FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

# Report to the Fachbeirat
# Department of Physical Chemistry

# 2017

## Department of Physical Chemistry — Director: Martin Wolf

**Staff scientists:**

Kramer Campen
Markus Eiswirth
Tobias Kampfrath *until 6/2017*
Takashi Kumagai
Alexey Melnikov *until 6/2016*
Alexander Mikhailov *until 06/2017*
Melanie Müller *since 5/2017*
Alexander Paarmann
Laurenz Rettig *since 2/2016*
Mohsen Sajadi

Gerhard Ertl (Emeritus)

**Scientists, staying for at least six months, paid by FHI:**

Vasileios Balos *since 7/2017*
Lukas Braun
Maciej Dendzig *since 6/2017*
Laura Foglia *until 4/2016*
Karsten Horn *until 12/2016*
Matthias Koch *since 8/2016*
Chenfang Lin *since 8/2017*
Sebastian Mährlein
Lukáš Nádvorník *since 11/2016*
Ilya Razdolski
Natalia Martín Sabanés *since 9/2017*
Christian Schewe *until 12/2016*
Martin Thämer
Hendrik Vita *until 7/2016*
Yoav William Windsor *since 2/2017*

**Scientists, staying for at least six month, paid from external funds:**

| | | | |
|---|---|---|---|
| Delroy Baugh *until 8/2016* | *UCLA* | Francoise Lapointe *until 4/2016* | *Quebec/MPG* |
| Majed Chergui *until 3/2017* | *AvH* | Fumito Mori *until 12/2015* | *VW* |
| Franz Geiger *until 8/2017* | *Northwestern/AvH* | Jeffrey Noel | *AvH* |
| Marc Herzog *until 1/2016* | *EU/DFG* | Amartya Sarkar *until 12/2015* | *VW/MPG* |
| Harald Kirsch | *SFB 1109* | Vasily Temnov *until 12/2016* | *AvH* |
| Janina Ladenthin *since 1/2017* | *SFB 951/JST* | Yujin Tong | *SFB 658* |

| | | |
|---|---|---|
| Graduate students: | 32 | (14 from external funds) |
| Master students: | 5 | |
| Trainees: | 7 | |
| Technicians: | 11 | |

**Max Planck Research Group: Structural and Electronic Surface Dynamics**

**Head:** Ralph Ernstorfer

6 post doc
3 graduate students
1 master student

**Max Planck Research Group: Electronic Dynamics**

**Head:** Julia Stähler
*(maternity leave 11/2016 - 8/2017)*

4 post doc
8 graduate students
1 bachelor student
1 scientific assistant

**Service Group Mechanical Workshop**

**Head:** Petrik Bischoff — 19 staff members — 1 apprentices

# Recent Developments in the Department of Physical Chemistry

## Director: Martin Wolf



**Max Planck Research Group: Structural and Electronic Surface Dynamics**

**Head: Ralph Ernstorfer**

**Max Planck Research Group: Electronic Dynamics**

**Head: Julia Stähler**

## 1. General Remarks

Since June 2017 the Department of Physical Chemistry has moved into the new building on the FHI campus and now all members of the department enjoy working together and communicating with each other in one building. Unfortunately, a part of the lab space is still not operational due to technical problems with the cooling water system. We hope that at the time of the Fachbeirat the experimental research infrastructure will finally be fully operational.

Several changes have occurred among the group leaders of the department since the last meeting of the Fachbeirat:

- *Dr. Julia Stähler* has started her Max Planck Research Group (MPRG) in January 2016 and is now expanding her experimental infrastructure by a versatile high-repetition rate laser system for her studies on interfacial electron dynamics
- Since February 2016 *Dr. Laurenz Rettig* is leading the research group on ultrafast dynamics of correlated materials employing XUV based time-resolved ARPES. With the successful implementation of his Emmy Noether Group he will expand these activities by combining time-resolved ARPES with x-ray diffraction experiments and dedicated sample growth using pulsed laser deposition (PLD).
- In January 2017 *Dr. Mohsen Sajadi* started a new research group on ultrafast molecular dynamics in liquids driven by high-field THz pulses.
- *Dr. Melanie Müller* has started in May 2017 her new research group to develop ultrafast scanning probe microscopy for studies of local carrier and molecular dynamics at surfaces.
- *Prof. Tobias Kampfrath* received an offer for a full professorship at the Freie Universität Berlin and has started on this position in July 2017. He will operate his group in our department for approximately two more years until his laboratory space is available at the FU Berlin.
- *Dr. Alexey Melnikov* moved to a position at the University of Halle in July 2016, but continues his research on spin and magnetization dynamics using the dedicated experimental setup at the FHI. Once the collaborative research center TRR 227 between Berlin and Halle on ultrafast spin dynamics will be established these activities shall move to Halle.
- After his retirement *Prof. Alexander Mikhailov* is associated as guest scientist both with the department and the Hiroshima University in Japan.

The Mechanical Workshops, headed by *Petrik Bischoff*, are still associated with the PC department whereas the Electronic Lab is now connected to the Molecular Physics Department. The machine infrastructure and organization of the workshop has been further improved and the high quality output is well received by all scientists.

During the last two years a remarkable number of younger scientists in the department received awards and distinguished research grants, for example, from the European Reserach Council (ERC), the German Research Foundation (DFG) and the Japanese Science and Technology Agency (JST). This is considered as an indicator demonstrating the success of the department in the promotion and guidance of younger scientists in their career development: *Ralph Ernstorfer* (ERC consolidator grant 2015), *Tobias Kampfrath* (ERC consolidator grant 2016, full professor at Freie Universität Berlin 2017), *Takashi Kumagai* (JSTS PRESTO grant 2017, Gerhard Ertl Young Investigator Award 2016), *Claude Monney* (SNF professorship University of Fribourg 2017), *Laurenz Rettig* (DFG Emmy Noether Research Group 2017), *Julia Stähler* (Max Planck Research Group (MPRG) 2015, Gaede Award 2016 of the German Vacuum Society 2016, Edith Flanigen Award 2016), *Lutz Waldecker* (Carl Ramsauer Award of the Physical Society Berlin 2016, Feodor Lynen Fellowship 2016, AvH), *Nicolai Paßler* (Physics Study Award 2017 of the Physical Society Berlin).

Furthermore, the PC department is hosting several winners of the Alexander von Humboldt and the Friedrich Wilhelm Bessel Research Award as well as winners of the Alexander von Humboldt Research Fellowships.

## 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 the coupling between various (electronic, spin and lattice) degrees of freedom and mechanistic insights into selected dynamic phenomena like ultrafast phase transitions, excited state dynamics or single molecule reactions at surfaces. We follow the strategy 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 in the department is performed by small teams with specific, often complementary expertise, creating various synergies between the different groups.

*Structure:* The research topics of the department focus on two main directions.
*(I) Ultrafast dynamics of elementary processes* in solids and at interfaces with specific focus on the interactions between electrons, phonons and spins: This line of research addresses the dynamics of elementary processes on their relevant time scales, employing ultrafast laser spectroscopy (with, typically, femtosecond time resolution). Both existing and newly developed spectroscopic techniques are used to study the electronic structure, excited state dynamics, optically induced phase transitions and low-energy excitations including lattice dynamics and spin dynamics in solids and at interfaces.
*(II) Molecular processes at interfaces and in condensed phase* systems including gas-solid, liquid-solid as well as electrochemical interfaces and liquids: Here 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. Furthermore, nonlinear optical sum-frequency and high field THz spectroscopy provides insights into the molecular structure at interfaces and into the dynamics of liquids. In particular, with these activities we implement the new direction of the FHI for the evolution of the institute into the next decade towards atomistic studies of processes at complex interfaces (i.e. beyond gas-solid in UHV) including liquid-solid, liquid-gas and electrochemical interfaces.

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

**Ultrafast Dynamics of Solids: Electrons, Phonons and Spins**

- Dynamics of Correlated Materials (*Laurenz Rettig*)
- Ultrafast Scanning Probe Microscopy (*Melanie Müller*)
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)
- Time-resolved Second Harmonic Generation Spectroscopy (*Alexey Melnikov*)

**Molecular Processes at Interfaces and in Condensed Phase**

- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- THz Driven Molecular Dynamics (*Mohsen Sajadi*)
- Complex Chemical and Biological Systems (*Alexander Mikhailov*)

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

- Structural and Electronic Surface Dynamics (*Ralph Ernstorfer)*
- Electron Dynamics (*Julia Stähler)*

Both the MPRG of *Ralph Ernstorfer* and *Julia Stähler* are embedded in the department by various collaborations and their research on ultrafast structural dynamics and interfacial electron dynamics, respectively, nicely complements corresponding research topics of other groups.

*New developments:* In the last few years the department has started to address several new research topics, which are often linked to the development of new techniques, and several new research groups have been initiated. One example is the research group of *Alexander Paarmann* who exploits the potential of the FHI free electron laser (FEL) for spectroscopy in solids (in particular surface phonon polaritons) and develops laser synchronization with the FEL. In the future this will have a strong impact on interfacial molecular spectroscopy at the FEL using nonlinear optics enabling studies of *e.g.* electrochemical interfaces.

More recently the department has put increasing emphasis on liquids and their interfaces: This includes studies of (i) liquid-solid or liquid-gas interfaces and electrochemical processes employing nonlinear vibrational sumfrequency spectroscopy with specific designed sample cells in the group of *Kramer Campen* and (ii) THz driven molecular dynamics in liquids using high field THz pulses to excite low frequency (e.g. rotational or librational) modes in the new group of *Mohsen Sajadi*. The activities based on high-field THz generation will be further boosted by an upgrade of the existing high power laser system at the FHI enabling several new experiments including application to solids in the group of *Tobias Kampfrath*.

Furthermore several new scanning probe setups are currently being developed for studies of light-induced single molecule processes on and for local spectroscopy and transport measurements at the nanoscale. Our goal is to bring together the expertise from (spatial averaging) optical spectroscopy together with local probes. This includes a project developing ultrafast scanning probe microscopy in the new group of *Melanie Müller* and a project developing a setup for a nanoscale integrated circuit single molecule transport measurements in low-temperture STM by *Matthias Koch*.

*Promotion of younger scientists:* Guidance and promotion of younger scientists in their career development is an important goal of the department, and is implemented by several measures (*e.g.* within the IMPRS graduate school, PhD student days and department workshops, regular status discussions, the nomination for awards or invited talks). As one specific measure, junior group leaders and advanced postdocs are guided to obtain experience in grant applications and to become also project leaders in ERC, DFG or JST funded projects. In particular, establishing an independent junior research group with substantial own funding is a

major achievement and career step for younger scientists. Recently the department has been very successful in this regard and currently five such research groups are funded:

- Max Planck Research Group & ERC Group of *Ralph Ernstorfer*
- ERC Group of *Tobias Kampfrath*
- DFG Emmy Noether Group of *Laurenz Rettig*
- Max Planck Research Group of *Julia Stähler*

In addition, several group leaders have projects as PIs in DFG funded collaborative research centers (Sfb 658, Sfb 951, Sfb 1109), one DFG research unit (FOR 1700) or have received individual research grants funded by DFG or JST (see section 3 for a complete list of all projects). The department has been strongly involved in the development of the concept for a new collaborative research center between Berlin and Halle (TRR 227) on Ultrafast Spin Dynamics. Several members of the department are PIs in this initiative.

### 1.2 Recent Research Highlights

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

- Semiconducting transition metal dichalcogenides (TMDCs) exhibit a hidden spin texture in the electronic ground state despite the inversion symmetry of the crystal structure. Employing spin-selective optical excitation combined with time- and angle-resolved photoemission spectroscopy (trARPES) with XUV probe pulses, the preparation of spin-, valley- and layer-polarized excited states in bulk $WSe_2$ crystals has been demonstrated suggesting opto-spintronic applications of these materials [Phys. Rev. Lett. **117**, 277201 (2016)].
- Using XUV trARPES, we studied the ultrafast dynamics of a spin density wave (SDW) in Chromium. Surprisingly, the suppression of the SDW gap in the electronic structure can be well understood in a thermal picture driven by the hot thermalized electronic heat bath. This shows that for phases governed by the temperature of a single (e.g. electronic, phononic) sub-system concepts from thermodynamic equilibrium are still applicable [Phys. Rev. Lett. **117**, 136801 (2016)].
- An advanced femtosecond XUV laser source at 500 kHz repetition rate has been implemented for trARPES providing access to band mapping of excited state and scattering processes throughout the full Brillouin zone with unprecedented sensitivity. In a first application the transient electronic band structure during the photo-induced (8x2) ↔

(4x1) transition of Indium nanowires on Si(111) has been elucidated providing detailed insights into excitation mechanism and timescales of this Peierls type transition. Moreover, the distinct dynamic changes of the bandstructure can be correlated with bond formation and the structural changes in real space.

- Using THz emission spectroscopy, ultrafast photoinduced charge transfer from Se to Bi atoms was revealed at the surface of the three-dimensional topological insulator $Bi_2Se_3$. The results show that previously suggested models of photocurrent generation in $Bi_2Se_3$ require refinement. This experiment renders THz emission spectroscopy to be an ultrafast surface-specific probe [Nature Commun. **7**, 13259 (2016)].
- Ultrafast manipulation of an electronic band gap was achieved in the layered semiconductor $Ta_2NiSe_5$ which exhibits an excitonic insulating ground state: By tuning the excitation density, the electronic band gap can be either decreased due to enhanced dynamical screening, or enlarged around the Γ point of the Brillouin zone, where the order parameter of the excitonic insulating phase is the strongest. The band gap enhancement is related to an increase of the exciton condensate density and persists for approximately 1 ps until the quasiparticle distribution thermalizes across the band gap [Phys. Rev. Lett., **119**, 086401 (2017)].
- Femtosecond electron diffraction provides snapshots of the atomic structure atom motion in a crystal. From the momentum- and time-resolved inelastic scattering signal of $WSe_2$, a momentum-resolved picture of the phonon dynamics was obtained enabling to directly visualize transient non-thermal phonon populations in momentum space [Phys. Rev. Lett., **119**, 036803 (2017)].
- Surface phonon polaritons (SPhPs) in polar dielectric crystals provide a novel platform for mid-infrared low-loss nanophotonics. Using the FHI infrared free-electron laser, the nonlinear response of localized surface phonon polaritons in sub-diffractional nanostructures has been studied as well as propagating polaritons using prism coupling [Nano Letters **16**, 6954 (2016) & ACS Photonics **4**, 1048 (2017)].
- Atomic-scale heterostructures of polar dielectric crystals, so-called crystal hybrids, offer a new pathway for active tuning the frequency of mid-infrared phonon polaritons, which was demonstrated for GaN/AlN superlattices.
- Spin-polarized currents can arise from a temperature gradient across a ferromagnetic/ normal-metal interface, also known as the spin-dependent Seebeck effect. The ultrafast,

non-thermal counterpart of this effect was demonstrated, whereby the spin-dependent transmittance for non-thermalized, high-energy hot carriers leads to generation of ultrashort spin current pulses with a duration defined by the hot carrier thermalization time [Phys. Rev. Lett. **119**, 017202 (2017)].

- Ultrashort spin current pulses can induce magnetization dynamics by spin transfer torque when injected into a ferromagnet opening the time domain for probing non-uniform magnetization dynamics. Laser-excited spin current pulses injected into a ferromagnetic Fe film were found to excite inhomogeneous high-frequency spin wave dynamics up to 0.6 THz, indicating that the perturbation of the ferromagnetic magnetization is confined to only 2 nm [Nature Commun. **8**, 15007 (2017)].
- A conceptually new emitter of broadband THz electromagnetic pulses has been developed consisting of metallic thin film of a heavy-metal (HM) layer on top of a ferromagnetic (FM) layer. Excitation with a 10 fs laser pulse triggers spin transfer from the FM into the HM layer where the spin flux is converted into a transverse charge current, which acts as a source of an ultrashort electromagnetic pulse covering the frequency range from 0.5 to 30 THz without gap. The spintronic source outperforms state-of-the-art semiconductor emitters in terms of bandwidth, efficiency and cost [Nature Photonics **10**, 483 (2016)].
- Single-molecule force-induced chemistry is an emerging field and the microscopic reaction mechanisms are so far poorly understood. Using low-temperature non-contact atomic force microscopy force-induced tautomerization of a single porphycene molecule on Cu(110) has been directly observed. The mechanism and energetics of this reaction was revealed by combining atomic force spectroscopy and density functional theory calculations [Nature Chemistry **6**, 41 (2016)].
- Controlling a photo-switchable molecule on surfaces provides a novel way to attain photo-active functional interfaces. Photo-induced tautomerization in single porphycene molecules has been directly studied on Cu(111) by using low-temperature scanning tunneling microscopy combined with a wavelength tunable laser. It was revealed that the reaction occurs via substrate-mediated indirect charge transfer mechanism and vibrational excitation of the porphycene plays a crucial role [Nano Lett. **16**, 1034 (2016)].
- Excited electrons observed with two-photon photoemission spectroscopy can be trapped at the vacuum/amorphous solid water interface in unoccupied electronic states with lifetimes of tens of seconds. The energy release in the electron trapping process is sufficient to cause chemical reactions; namely a two-electron reaction occurring with water, splitting

water molecules and forming hydroxide anions at the amorphous solid water/vacuum interface [J. Phys. Chem. C. **121**, 7379 (2017)].

- Low-frequency dynamics of molecular liquids is believed to have large impact on the outcome of chemical reactions. Strong THz electric field pulses have been employed to drive orientational dynamics in polar liquids leading a transient optical anisotropy that is significantly enhanced as compared to optical pump pulses. This observation is a hallmark of the torque the THz electric field exerts on the permanent dipole moments of the solvent molecules. Our approach provides insights into the character of THz absorption resonances, the coupling between low-frequency modes, namely librational and reorientational motions and the sign of the polarizability anisotropy of the solvent molecules [Nature Commun. **8**, 14963 (2017)].
- Probing the mechanism of electrochemical reactions experimentally is challenging because it requires detecting species that typically exist in small concentrations and have very short lifetimes. Using a thin layer electrochemical cell it is possible to initiate, using a femtosecond laser pulse, the hydrogen evolution reaction at a Au and Pt electrode and track the progress of the reaction both optically and electrically with femtosecond time resolution.
- Understanding water structure at electrode/aqueous interfaces is a necessary first step in a mechanistic description and understanding of essentially all aqueous phase electro-chemistry. A previously unobserved, population of hydrophobic interfacial water, namely water molecules with one OH group pointing towards the electrode, has been experimentally characterized at the Au electrode/water interface and its abundance varying with applied bias [Angew. Chemie, **56**, 4211 (2017)].
- The intermolecular interaction of interfacial water has been typically investigated experimentally by examination its OH stretch vibration, i.e. changes of the *inter*molecular potential were characterized by probing an *intra*molecular vibration. For the first time, an intermolecular mode of interfacial water, the libration, has been studied. Interstingly, the effect of the interface is to stiffen water's rotational potential while virtually all other structural properties are similar to the bulk liquid [PCCP **18**, 18424 (2016)].
- We have constructed a vibrationally resonant sum frequency (VSF) spectrometer with a novel phase referencing scheme that improves the signal to noise ratio over conventional VSF by > 15 times. This collinear, time-domain, heterodyned, balance detected VSF setup provides phase information cannot be obtained in conventional (homodyne) approaches.

- The complete stochastic thermodynamics in a complex chemical nano-machine, the channeling enzyme tryptophan synthase, has been reconstructed for the first time based on experimental data, entropy production and flow and considering the interactions between the tryptophans subunits [J. Chem. Phys. **146**, 025101 (2017)].

## 2. Progress Report

### 2.1 Ultrafast Dynamics of Solids: Electrons, Phonons and Spins

Elementary processes in solids and at interfaces such as vibrational or electronic excitations, electron transfer, and the coupling and energy exchange between electronic, lattice and spin degrees of freedom are the underlying microscopic processes of much more complex non-equilibrium phenomena. The study of the non-equilibrium, ultrafast dynamics of such fundamental processes provides mechanistic insights into various phenomena like structural and electronic phase transitions, dynamics and relaxation of excited states, or processes driven by spin-lattice or exchange coupling. 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 Excited State Spectroscopy and Ultrafast Dynamics of the Electronic System

A detailed analysis of the electronic structure is of fundamental importance for understanding various physical and optical properties of solids. Angle-resolved photoemission spectroscopy (ARPES) is well established to provide a detailed view on the occupied electronic structure, however, the unoccupied band structure remains inaccessible for conventional ARPES. Furthermore, the dynamics of typically short-lived excited state cannot be resolved. To overcome these limitations, the department has developed and commissioned a novel high-repetition rate apparatus for XUV-based time-resolved ARPES (trARPES) in close collaboration between the group of *Laurenz Rettig* and the MPRG of *Ralph Ernstorfer* (see also MPRG report). In this setup a home-built 20 fs OPCPA laser system running at 500 kHz is used to drive High-Harmonic Generation (HHG) in Argon to generate XUV photons at ~22 eV, which provides sufficiently high photon energy to cover the complete first Brillouin zone (BZ) of most solid state materials. Owing to this exceptionally high repetition rate, which exceeds typical HHG systems by ~2 orders of magnitude, the spectroscopy of transiently populated excited states in the normally unoccupied band structure becomes feasible. Such excited state spectroscopy extends static Fermi-surface mapping to time domain studies of transiently populated excited states throughout the whole BZ, which has previously been only explored close to the BZ center using time-resolved photoemission at low photon energies (see Fig. 1a). Using this system, the conduction band dispersion in the quasi-2D transition-metal dichalcogenite (TMDC) semiconductor $WSe_2$ could be probed in the whole BZ up to 3.1 eV above the valence band maximum (Fig. 1b). This allows to directly

observe and quantify the indirect band gap of the surface layer of $WSe_2$. Furthermore, the excellent time-resolution < 40 fs enables the analysis of the ultrafast intervalley scattering of resonantly excited excitons from the K to the Σ valley due to phonon emission on the timescale of ~15 fs.

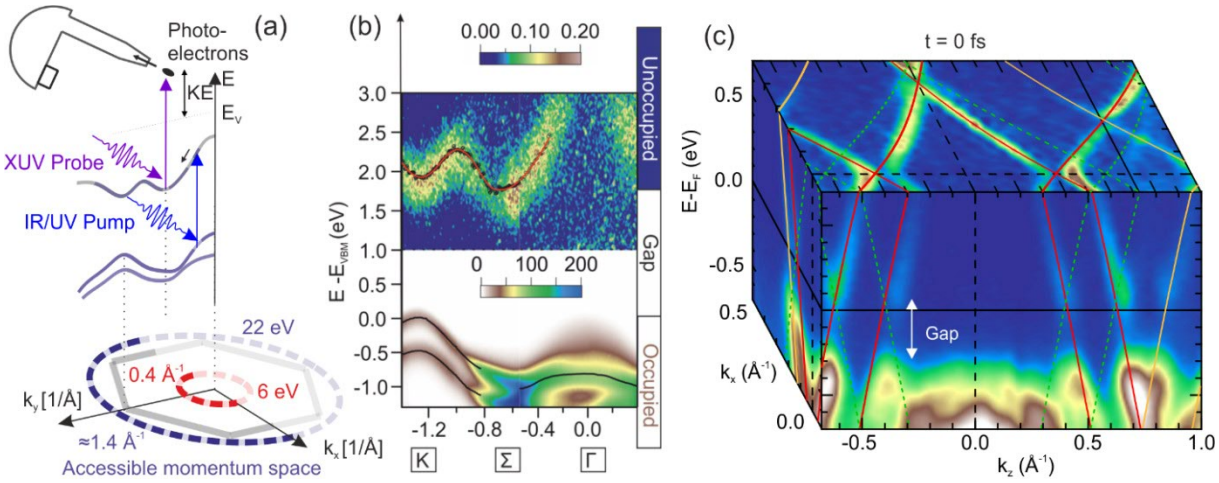


***Figure 1:*** *Excited state spectroscopy using XUV trARPES. (a) HHG-based trARPES with photon energies exceeding 20eV alllow access to the complete BZ of most materials, as exemplarily shown for the hexagonal BZ of the layered TMDC semiconductor $WSe_2$. (b) At 100 fs after excitation by 3.1 eV pump photons, the complete valence and conduction band dispersion and the indirect band gap of bulk $WSe_2$ can be simultaneously observed in a large energy range both below and above the Fermi energy. (c) In the CDW material $TbTe_3$, the unprecedented data quality achievable with the novel high-repetition rate XUV trARPES setup allows comparison to tight binding band structure calculations (lines) and reveals signatures of the CDW ordering such as energy gaps and spectral weight transfer into shadow bands (dashed green lines) in the ground and excited state band structure in the whole BZ.*

Furthermore, in a collaboration with the ARTEMIS facility at Rutherford Appleton Lab, the extreme surface sensitivity in trARPES using 20 eV XUV laser pulses allowed the observation of a hidden spin- and valley polarization induced by circularly polarized light excitation even in the centro-symmetric bulk material [1]. The high spin polarization of this transient population and the subsequent spin relaxation during the intervalley relaxation has been demonstrated by spin- and time-resolved ARPES experiments.

