganic/Organic Systems for Opto-Electronics" (HIOS), Berlin, Germany
*Local Characterization of Ultrathin ZnO Layers on Ag(111) by STM and AFM*

**Alexey Melnikov**

Jan 2014 Department Seminar, Department Molecular Spectroscopy, Max Planck Institute for Polymer Science, Mainz, Germany
*Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Jul 2014 Group Seminar, Institut für Materialsphysik (AG Cynthia A. Volkert), University of Göttingen, Göttingen, Germany
*Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Jul 2014 Moscow International Symposium on Magnetism MISM-2014, Moscow, Russia
*Non-Locality of Ultrafast Spin Dynamics in Au/Fe/MgO(001) Bi-Layers due to Spin-Dependent Hot Carrier Transport*

Oct 2014 Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany
*Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Nov 2014 Seminar, Department of Quantum Electronics, Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia
*Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Nov 2014 Seminar, P.L. Kapitza Institute for Physical Problems of the Russian Academy of Sciences, Moscow, Russia
*Ultrafast Non-Local Spin Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

Mar 2015 Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany
*Direct Monitoring of Hot Carrier-Formed Spin Currents in Metallic Multi-Layers by Time-Resolved Magneto-Induced Second Harmonic Generation*

Sep 2015 CECAM Workshop, Exploration of ultra-fast timescales using time dependent density functional theory and quantum optimal control theory, Lausanne, Switzerland
*Ultrafast Charge- and Spin-Dynamics Induced by the Transport of Laser-Excited Spin-Polarized Hot Carriers in Metallic Multi-Layers*

**Alexander S. Mikhailov**

Jun 2014 Lecture, Nanoscience Center, University of Barcelona, Barcelona, Spain
*Simple Elastic Models of Protein Machines and Elastic Motors*

Sep 2014 Lecture, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan
*Simple Elastic Models of Protein Machines*

Sep 2014 Seminar, RIKEN Center for Developmental Biology, Kobe, Japan
*Simple Elastic Models of Protein Machines*

Nov 2014 Seminar, Department of Basic Science, The University of Tokyo, Tokyo, Japan
*Simple Elastic Models of Protein Machines and Synthetic Motors*

Nov 2014 Seminar, Department of Physics, The University of Tokyo, Tokyo, Japan
*Autonomous Learning by Simple Dynamical Systems with Delayed Feedback*

Feb 2015 Lecture, International WE-Heraeus Physics School on "Model systems for understanding biological processes", Bad Honnef, Germany
*Hydrodynamic Collective Effects of Active Protein Machines*

Feb 2015 Lecture, International WE-Heraeus Physics School on "Model systems for understanding biological processes", Bad Honnef, Germany
*Simple Elastic Models of Protein Machines*

Mar 2015 Lecture, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan
*Hydrodynamic Collective Effects of Active Protein Machines*

Mar 2015 Seminar, Department of Biomedical Engineering, Faculty of Life and Medical Sciences, Doshisha University, Kyotanabe, Japan
*Hydrodynamic Collective Effects of Active Protein Machines*

Mar 2015 Seminar, Department of Information Sciences, Ochanomizu University, Tokyo, Japan
*Simple Elastic Models of Protein Machines*

Mar 2015 Seminar, Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto, Japan
*Simple Elastic Models of Protein Machines*

Jun 2015 Lecture, 8th International Conference, Engineering of Chemical Complexity, Garching, Germany
*Hydrodynamic Collective Effects of Active Proteins*

**Claude Monney**

Jan 2014 Artemis User Meeting, Abingdon, UK
*Time-Resolved Photoemission Study of an Electronically-Driven Charge Density Wave Phase*

Apr 2014 Seminar, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
*Time-Resolved Photoemission Study of an Electronically-Driven Charge Density Wave Phase*

Sep 2014 SUCCESS-2014: School on UV and X-Ray spectroscopies of correlated electron systems, Les Houches, France
*Resonant Inelastic X-Ray Scattering on Correlated Materials*

**Selene Mor**

Apr 2014 Specially Selected Young Scientist Talk, From the witches cauldrons in materials science, Center of Interface Science (CIS), Goslar, Germany
*Ultrafast Optical Spectroscopy of Quasi One Dimensional $Ta_2NiSe_5$*

**Melanie Müller**

Jul 2015 Seminar, Helmholtz-Zentrum Berlin
*Femtosecond Low-energy Electrons as Probes for Ultrafast Dynamics on the Nanoscale*

**Christopher Nicholson**

Jul 2014 Group Seminar, Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany
*Ultrafast Photoemission Study of Cr:W(110) Thin Films*

**Alexander Paarmann**

Jul 2014 FHI FEL Symposium, Berlin, Germany
*Ultrashort Pulse Operation of the FHI IR-FEL*

May 2015 FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany
*Nonlinear Phonon Spectroscopy of Solids Using the FHI IR-FEL*

**Alexander Saywell**

Nov 2013 Seminar, Department of Physical Chemistry, University of Graz, Graz, Austria
*Complex Organic Molecules Studied under Ultra-High Vacuum: Electrospray Deposition and On-Surface Synthesis*

