FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Report to the Fachbeirat
Department of Physical Chemistry

2019

Department of Physical Chemistry
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Recent Development of the Department of Physical Chemistry

General remarks

Since early 2018 the Department of Physical Chemistry became fully operational in its new building, which provides a very high quality laboratory infrastructure and an excellent working environment with close interaction between all members of the department. In this stimulating atmosphere we have sharpened our research profile with a stronger focus on light-matter interaction and elementary processes. This development is supported by the implementation of new techniques and instrumentation in the various research groups headed by younger scientists. We have celebrated the opening of the new building in an inauguration ceremony on March, 21st 2018 including scientific lectures, speeches, lab tours and an opening party (see Fig. 1).

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

- *Dr. Yujin Tong* has started in January 2018 a new research group on "*Non-linear Spectro-electrochemistry*" to investigate electrochemical reactions and molecular species at electrified interfaces by vibrational sum-frequency generation spectroscopy.

- *Dr. Matthias Koch* has started in July 2018 a new research group entitled "*Quantum Transport and Nanoelectronics*" and develops experiments for electronic transport in nanostructures on a silicon platform combining top-down with bottom-up techniques in low temperature scanning microscopy.

- *Prof. Kramer Campen* received an offer for a W3 professorship in physics at the University of Duisburg-Essen and has started on this position in July 2019. He will move his group to Duisburg early next year. Also *Dr. Yujin Tong* will take up a permanent scientist position in his group, but will continue in parallel with his research at the FHI and will pursue spectro-electrochemistry experiments at the FHI FEL exploiting the newly developed capabilities for MIR-Vis vibrational SFG spectroscopy.

- In December 2018 *Dr. Michael Zürch* assumed a W2 position to set up a new independent Max-Planck-Research-Group (MPRG) for attosecond time-resolved

X-ray absorption and diffraction experiments on solids. Soon later he received an offer for an assistant professorship from the University of California at Berkeley and started on this tenure track position in July 2019. He will finish the construction of an experimental chamber at FHI during a phase-out period and will setup his experiments in the new labs at Berkeley in 2020.

- Most recently *Dr. Julia Stähler* received an offer for a W3 professorship at the Humboldt University Berlin and will likely relocate her activities to the HU Chemistry Department in the next two years.

The Mechanical Workshops of the institute are associated with our department and are now headed by *Franck Kubitz*. Their service and high quality output is well received by all scientists. In the context of a necessary reconstruction of workshop building, we have developed a concept for future reorganization, which will incorporate the activities of the crystal lab and will enable improved workflow and machine infrastructure.

Figure 1: The inauguration ceremony for the new building of the Department of Physical Chemistry took place on March, 21st 2018 (front page of the invitation).

Promotion of younger scientists

Guidance and promotion of younger scientists in their career development is an important goal of our 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). During the last two years a remarkable number of younger scientists in the department received academic offers, awards, distinguished research grants or fellowships. This can be considered as an indicator demonstrating the success of the department in the promotion of younger scientists:

Kramer Campen (ERC consolidator grant 2018, W3 professorship, University of Duisburg-Essen, Dep. of Physics 2019), *Sarah King* (AvH fellowship 2018, assistant professorship with tenure track, University of Chicago, Dep. of Chemistry 2018), *Julia Stähler* (offer for W3 professorship, Humboldt University Berlin, Dep. of Chemistry 2019), *Michael Zürch* (Max Planck Research Group (MPRG) 2018, assistant professorship with tenure track, University of California at Berkeley, College of Chemistry), *Helene Seiler* (SNF postdoc mobility grant, Switzerland 2019), *Samuel Beaulieu (*Banting postdoctoral fellowship, Canada 2019), *Chris Nicholson* (Carl-Ramsauer-Award for excellent PhD thesis, Physical Society Berlin 2018), *Daniela Zahn* (Physics Study Award 2018, Physical Society Berlin 2018).

An important career development for advanced postdocs and junior group leaders is gaining experience with grant applications and becoming project leader with grants from, e.g., German Research Foundation (DFG), European Research Council (ERC), or Japanese Science and Technology Agency (JST). In particular, establishing an independent junior research group with substantial own funding is one major achievement and career step for younger scientists. The department has been very successful in this regard as currently six research groups receive such independent funding and are hosted by the department: ERC Group of *Kramer Campen,* ERC Group of *Ralph Ernstorfer,* ERC Group of *Tobias Kampfrath,* DFG Emmy Noether Group of *Laurenz Rettig,* Max Planck Research Group of *Julia Stähler,* and Max Planck Research Group of *Michael Zürch.* Four of these group leaders have recently been appointed as professors (or received offers). In addition, several group leaders are project leaders in DFG funded collaborative research centers (Sfb 951, Sfb 1109, TRR 227), the DFG research unit FOR 1700 or have received individual research grants funded by DFG, JST, or from the European Commission.

Research profile and structure

Our research focusses on the dynamics of elementary processes at surfaces, interfaces and in solids aiming at a microscopic understanding of the coupling between various degrees of freedom (electrons, spins and phonons/vibrations). The goal is to obtain mechanistic insights at an atomistic or molecular level into various dynamic phenomena like ultrafast phase transitions, excited state dynamics or molecular processes and (electro-)chemical reactions at interfaces. Our strategy is to address these problems from several sides using complementary approaches, in particular by the development and application of various time- or spatial-resolved spectroscopic techniques dedicated to the specific physical questions. Research in the department is performed by small teams with specific, complementary expertise, creating various synergies and exchange between the different groups.

The current research topics of the department consist of three pillars: (1) Ultrafast dynamics of elementary processes and phase transitions in solids with specific focus on the coupling between electrons, phonons and spins. These processes are probed on their relevant time scales by *time-resolved spectroscopy* using ultrashort laser pulses from THz to XUV and ultrafast electron diffraction (UED). (2) A rather recent development is our new focus on localized excitations and transport phenomena at the nanoscale. Here we employ *scanning probe microscopy* to investigate plasmonic excitations and light confinement and inelastic scattering in STM junctions as well as electronic transport. The increasing emphasis on spatial-temporal phenomena combining ultrafast lasers with local scanning probe techniques is nicely complemented by ultrafast diffraction methods like UED. (3) The third pillar addresses molecular structure of adsorbates, electro-chemical reactions and dynamical processes at interfaces and in (molecular) liquids. These are probed by *nonlinear optical techniques,* in particular IR-vis vibrational sum frequency generation and nonlinear THz spectroscopy. Based on these pillars the department currently supports the following groups:

Time-resolved Dynamics of Solids: Electrons, Phonons and Spins
- Dynamics of Correlated Materials (*Laurenz Rettig*)
- Structural & Electronic Surface Dynamics (*Ralph Ernstorfer)*
- Lattice Dynamics (*Alexander Paarmann*)
- Terahertz Physics (*Tobias Kampfrath*)

Localized Excitations and Transport
- Nanoscale Surface Chemistry (*Takashi Kumagai*)
- Ultrafast Scanning Probe Microscopy (*Melanie Müller*)
- Quantum Transport & Nanoelectronics (*Matthias Koch*)

Molecular Processes and their Dynamics
- Interfacial Molecular Spectroscopy (*Kramer Campen*)
- Nonlinear Spectro-Electrochemistry (*Yujin Tong*)
- THz Driven Molecular Dynamics (*Mohsen Sajadi*)

Max-Planck-Research Groups
- Electron Dynamics (*Julia Stähler)*
- Transient X-ray Spectroscopy & Diffraction (*Michael Zürch)*

This structure reflects a number of new research topics developed over the last few years, which are often linked with the development of new techniques and instrumentation together with the inauguration of new research groups. This includes: (1) Far-infrared nonlinear optical spectroscopy of solids and photonic structures of phonon polaritons) at the FHI FEL and development of laser synchronization at the FEL by *Alexander Paarmann*. (2) Spectro-electrochemistry of electrochemical interfaces employing vibrational SFG and dedictated sample cells by *Kramer Campen* and *Yujin Tong* (3) Generation of high field THz pulses to study THz driven molecular dynamics in liquids and confined environment by *Mohsen Sajadi*, (4) Light coupling into a custom designed low-temperature STM for atomic-scale optical spectroscopy and studies of plasmon-mediated physical and chemical processes in nanocavities by *Takashi Kumagai*. (5) Ultrafast THz scanning probe microscopy developed by *Melanie Müller* and (6) Electronic transport and scanning gate microscopy using nanoscale integrated circuits on silicon performed by *Matthias Koch*. As several senior group leaders will move onto academic positions in near future, the number of research groups will consolidate. However, we will continue with our policy to create new groups headed by young scientists with their specific profile as pursued in the past.

Furthermore, we also provide lab space for the new experimental setup of *Hendrik Bluhm* (FHI Department of Inorganic Chemistry), who proposes challenging surface science experiments to probe chemical reactions on liquid surfaces (like water) using high pressure photoemission (HPXPS) and other characterization tools. We are looking forward to collaborate with him and plan to add an interface-sensitive, phase-resolved SFG spectroscopy setup to this experiment in a later stage.

Research Highlights of the Department

The following topics give a selection and comprehensive overview of research achievements as well as instrument developments in the department, obtained in the last two years. For more details see reports by the individual research groups:

- Multidimensional time- and angle-resolved photoelectron spectroscopy has been developed combining a 500 kHz extreme ultraviolet (XUV) laser source with a time-of-flight momentum microscope. Together with novel multidimensional data analytics, this development enables the reconstruction of the equilibrium and non-equilibrium electronic band structure of solids with exceptional high sensitivity and paves the way for future experimental electronic structure benchmarking [*Rev. Sci. Inst.* 90, 023104 (2019)].

- The sensitivity of the core level spectral function to excitonic excitations in the semiconductor WSe_2 has been demonstrated using the free-electron laser FLASH at DESY in conjunction with a momentum microscope. Based on an analytical model for the screening of the core holes by the excited states, the dynamics of a Mott transition could be revealed.

- Photo-induced chemical reactions and phase transitions are typically governed by dynamics on a Born-Oppenheimer potential energy surface, which depends on the transient electronic structure and its occupation. Using XUV time- and angle-resolved photoemission spectroscopy in conjunction with *ab-initio* molecular dynamics simulations, a detailed reaction pathway of a structural phase transition of In/Si(111) nanowires could be unraveled, revealing a close correspondence between changes of bonds in real space and the electronic band structure [*Science* 362, 821 (2018) & *Phys. Rev. B* 99, 155107 (2019)].