The capabilities of our novel setup are further demonstrated in the quasi 2-dimensional charge density wave (CDW) material $TbTe_3$. The excellent data quality achievable with this high-repetition rate system allows us to investigate the whole ground and excited state band structure close to the Fermi level. Signatures of the CDW ordering such as the opening of energy gaps and spectral weight transfer into shadow bands can be identified and quantified, and compared to theoretical tight binding band structure calculations (Fig. 1c).

[1] R. Bertoni, *et al.*, Phys. Rev. Lett. **117**, 277201 (2016).

### 2.1.2 Photoinduced Phase Transitions in Strongly Correlated Materials

The coupling of electronic to lattice and spin degrees of freedom in solids gives rise to various ordering phenomena and phase transitions in strongly correlated materials. The study of non-equilibrium dynamics of such materials following ultrafast photoexcitation can provide novel insights into the mechanisms and couplings leading to such ordered phases and eventually to ultrafast phase transitions. The high-repetition rate XUV trARPES setup is ideally suited to study the excited state dynamics and transient electronic structure during photoinduced phase transitions starting from an ordered, well defined ground state. In the quasi-2D CDW system $TbTe_3$, the group of *Laurenz Rettig* could identify the photo-induced closing of the charge-density wave gap and the concomitant suppression of shadow band spectral weight in the whole Brillouin zone (see Fig. 1c) and follow the dynamics of the CDW order parameter, extracted from the transient energy gap size and shadow band intensity, for a large range of fluences. Moreover, the analysis of the CDW gap dispersion along different directions in momentum space reveals a transient enhancement of the nesting conditions in the excited state, which results in a persistent finite CDW energy gap size in the transient metallic state [1].

Another prototypical system exhibiting a Peierls-type insulator-to-metal transition are quasi one-dimensional Indium nanowires on Si(111). The ultrafast electron dynamics upon the optically driven structural phase transition from the low-temperature (8x2) to the high-temperature (4x1) phase has been studied, concomitant with an insulator-to-metal transition (Fig. 2). Starting from the 8x2 phase the gradual evolution of the electronic structure into the 4x1 phase could be followed by XUV trARPES on a femtosecond time scale. Remarkably, three distinctive time scales were found: (i) the insulator-to-metal transition associated with the gap closing at the 8x2 BZ boundary is observed already after 200 fs, while (ii) the Indium derived $m_1$ band at the BZ center shifts from above to below the Fermi level within 500 fs. Both processes occur faster than the structural transition into the 4x1 phase, as manifested (iii) by the splitting of the $m_2$-$m_3$ bands, which is completed after 700 fs (Fig. 2e). Such distinct timescales of the insulator-to-metal and structural transitions clearly differ from expectations for a "standard" Peierls-like scenario. The momentum space distribution of excited carriers observed by trARPES served as an input for *ab initio* calculations with realistic initial conditions (collaboration with University of Paderborn). From these simulations, which well reproduce the three timescales found in the experiment (see Fig 2e), we conclude that the depopulation of antibonding orbitals by photoexcited holes is the main driving force

triggering the photoinduced structural phase transition. Furthermore, the combined experimental and theoretical approach allows to elucidate the real-space dynamics of bond formation and breaking during the ultrafast transition.

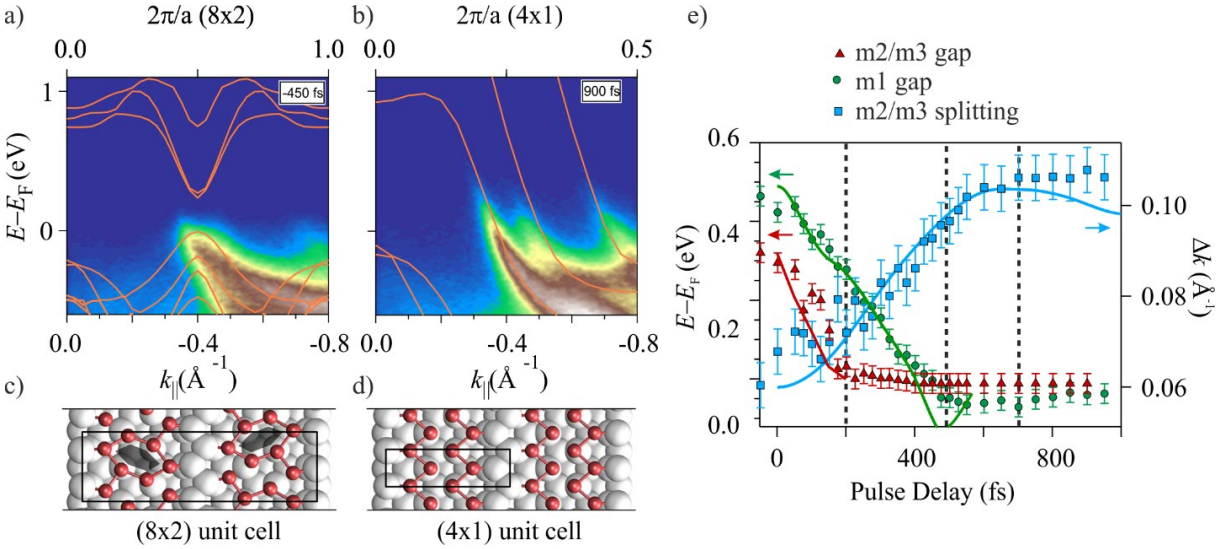


***Figure 2**: Ultrafast phase transition in In/Si(111) nanowires. (a,b) Energy/momentum maps of the trARPES intensity (a) before and (b) 900 fs after photoexcitation, overlaid by GW band structure calculations of the 8x2 and 4x1 phase, respectively. (c,d) Unit cell of the 8x2 and 4x1 phase. (e) Time dependence of the metal insulator transition (m2/m3 gap, red triangles), the closing of the m1 band gap (green circles) and the m2/m3 band splitting (blue squares), showing distinctly separate timescales for the three features. Solid lines are results of an ab-initio molecular dynamics simulation.*

Complementary ordering phenomena involving electron and spin degrees of freedom are present in magnetically ordered systems, where the role of structural degrees of freedom is minimized. The dynamics of the spin-density wave (SDW) transition in Chromium has been investigated using XUV trARPES, and by comparison with a mean field model the group was able to quantitatively extract the evolution of the SDW order parameter through the ultrafast phase transition, and show that it is governed by the transient temperature of the thermalized electron gas [2]. In contrast, the transient suppression of long-range collinear anti-ferromagnetic order in the rare-earth intermetallic $GdRh_2Si_2$, observed by the time-dependent suppression of the exchange splitting of a Si-derived ferromagnetic surface state, proceeds on a much slower timescale of ~10 ps. This slow demagnetization of the 4f antiferromagnet is limited by the angular momentum transfer between localized 4f and delocalized 5d electrons, due to the absent 4f orbital momentum in Gd. This conclusion is corroborated by the much faster demagnetization in the isotructural $SmRh_2Si_2$ compound with a finite 4f orbital momentum, which proceeds on a much faster timescale of less than 500 fs.

[1] L. Rettig, *et al.*, Nature Commun. **7**, 10459 (2016).

[2] C. W. Nicholson, *et al.*, Phys. Rev. Lett. **117**, 136801 (2016).

### 2.1.3 Mid-Infrared Nonlinear Optical Spectroscopy of Phonon Polaritons

Surface polaritons are the key building block of nanophotonics, since these excitations provide sub-diffractional light localization accompanied by significant optical field enhancements. Many previous studies have focused on surface plasmon polaritons at noble metal surfaces. Recently, an alternative approach was introduced using surface phonon polaritons (SPhPs) which can be excited in the mid-infrared at the surface of polar dielectric materials, where optical phonon resonances lead to the negative dielectric permittivity required for the surface polariton formation. Particularly, the active tuning of the phonon polariton resonances in nanometer and atomic scale structures represents a major goal in modern nanophotonics. The group of *Alexander Paarmann* is studying such systems with newly developed experimental techniques, employing the free-electron laser (FEL) at the FHI as an intense and tunable infrared light source.

Light localization in nanophotonic structures is typically accompanied by considerable enhancements of the local electric fields, which can be conveniently probed using nonlinear optical techniques such as second harmonic generation (SHG). While SHG spectroscopy is well-established in the visible spectral region, the group has now established this technique also in the mid-infrared using the FEL. Subsequent experiments on sub-diffractional nanostructures demonstrated a drastic enhancement of the SHG yield for localized SPhP resonances, opening the field of mid-infrared nonlinear nanophotonics based on SPhPs [1]. Additionally, a versatile prism coupling approach has been implemented based on the Otto geometry, enabling the systematic study of SPhP resonances in polar dielectric heterostructures [2].

With these unique experimental methods at hand, various strategies for active control of phonon polaritons in nanoscale systems are now explored. Already for single AlN thin films (10-100 nm) on SiC substrates, strongly coupled modes were observed, providing a simple way for tuning the frequency of phonon polaritons. The major focus of this work, however, lies on atomic scale heterostructures of polar dielectrics, so-called crystalline hybrids. Here, phonon polariton hybridization has been predicted for layer thicknesses reaching to the atomic scale. A first model study of AlN/GaN heterostructures indeed demonstrates the emergence of hybrid phonon polariton modes in these systems, as well as monolayer-level control of their frequencies, linewidths, and polar strengths, see Fig. 3. Hereby, the drastic improvement of sensitivity and contrast provided by SHG phonon spectroscopy over linear optical techniques (reflectivity) enables a clear assignment of the hybrid modes.

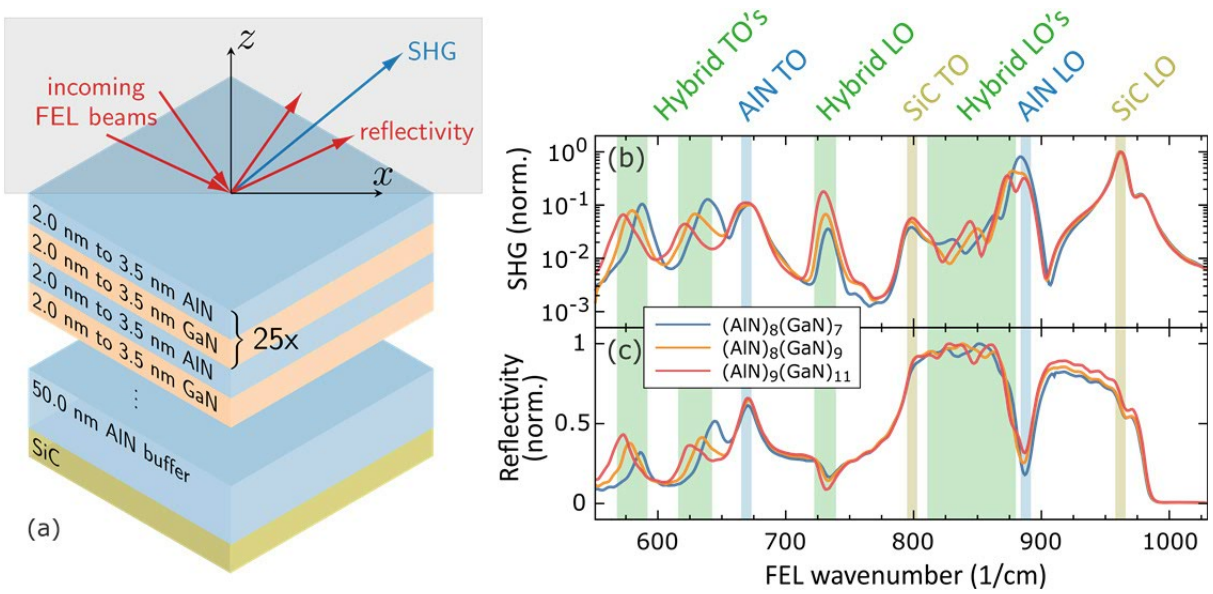


***Figure 3:*** *Control over phonon polariton hybridization on the atomic scale. (a) Schematic of the experiment and the atomic scale AlN/GaN heterostructure. Experimental second harmonic (b) and reflectivity (c) spectra of AlN/GaN superlattice structures with different AlN and GaN layer thicknesses. Several hybrid modes (green shaded) can be observed to shift with the layer thicknesses, while the SiC substrate (yellow shaded) and the AlN buffer layer (blue shaded) features are unaffected.*

Furthermore, a table top near-infrared laser oscillator synchronized to the FEL was recently implemented together with a timing infrastructure providing synchronization to the FEL with better than 100 fs precision (see FEL report for more details). A balanced optical cross correlator based on mid-infrared/near-infrared sum-frequency generation (SFG) allowed a first measurement of the FEL timing drift and jitter, whereby the jitter is found to be on the order of only 100 fs (rms). These measurements also reveal peculiar details of the FEL temporal pulse structure, highly relevant for prospective time-resolved FEL-pump near-infrared probe spectroscopy. Additionally, the group also develops the infrastructure for FEL-based SFG spectroscopy for studies of far-infrared surface vibrations, for instance, metal-oxide formation in electrochemical systems.

[1] Razdolski *et al.*, Nano Letters **16**, 6954 (2016).

[2] Passler *et al.*, ACS Photonics **4**, 1048 (2017).

### 2.1.4 Nonlinear THz Spectroscopy of Lattice Dynamics

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 and 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 current state of the art THz pulses can be generated in the lab with an electric-field amplitude of ~1 MV/cm it now possible to even drive and control such resonances on sub-

picosecond time scales [1]. The THz frequency range is thus of central relevance from a fundamental-scientific point of view but is also application-related as current information technology may soon approach data rates in the THz range. It is thus required to develop techniques to manipulate information carriers (such as electronic currents, 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

- 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 push physical effects so far studied at low frequencies into the THz range. Currently, a strong focus lies on fundamental spintronic effects such as the recently discovered ultrafast spin Hall effect and the spin-type Seebeck effects. These studies are conducted in the framework of the ERC Consolidator Grant project of *Tobias Kampfrath*.
- To develop new spectroscopic tools which permit, for example, control over elementary motions such as lattice vibrations and the detection of ultrafast spin currents ("ultrafast spin amperemeter"), with interface sensitivity.

Some recent examples on lattice control by THz pulses are illustrated below:
*Ultrafast spin-lattice coupling:* The coupling of lattice vibrations and ordered electron spins in magnetic solids is highly underresearched, despite its fundamental and applied relevance for ultrafast spin manipulation (femtomagnetism) and transport of spin angular momentum (spintronics and spin caloritronics). For example, the fundamental process of spin-lattice equilibration is far from being understood, even for model systems such as the ferrimagnet yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG), a central material in the field of magnonics. Estimates of the underlying time constants extend over as many as 6 orders of magnitude from ~1 μs down to ~1 ps.

To probe spin-lattice coupling in YIG, the THz physics group developed a pump-probe scheme in which an intense 20 THz pump pulse is used to resonantly excite optical phonons and the impact on the spin subsystem is monitored by measuring the transient Faraday effect over multiple time scales from femtoseconds to milliseconds (see Fig. 4a). The magnetic order is quenched on an ultrafast time scale of 1 ps and a slower scale of 0.1 μs. The ultrafast component is extremely surprising because decoherence of spin precession in YIG is known to occur over much longer times of 0.1 μs and more. Supported by measurements covering a

broad temperature range and by analytical and numerical calculations, the following consistent interpretation results: The THz pump pulse rapidly heats the YIG crystal lattice, thereby leading to additional stochastic modulation of the exchange interaction of the two ferrimagnetically coupled spin sublattices. On a 1 ps time scale, this modulation induces transfer of angular momentum between the spin sublattices and, thus, energy transfer from the phonon to the spin system.

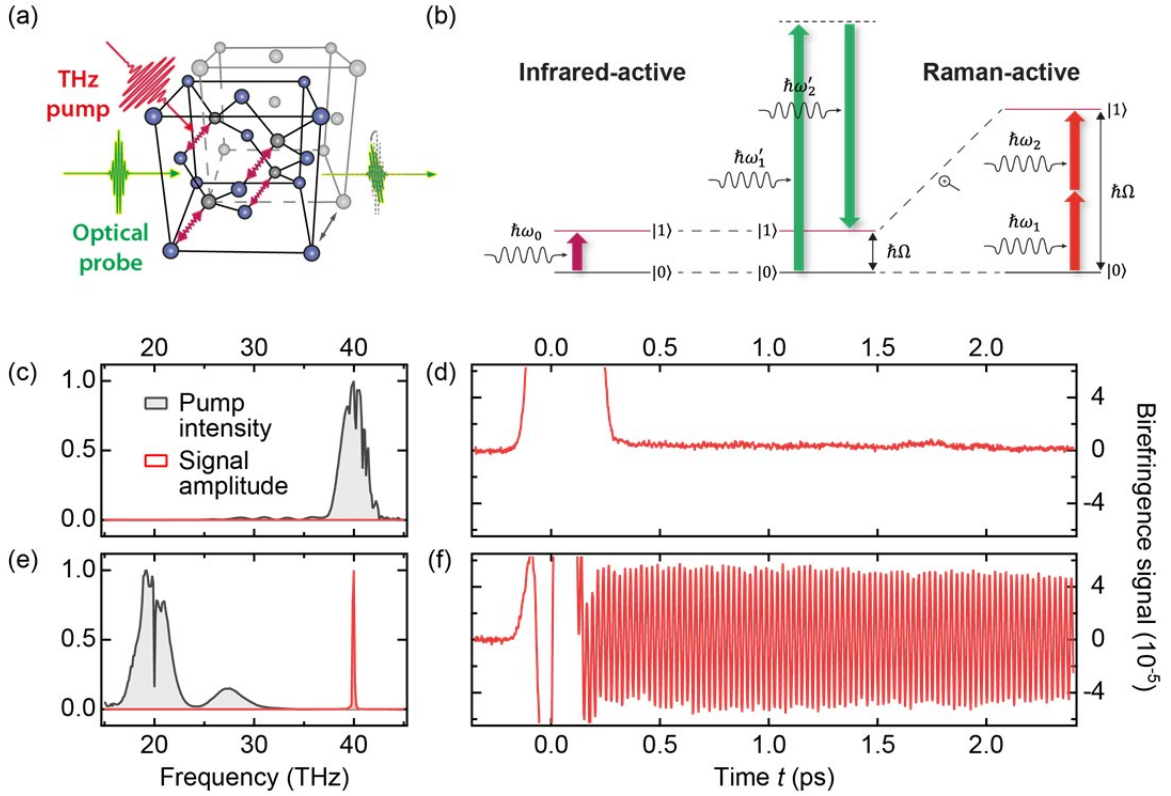


***Figure 4:*** *Excitation of coherent optical phonons by THz sum-frequency excitation. (a) Pump-probe scheme for driving and probing of coherent lattice vibrations in diamond or any other solid by femtosecond laser pulses. (b) Possible excitation pathways of a phonon with frequency* $\Omega$ *(from left to right): by one-photon absorption (1PA) with* $\omega_0 = \Omega$*, stimulated Raman scattering using two spectral components of the pump field with* $\omega_1' - \omega_2' = \Omega$*, and by sum-frequency Raman excitation with* $\omega_1 + \omega_2 = \Omega$*, which can also be considered as two-photon absorption (2PA) by a transition across adjacent vibrational levels. (c) A pump spectrum resonant with the 40 THz optical phonon of diamond. (d) Resulting optical birefringence as a function of time. (e,f) Analogous to (c,d), but with the pump spectrum overlapping with half the phonon resonance frequency.*

Note that the resulting quasi-equilibrium state is constrained by conservation of spin angular momentum and only accessible by ultrafast stimuli. This novel state finally decays by transfer of angular momentum and energy between phonons and spins on a 100 ns scale. In summary, our results reveal that the speed of spin-phonon relaxation in ferrimagnetic insulators with two spin sublattices depends on the dynamic observable one refers to. While energy transfer is dominated by exchange interaction and proceeds on picosecond time scales, angular-momentum equilibration is significantly slower and can easily extend to ~0.1 µs.

*Novel pathway to lattice control:* The above experiment on YIG relies on resonant excitation of infrared (IR)-active phonons with THz radiation. To drive IR-inactive yet Raman active phonons, stimulated Raman scattering (SRS) has been the method of choice so far. In SRS, a light pulse containing frequencies $\omega_2'$ and $\omega_2' = \omega_1' + \Omega$, both at roughly $2\pi \cdot 500$THz, generates a force that coherently drives the lattice at the difference frequency $\omega_1' - \omega_2' = \Omega$ (see Fig. 4b). Such rectification of optical fields is, however, often accompanied by unwanted electronic excitation due to one-photon and two-photon absorption (2PA), which is particularly severe in materials with small electronic band gaps. To avoid these issues, a novel scheme of coherent lattice control has been developed: the two incident frequencies are chosen such that their *sum* $\omega_1 + \omega_2 = \Omega$ is resonant with the target mode (Fig. 4b). This process can also be considered as 2PA by a transition across adjacent vibrational levels [2].

The IR-inactive yet Raman-active 40 THz optical phonon of diamond served as test system of our idea. The underlying pump-probe experiment is schematically shown in Fig. 4a. For a pump pulse centered about the phonon resonance (Fig. 4c), the optical probe signal (Fig. 4d) did not exhibit any indications of coherent lattice vibrations. However, when the pump center frequency is tuned to half of the 40 THz phonon frequency (20 THz), an oscillatory signal (Fig. 4f) is observed whose Fourier transform peaks at 40 THz (Fig. 4e).

This is a clear signature of the phonon intended to drive. In subsequent experiments, it could be shown that by tuning the carrier-envelope phase of the phase-locked THz pump pulse, we were able to shift the phonon oscillation phase at will. In addition to their fundamental relevance, our findings are important for action spectroscopy at the FHI free-electron laser as they open up a way to extend this method from IR-active to IR-inactive yet Raman-active vibrational modes of molecules [2].

[1] T. Kampfrath, K. Tanaka, K.A. Nelson, Nature Photon. **7**, 680 (2013).
[2] S. Maehrlein, A. Paarmann, M. Wolf, T. Kampfrath, Phys. Rev. Letter, in press (2017)

### 2.1.5 Teraherz Spin Transport

Future electronic device architectures will potentially employ the electron spin (and not only the electron charge) as an information carrier. Successful implementation of such spin-based electronics (spintronics) requires the transfer of spin angular momentum through space, preferably at speeds exceeding that of today's computers, that is, at THz frequencies. Currently, the group of *Tobias Kampfrath* studies the high-frequency (THz) behavior of only recently discovered fundamental spintronic effects that enable the generation and detection of

spin currents. While the spin-dependent Seebeck effect (SDSE) and the spin Seebeck effect (SSE), respectively, refer to the transport of spin angular momentum by electrons and spin waves induced by a temperature gradient, the inverse spin Hall effect (ISHE) refers to the conversion of a spin current into a transverse charge current.