**Julia Stähler**

| | |
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| Nov 2013 | Seminar, Physics Department (AG Aeschlimann), Technische Universität Kaiserslautern, Kaiserslautern, Germany<br>*Quasiparticle Dynamics at Oxide Surfaces: Electrons, Excitons and Polarons* |
| Dec 2013 | Seminar, Laboratory of Ultrafast Spectroscopy (AG Majed Chergui), École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland<br>*Quasiparticle Dynamics at Oxide Surfaces: Electrons, Excitons and Polarons* |
| Jan 2014 | 6th International Workshop and School on Time-Dependent Density-Functional Theory: Prospects and Applications, Centro de Ciencias de Benasque Pedro Pascual, Benasque, Spain<br>*Ultrafast Exciton Formation at the ZnO(10T0) Surface* |
| Apr 2014 | Seminar, Laboratory for Attosecond Physics, (Ferenc Krausz), Max Planck Institute of Quantum Optics, Munich, Germany<br>*Ultrafast Exciton Formation at the ZnO(10T0) Surface* |
| May 2014 | Institute Colloquium, Institiut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Kiel, Germany<br>*Ultrafast Exciton Formation at the ZnO(10T0) Surface* |
| Jul 2014 | SFB 767 Colloquium, Fachbereich Physik, Universität Konstanz, Constance, Germany<br>*Instantaneous Band Gap Collapse in Photoexcited Monoclinic $VO_2$* |
| Nov 2014 | 3rd International Ertl Symposium on Surface Analysis and Dynamics, Berlin, Germany<br>*Ultrafast Exciton Formation Dynamics at the ZnO Surface* |
| Dec 2014 | Colloquium Optics and Condensed Matter, Institiut für Angewandte Physik, University of Bonn, Bonn, Germany<br>*Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?* |
| Dec 2014 | Condensed Matter Seminar, Max Planck Institute for the Physics of Complex Systems, Dresden, Germany<br>*Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?* |
| Feb 2015 | Colloquium, Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany<br>*Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?* |
| Feb 2015 | Max Planck Research Group Selection Symposium, Harnack House, Berlin, Germany<br>*Transiently Functional Interfaces: Ultrafast Dynamics of Quasiparticles & Collective Phenomena* |
| Mar 2015 | 79. Jahrestagung der DPG und DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Surface Science Division, Berlin, Germany<br>*Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?* |

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| Apr 2015 | Department Seminar, The Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands<br>*A Real Time Movie about Ultrafast Phenomena at Hybrid Interfaces* |
| Apr 2015 | Meeting, From the witches cauldrons in materials science, Center of Interface Science (CIS), Goslar, Germany<br>*What Happens before Light Emission? A Real Time Movie about Exciton Formation and Decay, the Violation of Kasha's Rule and other Ultrafast Phenomena at Hybrid Interfaces* |
| May 2015 | Department Seminar, Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany<br>*Ultrafast Electron Dynamics at Oxide Surfaces: How Metallic is a Semiconductor?* |
| May 2015 | FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany<br>*Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption* |
| Aug 2015 | Women in Optics: The Castle Meeting 2015, Marburg, Germany<br>*Exciting! What Happens When Light is Absorbed in a Semiconductor?* |
| Sep 2015 | Highlights der Physik, Jena, Germany<br>*Es werde Licht! –Und zwar schnell!!* |

**Lutz Waldecker**

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|---|---|
| Jun 2015 | Group Seminar, Faculty of Physics (AG Uwe Bovensiepen), Universität Duisburg-Essen, Essen, Germany<br>*Electron-Lattice Interactions Probed with Femtosecond Electron Diffraction* |

**Martin Wolf**

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|---|---|
| Mar 2014 | APS March Meeting 2014, American Physical Society, Denver, CO, USA<br>*Dynamics of Electron Transfer and Exciton Formation at Interfaces* |
| May 2014 | FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany<br>*Current Topics and Developments in the PC Department* |
| May 2014 | Seminar, Energy Frontier Research Center, Columbia University, New York, NY, USA<br>*Probing the Transient Electronic Structure During Surface Reactions on Femtosecond Time Scales* |
| Jun 2014 | 5th International Conference on Photoinduced Phase Transitions and Cooperative Phenomena, PIPT5, Bled, Slovenia<br>*Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved ARPES* |
| Jun 2014 | International Workshop, Itinerant Magnetism and Superconductivity - IMS 2014, Dresden, Germany<br>*Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved ARPES* |
| Jun 2014 | Physikalisches Kolloquium, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany<br>*Dynamics of Electronic Structure Changes During Surface Reactions and Phase Transitions in Solids* |

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| Jul 2014 | Faraday Discussion 171, Emerging Photon Technologies for Chemical Dynamics, Sheffield, UK<br>*Coherent Dynamics of the Charge Density Wave Gap in Tritellurides Probed by Time-Resolved ARPES* |
| Jul 2014 | International Workshop on Nanoscale Spectroscopy and Nanotechnology (NSS-8), Chicago, IL, USA<br>*Electronic Structure and Exciton Formation at ZnO Interfaces* |
| Aug 2014 | International School and Workshop on Electronic Crystals ECRYS-2014, Cargèse, France<br>*Time-Resolved Spectroscopy and Ultrafast Dynamics of the Electronic Structure of Photoexcited Solids* |
| Oct 2014 | 16th Workshop on Dynamical Phenomena at Surfaces (WDPS-16), Madrid, Spain<br>*Ultrafast Dynamics of Electronic Structure Changes in Photoinduced Processes at Surfaces* |
| Oct 2014 | General Physics Colloquium, Aarhus University, Aarhus, Denmark<br>*Ultrafast Dynamics of Photoinduced Surface Reactions and Phase Transitions in Solids* |
| Jan 2015 | Workshop, Von Pico zu Femto - Time-Resolved Studies at BESSY II, Helmholtz-Zentrum Berlin, Berlin, Germany<br>*Ultrafast Dynamics of Photoinduced Surface Reactions* |
| Mar 2015 | International Workshop on Sum Frequency Generation, Wiesbaden, Germany<br>*Unconventional Approaches to Vibrational Spectroscopy at Interfaces* |
| Apr 2015 | International Workshop: The Future of Gas Phase and Surface Chemistry at FLASH, DESY, Hamburg, Germany<br>*Surface Femtochemistry: From Elementary Steps to Intricacy* |
| May 2015 | International Workshop, Photon Science Roadmap Symposium, DESY, Hamburg, Germany<br>*Surface Chemical Reaction Dynamics Studied with FELs* |
| May 2015 | Physikalisches Kolloquium, Institute of Physics, Universität Kassel, Kassel, Germany<br>*Transient Electronic Structure in Ultrafast Surface Reactions and Phase Transitions in Solids* |
| Aug 2015 | Dynamics at Surfaces, Gordon Research Conference (GRC), Newport, RI, USA<br>*Can we probe the transition state in surface reactions (Hot Topic)* |
| Aug 2015 | RACIRI Summer School 2015, Rügen, Germany<br>*Transient Electronic Structure in Ultrafast Surface Reactions* |
| Aug 2015 | Soft X-Ray in Energy and Time Workshop (SXET), Helmholtz-Zentrum Berlin, Berlin, Germany<br>*Transient Electronic Structure in Ultrafast Surface Chemistry* |