- The microscopic origin of non-equilibrium properties of ZnO was resolved by the combination of several complementary time-resolved spectroscopies. Previous conflicting results originate from the competition of intrinsic and defect-related relaxation dynamics of charge carriers and excitons. This first comprehensive picture of quasiparticle dynamics in ZnO offers the possibility of making use of the materials' susceptibility to defects that can be exploited to manipulate relaxation pathways on ultrafast timescales. [*Structural Dynamics* 6, 034501(2019)].

- Yttrium iron garnet (YIG) is a model insulating ferrimagnet with interesting applications in spintronics. The flow of energy and angular momentum between electron spins and ionic lattice has been directly probed after ultrafast resonant lattice excitation with intense THz pulses. On the 1-ps time scale, spins and phonons reach quasi-equilibrium in terms of energy through phonon-induced modulation of the exchange interaction. On the much slower, 100-ns scale, the excess of spin angular momentum is released to the crystal lattice, resulting in full equilibrium [*Science Advances* 4, eaar5164 (2018)].

- Spin angular momentum can be also transported out of YIG by just heating an adjacent metal layer. The initial steps of this spin Seebeck effect was analyzed with <27 fs time resolution using THz emission spectroscopy on YIG|Pt bilayers. After excitation of Pt with an infrared laser pulse, the spin Seebeck current rises on the same ~100 fs time scale on which the metal electrons thermalize and subsequently follows their temperature. This instantaneous response arises because the metal spins have a correlation time of only ~4 fs and deflect the ferromagnetic moments without inertia. In a first application, we used this principle to characterize spin-to-charge-current in various alloys [*Nature Communications* 9, 2899 (2018) & *Nano Letters* 18, 1064 (2018)].

- Only recently discovered antiferromagnetic metals such as CuMnAs are currently in the focus of magnetism research as their magnetic order parameter (the staggered magnetization or Neel vector *L*) can be rotated by 90° and back by simply applying an electrical current parallel to *L*. It has been demonstrated that such reversible switching can even be obtained by driving the current with an ultrashort terahertz electric-field pulse as stimulus [*Science Advances* 4, eaar3566 (2018)].

- Femtosecond time-resolved resonant soft-X-ray diffraction is used to systematically investigate the ultrafast magnetization dynamics in various members of the rare-earth (RE) intermetallics family $RERh_2Si_2$. Demagnetization timescales varying by almost three orders or magnitude reveal a fundamental dependence of the angular momentum transfer rate on the strength of indirect RKKY exchange interaction in this prototypical class of antiferromagnets.

- Nanoscale heterostructures show rich structural dynamics in non-equilibrium states. Hot-electron induced atomic disordering and ultrafast nanoparticle motion has been revealed by femtosecond electron diffraction in Au nano-cluster-thin film heterostructures [*ACS Nano* 12, 7710 (2018) & *Nanoscale Horizons* 4, 1164 (2019)].

- Inelastic light or electron scattering contains information on the momentum distributions of fundamental excitations in a material. Employing femtosecond electron diffraction, the time-dependent inelastic (diffuse) scattering reveals the localization of transient phonon distributions in momentum space arising from electron-phonon coupling or photo-induced phase transitions. This new approach has been successfully applied to different layered semiconductors and semimetals with thicknesses down to monolayers.

- In atomic-scale heterostructures, the macroscopic properties can be strongly influenced by the hetero-interfaces, due to the large interface-to-volume ratio. For optical phonons in Nitride semiconductor heterostructures, pronounced frequency shifts and the emergence of new interface modes have been demonstrated providing the possibility to modify the infrared dielectric function [*ACS Nano* 2019, 136, 6730].

- Strong coupling phenomena are ubiquitous in many areas of physics, providing hybrid modes with new physical properties. In ultrathin polar crystal films, the epsilon-near-zero phonon polariton hybridizes with the polar substrate polariton, resulting in a novel kind of hybrid polariton in the mid-infrared. [*Nano Letters* 2018, 18, 4285].

- Scanning probe microscope (SPM) pulling has the advantage that the structure of a molecule can be characterized before performing transport measurements. The influence of individual defects on the electromechanical properties of single graphene nanoribbons was obtained by combining SPM-Pulling experiments with atomistic simulations [*Phys. Rev. Lett.,* 121, 047701 2018].

- Plasmon-assisted resonant electron transfer under cw laser excitation has been demonstrated in nanoscale junctions of gold or silver tips and Ag(111). Resonant electron tunneling is induced from the tip to field emission resonances of Ag(111) through localized surface plasmon excitation in the STM junction [*Phys. Rev. Lett.* 121, 226802 (2018)].

- Near-field-induced tautomerization in single porpycene molecules on Cu(111) is mediated by photogenerated carriers and the reaction cross section is significantly enhanced in the presence of a Au tip through localized surface plasmon excitation [*Nano Lett.* 18, 152 (2018)].

- Using focused ion beam nanofabrication of gold tips, spectral features of a plasmonic STM junction can be manipulated. An exemplary Fabry−Pérot type resonator of surface plasmons is demonstrated by producing the tip with a single groove on its shaft and the spectral response is characterized by scanning tunneling luminescence [*Nano Lett.* 19, 3597 (2019)].

- Tip-enhanced resonant Raman scattering (TERRS) was demonstrated on ultrathin zinc oxide layers epitaxially grown on a Ag(111) surface. In this process both physical and chemical enhancement mechanisms support efficient TERRS with exceptional high (1-nm) spatial resolution arising from local variations of the electronic structure [Nano Lett. in press].

- Multi-angle reflectance measurements on Germanium in the extreme ultraviolet are used to recover the complex-valued index of refraction in unprecedented resolution. Besides resolving formerly undetected transitions, experimental proof is provided that critical angle reflectivity is largely insensitive to the electronic structure [*J. Opt. Soc. Am. B*, 36, 1716 (2019)].

- Sum frequency generation spectroscopy is interface specific within the electric dipole approximation for bulk phases with inversion symmetry. However many systems of interest may either have large quadrupole responses in the bulk or are non-inversion symmetric. A novel approach to quantitatively separate the two contributions from surface and bulk was demonstrated by taking advantage of the differing symmetries of bulk and surface contributions and performing high accuracy phase resolved SFG measurements. [*J. Chem. Phys*. 151, 064707 (2019)].

- Probing the mechanism of electro-catalytic reactions experimentally requires time domain characterization after rapid initiation of a reaction of interest. By quantifying photocurrents induced by fs optical pulse excitation we show the reactivity of Pt surfaces towards H_2 generation requires consideration of both ultrafast charge transfer and more slowly evolving electrolyte structural dynamics. [*ChemElectroChem.,* 6, 2675 2019].

- The potential dependent Stark shift in vibrational line shapes of adsorbates in electrochemical systems is typically described as a linear function of applied bias where deviations from linearity are often attributed to changes in surface structure or electrochemistry. For (bi)sulfate on a Pt(111) electrode SFG spectroscopy reveals such a nonlinear Stark shift. A microscopic model accounting for dipole-dipole coupling of adsorbates was developed showing that deviations from linearity are likely to occur in the absence of chemical or structural change. [*Surface Science* 678, 78–85 (2018)].

- Ion polarizability is important in understanding adsorption thermodynamics at liquid interfaces but has proven challenging to quantify. Using polarization resolved, vibrationally resonant sum frequency spectroscopy the anisotropy of perchlorate's polarizability at the air/water interface has been quantified, providing constrains on the anion and solvation shell structure as function of surface coverage [*Nature Communications* 9, 1313 (2018)].

- Low-frequency collective molecular motions in the terahertz (THz) and sub-THz frequency range are decisive to the thermodynamic properties and chemical reactivity of liquids. It is demonstrated that the microscopic nature of the collective molecular dynamics of liquids, as complex as methanol, can be revealed by comparing their THz pulse and optical pulse induced Raman responses. [*J. Phys. Chem. Lett.* 9 1279-1283 (2018)].

Outlook

Aiming at spatial-temporal resolution at atomistic length and ultrafast time scales we will *enhance our activities in scanning probe microscopy coupled with local optical excitation and spectroscopy* by several measures (e.g. low temperature operation in THz STM, fs-laser implementation to a LTSTM or significantly improved spectral resolution and sensitivity in TERS). Complementary to such local probes are diffraction techniques (like *ultrafast electron diffraction*). Here we plan to implement advanced detector technology to cover a much higher dynamic range for detection of very weak diffuse scattering together with the intense Bragg peaks. We also consider supporting a new junior research group in this area.

A further important direction will be the development of *nonlinear vibrational spectroscopy and microscopy* at the FHI FEL enabling investigations of (Chi(2) and Chi(3)) non-linear optical processes at wavelength not accessible with typical laboratory sources. In addition we will further develop phase-sensitive SFG spectroscopy and implement a new laser system. This will enable, e.g., spectroscopy of protons at liquid interfaces or oxide formation at electrochemical interfaces.

Furthermore we will improve our infrastructure and capabilities for sample preparation techniques for 2 D materials and heterostructures.

Emmy Noether Group Dynamics of Correlated Materials
Dr. Laurenz Rettig

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Dynamics of Correlated Materials Probed by trARPES and X-ray Diffraction

The Emmy Noether group Dynamics of Correlated Materials focusses on understanding the ultrafast dynamics of complex materials with many interacting degrees of freedom after optical excitation, and on characterizing photo-induced phase transitions and out-of-equilibrium states using momentum-resolved techniques such as femtosecond time-resolved photoelectron spectroscopy (trARPES) or time-resolved (resonant) X-ray diffraction. Using a combination of such techniques, we aim at understanding the interactions between the various degrees of freedom inside such materials (e.g. electrons, spins or lattice), which in complex materials often lead to novel ground states with fascinating physical properties.