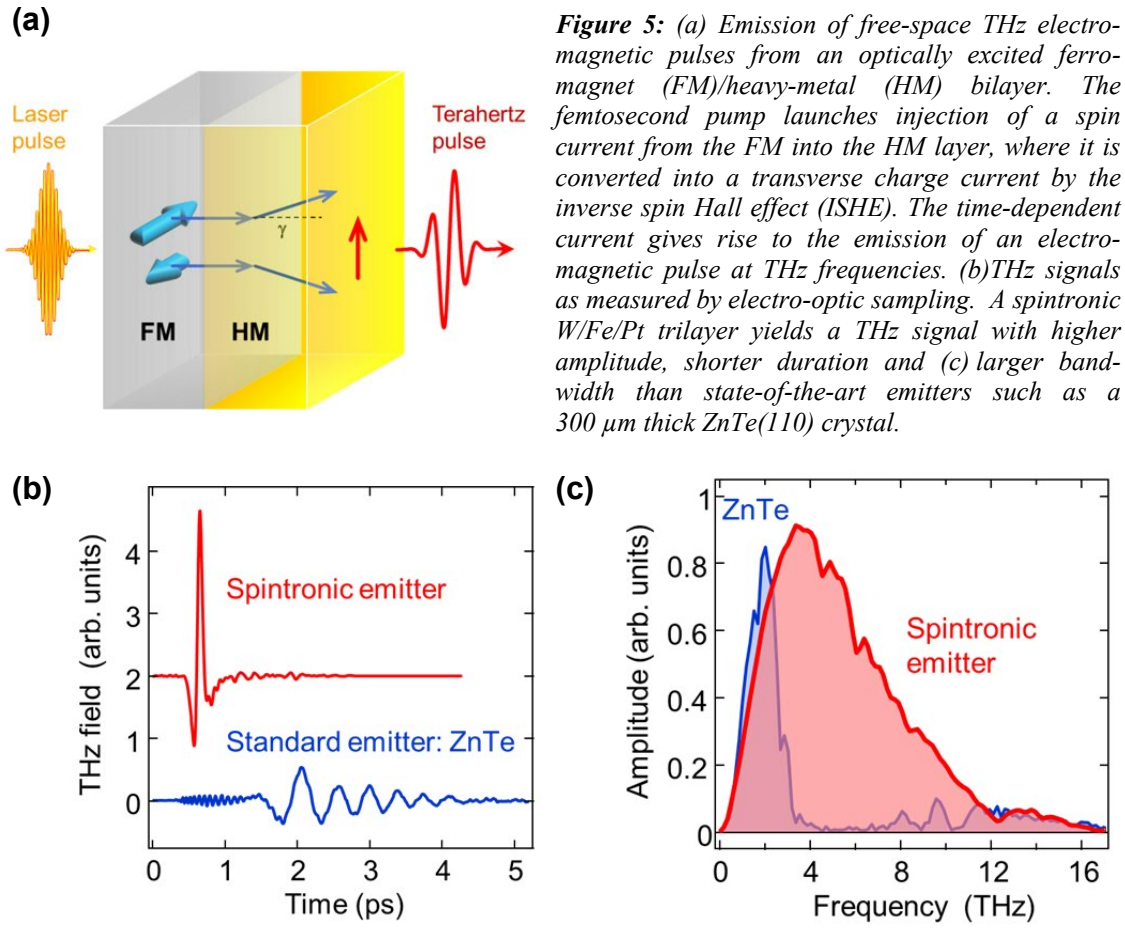


***Figure 5:*** *(a) Emission of free-space THz electromagnetic pulses from an optically excited ferromagnet (FM)/heavy-metal (HM) bilayer. The femtosecond pump launches injection of a spin current from the FM into the HM layer, where it is converted into a transverse charge current by the inverse spin Hall effect (ISHE). The time-dependent current gives rise to the emission of an electromagnetic pulse at THz frequencies. (b)THz signals as measured by electro-optic sampling. A spintronic W/Fe/Pt trilayer yields a THz signal with higher amplitude, shorter duration and (c) larger bandwidth than state-of-the-art emitters such as a 300 µm thick ZnTe(110) crystal.*

*THz spin transport:* To test the speed limit of the SDSE and ISHE, a THz emission experiment was conducted as schematically shown in Fig. 5a. Here, a femtosecond pump pulse is used to launch ultrafast spin transport from a ferromagnetic (FM) thin film into an adjacent heavy-metal (HM) layer through an ultrafast version of the SDSE. The longitudinal spin current is in part converted into a transverse charge-current burst by the ISHE, resulting in the emission of a THz electromagnetic pulse [1]. A typical THz waveform emitted by a Fe/Pt metal film of only 5 nm thickness driven by pulses of 10 fs duration from a simple laser oscillator is shown by Fig. 5b. An inversion procedure allows extraction of the ultrafast current generating the measured THz signal [2]. These results imply that the SDSE has a response time of less than 30 fs, pointing to an extremely fast generation process of the spin current, a point that is currently under study.

The above results have important applications. First, one can use the THz emission signal to obtain a relative estimate of the strength of the ISHE and the strength of the SDSE for a given HM and FM material respectively. The newly developed characterization method is straightforward because it works in a contact-free manner with standard thin film samples. In contrast, electronic approaches require relatively tedious preparation steps such as microstructuring and contacting. Second, FM/HM bilayer and trilayer stacks can be used as novel emitters of THz radiation which outperform standard emitters such as a 300 μm ZnTe crystal in terms of peak amplitude, THz pulse shortness (Fig. 5b) and bandwidth (Fig. 5c). In particular, the metallic spintronic emitters do not suffer from attenuation as is the case in semiconductor emitters owing to their Reststrahlen band (see e.g. the ZnTe spectrum in Fig. 5c). By upscaling the emitter diameter to 7.5 cm and the pump-pulse energy to 5 mJ, we were able to generate THz electric fields with peak amplitudes of as high as 300 kV/cm over the spectral range from 1 to 10 THz. These field strengths facilitate nonlinear control over matter on the sub-picosecond time scale, also in the 5-10 THz frequency range, which was challenging to access up to now [3].

*Interface sensitivity:* THz emission experiments on Fe/Pt bilayers were also conducted as a function of the film thickness. Remarkably, these measurements showed that the charge current generating the THz pulse flows in an only 1 nm thick Pt sheet directly at the Fe/Pt interface [1]. This result attests to a significant surface sensitivity of the emitted THz waveform and shows that THz spectroscopy is capable of addressing both the bulk (as done in the overwhelming majority of works to date) and interfaces of condensed matter.

Another THz emission experiment took advantage of this high degree of interface sensitivity in which the THz group was able to optically launch and detect THz currents flowing at the surface of the topological insulator $Bi_2Se_3$ by. It was found that excitation by a laser pulse (duration 10 fs, photon energy 1.55 eV) shifts electron density from the Se atoms toward the Bi atoms. The data indicate that this shift current flows predominantly in the first ~2 nm of the surface region [2]. In addition, the results show that previously suggested scenarios based on optically induced changes in the electron group velocity are not operative or at least result in much less efficient photocurrents than previously assumed.

[1] T. Seifert, *et al.,* Nature Photon. **10**, 483 (2016).

[2] L. Braun, *et al.,* Nature Commun. **7**, 13259 (2016).

[3] T. Seifert, *et al.,* Appl. Phys. Lett. **110**, 252402 (2017).

### 2.1.6 Ultrafast Spin Dynamics in Epitaxial Metallic Multilayers

Ultrafast spin dynamics induced by transport of photoexcited spin polarized carriers is of fundamental interest for applications in 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. 6b). The spin dynamics is probed by time-resolved second harmonic generation (SHG) [1] and magneto-optical Kerr effect (MOKE) [2]. One particular focus lies on the development of generation, control, and detection techniques for ultrashort spin current pulses [1] and studies of their induced spin transfer torque acting on a ferromagnet (FM) [2]. The spin transfer torque is an elegant and promising way to excite ultrafast magnetization dynamics: When spin-polarized hot carriers propagating in a non-magnetic (NM) spacer reach a FM layer, the magnetization experiences an ultrafast torque confined to the NM/FM interface and starts rapidly moving out of the equilibrium at terahertz rates.

In metals, spin currents can be produced by temperature gradients in a bulk FM or across interfaces known as the spin-dependent Seebeck effect. Recently, the ultrafast, non-thermal counterpart of this effect has been demonstrated [1]. It is based on the spin-dependent transmittance of FM/NM interface for non-thermalized laser-excited hot carriers at energies $E$ considerably different from the Fermi energy $E_F$ (see Fig. 6a): The large Fe/Au interface transmittance for majority electrons at $E > E_F + 0.3$ eV provides a spin flux from Fe to Au forming a spin current pulse with a polarization set by the direction of magnetization in the Fe emitter $\mathbf{M_E}$. Its duration is determined by the hot carriers thermalization time on the order of 200 fs: once the hot carriers relax towards $E_F$ the transmission difference vanishes and thus the hot carriers emission stops. Experimentally, hot carriers were excited by 14 fs, 800 nm laser pulses in a layered Fe/Au/Fe/MgO(001) structure (Fig. 6b) leading to generation of ~250 fs-long spin current pulses (Fig. 6d) detected by SHG which is sensitive to breaking of the inversion symmetry due to the spin current pulses in the Au. The study of spin current reflected from the Au/Fe interface has shown that the component polarized orthogonally to the magnetization of Fe collector $\mathbf{M_C}$ is lost upon the reflection and thus the spin current becomes polarized anti-parallel to $\mathbf{M_C}$ [1]. Subsequent picosecond precessional dynamics of $\mathbf{M_C}$ excited by the spin transfer torque in the collector has been monitored with MOKE [2]. Owing to interfacial confinement of the spin transfer torque, several standing spin wave modes with frequencies up to 0.6 THz are excited (Fig. 6d, e). Spectral analysis of the excited

modes (Fig. 6c) allows for an estimation of the spin accumulation depth due to confinement of the spin transfer torque at the interface. The spin accumulation depth is found to be below 2 nm in Fe.

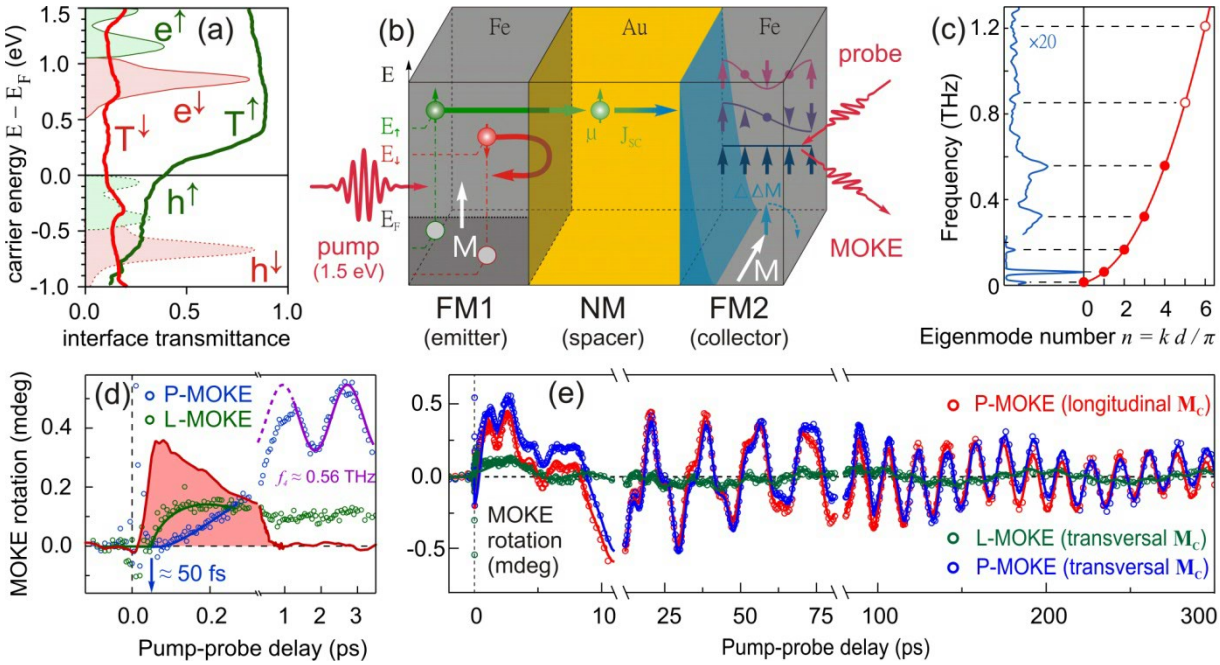


***Figure 6:*** *(a) Calculated momentum-averaged transmittance of the Fe/Au interface for majority ($T^{\uparrow}$) and minority ($T^{\downarrow}$) carriers moving from Fe to Au [1]. Shaded areas reproduce schematically the spectrum of primary carriers are excited by the 1.5 eV pump. (b) Experimental approach: Since only majority electrons at $E>E_F+0.3$ eV have large interface transmittance, a spin-current pulse is generated by laser excitation of a ferromagnetic emitter layer on the left-hand side with the duration limited to the electron thermalization time. This pulse exerts a torque on a ferromagnetic collector layer, which triggers ultrafast spatially non-uniform spin dynamics including the excitation of high-frequency standing spin-wave modes, which are subsequently probed magneto-optically. (c) Fourier spectrum of the MOKE signal (left) and spin waves dispersion calculated analytically (right). The frequencies of the standing spin waves in a 14 nm-thick Fe film are shown with red symbols. Along with the uniform precession (n=0), four higher modes are shown which were detected in the experiment (full dots). [2] (d) Transient MOKE rotation on the ultrashort timescale [2]. The rapid onset of the longitudinal component (green circles) is followed by a slower increase of the polar one (blue circles) due to the magnetization precession. The red shaded area reproduces the SC pulse as measured with SHG [1]. The purple line illustrates the $4^{th}$ spin wave eigenmode. (e) Transient MOKE rotation on longer timescales [2]. Polar (P-) and longitudinal (L-) MOKE effects are separated. Solid lines are the results of the fitting procedure with a set of exponentially decaying oscillations, with their frequencies given by the analytical equation [2]. The pronounced similarity between the two P-MOKE traces (red and blue dots) demonstrates the robustness of the measurements.*

These findings shed light on the properties of the ultrafast laser-driven spin currents and elucidate their interaction with a non-collinear magnetization in thin ferromagnetic films. The results demonstrate the extreme ability of spin-current pulses to excite non-uniform spin dynamics, as compared to other ultrafast mechanisms, such as the heat-induced quenching of magnetic anisotropy. Moreover, the density of magnetic moment transferred across the Au/Fe interface per pulse is found to amount ~7 $\mu_B/nm^2$, which shows a high promise for the magnetization switching in thin FM layers.

[1] A. Alekhin *et.al.*, Phys. Rev. Lett. **119**, 017202 (2017).
[2] I. Razdolski *et.al.*, Nature Commun. **8**, 15007 (2017).

## 2.2 Molecular Processes at Interfaces and in Condensed Phase

Understanding molecular dynamics at gas-solid, liquid-solid interfaces and in the liquid phase is of fundamental importance for surface chemistry, electrochemistry and biological processes. Fundamental studies in this area are performed by several groups in the department with complementary microscopic and spectroscopic techniques, enabling high spatial resolution using scanning probe microscopy, chemical identification using vibrational spectroscopy, and ultrafast dynamics using nonlinear optical spectroscopy.

### 2.2.1 Dynamics of Individual Molecules at Surfaces

Studies on single-molecule structures and dynamics at surfaces provide important information for a microscopic understanding of surface reactions and for development of molecular scale electronics. The group of *Takashi Kumagai* investigates chemistry and physics of single molecules on well-defined surfaces using several low-temperature scanning probe techniques including scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM), and tip-enhanced Raman spectroscopy (TERS) under UHV conditions. These methods enable direct observation and manipulation of single atoms and molecules on surfaces and eventually the local control of reactions. The group has investigated intramolecular hydrogen-atom transfer (tautomerization) reactions and recently focused, in particular, on force-induced processes (‘mechanochemistry’), tunneling dynamics in hydrogen transfer reactions, and single-molecule photochemistry at metal surfaces.

*Force-induced tautomerization in single porphycene molecules***:** Beside thermal, electronic and optical excitation to activate chemical processes an externally applied force provides an alternative way to perturb a chemical system and eventually induce a reaction. However, dedicated studies for such a mechanical activation are rare and the underlying microscopic mechanisms remain poorly understood *at the single-molecule level*. Recently, force-induced tautomerization in a single porphycene molecule was demonstrated on a Cu(110) surface at 5 K combining nc-AFM and density functional theory (DFT) calculations [1]. Force spectroscopy quantifies the force needed to trigger tautomerization with sub-molecular spatial resolution (see Fig. 7). DFT calculations show how the reaction pathway and barrier for the tautomerization are modified upon approch of a copper tip to the porphycene and reveal the atomistic origin of the process. Interestingly, it could be shown that a chemically inert tip

whose apex is terminated with a xenon atom cannot induce the tautomerization reaction due to a weak interaction with porphycene and the strong relaxation of the Xe atom on the tip as contact to the molecule is formed.

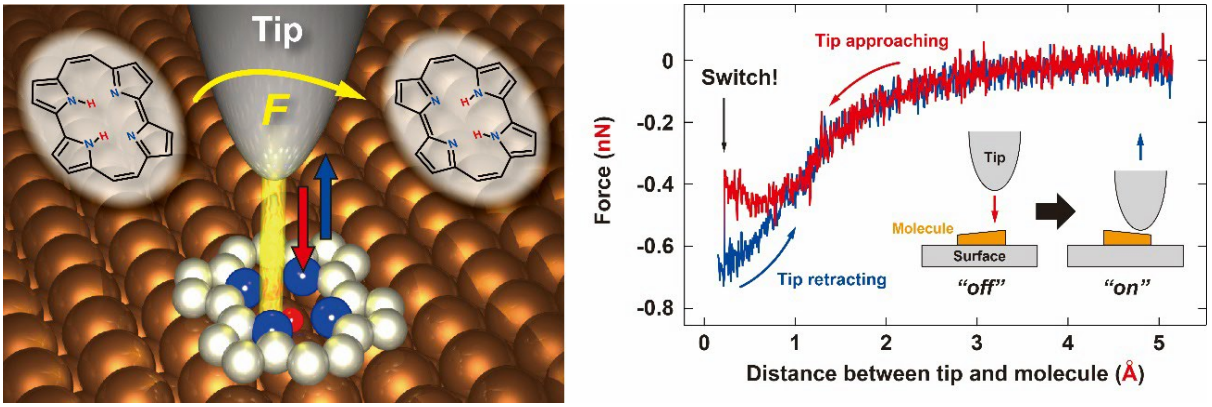


***Figure 7:*** *Force-induced cis ↔ cis tautomerization in a single porphycene molecule on Cu(110) at 5 K. Left: Schematic of the experiment with nc-AFM. The tip is brought toward and retracted from the porphycene while detecting the interaction acting between the tip apex and the molecule. Right: Force curve measured over the porphycene. The sudden drop of the force in the approaching curve corresponds to the moment of one tautomerization event underneath the tip.*

*Quantum tunneling of hydrogen atoms* plays a crucial role in many physical, chemical and biological processes. Although tunneling of a single particle has been examined extensively in various one-dimensional potentials, many-particle tunneling in high-dimensional potential energy surfaces remains poorly understood. The direct observation of a double hydrogen atom transfer (tautomerization) within a single porphycene molecule on a Ag(110) surface was recently demonstrated using a STM. Below ~14 K the tautomerization rate is temperature-independent and a large kinetic isotope effect (~100) is observed upon substituting the hydrogen atoms by deuterium. This clearly indicates a dominant contribution of quantum tunneling in the reaction. Additionally, detailed analysis reveals a sequential (step-wise) tunneling process of the H-atoms, rather than a concerted one. It is also found that the tautomerization rate is increased by vibrational excitation via an inelastic electron tunneling and that the STM tip can be used to manipulate the tunneling dynamics through modification of the potential landscape.

[1] J. Ladenthin *et al.*, Nature Chem. **8**, 935 (2016).

### 2.2.2 Local Photochemistry and Near-Field Induced Processes

*Tip-enhanced photochemistry:* Photochemistry can lead to enhanced selectivity and different reaction products compared to thermally-induced chemistry. Using low- temperature scanning tunneling microscopy combined with a wavelength tunable light source the direct observation of photoinduced tautomerization in single porphycene molecules on a Cu(111) surface has been demonstrated [2]. It is found that the thermodynamically stable *trans* configuration of the porphycene is converted to the metastable *cis* configuration in a unidirectional fashion through photo-irradiation, whereas the backward *cis* → *trans* conversion can be induced by heating the surface (Fig. 8). The wavelength dependence of the tautomerization cross section exhibits a steep increase around 2 eV, indicating that excitation of the Cu *d*-band electrons and the resulting hot carriers play a dominant role in the photochemical process. Additionally, a pronounced isotope effect in the cross section (~100) is observed when the transferred hydrogen atoms are substituted with deuterium, indicating a significant contribution of zero-point energy in the reaction. Combined with the study of inelastic tunneling electron-induced tautomerization with the STM, we proposed that the tautomerization occurs via excitation of molecular vibrations after photoexcitation. Currently we investigate near-field coupled process where the photo-induced tautomerization is largely enhanced in the presence of a metallic tip under photo-irradiation. It is found that the tip-enhanced process is particularly enhanced by using an Au tip (Fig. 8, lower panel), which is explained by localized plasmon excitation in the STM junction.

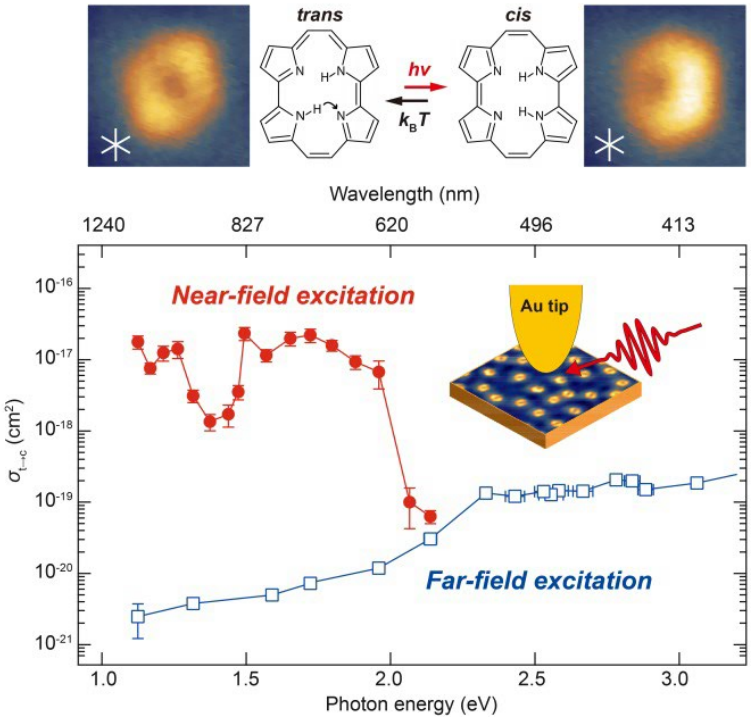


***Figure 8:*** *Upper panel: STM images and chemical structures of the trans and cis porphycene on a Cu(111) surface. The conversion can be selectively induced either by irradiation or by thermal activation. Lower panel: Cross section of the trans → cis tautomerization a function of photon energy in the presence and absence of an Au tip, denoted as near-field and far-field excitation, respectively.*

*Development of low-temperature optical scanning probe microscopy (SPM)*: Many important physical, chemical, and biological processes are based on light driven processes in molecular systems. For molecules at interfaces such processes will critically depend on the local environment. In particular, optical excitations of molecules mediated by metallic nanostructures have a wide range of applications such as surface-enhanced Raman spectroscopy (SERS), enhanced molecular luminescence, and photo-catalysis. Similarly, tip-enhanced Raman spectroscopy (TERS) has recently emerged as a powerful tool of single-molecule spectroscopy. In order to probe locally the coupling of single adsorbates to optical excitation and detect (inelastic) scatted light with high efficiency, we have designed a new low-temperature *optical* scanning probe microscope. In this setup a motorized *in-situ* parabolic mirror and a lens with a sufficiently high numerical aperture have been installed on the low-temperature SPM stage in proximity to the tip apex. This will enable various experiments such as single-molecule TERS, near-field optical excitation, photoluminescence spectroscopy, and possibly ultrafast spectroscopy in combination with THz or femtosecond laser excitation. The new system is currently being implemented in the new SPM laboratory and first preliminary experiments are carried out.

*Development of ultrafast THz-STM combined with optical near-field photoexcitation:* The new group of *Melanie Müller* is currently developing a THz-pulse gated STM which will be combined with optical photoexcitation of few-femtosecond laser pulses. Building on the

previously demonstrated gating technique of the STM tunneling bias by an ultrashort THz-pulse, the concept of plasmonic nanofocusing of broadband surface plasmon polaritons (SPPs) will be employed to enable versatile ultrafast optical excitation of the tip-sample junction. Nanofocused SPPs can be used to trigger nonlinear photoemission from the tip apex with higher quantum efficiency compared to direct apex illumination [2], as shown in the MPRG of Ralph Ernstorfer, thus promising less thermal load on the tip-sample junction and increased excitation efficiency of the sample. As a first step in this direction, a home-built room-temperature STM at ambient conditions has been constructed, providing easy and flexible optical access to explore the suitability of SPP nanofocusing for ultrafast STM. Such experiments may provide access to spatio-temporal dynamics of nanostructures and molecules at surfaces on their natural length and time scales.

[1] H. Böckmann *et al.*, Nano Lett. **16**, 1034 (2016).
[2] M. Müller *et.al.*, ACS Photonics **3**, 611-619 (2016).