Sep 2015 International Conference on Laser Ablation (COLA 2015), Cairns, QLD, Australia
*Fundamental Aspects of Laser-Matter Interaction: Ultrafast Dynamics of Insulator-to-Metal Transitions Probed by Time-Resolved Photoemission*

Sep 2015 Center for Quantum Computing & Quantum Technology Seminar, University of New South Wales, Sydney, NSW, Australia
*Ultrafast Dynamics of Photoexcited Insulators Probed by Time-Resolved Photoemission*

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

## Group members

### Scientists:

Roman Bertoni

### Doctoral students:

Melanie Müller
Michele Puppin
Thomas Vasileiadis
Lutz Waldecker

### Diploma and master's students:

Johannes Feldl

## 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 (until 03/2015).
- 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.

**Scientific Scope**

Many-body phenomena and the coupling between electron, lattice and spin degrees of freedom are of fundamental importance as they govern the ground state properties of materials as well as relaxation and dissipation effects in non-equilibrium states. Whereas such coupling effects are no physical observables, they can be assessed indirectly through an experimental perturbative approach, as illustrated in Fig. 1: femtosecond light pulses excite a specific subsystem, typically the electrons, and the same or another subsystem's response is observed with various time-resolved probes.

We develop and employ several complementary, ultrafast probes sensitive to the ultrafast response of electrons and crystalline structure: femtosecond electron diffraction (FED) reveals the level of vibrational excitation and the evolution of crystalline long-range order, femtosecond time- and angle-resolved photoelectron spectroscopy (trARPES) shows the temporal evolution of the electronic structure and of excited states, and time resolves optical spectroscopy provides the material's dielectric function. In addition, we established low-energy electrons as an ultrafast probe for transient electric fields and related photocurrents in nanoobjects.

We apply this set of techniques to a range of material systems ranging from bulk crystals, 2D materials, nanowires to clusters. The following section highlights the main research achievements since the last Fachbeirat's evaluation.

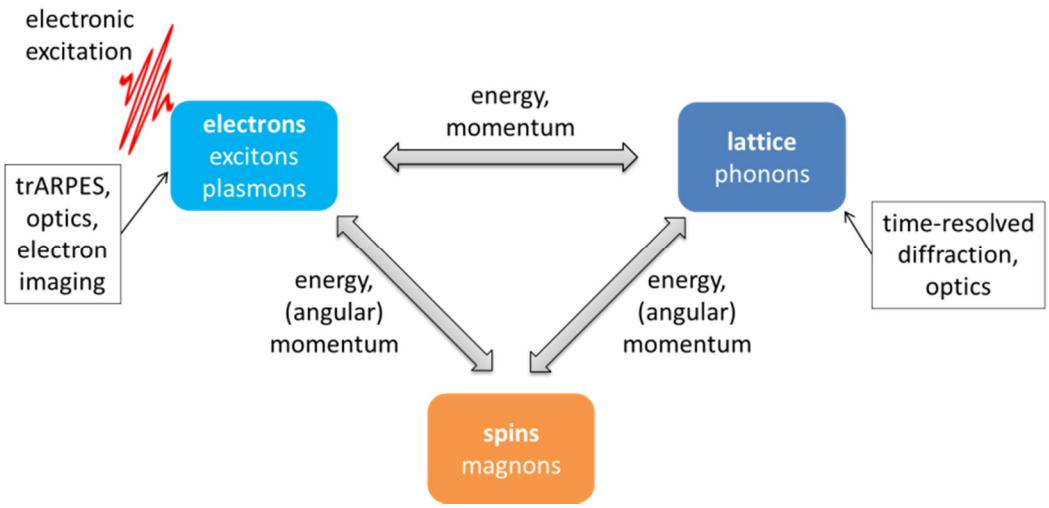


***Figure 1:*** *Illustration of the relation between employed experimental techniques and the accessible physical quantities. The coupling between electronic, phononic and spin degrees of freedom is investigated by different subsystem-specific ultrafast probes through the response of the electronic structure, the crystalline structure and the dielectric function to impulsive excitation of electrons. The research activities comprise the application as well as the development of ultrafast techniques.*

## Research Activities

### Development of a 500 kHz Femtosecond DUV and XUV Light Source

Time- and angle-resolved photoelectron spectroscopy (trARPES) provides access to electronic structure with time, energy and momentum resolution. The time scale of the relaxation of photo-excited states potentially reveals the relevant coupling mechanisms, which are reflected in the momentum- and energy-dependent self-energy [1]. Current approaches to trARPES are either limited in ***k***-space access due to low probe photon energies or limited in counting statistics due to limited repetition rate. Based on a novel laser system we bridge this technology gap. In collaboration with the *Dynamics of Correlated Materials* group headed by Martin Wolf, an optical parametric chirped pulse amplifier (OPCPA) operating at 500 kHz repetition rate and providing tunable short pulses with a pulse energy exceeding 30 µJ has been developed [2]. The output of this laser system is frequency up-converted to either the deep ultraviolet (DUV) spectral range by means of nonlinear crystals or the extreme ultraviolet (XUV) spectral range by high harmonic generation (HHG) in noble gases, see Fig. 2.