Multidimensional photoelectron spectroscopy

Many of the group's activities are performed in close collaboration with the ERC group of Ralph Ernstorfer, with which we share our high-repetition rate XUV trARPES setup. A new electron detector, a momentum microscope (SPECS Metis), was installed during the last two years allowing simultaneous and very efficient detection of transient electronic band structures in the complete surface Brillouin zone (BZ) of most materials. This development of multidimensional photoelectron spectroscopy (MPES) enables a completely new approach towards the investigation of transient electronic band structures and their properties, as well as its dynamics, treating three (energy, k_x, k_y) or even four dimensions (including time) on the same footing (see also report of the Ernstorfer group).
This approach is particularly useful for the investigation of anisotropic electronic

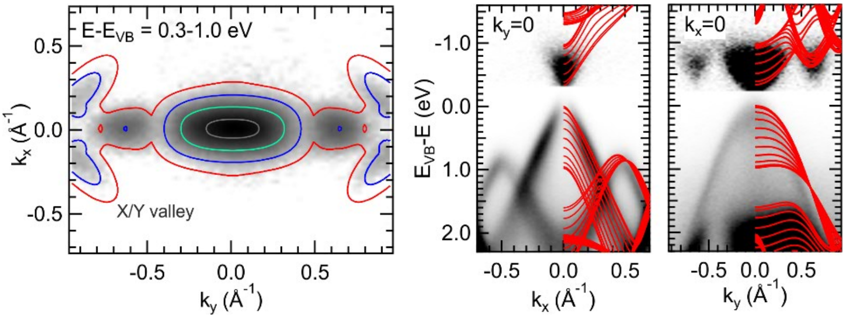

Figure 1: Time-resolved ARPES data of black phosphorous. Left: Constant energy contour of the conduction band states, showing the “hidden” X/Y valleys close to the BZ boundary. Right: Energy-momentum cuts along the armchair (k_x) and the zigzag (k_y) direction. Overlaid red lines are DFT calculations for different k_z values.

systems, such as e.g. the layered semiconductor black phosphorous (Fig. 1). This material shows strong in-plane anisotropy associated with a glide-plane symmetry, leading to a large polarization contrast in the photo-absorption cross-section. Using MPES, we could identify a new "hidden" Y/X valley in the conduction band dispersion off the high symmetry directions, which was not observed before, and which plays an important role for the relaxation of excited carriers. Owing to the full momentum and energy information obtained, we could carry out a detailed analysis of the carrier relaxation between the different valleys, and for different excitation conditions, and reveal a long memory effect of the initial carrier distribution on the final state, governed by the glide plane symmetry in the system.

Photoinduced phase transitions

The spectroscopic access to the momentum-resolved unoccupied electronic band structure provided by MPES is also particularly useful to investigate photoinduced phase transitions (PIPTs) in complex materials, e.g. of changes in the topology of the electronic structure or from an insulating ground state into a metallic excited state. A key goal is to reveal the underlying reaction mechanisms and pathways. In addition, by comparison of the experimental data to electronic band structure calculations, their validity for predicting excited state band dispersion and potential deviations e.g. due to many-body phenomena can be assessed.

A fascinating system that we recently studied is the type-II Weyl semimetal T_d-$MoTe_2$, where a strong sensitivity of the γ conduction band pockets on the electron-electron interaction has been predicted by DFT calculations (Fig 2, c-d), leading to a Lifshitz transition. Such a scenario can also happen in a photoexcited semiconductor or semimetal, where the photoexcitation of a large number of free carriers strongly enhances electronic screening and thereby suppresses electronic correlations. Indeed, using MPES, we observe the emergence of additional pockets on the Fermi surface after strong infrared photoexcitation (Fig. 2 b), supporting this scenario. The strong correlation of the excited state carrier population and the energy position of the γ pocket provide further evidence, supported by theory.

A model system for a structural phase transition, concomitant to an insulator-metal transition, are In nanowires on a Si(111) surface. In this system, a detailed comparison of the unoccupied electronic band structure to DFT and GW calcula-

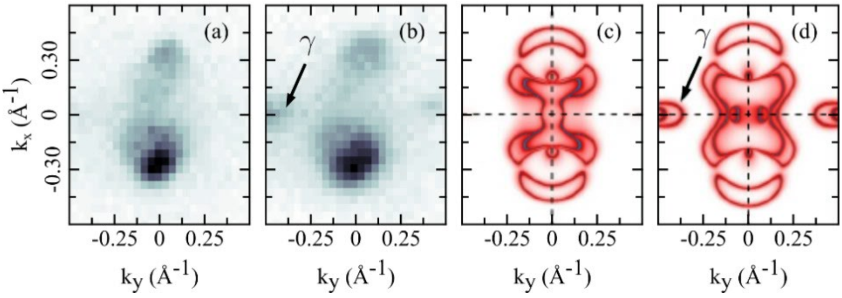

Figure 2: Time-resolved Fermi surface spectroscopy of $MoTe_2$. Fermi surface of $MoTe_2$ before (a) and at 500 fs after (b) excitation with 1030 nm pump pulses (0.64 mJ/cm^2). DFT+T calculated Fermi surface with (c) U=3 eV and (d) U=0 eV. Calculations adapted from PRL 121,136401 (2018).

tions revealed a distinct momentum-dependent deviation pointing towards excitonic contributions in the low temperature phase. Furthermore, the structural PIPT has been probed by trARPES and a detailed reaction pathway with several distinct timescales of the transition in the electronic structure identified. Remarkably, the momentum-resolved dynamics is completely determined by the transient electronic temperature after excitation.

A similar mechanism is present in the prototypical charge density wave (CDW) model system $TbTe_3$, where large energy gaps open up in the energy dispersion due to a coupled structural and electronic instability. Using the momentum microscope, we are now able to investigate the transient electronic fingerprints of this transition in a wide energy and momentum range throughout the BZ, including the unoccupied band structure (Fig. 3a), which is well described by DFT band structure calculations. Upon optical excitation, the CDW distortion is transiently suppressed, as seen by a large transfer of spectral weight on the Fermi surface, and closing of the energy gaps (Fig. 3b). A detailed investigation of the fluence dependent dynamics of the spectral weight in the gapped regions yields access to the dynamics of the electronic order parameter of the CDW (Fig. 3c). Within a time-dependent Ginzburg-Landau model, we can extract the time and fluence dependent transient energy potential, which we find to be dominated by the evolution of the energy content in the electronic system. In conjunction with time-resolved structural dynamics of the CDW superlattice reflections measured by time-resolved X-ray diffraction, this model yields a detailed description of the dynamics of CDW suppression and recovery.

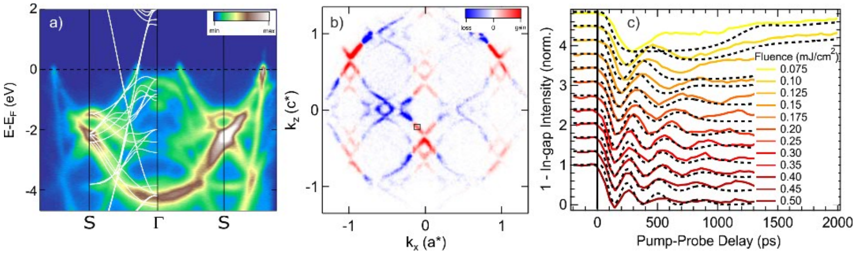

Figure 3: Ultrafast CDW dynamics in $TbTe_3$: (a) Band structure along the Γ-S high symmetry direction in a wide energy range, alongside with DFT band structure calculations (for YTe_3). (b) Differential Fermi surface, at 250 fs after excitation with 800nm laser pulses. The transfer of spectral weight from the metallic (blue) to the gapped (red) Fermi surface regions indicates the transition into the high-temperature state. (c) The coherent dynamics of the spectral weight inside the gap (black box in (b)) is well described by a modified time-dependent Ginzburg-Landau model.

Ultrafast dynamics of antiferromagnetic systems

The technique of time-resolved resonant soft X-ray diffraction is sensitive to the dynamics of magnetic ordering, in particular, of antiferromagnetic (AFM) systems. We have performed a series of experiments at the FemtospeX slicing source of BESSY II to investigate the ultrafast demagnetization dynamics of prototypical rare-earth (RE) intermetallic antiferromagnets, $RERh_2Si_2$. In this system, the rare-earth ions are enclosed in a fixed crystal lattice of Rh and Si atoms (Fig. 4a), and replacing the RE ions changes the electronic and magnetic properties relatively little. Therefore, this system is ideally suited to study the influence of the indirect

RKKY exchange interaction on the demagnetization dynamics in an antiferromagnetic system. The transient diffraction intensity of the (001) magnetic reflection shows a drastically different behavior for different rare-earth ions in the system, ranging from a sub-picosecond demagnetization in $SmRh_2Si_2$ up to several 100 ps in $PrRh_2Si_2$ (Fig. 4b). In addition, we find a pronounced critical slow-down of the dynamics upon approaching a critical fluence in all materials (Fig. 4c). This strongly varying demagnetization behavior can be well understood by considering the transfer rate of angular momentum, and its dependence on the strength of the RKKY interaction, which we parametrize by the de Gennes factor (g-1)2 J(J+1). Thereby, our systematic study of AFM demagnetization dynamics in this system reveals the indirect exchange interaction as the fundamental process responsible for angular momentum transfer. In addition, in $GdRh_2Si_2$, we could identify a coherent in-plane rotation of the whole AFM structure after excitation, due to a transient change of the magnetocrystalline anisotropy.

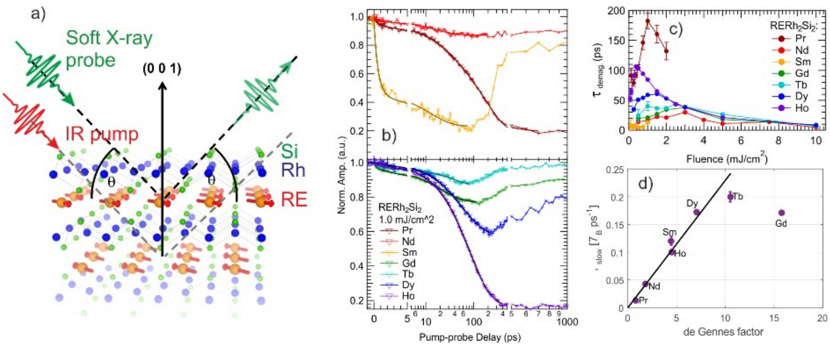

Figure 4: Time-resolved resonant x-ray diffraction in $RERh_2Si_2$. (a) RE atoms are embedded in a fixed Rh/Si matrix, and always order in a similar AFM structure. Soft x-rays tuned to the RE M4/5 absorption edges are used to detect the out-of-plane (001) magnetic diffraction peak. (b) Normalized magnetic diffraction signal for various $RERh_2Si_2$ compounds. Lines are biexponential fits. (c) Extracted slow time constants as a function of excitation fluence. (d) Derived angular momentum transfer rate as a function of the de Gennes factor.