### 2.2.3 Nonlinear Vibrational Spectroscopy of Interfacial Molecular Structure

Probing most liquid interfaces requires using appropriate photons as probes and interface-specific nonlinear optical, *i.e.* sum frequency (SF), spectroscopy that is vibrationally (VSF) or electronically (ESF) resonant. The group of *Kramer Campen* studies molecular-scale structure and ultrafast structural dynamics at liquid-solid, liquid-air and gas-solid interfaces using SF spectroscopy, both in and out of equilibrium. To explore equilibrium structural fluctuations at liquid interfaces additional pulsed infrared excitation is added and the temporal evolution of interfacial vibrationally-labeled ensembles followed. Non-equilibrium conditions that drive redox chemistry are investigated by steady-state approaches, *i.e.* electrochemical interfaces under reactive conditions, as well as ultrafast charge transfer induced by femtosecond laser pulses. Some recent examples of such structural studies and method development are illustrated below:

*(Electrified) Liquid-Solid Interfaces:* Prior work has shown that the liquid water/α-$Al_2O_3$(0001) interface exhibits surface aluminol (*i.e.* $(Al)_2$-OH) groups that are *non-H-bonded*, i.e. part of this surface is microscopically hydrophobic even as it macroscopically wets. However, how such groups exist in contact with liquid water ($H_2O(l)$) and their influence on surface chemistry is not well understood. By adding an additional IR pulse to a VSF probe it was shown that the vibrational relaxation of this type of aluminol depends sensitively on solution chemistry. In collaboration with theorists at the University of Potsdam it has been clarified that the mechanism of vibrational relaxation is through coupling to

neighboring *H-bonded* surface aluminols and subsequently to molecular water. This mechanism depends sensitively on α-$Al_2O_3$ crystal face and the solution chemistry and thus explains the dramatic changes in dynamics observed with changing solution chemistry and the low reactivity of the (0001) relative to other α-$Al_2O_3$ surfaces in contact with $H_2O(l)$.

Along similar lines a VSF study of the water structure at the $H_2O(l)$/Au electrode interface as a function of bias has identified a previously unobserved population of interfacial water molecules that have one OH group pointing towards the gold electrode [1]. Because these OH groups are only weakly H-bonded they are expected to play a significant role in aqueous electrochemistry. Curiously, and counter to simple electrostatics, the density of this type of interfacial water increases as the surface potential became more positive (see Fig. 9).

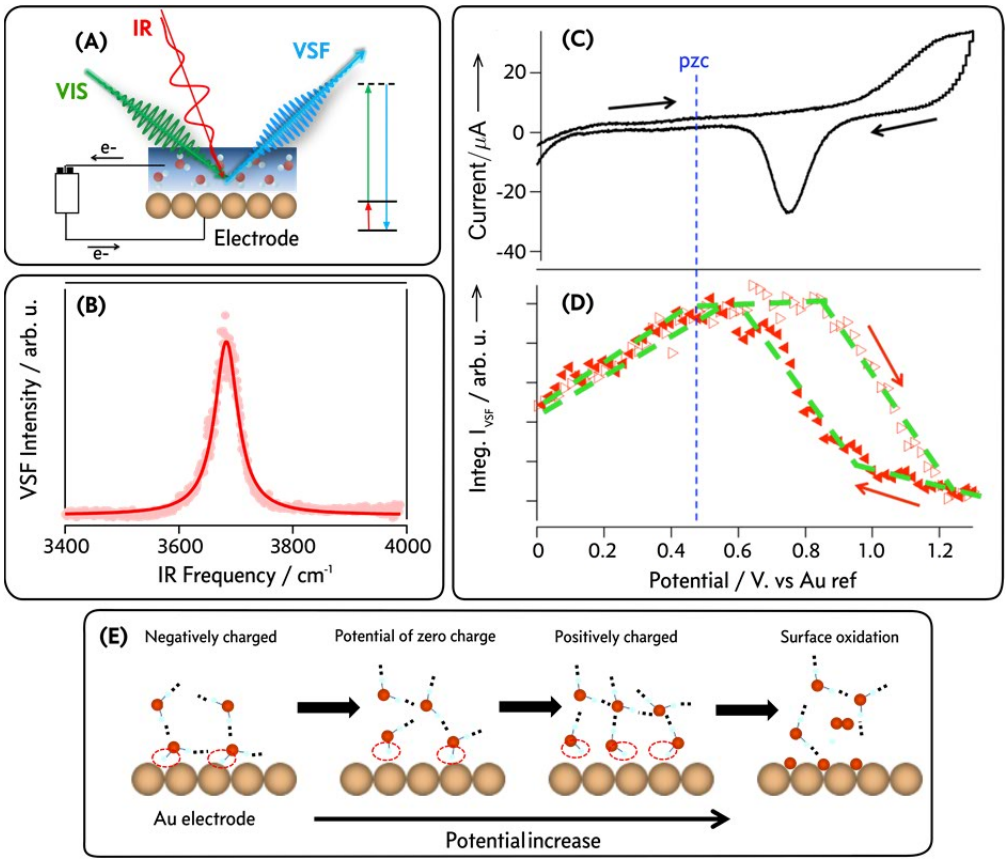


***Figure 9***: *(A) Thin-film VSF spectro-electrochemical set-up used to probe water structure at the Au electrode/ water interface [1]. (B) The VSF spectral response of water with one OH group pointing towards the electrode at open-circuit potentials. (C) Cyclic voltammogram in our thin-film spectro-electrochemical cell. (D) Integrated VSF intensity of the feature in (B) as a function of bias. (E) Cartoon of water structure consistent with observations in (B) and (D).*

Creating self-assembled monolayers (SAMs) of bistable optically switchable chromophores on electrodes is a pathway towards a variety of next-generation, gated, switchable sensors. While quantitative characterization of such chromophores is relatively straightforward in solution, gaining such insight in a SAM at an electrified liquid- solid interface is more

challenging. Systematic VSF measurements of a Spiropyran based SAM on Au electrodes were conducted and it was shown how the composition of its photo stationary state(s) and kinetics of photo switching vary as a function of bias [2].

*$H_2O(l)$-Air Interface:* The first measurement of the libration mode of interfacial water was reported, which is blue-shifted by 160 $cm^{-1}$ from bulk liquid water [3]. This indicates that the rotational potential of interfacial water is stiffened relative to bulk water in a manner similar to that on cooling ambient liquid water to form ice. Curiously, many other more local indicators of water structure (like hydrogen bond distance or angle) show only small changes between ambient bulk water and the air-water interface.

Contradicting classical, Debye-Hückel derived, theory, over the last 25 years, chemical kinetics measurements and surface sensitive spectroscopy have clarified that large, relatively polarizable anions tend to partition favorably to the $H_2O(l)$/air interface. Despite this insight challenging questions remain: *e.g.* (i) what role does anion polarizability play in adsorption and (ii) what effect does the interface have on ion pair formation? Both questions have been addressed for the example of perchlorate at the $H_2O(l)$/air interface. From bulk concentrations of 0-1 M the interfacial polarizability of perchlorate differs from bulk and continues to evolve with increasing concentration. Above 1 M bulk concentration interface induced ion pairing sets in. While in bulk water ion pairing occurs in solutions more concentrated than 11 M, at interfaces such effects occur at an order of magnitude lower concentration.

*Gas-Solid Interface:* A complete understanding of water-oxide interaction should encompass all water pressures from the single molecule to the liquid. The group also worked on the low-pressure end of this range. In collaboration with theoreticians from the University of Potsdam it was demonstrated that for the $\alpha$-$Al_2O_3$ $1\bar{1}02$ surface, with sub-monolayer coverages of water in UHV, a population of OH bonds exists that is sufficiently anharmonic that the proton is delocalized [4]. Extending this approach to the $Al_2O_3$ $11\bar{2}0$ surface an unusual arrangement of surface metal atoms was found that allow strong bidentate coordination of adsorbed OH groups and explains this surfaces high reactivity.

*Building a better SF Spectrometer:* Current work is limited by detecting only the emitted SF intensity, not the SF field (phase resolved), and by the relatively intense powers required for the incident fields. Overcoming the first limitation is important in correctly describing spectral line shapes while dramatically increasing signal to noise would both allow the direct probing of weakly adsorbing species (*e.g.* Zundel or Eigen cations in interfacial water) and/or allow

application of weaker continuum sources to collect broadband spectra spanning multiple decades in the infrared in a single shot. Recently both limitations have been adressed by building a collinear, time-domain, heterodyned, balance detected sum frequency spectrometer

[1] Tong *et al.* Angw. Chem., **56**, 4211-4214 (2017).
[2] Garling *et al.,* J. Phys.: Cond. Matt., **29**, 41 (2017).
[3] Tong *et al.,* Phys. Chem. Chem. Phys., **18**, 18424-18430 (2016).
[4] Wirth *et al.*, Phys. Chem. Chem. Phys., **18**, 14822-14832 (2016).

### 2.2.4 Reactions at Electrochemical Interfaces

Gaining molecular level insight into the chemistry at electrochemical interfaces requires the development of interface specific molecular spectroscopy for detection of small concentrations of interfacial species, with the interface under bias, in the presence of much larger amounts of similar moieties in the electrolyte. Furthermore, during electrochemical reactions intermediates often exist in small concentrations and have ultrashort lifetimes. The group of *Kramer Campen* is on the way to address these challenges by performing vibrational and electronically resonant sum frequency (VSF or ESF) spectroscopy in thin-film and meniscus spectro-electrochemical cells and by employing fs laser driven ultrafast perturbation of the electrode potential to initiate electron transfer and tracking the resulting products.

*Electrooxidation of Au:*. Understanding the mechanism of the oxygen evolution reaction on metal electrodes is challenging because often the electrode oxidizes in the same potential range as water, i.e. when the chemistry of interest is happening the electrode surface is often covered by a nm thick layer of poorly defined (hydr)oxide. The Au-O vibrational response (of oxide surface phonons) has been characterized *in-situ* under bias. These results suggest, contrary to thermodynamic expectations for idealized surfaces, that the Au surface is covered by a gold hydroxide phase at potentials at which the oxygen evolution sets in.

*Oxygen Evolution Reaction (OER) on Hematite.* Hematite ($\alpha$-$Fe_2O_3$) is a promising photoanode material for water splitting applications due to its relatively small bandgap and natural abundance. The role of electronic surface states in the OER at the Hematite photoanode has proven controversial: it's unclear whether they are trapped carriers, actively stabilize OER intermediates or neither. So far preliminary ESF measurements at the liquid water-hematite interface were conducted that reveal a previously unobserved intra-bandgap state. The bias-dependent spectral response suggests that this surface state must be depopulated for OER.

*Hydrogen Evolution Reaction (HER) on Au and Pt:* As neither protons nor water adsorb strongly on Au, theory suggests that the hydrogen evolution reaction on Au electrodes proceeds via an interfacial solvated electron. Because solvated electrons have relatively short lifetimes in water, understanding this chemistry requires the ability to start the HER at a well-defined time and then monitor the appearance of intermediates with high time resolution. Recently an experiment was developed in which, beginning with an Au electrode in contact with water, the HER is initiated by injecting photoexcited electrons from the electrode into the water conduction band using an intense femtosecond UV pulse. The fate of these (solvated) electrons are tracked both electrically, using a two-color laser induced perturbation of the open circuit potential, and by optical spectroscopy (see Fig. 10). Both types of probes suggest that, upon laser excitation, a delocalized solvated electron is generated that lives for 200 fs before localization. Some fraction of these localized solvated electrons relax back to the electrode on picosecond timescales, with a strongly potential dependent dynamics, while the remainder diffuses away from the surface and eventually drive chemistry.

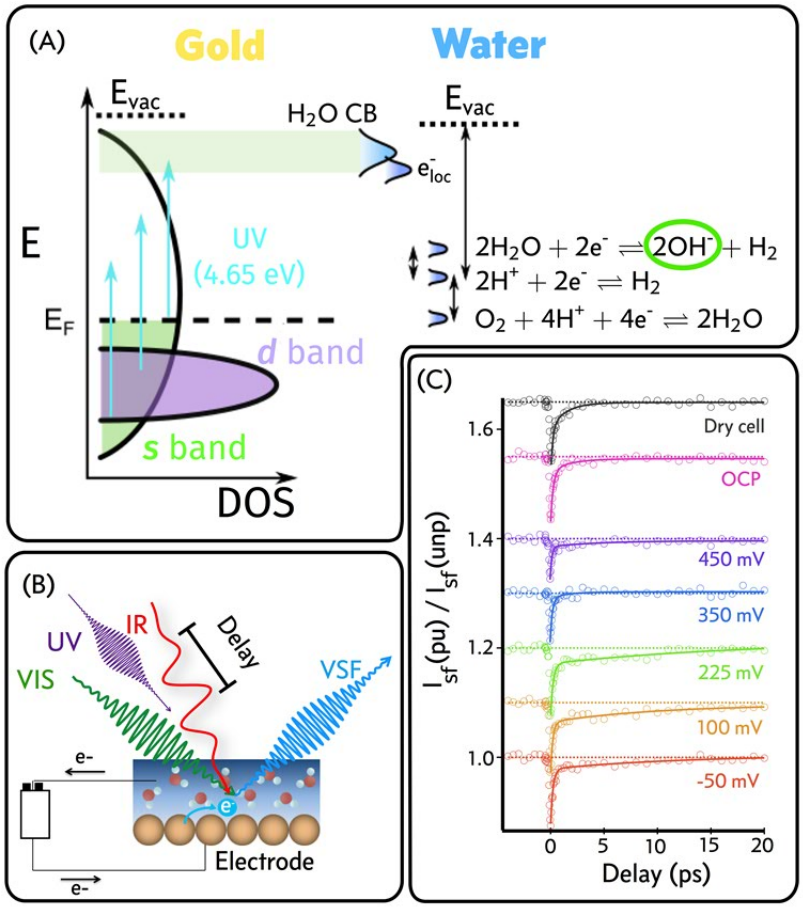


***Figure 10**: (A) Scheme for an experiment in which a fs UV pulse is used to adiabatically transfer an electron into the conduction band of water from which it drives chemistry (B) Experimental scheme illustrating the generation of an interfacial solvated electron and its characterization with a sum frequency probe pulse pair (C) Data from a normalized UV pump / SF probe scheme (mixing of 4 μm and 800 nm light). The results clearly show the 100 fs lifetime of the delocalized electron and the potential dependent ps lifetime of the localized solvated electron.*

In contrast to gold hydrogen adsorbs more strongly on platinum leading to dramatically higher electrocatalytic efficiency of the HER. However exactly how the HER proceeds on Pt is not clear: there is no mechanism that explains the dramatic dependence of the HER rate on pH, Pt crystal face, and electrolyte. Part of the challenge is that hydrogen adsorbs on Pt at potentials more oxidizing than hydrogen evolution and the relationship of this under potential deposited hydrogen to the HER is not clear. To help address this question an experiment was built whereby a femtosecond visible pulse was used to initiate electron transfer and the Pt-H surface probed by VSF. The results illustrate that, on sub ps time scales, Pt-H population is generated at the interface, presumably from molecularly adsorbed water, and that on a few picosecond time scale the Pt-H population decreases, presumably due to the generation of $H_2$.

### 2.2.5 Nonlinear THz Spectroscopy of Liquids

Low-frequency collective dynamics in molecular liquids are believed to have large impact on the outcome of chemical and biological processes. These complex motions include hindered rotations (librations) and translations and reorientational diffusive relaxation processes. The collective nature of these motions is a consequence of the intermolecular interactions and the coupling between different types of molecular motions, in particular, intermolecular modes. The group of *Mohsen Sajadi* aims at understanding the nature of these collective dynamics and mapping the potential energy of the intermolecular interactions, using linear and nonlinear THz spectroscopy.

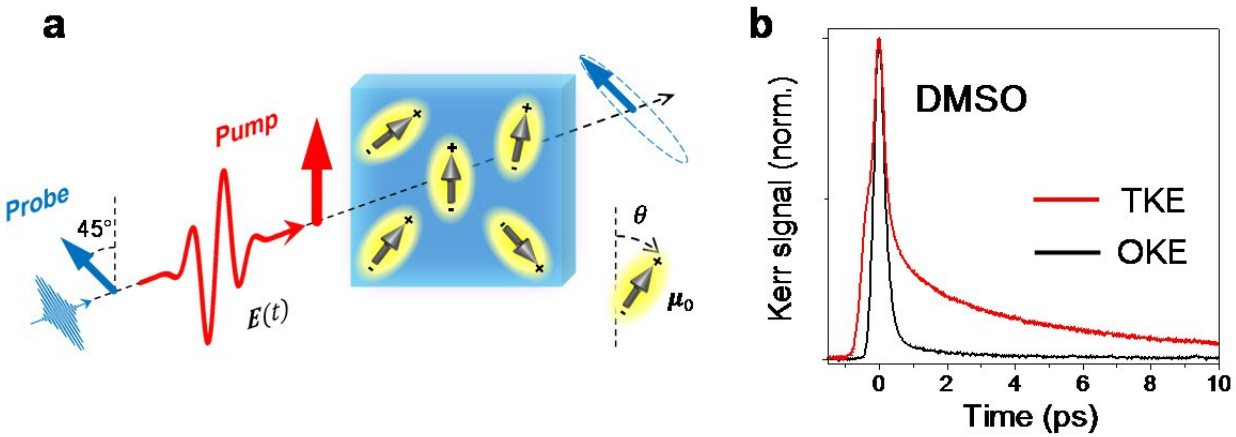


***Figure 11***: (a) *An intense THz or optical pump pulse induces birefringence in a polar liquid which is measured by an optical probe pulse that becomes elliptically polarized upon propagation through the medium. (b) TKE (red line) and OKE (black line) signals of DMSO are normalized to the instantaneous electronic contribution.*

*Direct observation of the intermolecular mode coupling in liquids*: Strong THz electric-field pulses have been applied to drive orientational dynamics in polar liquids leading a transient optical anisotropy induced by the torque of the THz field exerted on the permanent dipole

moments of the solvent molecules. The THz induced optical birefringence is monitored by an optical pulse as shown schematically in Fig. 11a. This THz Kerr effect (TKE) is significantly enhanced as compared to off-resonant optical excitation (OKE) as exemplified for the dipolar liquid dimethyl sulfoxide (DMSO, Fig. 11b). The amplitude enhancement in the TKE implies a direct coupling of the THz electric field to the permanent dipole moment of the liquid. Note that, optical pulses interact with the induced electronic dipoles where the nuclear dynamics is frozen during the light-matter interaction. Here, we use intense THz pulses to drive orientational molecular dynamics in polar liquids such as dimethyl sulfoxide or acetonitrile by coupling directly to their low-frequency resonances.

This approach provides insights into the character of THz absorption resonances, the coupling between low-frequency modes, namely librational and reorientational motions and the sign of the polarizability anisotropy of the solvent molecules. In light of a simple but quite general model and for excitation at different THz frequencies, it can be shown that the observed enhancement arises from the coupling between two intermolecular modes in the liquids, namely the resonantly excited librational (hindered rotational) motions and the optically resolved reorientational relaxation in the liquid. Here, the enhanced part of the TKE signal is assigned to the single molecule reorientational relaxation while the excited mode is the librational mode of DMSO.

Currently this approach of comparing transient optical anisotropy induced by THz and optical excitation has been expanded to liquid water. As water is highly polar, strong coupling of the THz electric field and the permanent dipole moment occurs. Such studies will provide insights into the coupling between the intermolecular modes associated with the hydrogen bonding network of water.

[1] M. Sajadi, M. Wolf, and T. Kampfrath, Nature Commun. **8**, 14963 (2017).

### 2.2.6 Theoretical Investigations of Molecular Machines

The group of *Alexander Mikhailov* continued theoretical studies of molecular protein machines, with the emphasis on understanding conformational dynamics and kinetics of their operation cycles, and studies of their hydrodynamic effects.

The enzyme tryptophan synthase represents an extensively experimentally investigated chemical nano-machine. Based on the available experimental data, a stochastic model for the operation of tryptophan synthase has been constructed and it became possible, for the first time, to reconstruct its complete stochastic thermodynamics, quantifying energy dissipation,

entropy and information production in all steps within the operation cycle, as well as the information and entropy flow within the enzyme [1].

In a collaboration with the Max Delbrück Center (MDC) in Berlin and the Kanazawa university in Japan the molecular motor dynamin has been extensively studied. This protein forms filaments that coil around a membrane tube (see Fig. 12) and, through the motor operation, induce its constriction and breakup. Using the structural data from X-ray diffraction studies and FRET experiments at MDC in Berlin together fast atomic force microscopy (AFM) imaging at about 10 frames/s at the Bio-AFM Research Center in Kanazawa and reduced coarse-grained simulations, the full molecular-dynamics and the operation mechanism of this molecular machine has been explored.

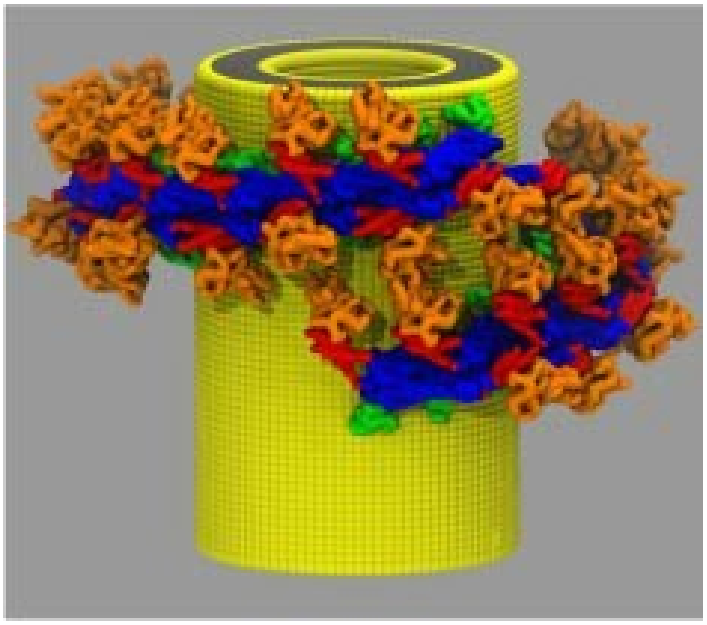

***Figure 12**: The dynamin filament coils itself around the membrane tube and, by constriction, induces its breakup.*

When active proteins are cyclically changing their conformations this results in fluctuating non-thermal flows in the cytoplasm and fluctuating strains in the elastic network of a cell. Systematic investigations of these effects were performed in viscoelastic media that represent active gels and in biological membranes populated by active protein inclusions [2] and presented in a review [3]. Furthermore, Alexander Mikhailov has also written together with Gerhard Ertl a book on *Chemical Complexity: Self-Organization Processes in Molecular Systems* [4].

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## 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, until 6/2017).

**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:**

- ERC Consolidator Grant #482843 “*FLATLAND: Electron-lattice-spin correlations and many-body phenomena in 2D semiconductors and related heterostructures*” (electron, phonon, and spin dynamics in van der Waals heterostructures investigated with trARPES, femtosecond electron diffraction and microscopy, from 10/2016).

**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 11/2015).

**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 ultrathin oxide films with STM and AFM, from 7/2015).

**Takashi Kumagai:**

- JST funded project on "***Eluciation of microscopic mechanism of catalytic effects via localized plasmon excitation***", within the PRESTO program on "Science and Creation of Innovative Catalysts" (surface reactions induced by localized plasmon excitation, low-temperature STM/ncAFM, from 10/2016)

**Tobias Kampfrath:**

- ERC consolidator grant TERAMAG, "*Ultrafast spin transport and magnetic order controlled by terahertz electromagnetic pulses*" (control of spin currents and spin dynamics by intense THz electromagnetic fields, from 07/2016).
- 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 7/2016).
- 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).

**Alexander Mikhailov:**

- Volkswagen Foundation, international project ***"Self-organizing networks of interacting machines"*** (design and analysis of the networks of molecular machines), until 12/2016.

**Laurenz Rettig**

- DFG Emmy Noether grant (RE 3977/1-1), ***"Beyond time constants: Quantifying interactions in correlated materials by complementary ultrafast time-domain approaches"*** (combined time-resolved ARPES and time-resolved diffraction experiments in strongly correlated materials across phase transitions, setup of Pulsed-Laser-Deposition (PLD) for oxide films, from 9/2017).

**Julia Stähler**

- DFG 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"*** (photoinduced electron transfer, two-photon photoemission spectroscopy of electronic states, from 7/2015).

## 4. Publications of the Department of Physical Chemistry

### 2015 (late publications)

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### Doctoral Thesis

*Bogner, L.*: Ultrafast Relaxation Dynamics after Optical Excitation of Hybrid Inorganic/Organic Systems. Freie Universität Berlin 2015.

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**Bachelor Thesis**

*Mayan, I.*: Charakterisierung amorpher Eisschichten auf der Cu(111)-Oberfläche mittels thermischer Desorptions- und Photoelektronenspektroskopie: Mittlere freie Weglänge niederenergetischer Elektronen in amorphem Eis. Universität Potsdam 2015.