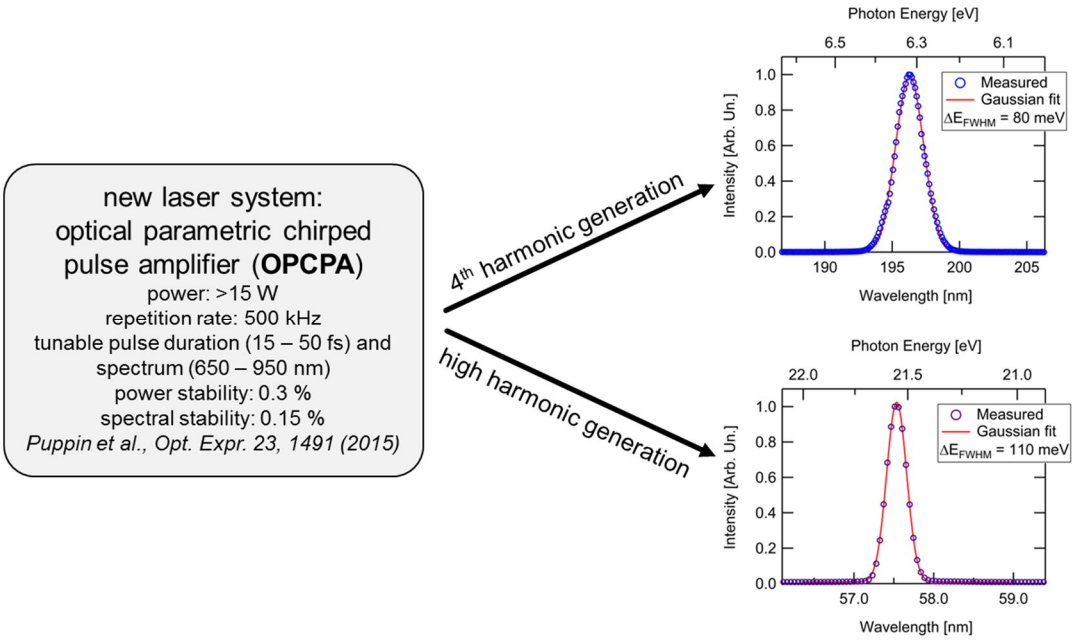


***Figure 2:*** *Generation of high-repetition rate femtosecond DUV and XUV pulses. A novel optical parametric chirped pulse amplifier providing high average power at 500 kHz repetition rate has been developed and is used for generating high-photon energy probes by frequency up-conversion. 4th harmonic generation in nonlinear crystal provides DUV pulses with photon energies up to 6.4 eV and bandwidth supporting sub-30 fs pulse duration (top right panel). Spectrally isolated XUV pulses exceeding 20 eV photon energy with a bandwidth of approximately 100 meV are generated by HHG of the frequency-doubled OPCPA output (bottom right panel). Puppin et al., Optics Express 23, 1491 (2015); poster PC 8.*

Employing a tight-focusing geometry and the 2nd harmonic of the OPCPA output as fundamental of the HHG process, a single isolated harmonic at ~21.5 eV photon energy with a bandwidth of ~100 meV is generated.

**Femtosecond Low-energy Electrons as Probes: Visualization of Photocurrents in Nanoobjects**

We developed a novel concept for femtosecond point-projection microscopy (fsPPM) and femtosecond low-energy electron diffraction (fsLEED) utilizing laser-triggered electron emission from metal nanotips as pulsed electron source, delivering either divergent or collimated femtosecond single-electron wave packets in the sub-kV energy range. Due to the large scattering cross-section of low-energy electrons and their high sensitivity to electric fields, such electrons represent sensitive probes for the investigation of ultrafast currents and transient electric fields in nanoobjects as well as of atomic structure in low-dimensional materials with femtosecond time resolution [3].

As a proof of concept, we demonstrated the visualization of ultrafast photo-induced currents in III-V semiconductor nanowires, see Fig. 3. Band bending along the radial coordinate of an InP nanowire results in a separation of photo-excited carriers with a flow of electrons from the interior to the surface of the nanowires. The photo-current results in a transient lifting of the band bending, which is reflected in a time-dependent change of the vacuum level in the vicinity of the nanowire. As low-energy electrons are sensitive to small changes of the electrostatic potential on the nanoscale, the fsPPM image of the nanowire reveals the net photocurrent inside the nanowire with approximately 100 fs temporal resolution, see Fig. 3c.

The temporal and spatial resolution of the fsPPM approach is currently limited by the need of keeping the laser pulses exciting the sample and triggering the electron source spatially separated. In order to overcome this limitation, we realized plasmon-driven electron emission from a gold nanotip in collaboration with the group of Markus Raschke, Univ. of Colorado. By means of grating structures engraved in the shaft of nanotips [4], a broadband surface plasmon polariton (SPP) is launched by a femtosecond laser pulse, see Fig. 3d. The continuous focusing of the SPP during the propagation towards the apex leads to fields sufficient for the nonlinear emission of electrons from the tip's apex. Interferometric autocorrelation measurements indicate that the SPP-induced electron emission occurs on the sub-10 femtosecond time scale.