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ERC Group Structural & Electronic Surface Dynamics
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Ultrafast Dynamics of Electrons and Lattice in Nanoscale Matter

The Structural & Electronic Surface Dynamics Group aims for a microscopic understanding of fundamental interactions in nanoscale condensed matter, ultimately on the level of individual quantum states. To achieve this, we develop and employ experimental techniques providing momentum-resolved information on transient states of the electronic structure and the atomic structure. This methodology is applied to a broad spectrum of material systems ranging from thin-film (semi-) metals and semiconductors to nanoscale heterostructures and nanocrystals. We closely collaborate with the Dynamics of Correlated Materials Group headed by Laurenz Rettig.

Development of multidimensional photoemission spectroscopy

In recent years, we developed time- and angle-resolved photoemission spectroscopy (trARPES) based on a femtosecond extreme ultraviolet (XUV) laser source, which provides access to the non-equilibrium electronic structure in the entire Brillouin zone of crystalline materials. We extended this approach by adding a momentum microscope detector, which enables four-dimensional trARPES as depicted in Fig. 1(a). The high repetition rate (500 kHz) of the XUV source provides enough statistics for mapping the weak and transient excited state signal in addition to the occupied states in the material's valence band. This is illustrated in panels b and c, showing two snapshots from a 3D movie of the formation and evolution of excitons in WSe_2, a prototypical layered semiconductor. Additional examples of use of this approach can be found in the report of the Dynamics of Correlated Materials Group.

The combination of a high-repetition rate light source and an every-electron detection scheme generates large data volumes. Making such data accessible to a broader community, for instance for benchmarking electronic structure calculations, represents a new challenge for the photoemission community. Within the BiGmax Research Network, we develop unsupervised learning algorithms for extracting experimental band structure from multidimensional data sets. We share this development with the community by developing a general multidimensional photoemission data analytics toolbox (https://github.com/mpes-kit).

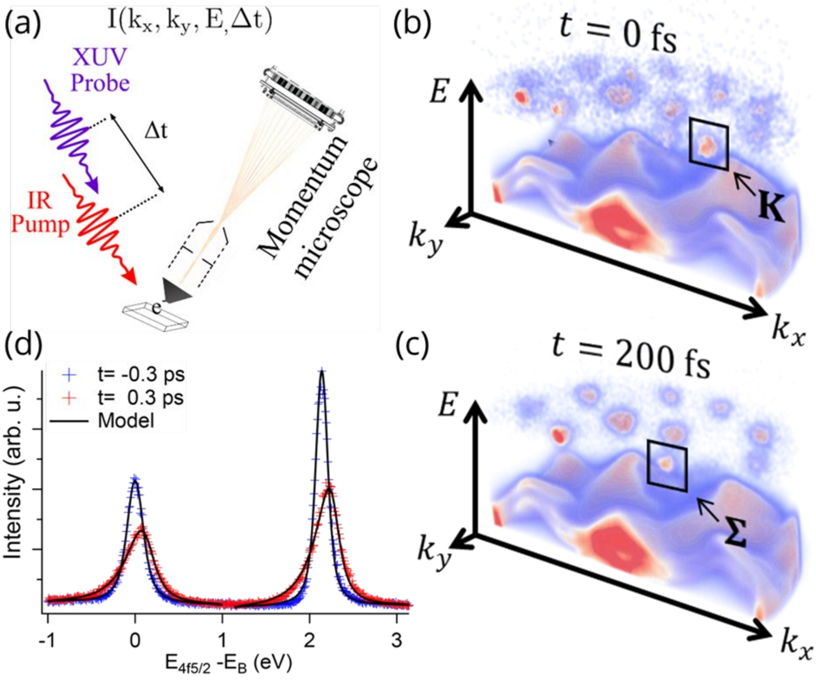

Figure 1: Multidimensional photoemission spectroscopy. (a) Illustration of the trARPES scheme with a momentum microscope spectrometer, which resolves the photoelectrons in energy, both parallel momentum dimensions and (pump-probe) time. Panels (b,c) show snapshots of the electronic structure of WSe_2 during the formation of an A exciton in the K valleys of the Brillouin zone (b) and after scattering of the bright A exciton to optically-dark excitons (c). The electronic contribution to the dark-exciton wave function is localized in momentum space near the Σ valleys of the conduction band. (d) Time-resolved spectral function of the W 4f core levels before (blue) and 300 fs after optical excitation of the A exciton resonance. The solid lines show fits with a time-dependent Doniach-Sunjic model, which reveals a Mott transition through the temporal evolution of the core-valence interaction.

Complementary to the study of ultrafast dynamics of valence electrons with trARPES, we investigated the response of core levels to excitations of the valence states in WSe_2. Using a momentum microscope and the free-electron laser FLASH at DESY, we probe the spectral function of W 4f core levels during the formation and evolution of excitons, see Fig. 1(d). The evolution of the spectral function is well reproduced by an analytic model, which extends the Doniach-Sunjic line shape model to excited semiconductors. The time-dependence of the spectral function is governed by the core-valence Coulomb interaction, which differs largely between excitonic and single-particle excitations of the valence electrons. Core-level photo-emission spectroscopy proves to be a sensitive tool for the investigation of electronic phase transitions like, as shown here, a Mott transition in a photo-excited semiconductor.

Elastic and inelastic femtosecond electron diffraction

Time-resolved diffraction techniques have primarily been employed for retrieving structural dynamics from elastic scattering signals, which reveal the net effect of all phonon modes on the atomic motion. Only recently, the analysis of inelastic scattering signal has been established as technique for obtaining momentum-resolved information on transient phonon populations. We employ this approach to study electron-phonon and phonon-phonon interactions as well as phase transitions in strongly coupled electron-lattice systems like charge density wave materials and certain topologically nontrivial semimetals. Fig. 2 shows exemplary data of the anisotropic semiconductor black phosphorous. The diffraction difference between excited and ground states shows the momentum distribution of the inelastic scattering, which reflects the transient phonon distribution in momentum space. After 300 ps, the pattern reflects a hot, yet thermal phonon distribution, see panel (b). On the sub-100 ps timescale, however, the inelastic scattering reveals nonthermal phonon distributions and highly anisotropic phonon population dynamics, as shown for small-momentum phonons in the armchair (red) and zigzag (black) crystalline directions, panel (c).

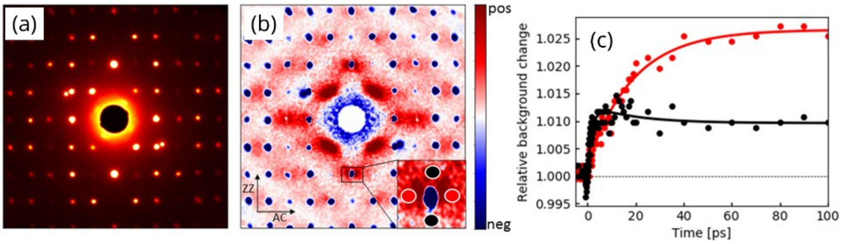

Figure 2: Femtosecond electron diffraction of a black phosphorous thin film. (a) Raw diffraction pattern showing the anisotropic structure in the armchair-zigzag plane. (b) Diffraction difference observed 300 ps after optical excitation of the electronic structure. Red signal: increase of star-shaped inelastic scattering, which reflects the transient phonon population at this time. The anisotropy of the phonon dynamics is retrieved from the momentum-dependent scattering signal, e.g., along the armchair (red dots) and zigzag (black dots) directions in the vicinity of elastic scattering peaks (see inset). Panel (c) shows the pronounced differences in the phonon dynamics along these high-symmetry directions (color code relates to the inset in (b)). These are explained by the anisotropy of the electron-phonon scattering phase space, which we independently measured with complementary trARPES measurements.

Ultrafast diffraction and microscopy of nanoscale materials

The large scattering cross section of nonrelativistic electrons allows for the investigation of structural dynamics in nanocrystals. We investigated size-selected magic-number Au clusters composed of ~920 atoms, which were soft-landed on different thin film substrates like graphene, see Fig. 3(a, b). The time-resolved diffraction patterns of these nanoscale heterostructures revealed the ultrafast flow of energy within each constituent as well as across the boundary and a hot-electron-assisted surface-melting mechanism. In the case of Au clusters on graphene, the dynamics of ultrafast restricted rotations, i.e., librations, could be extracted from the diffraction data. Molecular dynamics simulations reveal efficient coupling between flexural phonons of graphene and rotational motion of the cluster as quasi-impulsive driving mechanism of the librations.

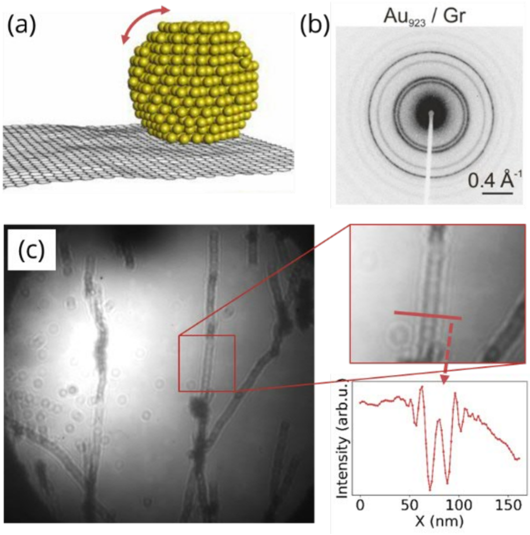

Figure 3: (a) Illustration of librational motion of Au-932 clusters on graphene. (b) The diffraction pattern of this 0D-2D heterostructure shows separated graphene and Au peaks, which allows retrieving ultrafast energy flow in the heterostructure. Deviations from Debye-Waller dynamics in the diffraction data could be identified as rotational motion of the entire nanocrystals. (c) Electron transmission image of free-standing graphene recorded with 220 eV electrons. A crack in the graphene causes single-slit scattering and single-electron interference (top right and lineout profile).