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**Doctoral Thesis**

*Krecinic, F.*: Ultrafast electron diffraction and imaging using ionized electrons. Freie Universität Berlin 2017.

*Müller, M.*: Femtosecond low-energy electron imaging and diffraction using nanotip photoemitters. Freie Universität Berlin 2017.

**Master's Thesis**

*Eisbach, M.*: Entropy, Dissipation and Information in Models of Interacting and Coarse Grained Systems. Technische Universität Berlin 2017.

*Müller, P.*: A 2D Spatial Light Modulator for femtosecond THz light modulation. Technische Universität Berlin 2017.

*Zahn, D.*: Structural dynamics of transition metal dichalcogenide heterostructures studied by ultrafast high-energy electron diffraction. Freie Universität Berlin 2017.

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

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

- Braun, Lukas: Ultrafast Spin- and Charge-Currents in Topological Insulators and Their Transport to Adjacent Ferromagnetic Layers. (Institutsseminar, Nano-Systems from Ions, Spins and Electrons, Max Planck Institute of Microstructure Physics, Halle, Germany, Nov 2016).

- Campen, R. Kramer: Probing of Surface Vibrational Modes with Optical SFG. (Block Course on Methods of modern interface and surface science, IMPRS Functional Interfaces in Physics and Chemistry, Berlin, Germany, Oct 2016).

- Campen, R. Kramer: Probing Molecular Structure and Chemistry at Electrochemical Interfaces in Real Time. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).

- Ernstorfer, Ralph: Development of a 500 kHz XUV Source Based on an OPCPA. (Seminar, Rutherford Appleton Laboratory, Didcot, UK, Oct 2015).

- Ernstorfer, Ralph: Photocurrents and Structural Dynamics in Nanomaterials Probed by Femtosecond Electron Pulses. (4th International Workshop on Ultrafast Nanooptics (UNO-4), Bad Dürkheim, Germany, Oct 2015).

- Ernstorfer, Ralph: Structural and Electronic Dynamics in Transition Metal Dichalcogenides: Accessing Coupling and Correlation Effect by Time-Resolved Techniques. (BESSY II - THz to Soft X-ray Workshop, Helmholtz-Zentrum Berlin, Berlin, Germany, Dec 2015).

- Ernstorfer, Ralph: Accessing Electron-Phonon Interaction with Time-Resolved Diffraction and XUV-Based trARPES. (Seminar, Philipps-Universität, Marburg, Germany, Jan 2016).

- Ernstorfer, Ralph: Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides. (Physikalisches Kolloquium, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, Feb 2016).

- Ernstorfer, Ralph: Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides. (SIMES Seminar, Stanford Institute for Materials & Energy Sciences, SLAC, Stanford University, Stanford, CA, USA, Feb 2016).

- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: From Electron-Phonon Coupling to Spin- and Pseudospin-Polarized Excited States. (Physical Seminar, Department of Chemistry, University of Rochester, Rochester, NY, USA, Feb 2016).

- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: From Electron-Phonon Coupling to Spin- and Pseudospin-Polarized Excited States. (Seminar, ICFO The Institute of Photonic Sciences, Castelldefels, Barcelona, Spain, Feb 2016).

- Ernstorfer, Ralph: Femtosecond Electrons Probing Ultrafast Phenomena in Nanostructures by Diffraction and Imaging. (SPIE Photonics West - OPTO: Ultrafast Phenomena and Nanophotonics XX, San Francisco, CA, USA, Feb 2016).

- Ernstorfer, Ralph: Accessing Electronic and Structural Dynamics with Time-Resolved Electron Diffraction and High Repetition Rate XUV-trARPES. (Kolloquium, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, Mar 2016).
- Ernstorfer, Ralph: Spin- and Pseudospin-Polarized Excited States in Bulk $WSe_2$. (Hauptvortrag, DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Ernstorfer, Ralph: Accessing Many-Body Effects and Coupling Phenomena in Transition Metal Dichalcogenides by Time-Resolved ARPES and Diffraction. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Ernstorfer, Ralph: Dynamics of Electrons, Spins and Phonons in Transition Metal Dichalcogenides. (1st WP2-Domain Workshop on Beyond CMOS, NEREID, NanoElectronics Roadmap for Europe: Identification and Dissemination, Espoo, Finland, May 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (Graz Advanced School of Science, Physics Colloquium of the University of Graz and the Graz University of Technology, Graz, Austria, Jun 2016).
- Ernstorfer, Ralph: A Momentum-Resolved View of Electronic and Structural Dynamics in $WSe_2$. (Seminar, 1. Physical Institute, Georg-August-Universität Göttingen, Göttingen, Germany, Jul 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (MPSD-Seminar, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, Jul 2016).
- Ernstorfer, Ralph: Electronic and Structural Dynamics in Solids: A Momentum-Resolved View on Microscopic Coupling and Correlation Phenomena. (Physikalisches Kolloquium, Institute for Nuclear Physics, Johannes Gutenberg University Mainz, Mainz, Germany, Jul 2016).
- Ernstorfer, Ralph: A Momentum-Resolved View of Electronic and Structural Dynamics in $WSe_2$. (CRC 1242 Kick-Off-Meeting, Non-Equilibrium Dynamics of Condensed Matter in the Time Domain, University of Duisburg-Essen, Bad Honnef, Germany, Nov 2016).
- Ernstorfer, Ralph: Ultrafast Electronic and Structural Dynamics on the Nanoscale. (The 32nd Annual Symposium on Chemical Physics, University of Waterloo, Waterloo, ON, Canada, Nov 2016).
- Ernstorfer, Ralph: Ultrafast Point-Projection Electron Imaging and Diffraction. (StEM Workshop at Ringberg Castle, Kreuth, Germany, Jan 2017).
- Ernstorfer, Ralph: Accessing Micro- and Mesoscopic Ultrafast Electron Dynamics in Low-Dimensional Materials. (DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Spatio-Temporal Multiscale Optical Spectroscopy Meets Functional Materials, Dresden, Germany, Mar 2017).
- Ernstorfer, Ralph: A Momentum-Resolved View on Electrons, Phonons and Their Coupling in Nanoscale Materials. (Kolloquium des Fachbereichs Physik, Freie Universität Berlin, Berlin, Germany, May 2017).

- Ernstorfer, Ralph: Momentum-Resolved View on Electrons, Phonons and Their Coupling in WSe2 through Ultrafast Techniques. (Workshop on Spectroscopy and Dynamics of Photoinduced Electronic Excitations, ICTP, Trieste, Italy, May 2017).
- Ernstorfer, Ralph: Accessing Microscopic Coupling in Solids with Momentum-Resolving Ultrafast Techniques. (Laser- und Quantenoptikseminar, Technische Universität Kaiserslautern, Kaiserslautern, Germany, Jun 2017).
- Ernstorfer, Ralph: Momentum-Resolved View on Electrons, Phonons and Their Coupling in $WSe_2$. (10th International Symposium on Ultrafast Surface Dynamics, Inzell, Germany, Jun 2017).
- Ernstorfer, Ralph: Nonthermal Structural Dynamics Probed by Momentum-Resolved Femtosecond Electron Diffraction. (ARD-ST3 Annual Workshop, DESY, Zeuthen, Germany, Jul 2017).
- Horn, Karsten: Graphene and Some of Its Interfaces – Electronic Structure. (3rd Erlangen Symposium on Synthetic Carbon Allotropes 2015, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany, Oct 2015).
- Horn, Karsten: Zehn Jahre Forschung an Graphen: ein Rück- und Ausblick. (Workshop, Graphenschichten: Abscheideverfahren und Eigenschaften, European Society of Thin Films, Dresden, Germany, Nov 2015).
- Horn, Karsten: Forschung an Graphen – ein Rück- und Ausblick. (Lecture, Leibniz-Institut für innovative Mikroelektronik, Frankfurt (Oder), Germany, Apr 2016).
- Horn, Karsten: Graphene and Its Relatives, and Their Fascinating Electronic Properties. (6th International Conference on NANOstructures and nanomaterials SElf-Assembly (NANOSEA), Catania, Italy, Jul 2016).
- Kampfrath, Tobias: Spintronics and Femtomagnetism with THz Radiation. (Photon Science Seminar, Paul Scherrer Institut (PSI), Villigen, Switzerland, Oct 2015).
- Kampfrath, Tobias: Terahertz Spectroscopy: From Ultrafast Probing Toward Control of the Motion of Electrons, Ions and Spins. (Workshop, SFB 1073 Atomic scale control of energy conversion, Doctoral Students' Seminar in Berlin, Berlin, Germany, Oct 2015).
- Kampfrath, Tobias: Terahertz Spectroscopy: From Ultrafast Probing Toward Control of the Motion of Electrons, Ions and Spins. (Physikalisches Kolloquium, Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany, Nov 2015).
- Kampfrath, Tobias: Spintronics with Terahertz Radiation. (Magnetism Three-Kings-Meeting, Deutsche Physikalische Gesellschaft, Bad Honnef, Germany, Jan 2016).
- Kampfrath, Tobias: Terahertz Magnetism. (TELBE Kick-Off Meeting, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, Feb 2016).
- Kampfrath, Tobias: Tutorial: Terahertz Spectroscopy. (Edgar-Lüscher-Seminar, Klosters, Switzerland, Feb 2016).
- Kampfrath, Tobias: Probing and Controlling Ultrafast Magnetism with Terahertz Radiation. (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Focus Symposium,

Ultrafast non-equilibrium dynamics in quantum materials, Regensburg, Germany, Mar 2016).

- Kampfrath, Tobias: Intense Terahertz Pulses: Probing the Dynamics of Electrons, Phonons and Spins. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Kampfrath, Tobias: Terahertz Spintronics. (Colloquium, Cluster of Excellence PRISMA, Johannes Gutenberg University Mainz, Mainz, Germany, Jun 2016).
- Kampfrath, Tobias: Probing and Controlling Ultrafast Magnetism with Terahertz Radiation. (International Workshop on "Terahertz Science, Nanotechnologies and Applications", Erice, Sicily, Italy, Jul 2016).
- Kampfrath, Tobias: Ultrathin Spintronic Metallic Multilayers as Efficient Emitters of Broadband Terahertz Electromagnetic Pulses. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Kampfrath, Tobias: Novel Emitters of Terahertz Radiation Based on Spintronic and Nanophotonic Concepts. (Leading Light Symposium with Kobus Kuipers, Amsterdam, The Netherlands, Oct 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (61st Annual Conference on Magnetism and Magnetic Materials (MMM), New Orleans, LA, USA, Oct 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Seminar, 1. Physical Institute (AG Stefan Mathias), Georg-August-Universität Göttingen, Göttingen, Germany, Nov 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Physikalisches Kolloquium, Grenz- und Oberflächenphysik (AG Markus Münzenberg), Ernst Moritz Arndt Universität Greifswald, Greifswald, Germany, Dec 2016).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Seminar, Magnetism and Spintronics (AG Mathias Weiler), Walther-Meißner-Institute for Low Temperature Research, Bavarian Academy of Sciences and Humanities, Garching, Germany, Jan 2017).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (MPSD Seminar, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, Jan 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Allgemeines Physikalisches Kolloquium, Physikalisches Institut (AG Rudolf Bratschitsch), Westfälische Wilhelms-Universität Münster, Münster, Germany, Jan 2017).
- Kampfrath, Tobias: The Thinner, the Better: Broadband Terahertz Emitters Made of Spintronic Metal Films. (German Terahertz Conference 2017, Bochum, Germany, Mar 2017).

- Kampfrath, Tobias: Ultrafast Spin Interactions Revealed with Terahertz Radiation. (DPG-Frühjahrstagung, Focus Session, Non-Equilibrium Dynamics in Light-Driven Materials: Theory Meets Experiment, Dresden, Germany, Mar 2017).
- Kampfrath, Tobias: Ultrafast Spintronics with Terahertz Radiation. (Optical Terahertz Science & Technology Conference (OTST 2017), London, UK, Apr 2017).
- Kampfrath, Tobias: Ultrafast Spincaloritronics Enables Efficient Emitters of Terahertz Radiation. (SPINCALORITRONICS VIII, Conference 2017, Regensburg, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Kolloquium der Fakultät für Physik, Physik Dünner Schichten und Nanostrukturen, Universität Bielefeld, Bielefeld, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Torque on Spins and Molecules: New Insights into Magnets and Liquids. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).
- Kampfrath, Tobias: Ultrafast Terahertz Spectroscopy: Probing and Controlling Fundamental Motions of Electrons, Spins and Ions. (Physikalisches Kolloquium, Fachbereich Physik, Technische Universität Kaiserslautern, Kaiserslautern, Germany, Jul 2017).
- Kumagai, Takashi: Direct Observation of H-Bond Dynamics Using Scanning Probe Microscopy. (CRC 1073 Workshop, Berlin, Germany, Oct 2015).
- Kumagai, Takashi: Direct Observation and Control of H-Bond Dynamics Using Scanning Probe Microscopy. (Seminar, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, Nov 2015).
- Kumagai, Takashi: Direct Observation of H-Bond Dynamics Using Scanning Probe Microscopy. (80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Kumagai, Takashi: Heat-/Electron-/Photo-/Force-Induced Tautomerization in a Single Molecule. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Surface and Interface Science Laboratory, RIKEN, Saitama, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Kyushu University, Fukuoka, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Institute for Molecular Science, Okazaki, Japan, Dec 2016).
- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Yokohama City University, Yokohama, Japan, Jan 2017).

- Kumagai, Takashi: Heat-/Electron-/Light-/Force-Induced Tautomerization in a Single Molecule. (Seminar, Atomic, Molecular & Optical Physics Laboratory, RIKEN, Saitama, Japan, Jan 2017).

- Kumagai, Takashi: Structure and Dynamics of Single Molecules Studied by Scanning Tunneling Microscopy. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2017).

- Ladenthin, Janina: Force-Induced Tautomerization in a Single Molecule. (Seminar, Department of Physics (AG Katharaina J. Franke), Freie Universität Berlin, Berlin, Germany, Nov 2016).

- Ladenthin, Janina: Force-, Heat-, and Electron-Induced Tautomerization of Single Porphycene Molecules Investigated with SPM. (Seminar, IBM Research, Zurich Research Laboratory, Rüschlikon, Switzerland, May 2017).

- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Seminar, Department of Physics (AG Katharina J. Franke), Freie Universität Berlin, Berlin, Germany, Oct 2015).

- Mährlein, Sebastian: Lattice Induced Ultrafast Phenomena. (Zhu group seminar, Department of Chemistry (X.-Y. Zhu), Columbia University, New York, NY, USA, Oct 2016).

- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Nanooptics Seminar, CIC nanoGUNE, Donostia – San Sebastian, Spain, Feb 2017).

- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Attoscience and Ultrafast Optics group seminar, ICFO The Institute of Photonic Sciences, Castelldefels, Barcelona, Spain, Mar 2017).

- Mährlein, Sebastian: Nonlinear Terahertz Phononics: A Novel Route to Controlling Matter. (Seminar, IBS Center for Correlated Electron Systems, Seoul National University, Seoul, South Korea, Jul 2017).

- Mährlein, Sebastian: Ultrafast Spin Dynamics Driven by Pure Phonon Excitation. (8th International Conference on Metamaterials, Photonic Crystals and Plasmonics (META 2017), Seoul, South Korea, Jul 2017).

- Melnikov, Alexey: Excitation and Propagation of Spin Currents in Fe/Au/Fe/MgO(001): Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescale. (Seminar, Institute of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany, Oct 2015).

- Melnikov, Alexey: Ultra-Short Spin Current Pulses in Metallic Multilayers: Non-Thermal Spin-Polarized Seebeck Effect and the Role of Interfaces in Fe/Au/Fe/MgO(001). (Workshop, Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans, France, Oct 2015).

- Melnikov, Alexey: Ultrashort Spin Current Pulses in Metallic Multilayers: Spin Seebeck and Spin Transfer Torque Effects on Ultrafast Timescales. (Seminar, Max-Born-Institut, Berlin, Germany, Oct 2015).

- Melnikov, Alexey: Ultrafast Spintronics Roadmap: From Femtosecond Spin Current Pulses to Terahertz Non-Uniform Spin Dynamics via Nano-Confined Spin Transfer Torques. (SPIE Optics and Photonics 2016, San Diego, CA, USA, Aug 2016).
- Melnikov, Alexey: Ultrafast Spintronics Roadmap: From Femtosecond Spin Current Pulses to Terahertz Non-Uniform Spin Dynamics via Nano-Confined Spin Transfer Torques. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (Department of Physics, Kyoto University, Kyoto, Japan, Oct 2015).
- Mikhailov, Alexander S.: Design Principles of Molecular Machines. (The AIMR International Symposium 2016, Tohoku University, Sendai, Japan, Feb 2016).
- Mikhailov, Alexander S.: Design Principles of Molecular Machines. (International Symposium, Department of Mathematical and Life Sciences, Hiroshima University, Hiroshima, Japan, Mar 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (71th Annual Meeting (2016), The Physical Society of Japan, Special joint Biophysics Session, Sendai, Japan, Mar 2016).
- Mikhailov, Alexander S.: Hydrodynamic Collective Effects of Active Proteins in Biological Cells. (Seminar, Tokyo Metropolitan University, Tokyo, Japan, Nov 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator $Ta_2NiSe_5$. (Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany, Apr 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator $Ta_2NiSe_5$. (Seminar, Department of Mathematics and Physics (AG Claudio Giannetti), Università Cattolica del Sacro Cuore, Brescia, Italy, May 2016).
- Mor, Selene: Ultrafast Electronic Band Gap Control in an Excitonic Insulator. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Paarmann, Alexander: Phonon-Driven Ultrafast Demagnetization in a Ferrimagnetic Insulator. (EMN Meeting on Ultrafast Research, Las Vegas, NV, USA, Nov 2015).
- Paarmann, Alexander: Ultrafast Demagnetization in a Ferrimagnetic Driven by Optical Phonons. (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Feb 2016).
- Paarmann, Alexander: Nonlinear Phonon Spectroscopy Using the FHI IR-FEL. (FHI-Workshop on Current Research Topics at the FHI, Potsdam, Germany, May 2016).
- Paarmann, Alexander: Nonlinear Mid-Infrared Solid State Spectroscopy Using Free-Electron Lasers. (United States Naval Research Laboratory, Washington, DC, USA, Jun 2016).

- Paarmann, Alexander: Nonlinear Phonon Spectroscopy with Infrared Free-Electron Lasers. (Colloquium, U.S. Naval Research Laboratory, Washington, DC, USA, Jun 2016).
- Paarmann, Alexander: Novel Concepts for Narrowband THz Excitation of Large Amplitude Lattice Motions. (Workshop on an accelerator based source for nonlinear THz science @ SwissFEL, Brugg-Windisch, Switzerland, Sep 2016).
- Paarmann, Alexander: Surface Phonon Polaritons for Mid-Infrared Nonlinear Nanophotonics. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Paarmann, Alexander: Coherent Phonon Spectroscopy Using TELBE: Challenges and Opportunities. (TELBE User Meeting at the HZDR, Dresden, Germany, Feb 2017).
- Paarmann, Alexander: Second Harmonic Phonon Spectroscopy: A New Tool for Studying Phonon Polaritons. (Group Seminar, Institut für Optik und Atomare Physik (AG Ulrike Woggon), Technische Universität Berlin, Berlin, Germany, May 2017).
- Paarmann, Alexander: Mid-Infrared Nonlinear Nanophotonics Using Surface Phonon Polaritons. (BerliNano, 4th mini workshop in Berlin on nanophysics and related nanosciences, Physical Chemistry Department of the Fritz Haber Institute, Berlin, Germany, Jun 2017).
- Paarmann, Alexander: Nonlinear Phonon Spectroscopy Using Infrared Free Electron Lasers. (FELIX Colloquium, Radboud University, Nijmegen, The Netherlands, Jun 2017).
- Paarmann, Alexander: Mid-Infrared Nonlinear Nanophotonics in Anisotropic Dielectrics Using Surface Phonon Polaritons. (8th International Conference on Metamaterials, Photonic Crystals and Plasmonics (META 2017), Seoul, South Korea, Jul 2017).
- Puppin, Michele: Excited-State Band Mapping with XUV-Based trARPES. (Workshop on Time-resolved Photoelectron Spectroscopy, Trieste, Italy, Jan 2017).
- Puppin, Michele: Excited-State Mapping with XUV-Based trARPES. (Seminar, Laboratory of Ultrafast Spectroscopy, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland, Mar 2017).
- Puppin, Michele: Excited-State Mapping with XUV-Based trARPES. (Seminar, Departement Physik, ETH Zurich, Zurich, Switzerland, Mar 2017).
- Razdolski, Ilya: Nonlinear Surface Photonics in Hybrid Magnetic Structures. (META'16, 7th International Conference on Metamaterials, Photonic Crystals and Plasmonics, Malaga, Spain, Jul 2016).
- Sajadi, Mohsen: Intermolecular Interactions in Liquids: Insight from Nonlinear THz Spectroscopy. (23rd Iranian Conference on Optics and Photonics (ICOP 2017), Tarbiat Modares University, Teheran, Iran, Jan 2017).
- Seifert, Tom: Spin Transport and Spin-Orbit Interaction at Terahertz Frequencies: Spectroscopy and Applications. (Hauptvortrag, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Ultrafast spin currents for spin-orbitronics: from metals to topological insulators, Regensburg, Germany, Mar 2016).

- Seifert, Tom: Ultrafast Spin Transport in Magnetic Thin Films Probed by Terahertz Spectroscopy. (Workshop, Spin Caloric Transport (SPP 1538), Bad Honnef, Germany, Mar 2016).
- Seifert, Tom: Efficient Metallic Spintronic Emitters of Ultrabroadband Terahertz Radiation. (EMN Meeting on Terahertz, Energy Materials Nanotechnology, San Sebastian, Spain, May 2016).
- Seifert, Tom: The Thinner, the Better: Nanometer-Thick Efficient Spintronic Emitters of Terahertz Radiation. (Kickoff mini workshop, BerliNano, Berlin, Germany, Dec 2016).
- Seifert, Tom: Terahertz Spectroscopy of Femtosecond Spins Currents in Magnetic Heterostructures. (DPG-Frühjahrstagung, Sektion Kondensierte Materie (SKM), Focus Session: Antiferromagnetic Spintronics, Dresden, Germany, Mar 2017).
- Seifert, Tom: The Thinner, the Better: Nanometer-Thick Spintronic Terahertz Emitters. (NanoOstrava 2017, Terahertz technology and nanostructures in photonics and electronics, Ostrava, Czech Republic, May 2017).
- Seifert, Tom: Spin Orbit Interaction at Terahertz Speeds: Probing and Driving Spins at Highest Frequencies. (Spin Dynamics in Nanostructures, Gordon Research Conference, Les Diablerets, Switzerland, Jul 2017).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (19. Deutsche Physikerinnentagung, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (IV. Physical Institute (AG Claus Ropers), Georg-August-Universität Göttingen, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (Institute Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria, Nov 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Colloquium, Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany, Dec 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Special Seminar, Department of Chemistry, University of California, Berkeley, CA, USA, Dec 2015).
- Stähler, Julia: Real Time Measurement of the Vertical Binding Energy during the Birth and Lifetime of a Solvated Electron. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Jan 2016).
- Stähler, Julia: Many Body Effects in Ultrafast Spectroscopy: Polarons, Excitons & Correlated Electrons. (Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany, Jan 2016).

- Stähler, Julia: Ultrafast Dynamics of Many Body Effects in Solids and at Interfaces: Polarons, Excitons & Correlated Electrons. (Prize Talk, Gaede Prize Symposium, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).

- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (Colloquium, Department of Chemistry, Technical University of Munich, Munich, Germany, Apr 2016).

- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (International conference, Internal Interfaces 2016, Marburg, Germany, May 2016).

- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (SFB 951 Colloquium, Humboldt-Universität zu Berlin, Berlin, Germany, Jun 2016).

- Stähler, Julia: Understanding Ultrafast Exciton Dynamics in ZnO and at Its Surfaces: Potential and Hazard of Impurities. (Gruppenseminar, Institut für Experimentelle Physik II (AG Marius Grundmann), Universität Leipzig, Leipzig, Germany, Jun 2016).

- Stähler, Julia: Photoinduced Transient Band Gap Enhancement in the Excitonic Insulator $Ta_2NiSe_5$. (International conference on dynamic pathways in multidimensional landscapes, Berlin, Germany, Sep 2016).

- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (Award Ceremony of the Edith Flanigen Award 2016, CRC 1109, Berlin, Germany, Oct 2016).

- Vempati, Sesha Pavan Kumar: Frontier Molecular Orbitals of $CO_2$ on ZnO Surfaces: Time-Resolved Photoelectron Spectroscopy. (Seminar, Indian Institute of Science Education and Research Mohali, Mohali, India, Feb 2017).