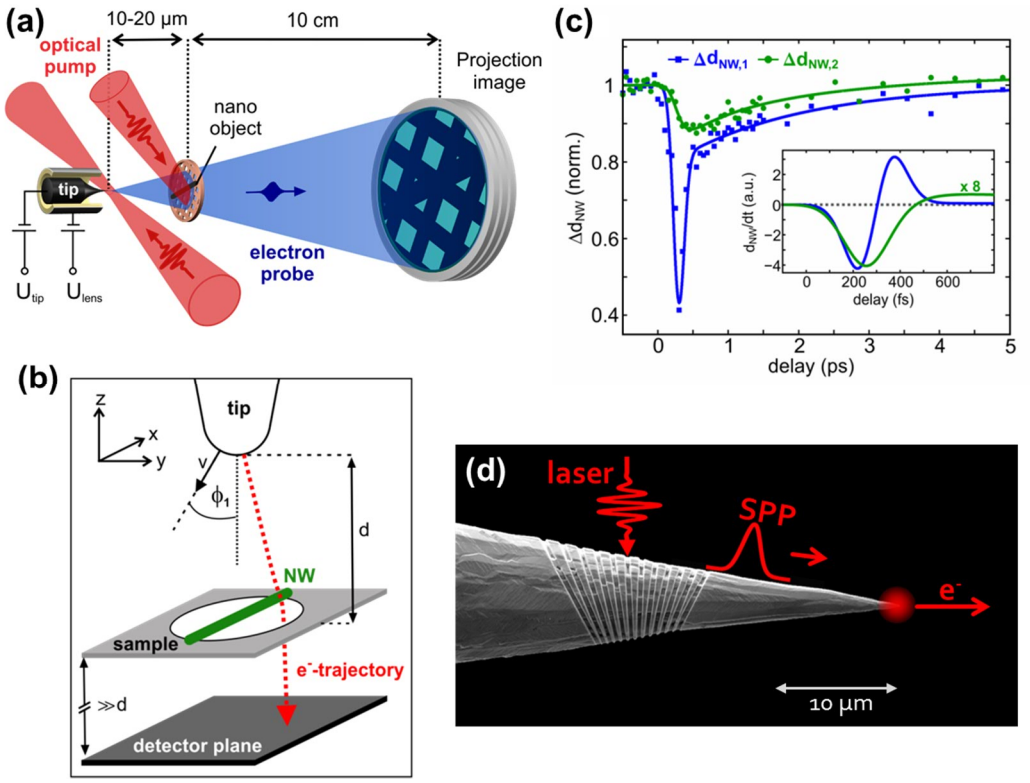


***Figure 3:*** *Visualization of photocurrents in a nanowire with low-energy femtosecond electrons (a-c) and plasmon-induced electron emission from a nanotip (d). Panel (a): Illustration of the experimental setup for fs point-projection microscopy comprising a laser-triggered nanotip as electron source. Panel (b): The trajectory of fs single electrons in the vicinity a nano-sized sample is sensitive to electric fields caused by variations of the electrostatic potential in the vicinity of the nanoobject. Panel (c): The time-dependent change of the projected diameter of a p-i-n-doped InP nanowire after optical excitation with femtosecond laser pulses centered at 800 nm. The photo-induced effect is interpreted as radial current of photo-excited electrons from the interior of the 30 nm thick nanowire to the surface in the p-doped (blue line) and n-doped (green line) segments, respectively. The inset shows the temporal derivative of the measured signal reflecting the time-dependence of the radial photocurrent. Panel (d): SEM image of a gold nanotip with a grating for the efficient coupling of a sub-10 fs laser pulse to a surface plasmon polariton (SPP). While propagating towards the apex, the SPP is focused and reaches intensities sufficient for nonlinear emission of electrons from the tip's apex. Müller et al., Nature Communications 5 (10), 5292 (2014); poster PC9.*

## Phase Change Materials: Relating Optical Properties and Crystalline Structure

Phase change materials employed in data storage applications are characterized by their large contrast of opto-electronical properties between their metastable amorphous and crystalline structural states. The ability to reversibly switch the material between those states has found numerous applications in modern data storage technology, where switching is achieved by tailoring temperature profiles in the system after heating with optical or electrical pulses.

Whereas the pathway of thermal phase transformation employed in devices is well established, the existence of non-thermal phase transitions [5], and the microscopic origin of the pronounced optical contrast [6] are still subject to debate. In collaboration with the group

of Simon Wall (ICFO, Castelldefels), we investigated the evolution of optical and structural properties of crystalline GST upon excitation with a femtosecond laser pulse by combining two complementary pump-probe techniques. The transient optical properties are investigated by femtosecond optical spectroscopy while the structural response of the lattice is probed with femtosecond electron diffraction, see Fig. 4. Above the threshold for switching, we employed single-shot optical and diffraction measurements to follow the system's response to photoexcitation during the crystalline-to-amorphous phase transition.

Large changes in the dielectric function of up to 30% occur instantaneously after photoexcitation, the amplitude of which increases with fluence, but saturates when crossing the threshold for permanent change. In earlier work on phase change materials, similar observations have been interpreted as non-thermal phase transitions to an amorphous or liquid state [7,8]. In contrast, time-resolved electron diffraction [9] reveals that energy transfer from excited electrons to the lattice occurs only on a few picosecond timescale independent of the excitation level. We interpret the ultrafast dynamics of optical and structural properties in terms of resonant bonding of this material [10]. While electronic excitation depopulates resonantly-bonded states, which dominate the optical properties, the crystalline structure is preserved by the covalently bound backbone until energy transfer due to electron-phonon