Complementary to the momentum-space technique trARPES, we also aim to observe ultrafast dynamics in real space with femtosecond electron point-projection microscopy. This technique is sensitive to the electric potential in the vicinity of nanostructures; time-resolved experiments hence reveal changes in the electric potential and allow the reconstruction of the underlying motion of charges. To enhance the sensitivity of the technique towards the limit of a single elementary charge, we aim to realize femtosecond electron holography. Improvements of the mechanical stability of the microscope and optimization of the photoemission process from nanotips in terms of source coherence have recently allowed us to record first images with clear signatures of electron interference, see Fig. 3.

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Nonlinear Phonon Spectroscopy using Infrared Free-Electron Lasers

The Lattice Dynamics group uses the FHI infrared Free-Electron Laser (FEL) to study optical phonons in polar dielectric crystals, and the associated resonances in the nonlinear-optical response of materials in the mid- to far-infrared spectral region. Specifically, we are interested in phonon polaritons in hetero- and nanostructures, where we use the structure to control the resonances while the polaritonic field confinement leads to enhancement of the nonlinear-optical signals. For these studies, we develop novel experimental approaches and instrumentation, as for instance FEL-based far-infrared surface-vibrational spectroscopy and microscopy. These new methods will, for instance, also be applied to investigations of transient structural motifs in electrochemical systems and domain structure in correlated oxide heterostructures in the future.

Phonon polaritons in polar dielectric heterostructures

Phonon polaritons – phonon-light coupled quasiparticles - arise in thin films or at surfaces of polar dielectric crystals due to the infrared-active optical phonons. They are supported in the negative permittivity region between transverse and longitudinal optical phonon resonances - the so-called Reststrahlen region. The long lifetimes of these excitations offer unique advantages for infrared nanophotonics over lossy, short-lived plasmon polaritons. However, a major drawback arises from the limited, material-specific spectral range over which phonon polaritons are supported, as well as their limited tunability. The Lattice Dynamics group follows various approaches to lift these restrictions by means of planar heterostructures, where the polariton modes can be tuned either via polariton-polariton coupling between the different layers, or even by phonon hybridization at the material interfaces in atomic-scale heterostructures.

For ultrathin polar dielectric films of 10-100 nm thickness, the phonon polariton dispersion is strongly modified, resulting in a unique mode that naturally resides at the zero-crossing of the dielectric function (epsilon-near-zero, ENZ). This ENZ condition has many attractive properties otherwise only accessible through carefully designed metamaterials, such as infinite phase velocity, scatter-free propagation, and drastically enhanced nonlinear-optical effects. When brought onto a polar dielectric substrate, the ENZ polariton in the thin film can hybridize with the substrate polariton, to generate strongly coupled modes with unique properties of both surface and ENZ polaritons.

In contrast, a (non-polar) dielectric ultrathin film placed on a polar crystal surface results in a compression of the substrate polariton dispersion. This is particularly interesting when using phase change materials like GST as the dielectric, where this compression can be modulated, see Fig. 1. Additionally, the perpendicularly polarized waveguide mode was found to, due to the polar crystal substrate, have very similar (polariton-like) properties, making the GST/polar crystal heterostructure an extremely attractive platform for infrared nanophotonics.

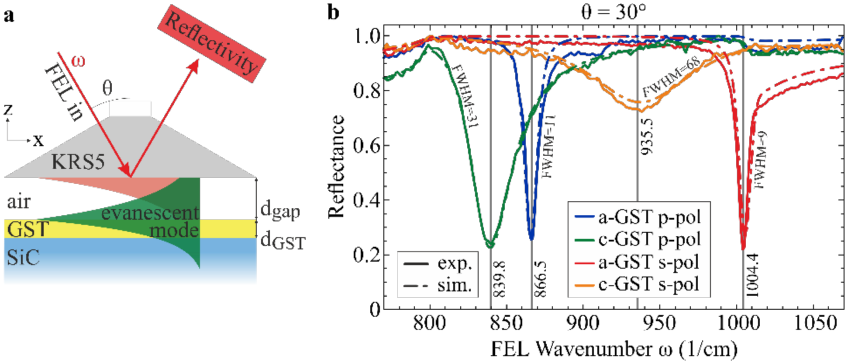

Figure 1: Tuning of phonon polariton resonances: (a) Schematic of Otto-type prism coupling experiment that allows mapping of the polariton dispersion in heterostructures. (b) For ultrathin layers of the phase-change material GST, switching of the of the GST phase results in tremendous tuning of the GST-compressed surface polariton (p-pol, blue/green) and the newly discovered polariton-like waveguided mode (s-pol, red/orange).

For heterostructures with ultrathin film thicknesses approaching atomic length scales, the modified chemical bonding at the layer interfaces additionally leads to hybridization of the optical phonons, and thereby modulation of the phonon polaritons. Simultaneously, due to strong anisotropy (in-plane vs. out-of-plane modes) of the heterostructure, this new material now also supports so-called hyperbolic polaritons – volume-confined modes with unbound momenta. As such, atomic-scale heterostructures establish a new way to design materials specifically for phonon-polariton-based nanophotonics.

Far-Infrared sum-frequency generation spectroscopy and microscopy

Infrared-visible sum-frequency generation (SFG) spectroscopy is a powerful tool to reveal the structure and symmetry of interfaces. This technique is well established in the mid-infrared range using table-top laser sources providing access to high-frequency vibrations. This has led to many major discoveries, for instance regarding the surface structure of liquid and solid water, or the transient interface structure in electrochemical systems. Using the FHI FEL, the Lattice Dynamics group is now pushing SFG spectroscopy into the far-infrared range, opening up a whole new field of exciting possibilities, owing to the vibrational and electronic excitations in that spectral range which are currently inaccessible. This applies for instance - but is by far not limited to - most optical phonon modes in the large class of metal oxides. Therefore, far-infrared SFG spectroscopy could be employed to study many important problems in, for instance, aqueous oxide chemistry or strongly correlated oxide heterostructures.

Many interface problems in physics, chemistry, and even biology involve significant spatial heterogeneity. Therefore, spatially resolved information about the interface structure and symmetry can tremendously enhance the understanding of underlying mechanisms. Notably, SFG is perfectly suited for infrared microscopy, whereby the spatial resolution is limited only by the wavelength of the visible SFG photons, i.e., well below the diffraction limit for infrared radiation. Motivated by these possibilities, we have started to implement FEL-based far-infrared SFG spectroscopy and microscopy.

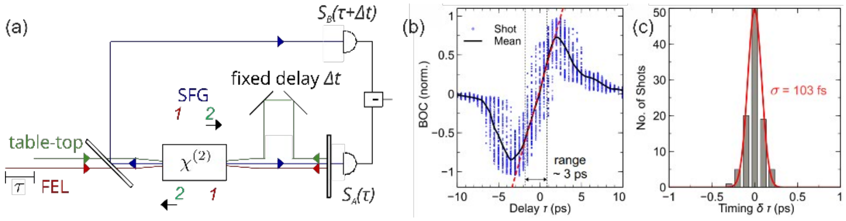

Figure 2: Timing tool for the FHI FEL: (a) Concept of balanced optical cross correlation (BOC) used for online monitoring of the relative arrival time of visible and FEL pulses. (b) BOC signal when scanning the delay time τ between FEL and visible laser. (c) The timing distribution function yields a timing jitter of ~ 100 fs.

To enable far-infrared SFG using the FHI FEL as the powerful far-infrared light source, a time-synchronized visible laser system is required. The Lattice Dynamics group has, over the last 4 years, established the respective instrumentation. A radio-frequency timing infrastructure at the FEL facility was installed, which was demonstrated to allow synchronization of a low-power fiber laser to the FEL pulses with ~100 fs precision (see Fig. 2). We also developed a new concept for and implemented a timing tool for online-monitoring of the relative timing between the two lasers, a crucial advantage of the current approach over earlier attempts at other FEL facilities.

Using the synchronized low-power visible laser for a proof-of-concept experiment, SFG spectroscopy and microscopy measurements were performed, see Fig. 3. Here we took advantage of the polaritonic field confinement in phonon polariton sub-diffractional resonators that leads to dramatic enhancement of the nonlinear signal, resulting in detectable signal levels despite the low visible laser power

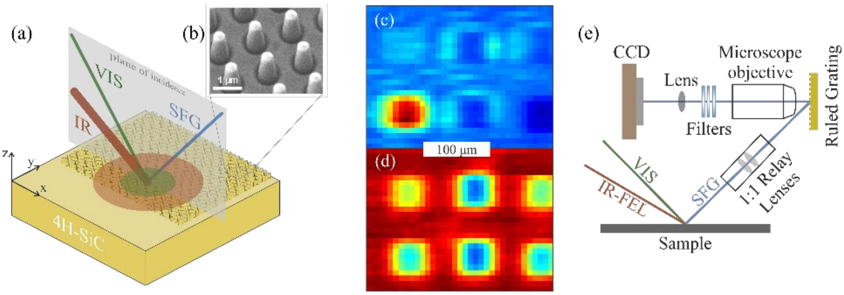

Figure 3: (a) Concept of scanning probe SFG microscopy of nanophotonic structures made of (b) Silicon Carbide nanopillars. Experimental resonant (c) and non-resonant (d) SFG images. (e) Concept for FEL-based wide-field SFG microscopy to be implemented

available. This also allowed for first far-infrared SFG microscopy experiments, here done with spatially scanning tightly focused beams.

To harvest the full potential of far-infrared SFG spectroscopy and microscopy, the department applied for and was recently granted financial support by the Max-Planck-Society to acquire a new high-power visible laser operating in burst mode, synchronized with the FEL. This new laser will be installed in early 2020, and our group will implement FEL-based SFG spectroscopy and microscopy as an experimental end station at the FHI FEL. Notably, the concept also includes to establish wide-field SFG microscopy. Once operational, this SFG end station will be used for many different experiments, ranging from infrared nanophotonics to quantum materials and electrochemistry.