- Vempati, Sesha Pavan Kumar: Hybrid Systems for Optoelectronic Applications and Photoelectron Spectroscopy. (Seminar, Material Research Center, Indian Institute of Science, Bengaluru, India, Mar 2017).

- Winta, Christopher: Second Harmonic Phonon Spectroscopy. (Group Seminar, Department of Physics (AG Wolfgang Kuch), Freie Universität Berlin, Berlin, Germany, Apr 2017).

- Wolf, Martin: Ultrafast Dynamics of Exciton Formation and Charge Transfer at Hybrid Interfaces. (1st funCOS International Workshop (FOR 1878), Erlangen, Germany, Nov 2015).

- Wolf, Martin: Ultrafast Dynamics of Photo-Induced Surface Reactions. (The 1st Sino-German Young Scientist Symposium on Structures & Dynamics at Surfaces, Beijing, China, Nov 2015).

- Wolf, Martin: Ultrafast Dynamics of Photoexcited Insulators Probed by Time- and Angle-Resolved Photoemission. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).

- Wolf, Martin: Dynamics in Complex Environments. (Photoionization & Photodetachment, Gordon Research Conference, Barga, Italy, Feb 2016).
- Wolf, Martin: Challenges and Prospects of Femtosecond Time-Resolved ARPES. (International Focus Workshop, Prospects and Limitations of Electronic Structure Imaging by Angle Resolved Photoemission Spectroscopy, Dresden, Germany, Apr 2016).
- Wolf, Martin: Ultrafast Bandgap Dynamics and Insulator-to-Metal Transitions Probed by Time-Resolved ARPES. (SPIE Defense + Commercial Sensing 2016, Baltimore, MD, USA, Apr 2016).
- Wolf, Martin: Ultrafast Electron Dynamics and Solvation at Interfaces. (Nilsson Symposium, Stockholm University, Stockholm, Sweden, May 2016).
- Wolf, Martin: Ultrafast Electronic Dynamics in Surface Reactions and 2D Materials. (Allgemeines Physikalisches Kolloquium, Fachbereich Physik, Westfälische Wilhelms-Universität Münster, Münster, Germany, May 2016).
- Wolf, Martin: Ultrafast Electronic Dynamics in Quasi 2D Materials Probed by Femtosecond Time-Resolved ARPES. (Ultrafast Dynamics at the Nanoscale 2016, Okinawa, Japan, Jul 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics in Low-Dimensional Materials Probed by Time-Resolved ARPES. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics in Quasi 2D Materials Probed by Time-Resolved ARPES. (NNN Telecom Workshop 2016, Nonlinear Nanophotonics and Nanofabrication at TELECOM frequencies, Le Mans, France, Sep 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Low Energy Excitations in Light-Driven Materials. (Physikalisches Kolloquium, Fakultät für Physik und Astronomie, Julius-Maximilians-Universität Würzburg, Würzburg, Germany, Nov 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Nonlinear Optical Spectroscopy of Interfaces and Solids. (Kolloquium SFB 1083, Fachbereich Physik, Philipps-Universität Marburg, Marburg, Germany, Nov 2016).
- Wolf, Martin: Ultrafast Excited State Dynamics and Insulator to Metal Transitions Probed by trARPES. (Workshop on Time-resolved Photoelectron Spectroscopy, Trieste, Italy, Jan 2017).
- Wolf, Martin: Transient Electronic Band Structure Mapping by Time-Resolved ARPES: The In/Si(111) (8x2) ↔ (4x1) Phase Transition. (Workshop, Physics at the borderline between 1D and 2D, Bad Honnef, Germany, Mar 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics and Nonlinear Optical Spectroscopy at Interfaces. (APS March Meeting 2017, New Orleans, LA, USA, Mar 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics and Structural Phase Transitions Probed by Time-Resolved ARPES. (Optics Seminar, Department of Applied Physics (Group Tony Heinz), Stanford University, Menlo Park, CA, USA, Apr 2017).

- Wolf, Martin: The Forefront of Time-Resolved Photoemission: From the Past to the Future. (10th International Symposium on Ultrafast Surface Dynamics, Inzell, Germany, Jun 2017).
- Wolf, Martin: Ultrafast Electronic Structure Changes During Photoinduced Phase Transitions: The Dynamics of the In/Si(111) (8x2) ↔ (4x1) Transition. (16th International Conference on the Formation of Semiconductor Interfaces (ICFSI-16), Hannover, Germany, Jul 2017).
- Wolf, Martin: Ultrafast Dynamics of Excited States and Light Induced Processes at Surfaces. (Plenary Session, 33rd European Conference on Surface Science (ECOSS-33), Szeged, Hungary, Aug 2017).
- Wolf, Martin: Ultrafast Excited State Dynamics Probed by Time-Resolved ARPES. (International School and Workshop on Electronic Crystals (ECRYS-2017), Cargèse, France, Aug 2017).

## Max Planck Research Group for Structural and Electronic Surface Dynamics

### Head: Ralph Ernstorfer

**Group members**

| | |
|---|---|
| Roman Bertoni | (*Postdoc, until 12/2015*) |
| Johannes Feldl | (*Master student, until 09/2016*) |
| Faruk Krecinic | (*Postdoc*) |
| Jannik Malter | (*Bachelor student*) |
| Melanie Müller | (*PhD student, until 08/2016, Postdoc, 09/2016 – 04/2017*) |
| Michele Puppin | (*PhD student, until 06/2016*) |
| Dong Shuo | (*Postdoc*) |
| Thomas Vasileiadis | (*PhD student*) |
| Lutz Waldecker | (*PhD student, until 09/2015, Postdoc, 10/2015 – 03/2016*) |
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| Daniela Zahn | (*Master student, until 05/2017, PhD student, since 07/2017*) |

**Research Projects Funded from Outside Resources**

- European Research Council Consolidator Grant (ERC-CoG #482843): *"*FLATLAND: *Electron-lattice-spin correlations and many-body phenomena in 2D semiconductors and related heterostructures"*. Start date: 10/2016.
- 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. 2nd funding period: 01/2017-31/2020.
  Project graduate student: Christopher Nicholson.

## 1. Scientific Scope

The ground state properties of complex materials as well as the reaction pathways of photo-excited states are governed by many-body phenomena and the mutual dependence of electron, spin and lattice subsystems. Ultrafast techniques provide access to these fundamental correlations and coupling phenomena as femtosecond light pulses allow for subsystem-specific excitations and time-resolved observation of the same or another subsystem's response.

We develop and employ complementary ultrafast probes sensitive to the ultrafast response of electrons and atomic structure in nanoscale materials. Most recently, we completed the development of a high-repetition rate extreme ultraviolet (XUV) laser and demonstrated the potential of this light source for mapping the excited state structure and dynamics in the entire Brillouin zone by time- and angle-resolved photoemission spectroscopy (trARPES), see Fig. 1. Femtosecond electron diffraction (FED) reveals the level of vibrational excitation and

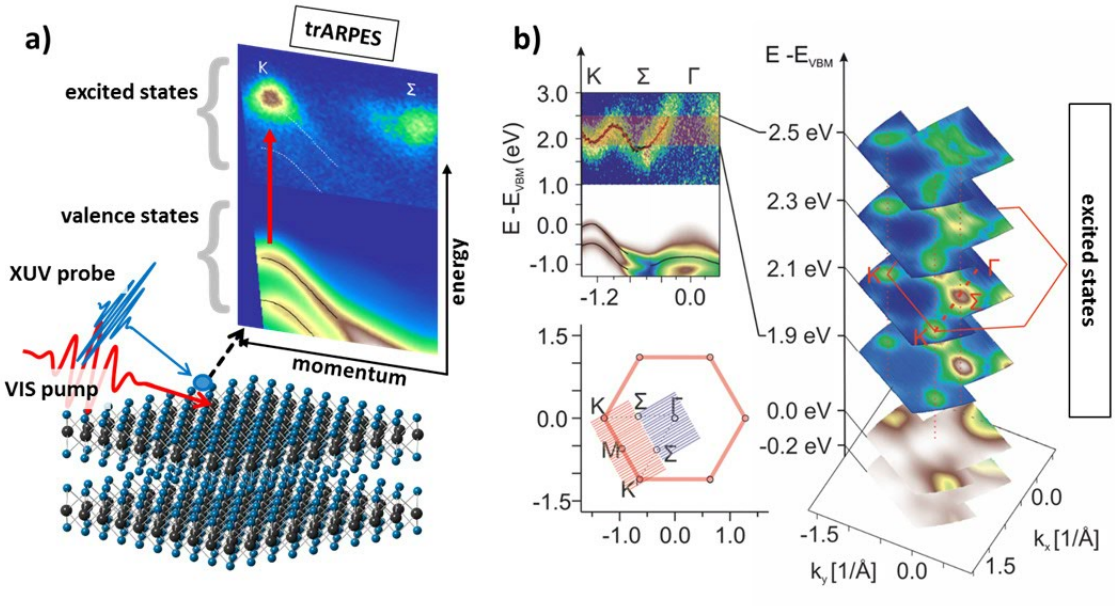


***Figure 1: Excited state spectroscopy with XUV-trARPES.*** *a) Principle of trARPES exemplified for excited state snapshots of $WSe_2$. Electrons are excited with a short visible laser pulse in resonance with a vertical transition (red arrow) at the K points of the Brillouin zone. The color plot shows the distribution of excited states in energy and momentum (along a linear cut through the Σ and K valleys) at temporal overlap of pump and probe pulses. b) Excited state map of $WSe_2$ taken 100 fs after optical excitation with 3.1 eV photons. After this time, the excited state population has spread over an extended region of the excited state structure and are photoemitted with a 20 fs XUV with 21.7 eV photon energy. For a given sample orientation, the employed electron spectrometer detects the electronic structure above and below the band gap along a line in the Brillouin zone, see left panels. By rotation of the sample, a 3D snapshot (resolved in $k_x$, $k_y$ and energy) of the excited state distribution is obtained, see right panel. This experimental approach extends the concept of band structure mapping by ARPES to transiently populated excited states. See posters PC 3 and PC 4.*

we recently demonstrated the investigation of ultrafast phonon dynamics with momentum resolution. In addition to these reciprocal space techniques, we utilize ultrashort low-energy electron wave packets for the microscopy of charge migration and 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.

## 2. Research Activities

### 2.1 Electronic Excited State Mapping and Dynamics with XUV-Based trARPES

Angle-resolved photoemission spectroscopy with extreme ultraviolet (XUV) and soft x-ray radiation is the key experimental method for the determination of the electronic structure of crystals and molecules. In collaboration with the *Dynamics of Correlated Materials* group headed by Laurenz Rettig, we developed a high-repetition rate femtosecond XUV laser which allows the time- and angle-resolve photoemission spectroscopy (trARPES) of excited electronic states (poster PC 3). The experimental scheme is illustrated in Fig. 1a: a femtosecond visible laser pump pulse excites a small fraction of the valence electrons to the conduction band. The distribution and evolution of the excited states in energy and momentum space is observed through subsequent photoemission with a short XUV probe pulse. Fig. 1a shows exemplary data for the layered semiconductor $WSe_2$, optically excited by a vertical transition at the K point in the Brillouin zone (red arrow). At temporal overlap of pump and probe pulses, the excited state distribution at the K point as well as the onset of population build-up in the Σ valley of the conduction band is visible.

The trARPES experiments records photoemission signal resolved in four dimensions, i.e., time, energy, and both parallel momentum components. Fig. 1b shows the excited state distribution in E, $k_x$ and $k_y$ at a fixed time of 100 fs after optical excitation of $WSe_2$ with 3.1 eV photons. This data set is constructed from individual two-dimensional acquisitions of the excited state spectrum along linear cuts through the irreducible part of the Brillouin zone, as illustrated on the left side of Fig. 1b. This proof-of-concept experiment demonstrates the extension of valence band structure mapping with ARPES to transient excited states (see poster PC 4). The new XUV-trARPES apparatus was additionally employed for studying ultrafast phase transitions of atomic indium wires on silicon substrates and to the charge

density wave material $TbTe_3$, see sections 2.1.1 and 2.1.2 in the PC report and posters PC 1 and PC 2.

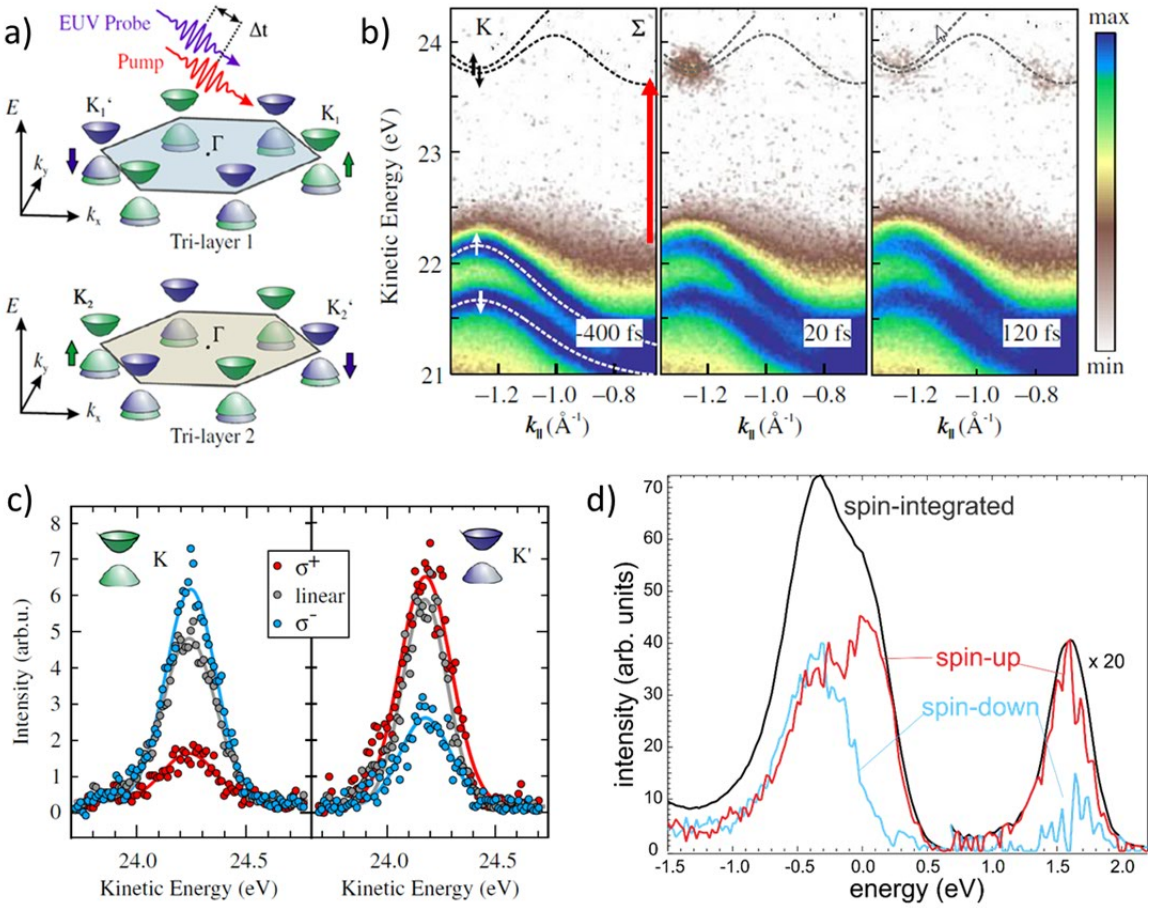


***Figure 2:*** *Observation of spin- and valley-polarized excited state in inversion-symmetric bulk $WSe_2$. a) Sketch of the electronic band structure in the K valleys. As these states have pronounced 2D character, the spin-valley correlation known from symmetry-broken TMDC monolayers [1–3] is present in each $WSe_2$ tri-layer. Time- and angle-resolved photoemission spectroscopy (trARPES) provides access to the transient electronic structure of the topmost tri-layer. b) TrARPES maps before (left), during (middle) and 120 fs after resonant excitation at the K point (red arrow) showing the build-up of excited state population. c) The excited state signal in the K valleys shows a pronounced circular dichroism which is inverted in the K' valleys. d) Additionally, the spin-polarization of the excited states is directly evidenced by spin-resolved trARPES. Figures a)-c) adapted from [4]. See poster PC 3.*

The technology enabling this type of photoemission spectroscopy is the XUV laser, which is based on a high-repetition rate, high-power optical parametric chirped pulse amplifier (OPCPA) developed in the department [5]. The near-infrared amplifier output is frequency up-converted to the $14^{th}$ harmonic by sequential processes, i.e., second harmonic generation in a nonlinear crystal followed by High-Harmonic Generation (HHG) in an Ar gas jet. After spectral filtering of a single harmonic with 21.7 eV photon energy, a 0.5 MHz train of XUV pulse with a duration of 20 fs and a photon flux up to $10^{12}$ ph/s is available at the sample. Details of this technological development are discussed on poster PC 4.

## 2.2 Spin-Polarized Excited States in Inversion-Symmetric Transition Metal Dichalcogenides

Layered semiconducting transition metal dichalcogenide (TMDC) materials like $WeSe_2$ exhibit fascinating properties arising from many-body interactions and the resulting spin texture promises new device concepts ranging from optoelectronic to spintronic applications. The strong spin-orbit coupling in combination with the highly anisotropic bonding and the lack of inversion symmetry within individual layers of these materials result in unusual spin-valley correlation in the electronic structure [2,6]: for monolayers (ML) of these materials, the valence band at the corners of the hexagonal Brillouin zone (K and K' points) exhibits spin-split bands separated by up to 500 meV with alternating spin polarization between neighboring valleys [2]. This coupling of spin polarization and valley index allows for the optical preparation of spin- and valley-polarized excited states in monolayers [1,3,7]. In thicker TMDC samples like bi-layers, however, inversion symmetry is restored due to the 2H layer stacking. Consequently, all electronic states in these centrosymmetric materials are spin-degenerate. However, it has recently been predicted that spin-polarized states may exist in a range of materials as a consequence of atomic site asymmetry despite the global inversion-symmetry of the crystal [8]. This hidden spin texture has been experimentally observed with spin-resolved photoemission spectroscopy [9,10]. Employing trARPES with spin-selective optical excitation, we demonstrated that the spin-polarized excited state populations can be generated [4].

## 2.3 Electron-Lattice Interaction Beyond the Two-Temperature Approximation

The energy exchange between electronic and vibrational degrees of freedom in a solid is typically described in the framework of the two-temperature approximation, i.e. the assumption of Fermi-Dirac and Bose-Einstein distribution functions for electrons and phonons, respectively. We challenge this approximation and its predictive power for microscopic energy flow for several prototypical materials. By probing the phonon population dynamics with ~100 fs resolution after impulsive excitation of the electrons with time-resolved electron diffraction [11], we quantify the electron-phonon coupling strength and compare to values obtained with first-principles calculations (J. Vorberger, Helmholtz-Zentrum Dresden-Rossendorf). Even for a simple metal like aluminium, we find that the assumption of thermal phonon distributions is insufficient as the electron-phonon energy

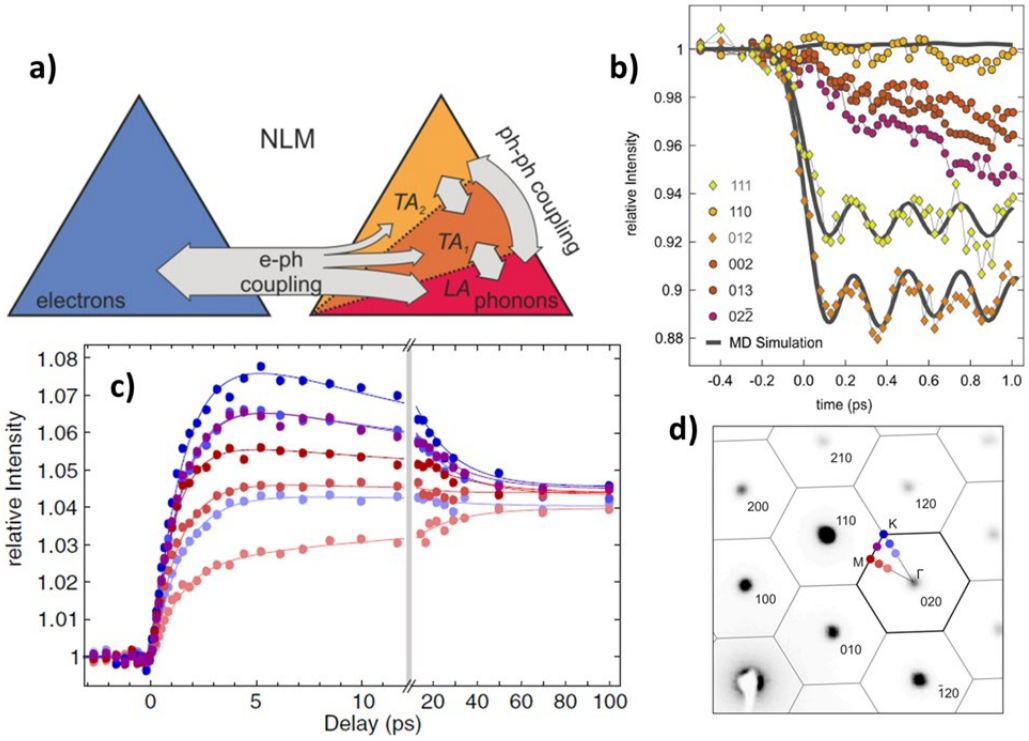


***Figure 3: Ultrafast nonthermal phonon dynamics in aluminium, antimony and $WSe_2$.*** *a) Schematic depiction of the nonthermal lattice model (NLM) proposed for an accurate description of the energy exchange between electrons and phonons in Al* [12]. *b) Simultaneous detection of coherent optical phonon dynamics ($A_{1g}$ mode, reflected by the 111 and 012 superlattice peaks) and incoherent phonon build-up. Again, a NLM is proposed and verified by comparison with first principle calculations* [13]. *c)&d) Momentum-resolved view on transient phonon populations in multilayer $WSe_2$. The analysis of the momentum-resolved inelastic scattering signal (colored dots in d) reveals a pronounced q-dependence of the dynamics and amplitude of the phonon population shown in c). This information is compared to the momentum-resolved electron-phonon coupling strength obtained from theory* [14]. *See poster PC 23.*

exchange rates are underestimated by a factor two [12]. This is caused by the preferential coupling of electrons to the high-energy longitudinal phonons. We proposed a nonthermal

lattice model (NLM), which treats coupling to the three phonon branches individually as depicted in Fig. 3a, as a minimal model capable of a quantitative description of electron-lattice relaxation.

For the semi-metal antimony, we extract the ultrafast dynamics of coherent and incoherent phonons from a single measurement from the temporal evolution and superlattice peaks and conventional Bragg peaks, respectively, see Fig. 3b. We differential energy flow from the electron to optical and acoustic phonons, and show that the electron-phonon coupling calculated from ab initio theory (Martin Garcia, Univ. Kassel) quantitatively is in good agreement with experiment as long as an NLM is employed for data analysis [13].

A direct momentum-resolved view on nonthermal phonon distributions can be obtained from the inelastic scattering background, as demonstrated before for x-ray diffraction [15] and

MeV FED [16]. We measure the momentum-dependent phonon dynamics in multilayer $WSe_2$ induced by optical excitation of the A exciton resonance, see Fig. 3c&d and [14]. The excited electrons relax to the conduction band minimum within the Σ valleys. We observed a rapid build-up of phonons corresponding to the M and K points in the Brillouin zone. These phonons connect 2nd- and 3rd-next Σ valleys in the electronic structure. Our measurements reveal that the electron relaxation is governed by intervalley rather than intravalley scattering processes [14], in agreement with ab initio calculations (Angel Rubio and co-workers, MPSD Hamburg).

### 2.4 Nanoscale Energy Flow in Heterostructures

Recently, we extended our FED studies to nanoscale heterostructures to study energy flow across heterostructure interfaces from the phonon perspective (for details, see poster PC 25). As 2D-2D heterostructure model system, we manually stack multilayers of $WS_2$ and $WSe_2$, see Fig. 4a&b. By tuning the photon energy of the pump pulses, the distribution of the initial electronic excitation can be controlled and the resulting structural dynamics in both materials can be extracted from the superposition diffraction pattern shown in Fig. 4b. In this semiconductor heterostructure with type-II band alignment, we find the electronic coupling to be highly efficient in spatially distribution the excitation energy.