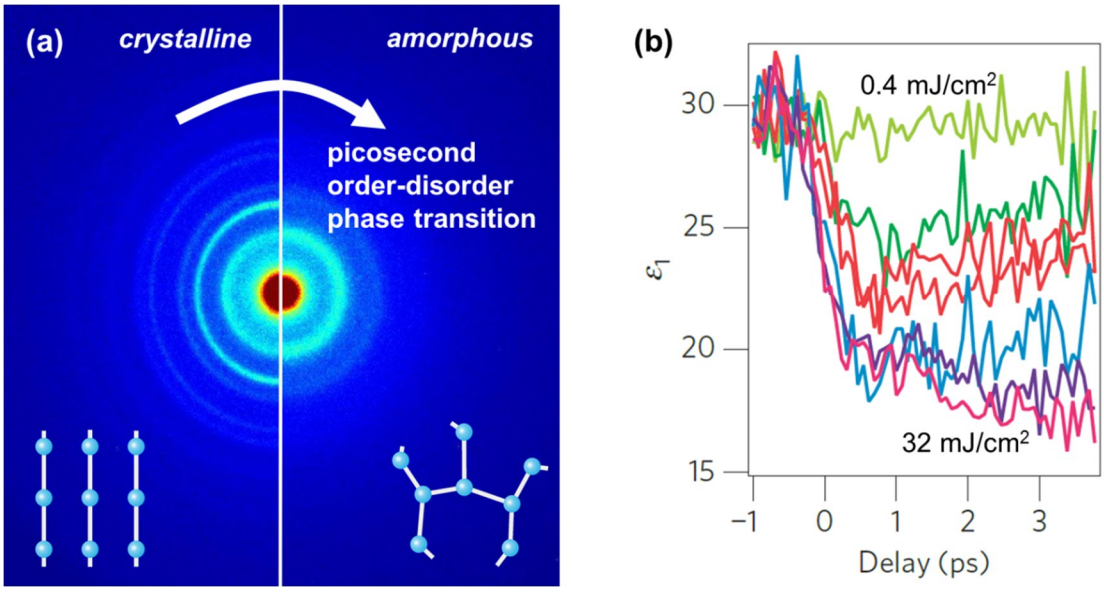


***Figure 4:*** *The response of structural and optical properties of the phase change material GST ($Ge_2Sb_2Te_5$) to electronic excitation is studied with femtosecond electron diffraction (left) and optical spectroscopy. The right panel shows the evolution of the real part of the dielectric function at 800 nm retrieved from simultaneous single-shot measurement of transmission and reflectivity for a range of excitation levels. The light blue curve corresponds to a fluence of 14 mJ/cm$^2$, which is the threshold fluence for a persistent crystalline-amorphous phase transition. While the dielectric function changes quasi-instantaneously by up to 30%, the loss of crystalline long-range order occurs by thermal melting on the picosecond time scale. Waldecker et al., Nature Materials, aop, doi: 10.1038/nmat4359; poster PC 10.*

coupling leads to melting of the crystal. The large transient change of the optical properties without structural transition may be utilized in optical modulators comprising GST-based heterostructures.

**Electron-lattice Interaction in Layered Transition Metal Dichalcogenides, Bulk Crystals and Clusters**

In addition to the temporal evolution of crystalline long-range order, femtosecond electron diffraction provides time-resolved information on the excitation level of phonons through the experimentally accessible mean-squared displacement of the atoms. Figure 4a shows the time-dependent atomic mean squared displacement of Al in response to optical excitation with an NIR pulse for three excitation levels. The increase in atomic motion reflects the transfer of energy from the photo-excited electrons to the lattice, which is typically described within a two-temperature model. The assumption, however, that phonon populations follow Bose-Einstein statistics on the femtosecond time scale, is highly questionable. In collaboration with Jan Vorberger (MPIKS Dresden), we introduce a non-thermal lattice model describing the coupling of electrons to individual phonon branches [11].

Besides bulk materials, we investigate the electron-phonon interaction in low-dimensional materials. In collaboration with the group of Richard Palmer (University of Birmingham), size-selected Au clusters on thin graphite are optically excited and studied with femtosecond

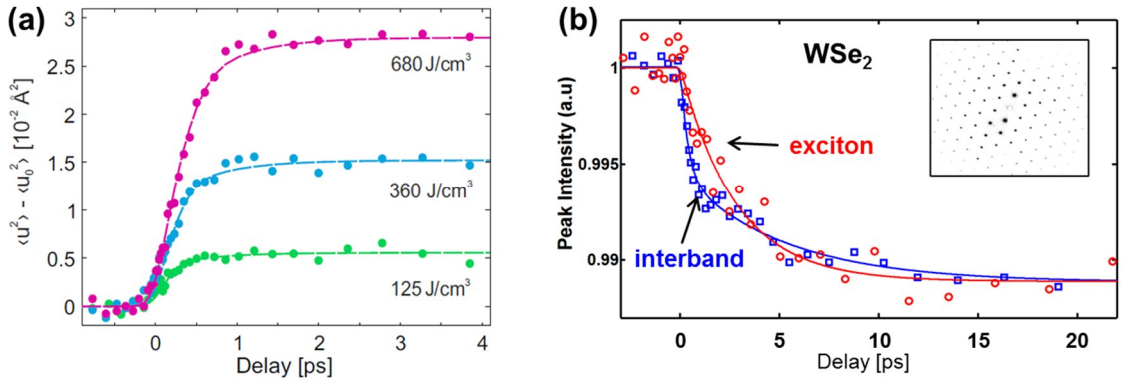


***Figure 5:*** *Investigation of electron-phonon coupling in aluminium and the 2D material $WSe_2$. Left panel: time-resolved electron diffraction reveals the increase in atomic mean squared displacement (dots) in a 30 nm thick film of Al subsequent to excitation of the electrons with three different energy densities. The data is fitted with a non-thermal lattice model (solid lines) describing the energy transfer from electrons to individual phonon branches with coupling constants from first principles calculations. Right panel: dynamics of Bragg peak intensity of multilayer $WSe_2$ in response to optical excitation resonant with the lowest energy excitonic transition (red circles) and with interband transitions at 400 nm (blue squares). Solid lines indicate exponential fits to the data revealing a sequential relaxation process of photo-excited free carriers (blue) due to electron-phonon coupling, in contrast to the mono-exponential relaxation of excitonic states (red). The inset shows a static diffraction of the sample before optical excitation. Waldecker et al., arXiv 1507.03743; poster PC 11.*

electron diffraction. Both, internal coupling between electrons and vibrations as well as coupling between clusters and substrate are investigated. Additionally, we study semiconducting transition metal dichalcogenides (TMDCs), which are a fascinating class of layered materials exhibiting highly anisotropic bonding, pronounced excitonic effects, transitions from indirect to direct bandgaps in the limit of single crystalline layers [12], and spin-valley-layer correlations [13,14]. Currently, we investigate relaxation dynamics subsequent to different kinds of optical excitation in multilayer $WSe_2$ by probing the evolution of the vibrational excitation of the crystal, see Fig. 5b. The mono-exponential relaxation dynamics subsequent to excitation in resonance with an excitonic band is ascribed to exciton dissociation and carrier relaxation towards the band extrema, whereas relaxation of electrons subsequent to classical interband excitation proceeds through fast intraband relaxation followed by a slower process likely involving intervalley scattering. In perspective, the structural dynamics studies with time-resolved diffraction experiments will be complemented by trARPES experiments providing direct access to momentum-resolved electron relaxation.