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Ultrafast Terahertz Spectroscopy of Complex Materials

The terahertz (THz) frequency range is attracting increasing interest for both applied and fundamental reasons. On one hand, bit rates in current information technology may soon approach the THz range. Therefore, it is warranted to study the behavior of materials at THz frequencies. This goal is, on the other hand, also highly interesting from a scientific viewpoint because its low photon energy (4.1 meV at 1 THz) makes THz radiation an excellent probe of many elementary excitations of solids, for instance lattice vibrations (phonons), electronic intraband transport, excitons and spin waves (magnons).

The Terahertz Physics Group makes use of ultrashort THz and optical laser pulses

- To gain insight into the interplay of low-energy excitations in complex materials. An example is the elusive interaction of lattice and electron spins in magnetically ordered solids.
- To push various physical effects so far studied at low frequencies into the THz range. Currently, the group has a strong focus on fundamental spintronic effects such as the only recently discovered spin Hall effect and the spin-type Seebeck effects. These studies are conducted in the framework of the PI's ERC Consolidator Grant project TERAMAG.
- 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.

Recent examples of these activities are illustrated below.

Ultrafast spin currents in magnetic bilayers

A fundamental operation of spintronic devices is the transport of spin information, for example from a magnetic layer into an adjacent nonmagnetic metal (see Fig. 1a). Remarkably, such spin current j_s can be triggered by simply heating the metallic layer, even if the magnetic layer is an insulator such as yttrium iron garnet (YIG).

To reveal the possibly ultrafast formation of this spin Seebeck effect in the model bilayer system YIG|Pt, we made use of a femtosecond laser pulse to instantaneously heat the Pt film (Fig. 1a). Note that any spin current j_c flowing from YIG to Pt is converted into a transient transverse charge current j_c by the inverse spin Hall effect of Pt. The time-dependent j_c gives rise to the emission of an electromagnetic pulse with frequencies extending into the THz range.

Using a highly sensitive electrooptic-sampling setup, we were able to measure the emitted THz pulse. We developed an inversion procedure to extract the ultrafast dynamics of the spin current $j_s(t)$ displayed in Fig. 1b. The decay of j_s on a 300 fs scale directly follows the cooling dynamics of the Pt electrons by the Pt lattice. Interestingly, the rise of j_s on a 100 fs scale is substantially slower than the 27 fs resolution of our setup. Analytical modeling and electron-dynamics simulations showed that this rise traces the thermalization of the Pt electrons. These findings are consistently explained by the formation scenario of the spin Seebeck effect that is summarized in Fig. 1c and its caption.

We have meanwhile confirmed these insights for other insulating ferrimagnets and take advantage of this scheme to rapidly characterize the strength of the spin Hall effect in various materials, to study the role of the interface and to understand how spin transport arises in the case of metallic rather than insulating magnetic layers.

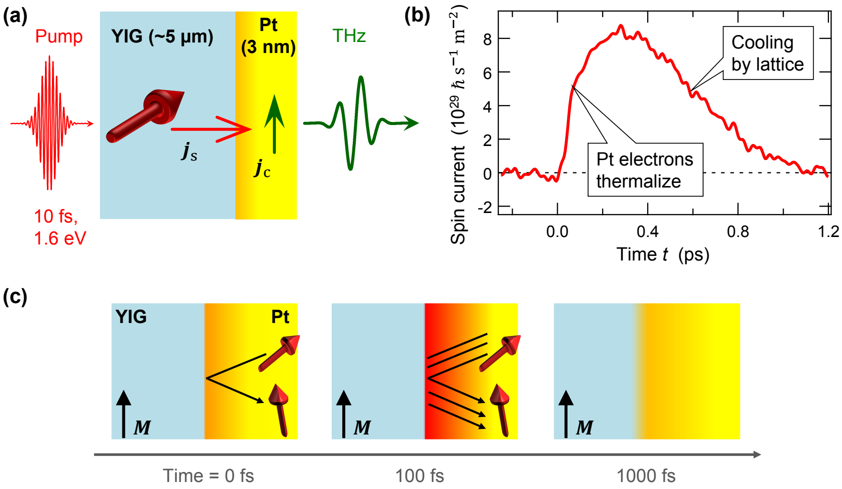

Figure 1: Ultrafast spin Seebeck effect. (a) Schematic of experiment. A pump pulse heats the Pt film, giving rise to a transient spin current *js* from YIG to Pt that is converted into a transverse charge current *jc* by the inverse spin Hall effect. Measurement of the concomitantly emitted THz pulse allows us to extract (b) the temporal dynamics of the transient spin current *js*(*t*) through the YIG-Pt interface. (c) Scenario of the formation of the spin Seebeck current. After heating of the Pt layer at time 0 fs, hot electrons scatter off the YIG-Pt interface, thereby partially aligning with the YIG magnetization through interfacial exchange interaction and transporting spin angular momentum into the N layer. The scattering rate is proportional to the number of occupied incident Bloch states times the number of unoccupied reflected states. It rises when the number of electrons and holes grows (here by a factor of ~40) in the course of electron thermalization.

Spintronic operations with intense THz fields

We not only use THz radiation to probe spin and charge dynamics, but also employ intense THz pulses to drive and finally control dynamics. A recent result is the switching of magnetic order of antiferromagnets as illustrated by Fig 2. Our sample was a thin film of the only lately discovered metallic antiferromagnet CuMnAs. Since the antiferromagnetically coupled and, thus, oppositely oriented (staggered) spins are located at sites with locally broken inversion symmetry, CuMnAs has a remarkable property: Driving a charge current through the metal is like applying a staggered magnetic field to the two spin sublattices. This effective field exerts a uniform torque on all spins and rotates them coherently (see Fig. 2a). The degree of alignment of the spin system can be probed by electrical measurement of anisotropic magnetoresistance (AMR).

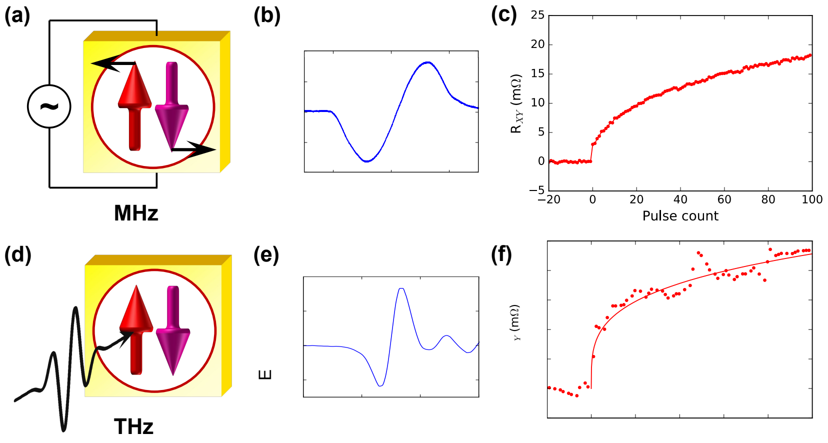

Figure 2: THz switching of antiferromagnetic order. (a) By applying an electric current pulse to the metallic antiferromagnet CuMnAs, a staggered magnetic field is applied to the antiferromagnetically coupled spin sublattices, resulting in coherent rotation of all spins. (b) Voltage vs time *t* of the electrical pulse applied to the Ohmic contacts of the sample. (c) AMR signal vs number of applied pulses. (d) Free-space THz pulses are applied to the sample to induce switching of antiferromagnetic order. (e) Transient electric field of the incident THz pulse. (f) AMR signal vs number of applied THz pulses.

To characterize our sample, we first applied microsecond voltage pulses (Fig. 2b) through Ohmic contacts to the sample. As expected from previous works of our collaborators, we observed that with every additional pulse, the AMR signal increased (Fig. 2c), indicating that an increasing number of spins had been rotated.

In a second experiment using the very same sample and setup, we excited the sample with free-space THz pulses (Fig. 2d) that featured a duration of ~1 ps and a peak field of ~0.3 MV/cm (Fig. 2e). Remarkably, we found the AMR signal to exhibit an increase when the number of applied pulses increased (Fig. 2f), fully analogous to the result of MHz-driving (Fig. 2c). Further checks showed that antiferromagnetic order of CuMnAs can indeed be switched (here rotated) using THz pulses. In complete analogy to the electrical approach (Fig. 2a), switching back was achieved by rotating the polarization of the THz beam by 90°.

We are currently working on time-resolving the switching dynamics. This goal requires the development of suitable ultrafast probes of antiferromagnetic order.

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Near-field Physics and Chemistry in Plasmonic Nanocavities

Near-field physical and chemical processes have gained increasing attention due to the potential for nanoscale imaging, ultrasensitive chemical analysis, and enhancement of photochemical reactions. Plasmonic nanocavities are key for various applications due to their strong field confinement and enhancement. The group of Takashi Kumagai has focused on investigation of near-field physics and chemistry in plasmonic nanocavities using a newly developed low-temperature STM for precise local optical excitation and detection (photon-STM). The photon-STM has been developed in collaboration with UNISOKU Co. Ltd. and was installed in the new STM laboratory in June, 2017. It has achieved high performance and the group has carried out the experiments described below. Part of this work is done in collaboration with the Ultrafast Scanning Probe Microscopy group of Dr. Melanie Müller.

Plasmon-assisted resonant electron tunneling

Light-induced electron transfer is of fundamental importance in nature and intimately related to energy conversion such as photovoltaics and photocatalysis. In particular, efficient electron transfer by visible light is a key to make use of solar energy. Plasmonic nanostructures can be used to harvest light and enhance photophysical and photochemical processes through surface plasmon excitation leading to dramatic enhancement of electromagnetic fields. Employng the photon-STM the group demonstrated plasmon-assisted *resonant* electron tunneling from an Ag or Au tip to field emission resonances (FERs) of a Ag(111) surface induced by irradiating an STM junction with a focused cw laser at visible wavelengths (Fig. 1a). As a hallmark of the plasmon-assisted resonant tunneling, a significant redshift of the FERs is observed whereby the shift of the first resonance equals the incident photon energy (Fig. 1b). STM-induced luminescence measurement for Ag and Au

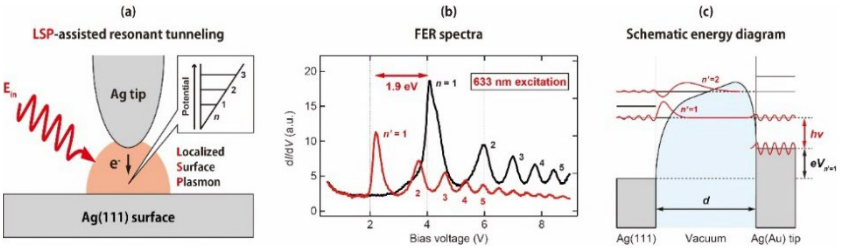

Figure 1: (a) Schematic of the experiment. (b) FER spectra with (red) and without (black) illumination. (c) Schematic energy diagram of plasmon-assisted resonant tunneling in the STM junction.

tips reveal a clear correlation between the laser-induced change in the FER spectra and the plasmonic properties of the junction. Our results demonstrate a novel resonant electron transfer mechanism in a plasmonic nanocavity (Fig. 1c).