In collaboration with the group of Richard Palmer (Swansea University), we investigate electron-phonon coupling and structural dynamics in size-selected $Au_{923}$ clusters and their electronic and vibrational coupling to various substrate materials, see Fig. 4c&d. We compare

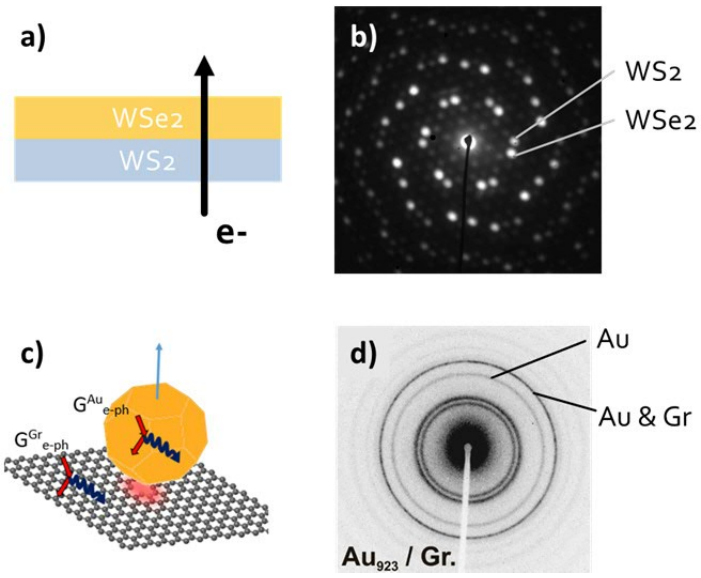


***Figure 4: Investigation of nano–scale energy flow in hetero–structures with FED.*** *a&b) FED reveals the phonon population dynamics in the individual compounds of a 2D-2D multilayer heterostructure through the time-dependent changes of the respective sub-lattice peaks shown in b). c&d) The photo-induced lattice dynamics of size-selected $Au_{923}$ nanoclusters are investigated for different support films. See poster PC 25.*

the same clusters on metallic, light-absorbing substrates (few-layer graphite or amorphous carbon) and on transparent silicon nitride films. The initial energy distribution as well as the resulting energy flow differ significantly for both scenarios, and we quantify the interfacial Kapitza conductance from the time-resolved data. Most importantly, we observe ultrafast surface disordering of the Au clusters induced by hot electron in the clusters. We describe this observation in terms of a modified electron friction model and discuss its potential implication for the enhanced photocatalytic activity of metal clusters [17].

## 2.5 Microscopy of Ultrafast Photocurrents in Nanoobjects: Towards Femtosecond Electron Holography

We developed femtosecond point-projection microscopy (fsPPM) as novel microscopic technique to visualize photoinduced charge migration in nanostructures, e.g., semiconductor nanowires [19]. This technique employs the emission of a single electron wave packet from metal nanotips by few fs laser pulses and visualizes time-dependent changes in the electric field distribution in the vicinity of a free-standing nanostructure. The temporal resolution is

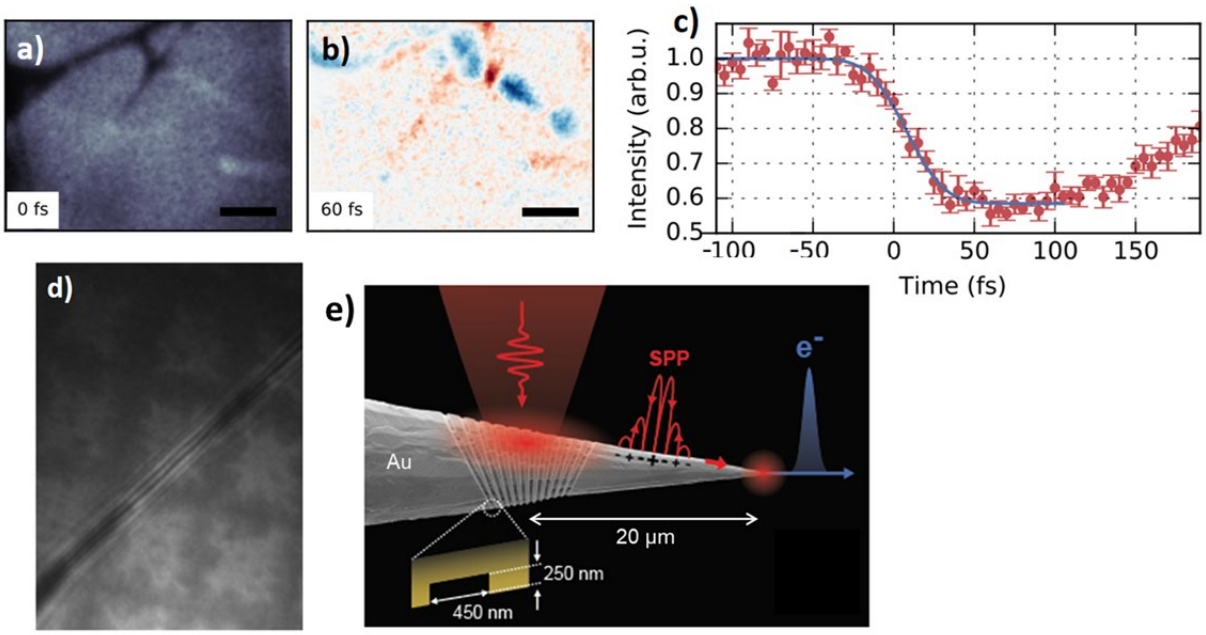


***Figure 5: Microscopy of photocurrents with femtosecond low-energy electron wave packets.*** *a) FsPPM image of 50 nm diameter Ag nanowires (bright) supported by a carbon mesh (black) at temporal overlap of optical pump and electron probe pulses. b) The transient space charge fields accompanying photoemission induced by the optical pulse is visible by the difference image taken at 60 fs delay and a pre-time zero image. c) The fastest temporal evolution of electron intensity shows dynamics shorter than the integral of Gaussian function with 40 fs FWHM. d) Hologram of a Ag nanowire recorded with in-line geometry. e) Illustration of non-local emission of sub-10 fs electron wave packets by propagating surface plasmon polaritons (SPP) from the apex of a gold tip* [18]. *See poster PC 24.*

below 40 fs, as demonstrated by the measuring the space charge fields accompanying photoemission from Ag nanowires, see Fig. 5a-c. To advance this technique further in terms of spatial and temporal resolution, in collaboration with the group of Markus Raschke (Univ. of Colorado) we demonstrated the non-local photoemission of electrons from the apex induced by a surface-plasmon polariton (SPP) generated ~20 μm away by illumination of a chirped grating [18], see Fig. 5d. The SPP duration at the apex is below 8 fs, resulting in 5 fs short single-electron wave packets emitted through multiphoton emission. In the future, we intend to utilize this plasmon-triggered electron point-source to develop femtosecond low-energy in-line holography. Our experimental setup is conceptually identical to the electron holography approach developed by the Fink group at the University Zurich, which recently has been demonstrated to be capable of imaging single molecules [20] or single charges [21]. The mechanical stability of our setup has been sufficiently improved to record holograms from metal nanowires, see Fig. 5d. In the future, we intend to utilize holographic recording in time-resolved experiments.

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## 3. Current cooperation partners

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Richard Palmer, Nanoscale Physics Research Laboratory, University of Birmingham, UK.

Valerio Pruneri, ICFO Barcelona, Spain.

Markus Raschke, Nano-Optics Group, University of Colorado, USA.

Angel Rubio and Hannes Hübener, Theory Department, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg.

Jan Vorberger, Helmholtz-Zentrum Dresden-Rossendorf, Germany.

Simon Wall, Ultrafast Optical Dynamics of Solids, ICFO Barcelona, Spain.

## 4. Publications (August 2015 - July 2017)

*L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio, and R. Ernstorfer*: A Momentum-Resolved View on Electron-Phonon Coupling in Multilayer $WSe_2$. Phys. Rev. Lett. **119**, 036803 (2017). Open access: arXiv:1703.03496.

*L. Waldecker, T. Vasileiadis, R. Bertoni, and R. Ernstorfer; T. Zier, F.H. Valencia, M.E. Garcia, and E.S. Zijlstra*: Coherent and incoherent structural dynamics in laser-excited antimony. Phys. Rev. B **95**, 54302 (2017). Open access: arXiv:1608.03486.

*R. Bertoni, C.W. Nicholson, L. Waldecker, H. Hübener, C. Monney, U. De Giovannini, M. Puppin, M. Hoesch, E. Springate, R.T. Chapman, C. Cacho, M. Wolf, A. Rubio, and R. Ernstorfer*: Generation and evolution of spin-, valley- and layer-polarized excited carriers in inversion-symmetric $WSe_2$. Phys. Rev. Lett. **117**, 277201 (2016). Open access: arXiv:1606.03218.

*C. Monney, M. Puppin, C.W. Nicholson, M. Hoesch, R.T. Chapman, E. Springate, H. Berger, A. Magrez, C. Cacho, R. Ernstorfer, and M. Wolf*: Revealing the role of electrons and phonons in the ultrafast recovery of charge density wave correlations in 1T-$TiSe_2$. Phys. Rev. B **94**, 165165 (2016). Open access: arXiv:1609.08993.

*T. Paasch-Colberg, S.Y. Kruchinin, Ö. Sağlam, S. Kapser, S. Cabrini, S. Mühlbrandt, J. Reichert, J.V. Barth, R. Ernstorfer, R. Kienberger, V.S. Yakovlev, N. Karpowicz, and A. Schiffrin*: Sub-cycle optical control of current in a semiconductor: from multiphoton to tunneling regime. Optica **3**, 1358 (2016).

*M. Müller, V. Kravtsov, A. Paarmann, M.B. Raschke, and R. Ernstorfer*: Nanofocused plasmon-driven sub-10 fs electron point source. ACS Photonics **3**, 611 (2016). Open access: arXiv:1512.07037.

*L. Waldecker, R. Bertoni, and R. Ernstorfer; J. Vorberger*: Electron-Phonon Coupling and Energy Flow in a Simple Metal beyond the Two-Temperature Approximation. Phys. Rev. X **6**, 021003 (2016).

*L. Waldecker, T.A. Miller, M. Rude, R. Bertoni, J. Osmond, V. Pruneri, R. Simpson, R. Ernstorfer, and S. Wall*: Decoupled optical response and structural transition in phase change materials. Nature Materials **14**, 991 (2015). Open access: arXiv:1412.0901.

**Doctoral Thesis**

*M. Puppin*: Time- and angle-resolved photoemission spectroscopy on bidimensional semiconductors with a 500 kHz extreme ultraviolet light source. FU Berlin, 2017.

*M. Müller*: Femtosecond low-energy electron imaging and diffraction using nanotip photoemitters. FU Berlin, 2016.

*L. Waldecker*: Electron-lattice interactions and ultrafast structural dynamics of solids. FU Berlin, 2015.

**Master's Thesis**

*D. Zahn*: Structural dynamics of transition metal dichalcogenide heterostructures studied by ultrafast high-energy electron diffraction, FU Berlin, 2017.

*J. Feldl*: A 500 kHz high harmonics generation XUV light source for photoelectron spectroscopy, LMU München, 2016.

**Bachelor Thesis**

*J. Malter*: Characterization of a nanotip electron source for femtosecond point-projection microscopy, FU Berlin, 2017.

## 5. Invited Talks (August 2015 - July 2017)

- Ernstorfer, R.: *Nonthermal structural dynamics probed by momentum-resolved femtosecond electron diffraction*, ARD WORKSHOP, DESY, Zeuthen, Germany, July 2017.
- Ernstorfer, R.: Accessing microscopic coupling in solids with momentum-resolving ultrafast techniques, Quantum Optics Seminar, University Kaiserslautern, Germany, June 2017.
- Ernstorfer, R.: Momentum-Resolved View on Electrons, Phonons and Their Coupling in $WSe_2$. Talk presented at the Ultrafast Surface Dynamics 10, Inzell, Germany, June 2017.
- Ernstorfer, R.: Momentum-Resolved View on Electrons, Phonons and Their Coupling in $WSe_2$ Through Ultrafast Techniques. Talk presented at the Workshop on Spectroscopy and Dynamics of Photoinduced Electronic Excitations, ICTP, Trieste, Italy, May 2017.
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- Ernstorfer, R.: *Electronic and Structural Dynamics in Simple Metals, Phase Change Materials and Transition Metal Dichalcogenides*. Talk presented at SIMES Seminar, Stanford Institute for Materials & Energy Sciences, SLAC, Stanford University. Stanford, CA, USA. 2016-02-16.
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- Ernstorfer, R.: *Photocurrents and Structural Dynamics in Nanomaterials Probed by Femtosecond Electron Pulses*. Talk presented at 4th International Workshop on Ultrafast Nanooptics (UNO-4). Bad Dürkheim, Germany. 2015-10-18 - 2015-10-22.
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## Max Planck Research Group for Electron Dynamiχ: Transient Functionality at Interfaces

**Head: Julia Stähler**
*(maternity leave: 11/2016-08/2017)*

### Group members

**Current:**

| | |
|---|---|
| Stefano Calati | (*PhD student*) |
| Angelika Demling | (*PhD student*) |
| Lukas Gierster | (*PhD student*) |
| Sarah B. King | (*Postdoc, Humboldt Fellow*) |
| Selene Mor | (*PhD student*) |
| Boubacar Tanda Bonkano | (*PhD student*) |
| Sesha Vempati | (*Postdoc*) |

**Former:**

| | |
|---|---|
| Katharina Broch | (*Postdoc, until 12/2016*) |
| Lea Bogner | (*PhD student, until 12/2015*) |
| Jan-Christoph Deinert | (*PhD student, until 01/2016*) |
| Laura Foglia | (*PhD student, until 12/2015*) |
| Marc Herzog | (*Postdoc, until 01/2016*) |
| Ines Mayan | (*Bachelor student, until 12/2015*) |
| Clemens Richter | (*scientific assistant, until 01/2016*) |

### Research Projects Funded from Outside Resources

- DFG 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"*** (photoinduced electron transfer, two-photon photoemission spectroscopy of electronic states, from 07/2015).

## 1. Scientific Scope

The current technological progress in seemingly different fields (e.g. light harvesting, opto-electronics, data processing, energy storage, catalysis…) relies on non-equilibrium phenomena that occur at the interfaces of different materials and on electronic time and energy scales, i.e. femtoseconds (fs) and electronvolts (eV). Examples span from ultrafast charge transfer processes initiating chemical reactions at electrochemical interfaces to quasiparticle interactions in strongly correlated systems triggering, for instance, insulator-to-metal phase transitions.

The group aims at the next step towards exploitation of ultrafast science beyond the research on non-equilibrium dynamics of matter by *utilizing* the transient properties of photoexcited systems. While the established methods for the investigation of non-equilibrium dynamics provide valuable insight into the excited state properties of matter, this new approach will *make use* of these properties to manipulate the functionality of materials and material combinations on the ultrafast timescale.

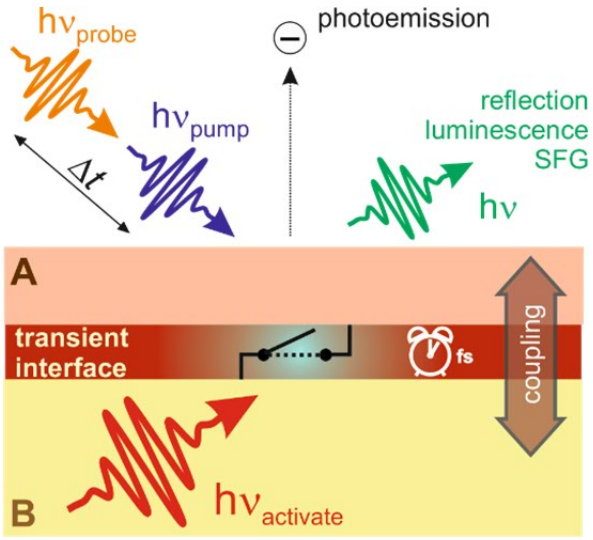


***Figure 1: Concept of transient functionality at interfaces (TRAFIC).*** *The functionality of the interface between material A and B is modified by an activation pulse $h\nu_{activate}$. The time-dependent properties of this transient interface are monitored by a complementary set of femtosecond time-resolved spectroscopies.*

"Conventional" ultrafast spectroscopy is often performed in a pump-probe scheme, where a first laser pulse ($h\nu_{pump}$) is used to bring the sample into non-equilibrium conditions and a second, time-delayed pulse ($h\nu_{probe}$) to probe the transient properties of the system by, for instance, photoelectron, linear or non-linear optical spectroscopy (Figure 1, top). We plan to use an additional, third laser pulse ($h\nu_{activate}$) in order to modify the properties and, thus, the functionality of the interface on an ultrafast timescales. This transient functionality at interfaces (TRAFIC) will be achieved in multiple ways: (i) modification of charge/exciton

density, (ii) chemical activation of adsorbed molecules, (iii) time-dependent changes of the electronic structure.

Since the last Fachbeirat evaluation, we have extended our complementary set of "conventional" state-of-the-art ultrafast spectroscopies. It now comprises: time- and angle-resolved (two-photon) photoelectron spectroscopy (tr-ARPES / tr- & ar-2PPE), transient reflection/transmission and time-resolved electronic sum frequency generation (tr-eSFG) based on a white light supercontinuum (WLC), time-resolved photoluminescence (tr-PL, single photon counting & optical down conversion) enabling the investigation of bulk materials, surfaces, and interfaces under ultrahigh vacuum to ambient conditions. It should be noted that we succeeded in setting up the first fs-time-resolved eSFG setup based on a WLC that is *applicable to solid state samples*. [1] These techniques were used to explore several different model systems ranging from electrochemical interfaces to strongly correlated low-dimensional materials as outlined in the following. These research highlights set the stage for TRAFIC once the third, strong activation laser pulse ($h\nu_{activate}$) can be added. A new powerful laser system with tunable repetition rate was installed in May 2017, but still requires further service to achieve its specifications.

## 2. Development of the Group

The Electron Dynamiχ Group has undergone several important changes in the last two years. Firstly, three PhD students and one long-standing postdoc left the group around the turn of the year 2015/16 and could only be replaced in late 2016 after an intensive search and interview time for suitable candidates. Secondly, Julia Stähler's maternity leave unexpectedly started one month earlier than specified by law (health condition) in November 2016 and ended as planned in August 2017. Lastly, the move of the laboratory to the new building in spring 2016 extended the experimental space for the group, but also, naturally, interrupted experiments. Although generally efficient and successful, the new lab is still in its infancy (e.g. water leakage, unexpected power shut-downs). The above challenges were faced and conquered with pragmatic, optimistic, and diligent attitude by all group members: The new PhD students have learned the ropes, the experiments mostly are up and running. As soon as child care is available, Julia Stähler will be able to return to a full time schedule.

## 3. Research Activities

### 3.1 Interfacial Electron Dynamics in Polar Solvents

Excess electrons in polar solvent environments play a crucial role in various different fields in physics, chemistry, and biology. Through the interaction with the molecular dipole moment, polaronic states form, in which the electron is stabilized (solvated) in a molecular cavity. In the vicinity of a metal surface, such states are particularly relevant for electrochemical reactions. We use tr- & ar-2PPE to investigate the formation, lifetime, and decay of solvated electrons and especially focus on their reactivity. In these experiments, as illustrated in figure 2(A), a first femtosecond (fs) laser pulse ($h\nu_{pump}$) injects excess electrons from the metal and the second, time-delayed laser pulse ($h\nu_{probe}$) is used to photoionize the sample. The ejected photoelectrons are then analyzed with regard to their kinetic energy and momentum parallel to the surface and, thus, provide information about the transient population and degree of localization of normally unoccupied states. One example of the multifaceted dynamics occurs in DMSO layers adsorbed on Cu(111) (figure 2(B)). Very similar to previous studies on amorphous solid water (ASW), alcohol, and ammonia layers on various metal surfaces [2-12], the excess electrons initially populate a delocalized state and increasingly localize with time, as indicated by the flattening dispersion depicted in the bottom panel. At the same time, the electronic state $e_S$ shifts down to lower energies due to the rearrangement of the surrounding polar molecules. We find the evolution of this interfacial electronic state to be localized within the first two monolayers of DMSO and, moreover, show that it persists for even larger coverages. [13]

Recently, we could show that a long-lived state with a lifetime of several seconds exists at the vacuum interface of ASW. As illustrated in figure 2(C), the enormous lifetime of these trapped electrons even enables water splitting: under illumination with UV light, the signature of the trapped electrons $e_T$ vanishes in a similar fashion as the work function $\Phi$ rises (bottom panel), indicating that an anionic species is formed that suppresses further electron trapping at the interface. The unusually long excited state lifetime in combination with the large binding energy gain upon electron trapping enables the *dielectron hydrogen evolution reaction*, which exhibits large activation barriers. [12] In very recent experiments, we were able to observe a similarly long-lived state at the DMSO/vacuum interface that shows clear indications of chemical reactivity with molecular oxygen. [14]

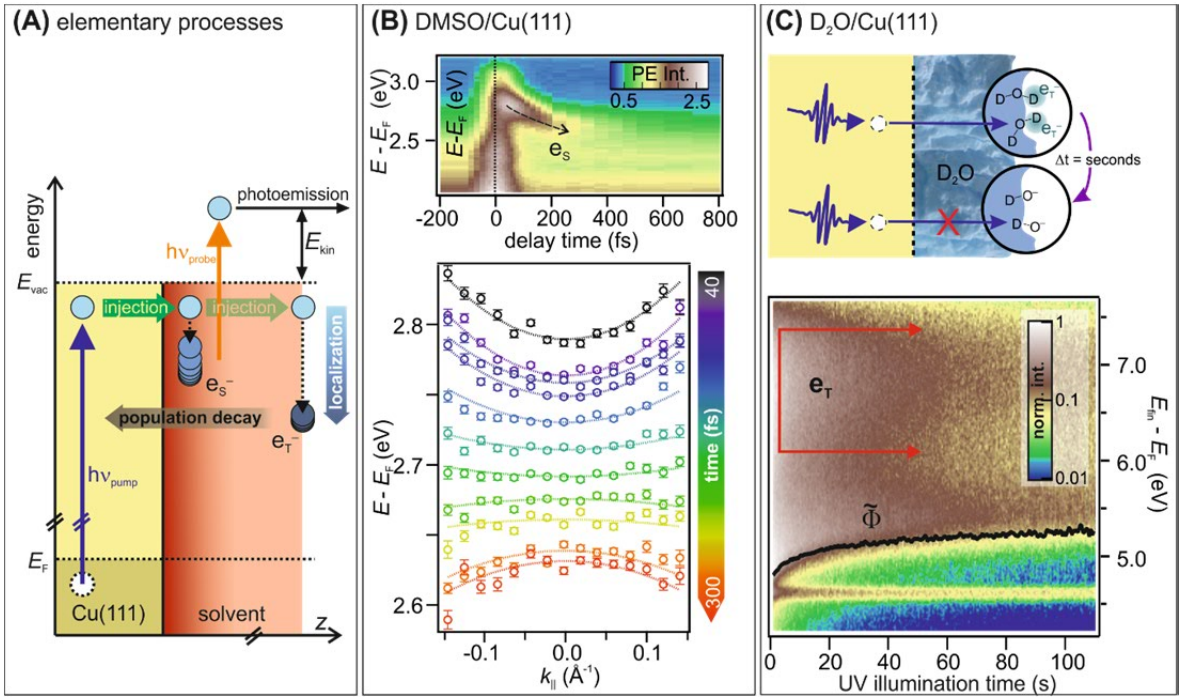


***Figure 2: Electron solvation, decay, and reactivity near solvent/metal interfaces.*** *(A) Experimental scheme for tr-2PPE and elementary processes: $h\nu_{pump}$ optically excites the metal and thereby injects electrons into the solvent layers. Two different types of electronic states are formed: Near the metal, the excess electron population decays on femtosecond timescales while it survives 14 orders of magnitudes longer at the vacuum interface. The dynamics are probed by a second laser pulse after an adjustable time delay: The transient electron population is excited above the vacuum level and detected using a hemispherical electron analyzer. (B) Ultrafast polaron formation near the DMSO/Cu(111) interface probed by 2PPE: Intensity in false colors as a function of time and intermediate state energy with respect to the Fermi level $E_F$ (top). Angle-resolved measurements show the time-dependent change of the dispersion, indicating increasing electron localization (bottom). (C) Long-lived electrons at the ice-vacuum interface react with $D_2O$ to form $OD^-$ (top), a reaction that causes a work function rise and reduction of $e_T$ intensity as a function of UV exposure (bottom).*

## 3.2 Ultrafast Charge Transfer-Induced $CO_2$ Activation on ZnO(10-10)

The man-made excess of $CO_2$ in the atmosphere is undoubtedly one important cause of global warming. Unfortunately, $CO_2$ also is energetically very stable and needs to be activated before it can be chemically transformed to, for instance, useful hydrocarbons (solar fuels). Catalytic surfaces can help to enhance reaction rates. On ZnO(10-10), $CO_2$ adsorbs in a tridentate (figure 3B) form [15] and both activated and non-activated species are observed. [16] We find a substantial work function increase of 1.2 eV for the full $CO_2$ monolayer up to 5.7 eV, which can be explained by its partial reduction upon adsorption and the corresponding dipole moment. This charge redistribution at the surface leads to surface band bending, causing surface photovoltage (SPV) effects when the sample is optically excited as illustrated in figure 3A.