**Observing the Motion of Electrons on Atomic Length Scales**

The propagation of electrons in crystals is described in terms of Bloch wave packets, i.e., coherent superpositions of Bloch states around a central wave vector. Free propagation of

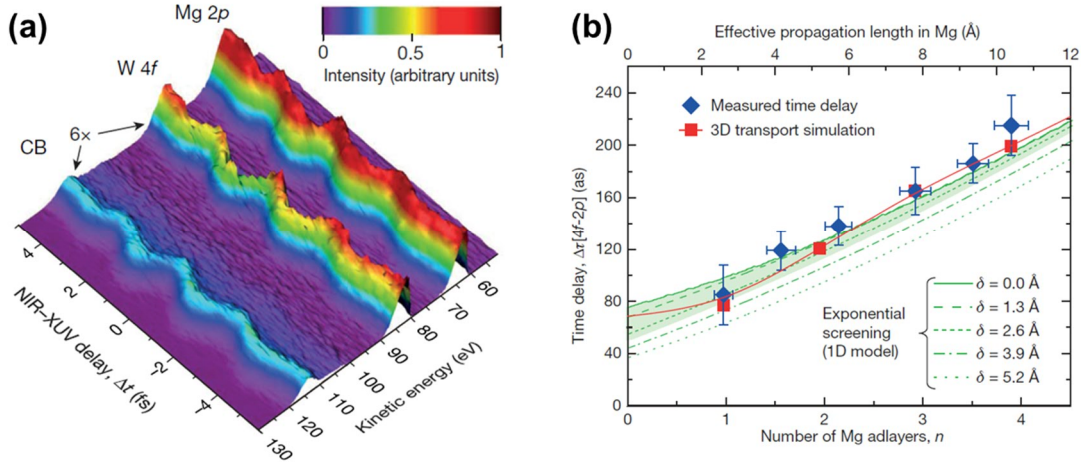


***Figure 6:*** *Investigation of electron propagation and dielectric screening on atomic length scales. Left panel: Attosecond streaking photoelectron spectroscopy from four monolayers of magnesium on a tungsten crystal showing emission from the Mg 2p and W 4f core levels and the sample's conduction band modulated in energy by a sub-2 cycle near-infrared streaking field. Right panel: the time delay between electrons originating from core levels of substrate and adlayer reveals the propagation of electron through the Mg layers and the length scale of dielectric screening of near-infrared light at the surface. Neppl et al., Nature 517 (7534), 342-346 (2015).*

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. In collaboration with the groups of Peter Feulner, Reinhard Kienberger (both TU Munich) and Ferenc Krausz (MPQ, Garching), electron wave packet motion has been investigated on the atomic length and the attosecond time scale [15]. These experiments reveal the electron motion through few layer of magnesium adsorbed on a tungsten crystal and provide information on the length scale of dielectric screening by the metal, see Fig. 6. Additionally, this type of experiments has been employed for investigating collective excitation in photoemission, in particular to discriminate between intrinsic and extrinsic excitation of plasmons [16].

**References**


[1] M. Sentef, A. Kemper, B. Moritz, J. Freericks, Z.-X. Shen, and T. Devereaux, *Phys. Rev. X* **3**, 041033 (2013).

[2] M. Puppin, Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf, and R. Ernstorfer, *Opt. Express* **23**, 1491 (2015).

[3] M. Müller, A. Paarmann, and R. Ernstorfer, *Nat. Commun.* **5**, 5292 (2014).

[4] S. Berweger, J. M. Atkin, R. L. Olmon, and M. B. Raschke, *J. Phys. Chem. Lett.* **3**, 945 (2012).

[5] A. V Kolobov, M. Krbal, P. Fons, J. Tominaga, and T. Uruga, *Nat. Chem.* **3**, 311 (2011).

[6] K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, and M. Wuttig, *Nat. Mater.* **7**, 653 (2008).

[7] K. Sokolowski-Tinten, J. Solis, J. Bialkowski, J. Siegel, C. Afonso, and D. von der Linde, *Phys. Rev. Lett.* **81**, 3679 (1998).

[8] J. Callan, A. M. Kim, C. Roeser, E. Mazur, J. Solis, J. Siegel, C. Afonso, and J. de Sande, *Phys. Rev. Lett.* **86**, 3650 (2001).

[9] L. Waldecker, R. Bertoni, and R. Ernstorfer, *J. Appl. Phys.* **117**, 044903 (2015).

[10] L. Waldecker, T. A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. E. Simpson, R. Ernstorfer, and S. Wall, *Nat. Mater.*, aop, doi: 10.1038/NMAT4359.

[11] L. Waldecker, R. Bertoni, R. Ernstorfer, and J. Vorberger, *ArXiv* 1507.03743v1 (2015).

[12] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).

[13] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, *Phys. Rev. Lett.* **108**, 196802 (2012).

[14] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, *Nat. Phys.* **10**, 343 (2014).

[15] S. Neppl, R. Ernstorfer, A. L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E. M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J. V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz, and R. Kienberger, *Nature* **517**, 342 (2015).

[16] C. Lemell, S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger, and J. Burgdörfer, *Phys. Rev. B* **91**, 241101(R) (2015).

**Publications (2014 - July 2015)**

*Müller, M., A. Paarmann and R. Ernstorfer:* Femtosecond electrons probing currents and atomic structure in nanomaterials. Nature Communications **5 (**10), 5292 (2014).