Near-Field manipulation in a scanning tunneling microscope junction with plasmonic Fabry-Pérot tips

Manipulation of near-field properties such as the spectral response, optical coupling to far fields, and local field enhancement, by metallic nanostructures is a is a key goal in plasmonics, providing a wide range of applications in nanooptics, single-molecule sensing, and enhancement of photovoltaics and photochemistry. Advances of nanoscale fabrication techniques have allowed to control surface plasmons at metal–dielectric interfaces, leading to the discovery of exotic properties of near-field optics, e.g., extraordinary high transmission through subwavelength holes. Plasmon excitation in nanoscale cavities is of particular importance due to dramatic enhancement and extreme confinement of an electromagnetic field, which result in strong light–matter interactions. The group demonstrated that the spectral features of a plasmonic STM junction can be manipulated by nanofabrication of Au tips using focused ion beam (FIB). An exemplary Fabry–Pérot type resonator of surface plasmons is demonstrated by producing the tip with a single groove on its shaft (Fig. 2a and 2b). Scanning tunneling luminescence spectra of these Fabry–Pérot tips exhibit spectral modulation resulting from inter-

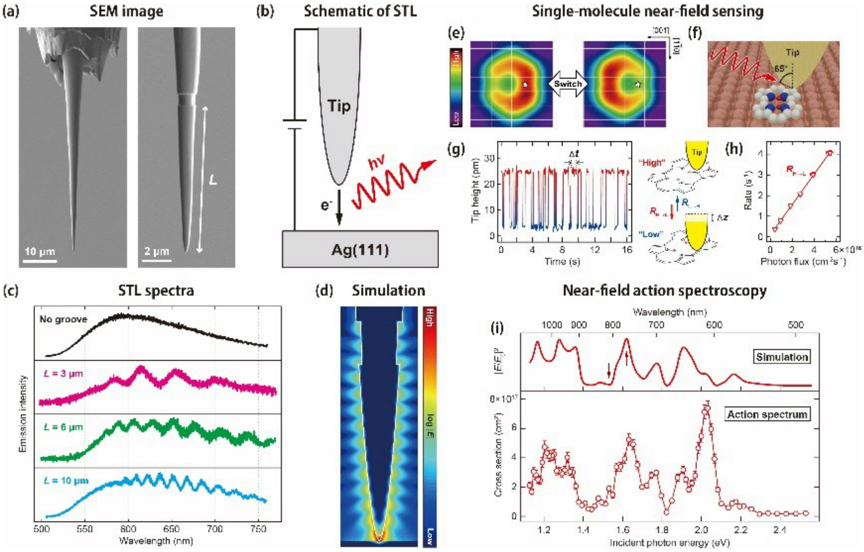

Figure 2: (a) SEM images of an Au FIB-tip with a single groove on the shaft at the distance L from the apex. (b) Schematic of STL. (c) STL spectra obtained for FIB-tips without the groove and with the groove at L=3, 6, 10 µm. (d) Electrodynamics simulation of plasmonic Fabry–Pérot interference in the grooved FIB-tip. (d) STM image of a single porphycene molecule on Cu8110) at 5 K, which acts as a nanoscale sensor to detect local field enhancement in plasmonic STM junctions. (e) Schematic of experiment. (f) Two-state switching of prophycene induced by localized surface plasmon excitation in the STM junction. (g) Fluence dependence of the tautomerization rate from which we can calculate the near-field cross-section. (h) Tautomerization cross section as a function of incident photon energy (near-field action spectrum).

ference between localized and propagating surface plasmon modes (Fig. 2c). The standing wave characteristic was reproduced by electrodynamic simulations (Fig. 2d). In addition, the quality factor of the plasmonic Fabry–Pérot interference can be improved by optimizing the overall tip shape. This approach paves the way for near-field imaging and spectroscopy with a high degree of accuracy. The group Furthermore, plasmonic FIB-tips we used to control single-molecule reactions and to demonstrate near-field action spectroscopy (Fig. 2e–i) which provides a unique way to characterize local field enhancement in plasmonic nanocavities. The FIB fabrication has been performed in close collaboration with Electron Microscope group in the AC department.

Resolving the correlation between tip-enhanced resonance Raman scattering and local electronic states with 1 nm resolution

Low-temperature tip-enhanced Raman spectroscopy (TERS) enables chemical identification with single-molecule sensitivity and extremely high spatial resolution down to the atomic scale. The large enhancement of Raman scattering obtained in TERS can originate from physical and/or chemical enhancement mechanisms. Whereas physical enhancement results from strong near-field enhancement through excitation of localized surface plasmons, chemical enhancement is governed by resonance in the electronic structure of the sample, which is also known as resonance Raman spectroscopy. The group applied tip-enhanced resonance Raman spectroscopy (TERRS) to ultrathin ZnO layers epitaxially grown on a Ag(111) surface (Fig. 3a and b) and demonstrated that both enhancement mechanisms are operative. Furthermore, in combination with scanning tunneling spectroscopy (STS), it is demonstrated that the TERRS intensity strongly depends

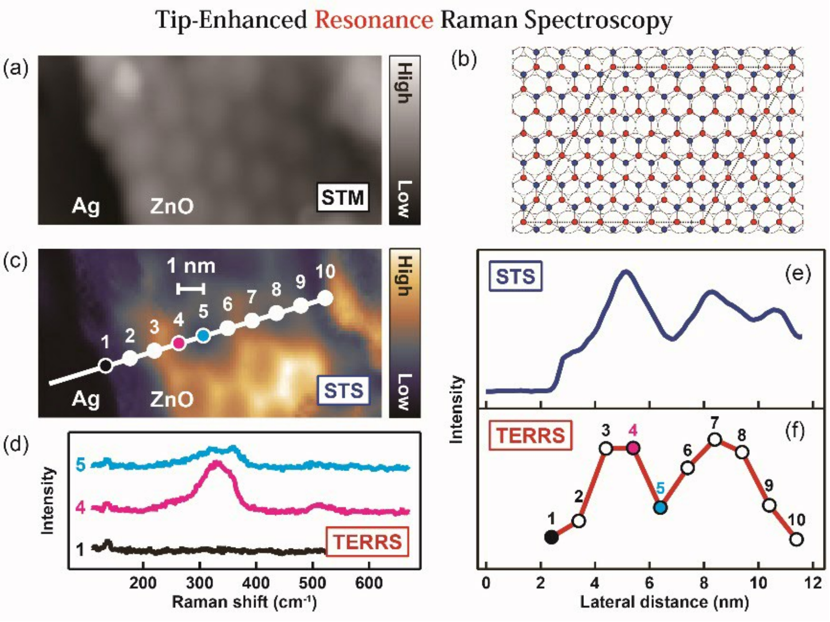

Figure 3: (a) STM image of ultrathin ZnO layers epitaxially grown on a Ag(111) surface. (b) Schematic structure of the ultrathin ZnO layer. (c) STS mapping over the ZnO layer. (d) TERRS spectra obtained at different positions. (e) Profile of the STS and TERRS intensity along the line in (c).

on the local variation of electronic states at the ZnO/Ag(111) interface (Fig. 3c and 3d). It was reveal that the spatial resolution of TERRS is dependent on the tip–surface distance and reaches nearly 1 nm in the tunneling regime (Fig. 3e and 3f). This can be rationalized by strong field confinement resulting from an atomic-scale protrusion on the tip apex. Comparison of STS and TERRS mapping clearly shows a correlation between resonantly enhanced Raman scattering and the local electronic states at near-atomic resolution. These results suggest that TERRS can provide a new approach for the atomic-scale optical characterization of local electronic states.

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THz-gated Scanning Tunneling Microscopy of Photoexcited Nanostructures

Since the start of the *Ultrafast Scanning Probe Microscopy Group* in 2017, much of our work concentrated on the development and implementation of a THz-gated Scanning Tunneling Microscope (THz-STM) specifically designed for the combination of broadband optical and THz excitation, respectively. The main goal of our research is to probe the local femtosecond dynamics of photoexcited systems like nanostructures or surfaces on the nanometer scale down to atomic length scales. Understanding the role of the local environment and surface conditions on ultrafast carrier dynamics and their relaxation pathways is a longstanding goal in surface dynamics. In this regard, using THz-STM we aim at combining femtosecond spectroscopic information with atomic spatial resolution, complementing the wide variety of time-resolved surface science techniques available in the department of physical chemistry.

In close collaboration with the group of Takashi Kumagai and Unisoku Co., Ltd. we developed an ultrahigh-vacuum STM/AFM system with two large-aperture motorized parabolic mirrors integrated on the SPM platform in UHV for broadband excitation and light detection covering the full spectral range from the visible to the THz. The setup is operational at room temperature since February 2019 and is fully compatible to be upgraded to cryogenic temperatures down to 5K. For ultrafast gating of the tunnel junction we employ broadband single-cycle THz pulses generated from a metallic spintronic emitter (STE), as developed in our department in the THz-group of Tobias Kampfrath. A broadband OPCPA laser system, shared with the group of Ralph Ernstorfer, with variable repetition rates from 0.2 – 2 MHz at few µJ pulse energies is used for THz-generation and simultaneous photoexcitation of the STM junction.