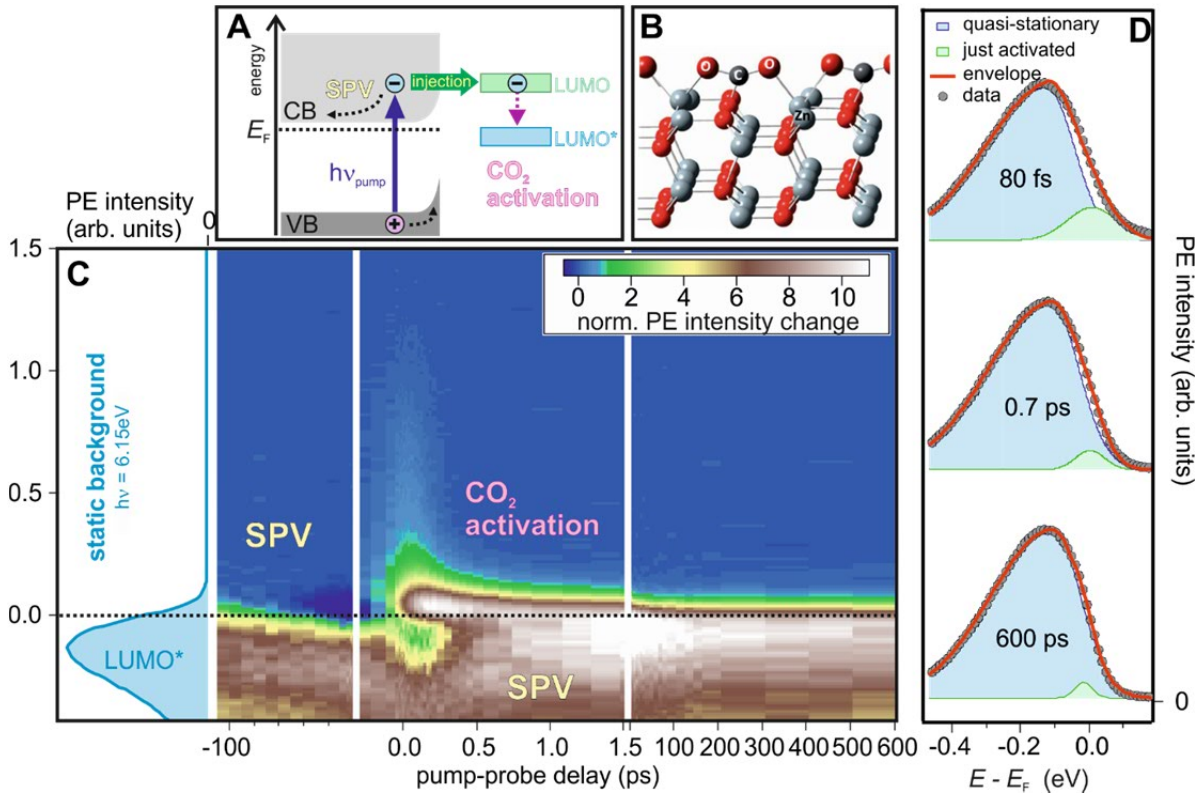


***Figure 3: Ultrafast dynamics at the $CO_2$/ZnO(10-10) interface.*** *(A) Across band gap excitation causes surface photovoltage and $CO_2$ activation dynamics. (B) Adsorption motif modified from [15] (C) Photoinduced changes to the static (left) photoelectron spectra. The $CO_2$ activation is evidenced by the transient electron population above $E_F$, shifting downwards within 1.4 ps. (D) Data analysis: The asymmetric Gaussian signature of activated $CO_2$ molecules (blue) shifts in energy due to surface photovoltage effects. The transiently populated LUMO of newly activated molecules (green) lies at higher energies and relaxes as time proceeds.*

Static photoemission (figure 3C, left) shows a (partially) occupied state just below the Fermi energy $E_F$, which we assign to the formally LUMO of the gas phase molecules, termed LUMO* for the activated, adsorbed species. The false color plots in figure 3C show the photoinduced change of photoelectron intensity after subtraction of the static background as a function of pump-probe time delay. The dynamics can be explained by (i) a shifting of LUMO* at positive and negative delays due to SPV similar to what has been recently observed for GaAs(110) [17] and (ii) a transient population of the LUMO of non-activated $CO_2$ molecules as illustrated in figure 3A. Data analysis (figure 3D) yields a charge transfer-induced activation time of 1.4(2) ps. [18] This work, which was initiated through a collaboration with Elias Frei and Robert Schlögl from the AC department, thus demonstrates the possibility of $CO_2$ activation through photoinduced charge transfer to the molecules at a catalyst surface. This is the proof-of-principle of monitoring photo-electrochemical reactions in real time.

### 3.3 Charge Carrier & Exciton Dynamics in ZnO

Beyond catalysis, ZnO is also a very promising material in the field of optoelectronics, in particular in combination with organic materials to form inorganic/organic hybrid systems. Unfortunately, ZnO also is a remarkably difficult material, which is highlighted by decades of research and partially conflicting results not only with regard to ultrafast dynamics (see, e.g. [19-21]). In order to achieve a complementary understanding, the group used the entire canon of experimental techniques to investigate a defined set of ZnO samples to ensure comparability of the results. We started with a thorough analysis of the electron and exciton dynamics at the ZnO(10-10) and ZnO(000-1) surfaces [22-25] in previous work using tr-ARPES and 2PPE, showing that these expose subsurface-bound excitons that form within 20-40 fs and decay in 100 ps. This report, however, highlights the most recent results on the carrier and exciton dynamics in bulk ZnO. [26]

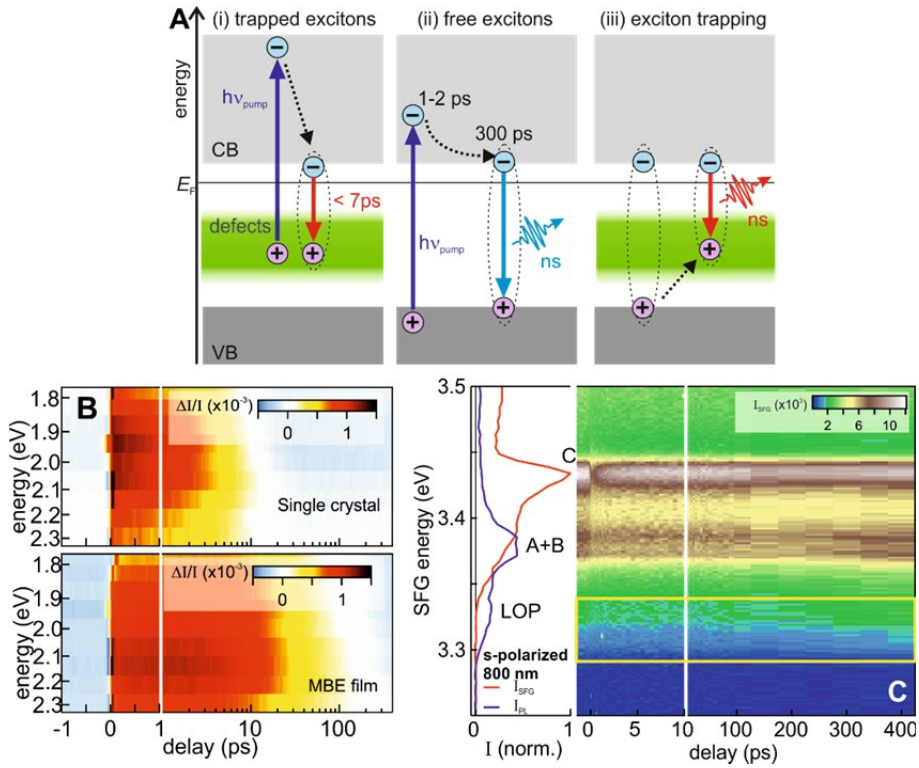


***Figure 4: Exciton dynamics in bulk ZnO.*** *(A) Illustration of the observed elementary processes: (i) Photoexcitation from in-gap defect states is followed by recombination within only 7 ps. (ii) Across band gap excitation is followed by carrier cooling and exciton formation within 300 ps. (iii) Free excitons with ns lifetimes are trapped at defect sites, leading to ns defect emission despite the 7 ps recombination rate. (B) Transient transmission using a WLC clearly shows faster dynamics in the single crystal sample compared to the MBE (molecular beam epitaxy) film with lower defect density. (C) tr-eSFG displays fast dynamics near the band edge due to carrier relaxation. The slow component (yellow box) reflects the formation dynamics of the free exciton.*

By femtosecond time-resolved transmission experiments using a WLC (figure 4B), we found that the optical response is dominated by depletion of the in-gap defect band as illustrated in figure 4A(i), which decays within 7 ps after photoexcitation. Interestingly, and seemingly in

contrast, the corresponding (defect) light emission continues for nanoseconds as evidenced by tr-PL (not shown). In addition to these defect-related dynamics, across band gap excitation was observed, yielding hot carrier relaxation times at the band edges on the order of a few ps (figure 4A(ii)). These results were confirmed by tr-eSFG, which is bulk-sensitive in non-centrosymmetric ZnO (figure 4C). Beyond the good agreement between linear and non-linear optical spectroscopy, the eSFG experiments furthermore show, in agreement with previous work, [27] that the bulk exciton forms within 300 ps. Its nanosecond lifetime is reflected in complementary time-resolved photoluminescence[1] experiments, strongly suggesting that free excitons are trapped at defect sites as illustrated in figure 4A(iii) and explaining the apparent discrepancy between optical and PL time constants. This first comprehensive study of the ultrafast carrier and exciton dynamics in ZnO, and at its surfaces, provides unprecedented insight into the elementary processes occurring upon photoexcitation of this material and demonstrate the severe impact of defects on the lifetimes and relaxation pathways. [26]

### 3.4 Ultrafast Phenomena in Layered Materials

The technological relevance of low-dimensional materials was evident already before the ascent of graphene. The miniaturization and optimization of layered functional elements (solar cells, transistors, LEDs etc.) requires advanced control and understanding of the involved materials. As any functionality involves non-equilibrium quasiparticle dynamics, ultrafast spectroscopy is a perfect tool to achieve these goals.

$Ta_2NiSe_5$ is a layered, orthorhombic, quasi-1D small band gap semiconductor (Figure 5A) that undergoes a transition to a monoclinic phase upon cooling across $T_C$ = 328 K. The low temperature phase is, moreover, characterized by a wider band gap, which is why the transition is termed semiconductor-to-insulator transition. Due to the low dielectric constant of $Ta_2NiSe_5$ and the anomalous flattening and broadening of the valence band (VB), the low temperature phase of $Ta_2NiSe_5$ is suspected to be an excitonic insulating phase. [28-32] In an excitonic insulator the exciton binding energy $E_B$ exceeds the gap size $E_G$ such that spontaneous exciton formation occurs, followed by exciton (boson) condensation, leading to a wider band gap $E_G + 2\Delta$ (figure 5B).

We investigated the transient changes to the electronic band structure and the ultrafast electron dynamics in $Ta_2NiSe_5$ using tr-ARPES in different parts of the surface Brioullin zone. As shown in figure 5D, photoexcitation below the critical fluence $F_C$ = 0.2 mJ/cm² leads to a depletion and shifting of the

[1] In cooperation with Sylke Blumstengel, Humboldt University Berlin.

VBs towards $E_F$, i.e. a shrinking of the band gap. This band gap renormalization is a common effect in semiconductors and is due to the photoinduced change of the screening of the Coulomb interaction. However, upon crossing the threshold fluence, we observe a band gap *widening* through a downward shift of the topmost VB at Γ (red, figure 5D), while the other bands continue to shift upwards (green, yellow). This exotic behavior can be explained by the excitonic insulating phase through Hartree-Fock calculations[2] and demonstrates the possibility to control the band gap of materials on the ultrafast timescale. [33]

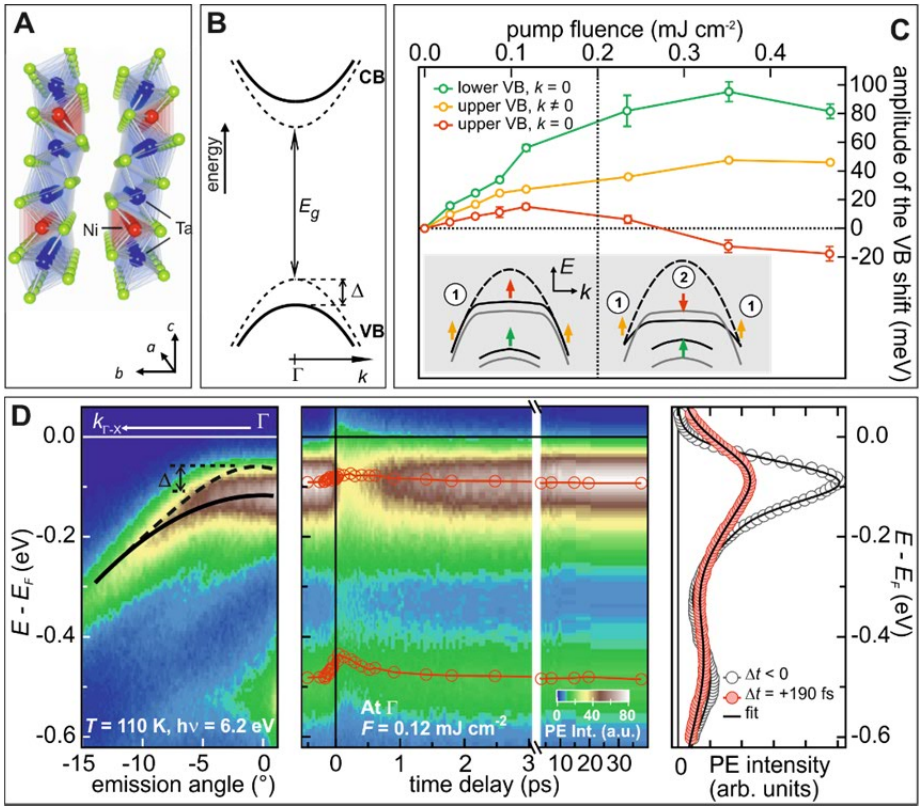


***Figure 5: Ultrafast electronic band gap control in $Ta_2NiSe_5$.*** *(A) Material crystal [28] and (B) electronic structure. (C) Fluence dependence of VB shifts. Upper valence band region of $Ta_2NiSe_5$ at low temperature as observed by ARPES (left), pump-induced dynamics at Γ for below threshold excitation (center), photoelectron spectra before and after excitation (right).*

Complementary to strongly correlated, low-dimensional materials such as $Ta_2NiSe_5$, thin, insulating oxide films are useful to electronically decouple materials from each other or to chemically protect electrodes. The group has, therefore, started to investigate the $SiO_2$ bilayer in collaboration with Hajo Freund and Thomas Schmidt's group in the CP department. The silica bilayer is found to form a specific, chemically inert structure when grown on Ru(0001) [34-36] and UPS experiments at SMART [37] already gave insights into the occupied

[2] In cooperation with Martin Eckstein (Univ. Erlangen-Nürnberg), Denis Golež and Philipp Werner (Univ. Fribourg).

electronic structure. In order to elucidate the properties of the (unoccupied) conduction band and the interplay with the significant image potential of the metal substrate, we use time- and angle-resolved 2PPE. As expected, we find quantum well-like states in the region of the $SiO_2$ conduction band with energy separations, lifetimes, and dispersions that clearly suggest a strong impact of the image potential. In forthcoming work, we will test in how far these states can serve as a mediator between adsorbed species and the Ru(0001) in terms of electronic coupling.

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## 4. Current cooperation partners

Sylke Blumstengel, Department of Physics, Humboldt University Berlin, Germany

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Karsten Reuter, Department of Chemistry, Technical University Munich, Germany

Andres Santander, University Paris-Sud, France

Philipp Werner, Department of Physics, University of Fribourg, Switzerland

## 5. Publications (August 2015 – August 2017)

*Foglia, L., L. Bogner, M. Wolf and J. Stähler*: Localization-dependent charge separation efficiency at an organic/inorganic hybrid interface. Chemical Physics Letters **646**, 25–30 (2016).

*Foglia, L., M. Wolf and J. Stähler*: Ultrafast dynamics in solids probed by femtosecond time-resolved broadband electronic sum frequency generation. Applied Physics Letters **109** (20), 202106 (2016).

*King, S.B., D. Wegkamp, C. Richter, M. Wolf and J. Stähler*: Trapped Electrons at the Amorphous Solid Water/Vacuum Interface as Possible Reactants in a Water Splitting Reaction. The Journal of Physical Chemistry C **121** (13), 7379–7386 (2017).

*Stähler, J. and P. Rinke*: Global and local aspects of the surface potential landscape for energy level alignment at organic-ZnO interfaces. Chemical Physics **485-486**, 149–165 (2017).

*Mor, S., M. Herzog, D. Golež, P. Werner, M. Eckstein, N. Katayama, M. Nohara, H. Takagi, T. Mizokawa, C. Monney, and J. Stähler*: Ultrafast electronic band gap control in an excitonic insulator. Physical Review Letters **119** (8), 086401 (2017).

*Wegkamp, D. and J. Stähler:* Ultrafast dynamics during the photoinduced phase transition in $VO_2$. Progress in Surface Science **90** (4), 464–502 (2015).

### Doctoral Thesis

*Bogner, L.*: Ultrafast Relaxation Dynamics after Optical Excitation of Hybrid Inorganic/Organic Systems. Freie Universität Berlin 2015.

*Deinert, J.-C.*: Zinc Oxide Surfaces and Interfaces: Electronic Structure and Dynamics2017 of Excited States. Technische Universität Berlin 2016.

*Foglia, L.*: Ultrafast dynamics and energy loss channels at a hybrid organic inorganic interface. Technische Universität Berlin 2015.

### Bachelor Thesis

*Mayan, I.*: Charakterisierung amorpher Eisschichten auf der Cu(111)-Oberfläche mittels thermischer Desorptions- und Photoelektronenspektroskopie: Mittlere freie Weglänge niederenergetischer Elektronen in amorphem Eis. Universität Potsdam 2015.

## 6. Invited Talks (August 2015 - August 2017)

- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (19. Deutsche Physikerinnentagung, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (IV. Physical Institute (AG Claus Ropers), Georg-August-Universität Göttingen, Göttingen, Germany, Oct 2015).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (Institute Seminar, Institute of Solid State Physics, Graz University of Technology, Graz, Austria, Nov 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Colloquium, Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany, Dec 2015).
- Stähler, Julia: Exciting! Ultrafast Physical Chemistry at Interfaces after Light Absorption. (Special Seminar, Department of Chemistry, University of California, Berkeley, CA, USA, Dec 2015).
- Stähler, Julia: Real Time Measurement of the Vertical Binding Energy during the Birth and Lifetime of a Solvated Electron. (The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem), Honolulu, HI, USA, Dec 2015).
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (Ultrafast Phenomena in Cooperative Systems, Gordon Research Conference, Barga, Italy, Jan 2016).
- Stähler, Julia: Many Body Effects in Ultrafast Spectroscopy: Polarons, Excitons & Correlated Electrons. (Colloquium, Department of Physics, Freie Universität Berlin, Berlin, Germany, Jan 2016).
- Stähler, Julia: Ultrafast Dynamics of Many Body Effects in Solids and at Interfaces: Polarons, Excitons & Correlated Electrons. (Prize Talk, Gaede Prize Symposium, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, Germany, Mar 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (Colloquium, Department of Chemistry, Technical University of Munich, Munich, Germany, Apr 2016).
- Stähler, Julia: Charge Carrier and Exciton Dynamics at Hybrid Inorganic/Organic Interfaces. (International conference, Internal Interfaces 2016, Marburg, Germany, May 2016).
- Stähler, Julia: Exciting! Ultrafast Dynamics in ZnO, at Its Surfaces, and Interfaces with Organic Molecules after Light Absorption. (SFB 951 Colloquium, Humboldt-Universität zu Berlin, Berlin, Germany, Jun 2016).
- Stähler, Julia: Understanding Ultrafast Exciton Dynamics in ZnO and at Its Surfaces: Potential and Hazard of Impurities. (Gruppenseminar, Institut für Experimentelle Physik II (Marius Grundmann), Universität Leipzig, Leipzig, Germany, Jun 2016).
- Stähler, Julia: Photoinduced Transient Band Gap Enhancement in the Excitonic Insulator Ta2NiSe5. (International conference on dynamic pathways in multidimensional landscapes, Berlin, Germany, Sep 2016).

- Stähler, Julia: Exciting! Ultrafast Dynamics in Condensed Matter after Light Absorption. (Award Ceremony of the Edith Flanigen Award 2016, CRC 1109, Berlin, Germany, Oct 2016).

**Cancelled/declined due to maternity leave:**

- Stähler, Julia: Ultrafast Dynamics at Inorganic/Organic Hybrid Interfaces. (Molecular Interactions & Dynamics, Gordon Research Conference (GRC), Easton, MA, USA, Jul 2016
- Stähler, Julia: Electronic Phase Transitions in Strongly Correlated Systems: When Does the Band Gap Collapse? (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Stähler, Julia: DIET15 (15$^{th}$ conference on Desorption Induced by Electronic Transitions), Shanghai, China, Oct 2017
- Stähler, Julia: Chemistry Colloquium, Johannes Kepler University, Linz, Austria, Oct 2017
- Stähler, Julia: CMD26 (26$^{th}$ EPS Condensed Matter Division Conference), Groningen, Netherlands, Nov 2016
- Stähler, Julia: Kick-off meeting Sfb 1242, Bad Honnef, Germany, Nov 2016
- Stähler, Julia: Department Seminar, Cornell University, Dept. of Chemistry and Chemical Biology, Ithaca, NY, USA, Nov 2016
- Stähler, Julia: COST general meeting, Action CM1401 (Chem. & Mol. Sci. & Techn.) Non-thermal desorption from cold surfaces Workshop, Faro, Portugal, Jan 2017
- Stähler, Julia: March Meeting of the American Physics Society, New Orleans, LA, USA, Mar 2017
- Stähler, Julia: ECSCD-13 (European Conference on Surface Crystallography and Dynamics), San Sebastian, Spain, Jun 2017
- Stähler, Julia: ICFSI 16 (International Conference on the Formation of Semiconductor Interfaces), Hanover, Germany, Jul 2017
- Stähler, Julia: RACI (Royal Australian Chemical Institute) National Centenary Conference, Melbourne, Australia, Jul 2017
- Stähler, Julia: Summer Workshop of Theoretical Chemistry at TU Munich "Frontiers of Multi-scale Modelling in Materials, Energy & Catalysis III", Germany, Jul 2017
- Stähler, Julia: E-MRS Fall Meeting, Warsaw, Poland, Sep 2017
- Stähler, Julia: FEMTO13 (13th Femtochemistry Conference - Frontiers of ultrafast phenomena in Chemistry, Biology, and Physics) Cancun, Mexico, Aug 2017
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator Ta2NiSe5. (Department of Physics (AG Martin Weinelt), Freie Universität Berlin, Berlin, Germany, Apr 2016).
- Mor, Selene: Transient Band Gap Enhancement by Photoexcitation of the Excitonic Insulator Ta2NiSe5. (Seminar, Department of Mathematics and Physics (AG Claudio Giannetti), Università Cattolica del Sacro Cuore, Brescia, Italy, May 2016).

- Mor, Selene: Ultrafast Electronic Band Gap Control in an Excitonic Insulator. (IMPACT 2016, International Research School: Electronic States and Phases Induced by Electric or Optical Impacts, Cargèse, France, Aug 2016).
- Vempati, Sesha Pavan Kumar: Frontier Molecular Orbitals of CO2 on ZnO Surfaces: Time-Resolved Photoelectron Spectroscopy. (Seminar, Indian Institute of Science Education and Research Mohali, Mohali, India, Feb 2017).
- Vempati, Sesha Pavan Kumar: Hybrid Systems for Optoelectronic Applications and Photoelectron Spectroscopy. (Seminar, Material Research Center, Indian Institute of Science, Bengaluru, India, Mar 2017).