*Paasch-Colberg, T., 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 **8 (**3), 214-218 (2014).

*Schiffrin, A., 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:* Addendum: Optical-field-induced current in dielectrics. Nature **507 (**7492), 386-387 (2014).

*Ernstorfer, R:* Im Fokus ultrakurzer Laser: das Wechselspiel von Elektronen und Kristallstruktur. MPG Jahrbuch 2015.

*Lemell, C., S. Neppl, G. Wachter, K. Tőkési, R. Ernstorfer, P. Feulner, R. Kienberger and J. Burgdörfer:* Real-time observation of collective excitations in photoemission. Physical Review B **91 (**24), 241101 (2015).

*Müller, M., A. Paarmann and R. Ernstorfer:* Visualization of Photocurrents in Nanoobjects by Ultrafast Low-Energy Electron Point-Projection Imaging. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 667-670 (2015). ISBN 978-3-319-13241-9.

*Neppl, S., R. Ernstorfer, A.L. Cavalieri, C. Lemell, G. Wachter, E. Magerl, E.M. Bothschafter, M. Jobst, M. Hofstetter, U. Kleineberg, J.V. Barth, D. Menzel, J. Burgdörfer, P. Feulner, F. Krausz and R. Kienberger:* Direct observation of electron propagation and dielectric screening on the atomic length scale. Nature **517 (**7534), 342-346 (2015).

*Puppin, M., Y. Deng, C. Nicholson, C. Monney, M. Krenz, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer:* 500 kHz OPCPA-based UV-XUV light source for time-resolved photoemission spectroscopy. In: Proceedings of Conference on Lasers and Electro-Optics (CLEO). OSA Publ., Washington, DC, SF2M.4 (2015). ISBN 978-1-55752-968-8.

*Puppin, M., Y. Deng, O. Prochnow, J. Ahrens, T. Binhammer, U. Morgner, M. Krenz, M. Wolf and R. Ernstorfer:* 500 kHz OPCPA delivering tunable sub-20 fs pulses with 15 W average power based on an all-ytterbium laser. Optics Express **23 (**2), 1491-1497 (2015).

*Puppin, M., Y. Deng, O. Prochnow, J. Matyschok, T. Binhammer, U. Morgner, M. Wolf and R. Ernstorfer:* Fiber-Slab-Pumped OPCPA for XUV-Based Time-Resolved Photoelectron Spectroscopy at 500 kHz Repetition Rate. In: Ultrafast Phenomena XIX. (Eds.) K. Yamanouchi, S. Cundiff, R.d. Vivie-Riedle, M. Kuwata-Gonokami and L. DiMauro. (Springer Proceedings in Physics, Vol. 162). Springer, Cham, 766-769 (2015). ISBN 978-3-319-13241-9.

*Waldecker, L., R. Bertoni and R. Ernstorfer:* Compact femtosecond electron diffractometer with 100 keV electron bunches approaching the single-electron pulse duration limit. Journal of Applied Physics **117 (**4), 044903 (2015).

*Waldecker, L., T.A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer and S. Wall:* Time-domain separation of optical properties from structural transitions in resonantly bonded materials. Nature Materials, advance online publication: doi: 10.1038/nmat4359.

**Invited Talks (2014 - July 2015)**

**Ralph Ernstorfer**

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| May 2014 | FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany<br>*Ultrafast Structural and Electronic Dynamics in Low Dimensional Materials* |
| May 2014 | Physikalisches-Kolloquium, RWTH Aachen University, Aachen, Germany<br>*Photo-Induced Structural Dynamics in Solids* |
| Aug 2014 | SPIE Optics and Photonics, Ultrafast Nonlinear Imaging and Spectroscopy II, San Diego, CA, USA<br>*Femtosecond Low-Energy Electron Diffraction and Imaging* |
| Sep 2014 | ELI-ALPS 2nd User Workshop, Extreme Light Infrastructure - Attosecond Light Pulse Source, Szeged, Hungary<br>*Towards Mapping Excited Electronic States in Molecules and Correlated Materials with tr-ARPES* |
| Oct 2014 | Workshop, DIET 14, Dynamics, Interactions and Electronic Transitions at Surfaces, Pacific Grove, CA, USA<br>*Femtosecond Low-Energy Electrons Probing Currents and Atomic Structure in Nanomaterials* |
| Feb 2015 | 4th Banff Meeting on Structural Dynamics Ultrafast Dynamics with X-Rays and Electrons, Banff, AB, Canada<br>*Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials* |
| Mar 2015 | 79. Jahrestagung der DPG und DPG-Frühjahrstagung der Sektion Kondensierte Materie (SKM), Focus Session: Structural Dynamics in Nanoscale Materials Probed by Ultrashort Electron Pulses, Berlin, Germany<br>*Femtosecond Electron Probes for the Investigation of Structural Dynamics and Ultrafast Currents in Nanomaterials* |
| Mar 2015 | Winter School on Ultrafast Processes in Condensed Matter (WUPCOM'15), Reit im Winkl, Germany<br>*Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents* |
| Apr 2015 | Seminar in Solid State Physics, Physik-Institut, University of Zurich, Zurich, Switzerland<br>*Femtosecond Electrons Probing Structural Dynamics and Ultrafast Currents* |
| Jul 2015 | Workshop of the Munich-Centre of Advanced Photonics and IMPRS-APS, Wildbad Kreuth, Germany<br>*Investigating correlation and coupling phenomena in solids: which physical quantities can we access?* |

**Melanie Müller**

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| Jul 2015 | Seminar, Helmholtz-Zentrum Berlin<br>*Femtosecond low-energy electrons as probes for ultrafast dynamics on the nanoscale* |

**Lutz Waldecker**

Jun 2015 Group Seminar, Faculty of Physics (AG Uwe Bovensiepen), Universität Duisburg-Essen, Essen, Germany
*Electron-Lattice Interactions Probed with Femtosecond Electron Diffraction*