First experiments include the investigation of THz near-field coupling to the tip, which requires time-domain sampling of the THz electric field directly in the STM junction as accomplished via ultrafast gating of photocurrents. Moreover, in this context we could probe nano-localized dynamics of photocarriers in a metallic STM junction on femtosecond timescales, manifested as deviations of the measured waveform from the real THz near-field. In terms of setup development, we analyzed the performance of the spintronic emitter using a curved-wavefront excitation geometry implemented for efficient pumping with few-femtosecond optical pulses at the µJ-level.

Waveform sampling of THz near-fields via ultrafast photocarrier gating

The transient electric field of a THz pulse acts as a quasi-static voltage applied to the STM, controlling current flow on femtosecond timescales. Optimal operation of a THz-gated STM evidently requires exact knowledge of the THz near-field waveform, which can differ significantly from the far-field waveform due to tip antenna effects. Moreover, the *local* waveform of the THz pulse critically depends on the position of the point-like tip in the THz focus, which additionally can suffer from strong chromatic aberrations, originating for instance from imperfect frequency-dependent collimation of the radiated THz beam. Whereas the tip itself acts as a low-pass filter to the THz pulse, the point-like character of the tip makes it difficult to compare the near-field to the far-field waveform measured via spatially integrating electro-optic sampling. It is thus essential to routinely measure the THz waveform directly in the STM for given settings of the setup.

In this regard, much of our effort was invested to show that the THz near-field waveform can be sampled via THz-induced modulation of photoemission currents through the STM junction excited by femtosecond optical pulses, as sketched in Fig. 1. This type of THz-VIS crosscorrelation sampling can be routinely used

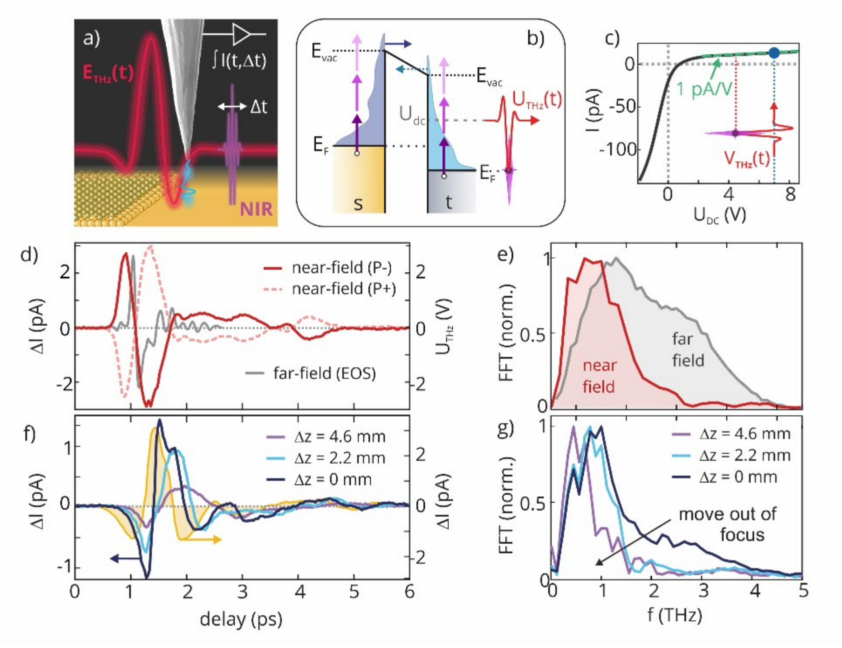

Figure 1: (a) Concept of photoexcited THz-STM. (b) Modulation of the potential barrier in the STM junction by the transient electric field of the THz pulse. (c) Photocurrent-voltage characteristics of the photoexcited junction of a W-tip on HOPG at few nm distance and illustration of transient bias modulation by the THz pulse. (d) THz-induced photocurrent modulation at 7 V bias and for opposite THz pulse polarities, sampled in the linear part of the photocurrent-voltage curve. The THz near-field waveform and applied THz voltage is revealed indicating a significant low-pass filter effect, as evident also from the corresponding spectra (e). (f) Change of the THz waveform as the tip is moved out of the THz focus by a distance Δz, and corresponding FFT spectra in (g). The yellow filled curve shows the waveform by tuning the Gouy phase shift at a fixed tip position in the THz focus via the incident THz beam divergence.

independent of the type of sample and at all temperatures. However, care has to be taken to exclude temporal broadening due to non-instantaneous effects such as long-lived photocarriers and electron-propagation effects. In their absence, the delay-dependent THz-induced change of the photocurrent is determined by the instantaneous THz electric field, with a dependence dictated by the photocurrent-voltage characteristic, as seen in Fig. 1c). In the particular case of a linear IV dependence, knowledge of its slope allows for easy quantitative calibration of the applied THz voltage. For the example shown in Fig. 1d) peak THz voltages of 4 V_{pp} are obtained in the junction.

Employing this method, we characterized the THz near-field dependence of the relative position of tip and THz focus, as shown in Fig. 1f) and 1g), where we see low-pass filtering due to frequency-dependent spatial overlap. We further can use the Gouy phase shift to tune the THz waveform from sinus-like to a cosine-like pulse (yellow curve). Together with straightforward control of the THz polarity and polarization via magnetization of the STE, our setup allows us to precisely tune the THz waveform according to the requirements for THz-STM.

Beyond characterization of the THz near-field, we started to investigate the dynamics of photoexcited charge carriers in the STM junction. Depending on sample bias and THz polarity, we find carrier dynamics on femtosecond to few picosecond timescales to contribute to the signal. For the example shown in Fig. 2a) using a W-tip and HOPG sample, photocarrier dynamics are observed several ps before arrival of the THz pulse. Whereas photoemission is a nearly instantaneous effect suitable for waveform sampling, tunneling of long-lived hot electrons at energies closer to the Fermi level requires convolution of the waveform with their respective lifetimes. Furthermore, for DC biases smaller than the applied THz voltage, slow photoelectrons can be decelerated back into the tip (or sample). To understand the observed dynamics, further modeling of photo-assisted tunneling through a time-dependent junction and calculation of photo-

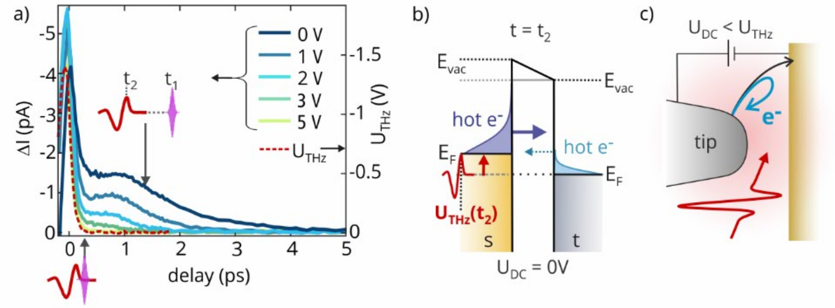

Figure 2. Dynamics of photocarriers measured for a W-tip and HOPG sample in a IR-pump - THz-probe scheme. (a) THz-induced photocurrent modulation for different sample biases at tunneling distances (I_{set} = 200 pA, U_{set} = 10 V). Note that the x-axis is reversed compared to Figures 1 (d) and (f). The red dashed line shows the first half cycle of the applied THz transient (right y-axis). Signal observed before arrival of the THz pulse can originate from either (b) long-lived hot electrons inside tip and sample, or (c) from slow photoelectrons decelerated back into the tip or sample by the THz field at low DC voltages $U_{DC}< U_{THz}$, for which photoelectron propagation is dominated by the spatio-temporal distribution of the THz field.

electron trajectories within the THz near-field is required. These experiments are a first step to demonstrate the ability of THz-STM to probe ultrafast carrier dynamics with femtosecond time resolution on THz sub-cycle timescales.

Curved-wavefront excitation of a spintronic THz emitter

Optimal operation of a THz-STM requires variable repetition rates between 100's kHz to few MHz, with µJ pulse energies for generation of THz pulses with sufficient field strength. Optically pumped emitters such as photoconductive antennas and spintronic emitters are very attractive for THz-STM as they allow for simple adjustment of the THz polarity and polarization, but they suffer from saturation effects and low damage thresholds. In the case of a spintronic emitter pumped with µJ optical pulses, depending on the pump spot size both ablation and thermal suppression of THz emission might occur. In this regard, placing the STE in the convergent or divergent part of a focused pump beam, we aimed for a flexible setup enabling tunable pump spot sizes which can be optimized for a specific repetition rate and pump pulse energy, respectively.

We find that the THz field strength decreases by more than 90% close to the pump focus independent of the pulse energy, excluding thermal heating effects. We attribute this large drop to a superposition of sub-wavelength emission (causing decreased radiation coupling to the far field) and THz beam propagation effects. Further investigation taking into account propagation of the THz beam are underway.

Further directions

After an initial period of implementation and experimental characterization of the setup, we will focus on using THz-STM as a nanoscale platform to study high-field THz-driven nonequilibrium states in matter with high spatial resolution using high repetition rate THz sources. We recently started to study room-temperature electroluminescence of p-doped GaAs out of the STM junction, aiming for the spatio-temporal investigation of THz-driven luminescence from semiconductor surfaces on sub-cycle timescales. Moreover, we are planning first time-resolved imaging experiments on photoexcited semiconductor surfaces and metal-semiconductor interfaces at room temperature. Furthermore we will upgrade our STM to cryogenic temperatures, which is necessary to access not only a wider class of samples, but also to improve the stability of the illuminated STM junction. This is a key aspect for experiments which conceptually do not require low temperatures, but which suffer from thermal instabilities of the tip and thermal drifts at room temperature.

Quantum Transport & Nanoelectronics Group
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High Resolution Scanning Gate Microscopy

Quantum transport on the nanoscale is often probed by electrical conductance measurements. However, these measurements typically lack spatial resolution and the observable, the current, is averaged over the whole junction. Especially at nanometer length scales the environment as well as the precise chemical composition of the junction will influence the measurement and the electronic properties of the material. Therefore, having utmost control over the junction is of importance. In our group we want to combine commercially available scanning probe microscopy (SPM) methods with additional electrodes integrated into the sample system, parallel to the surface, to electronically contact/gate nano-scale materials with nanometer precision. These additional electrodes in close proximity to the surface extend the functionality of the SPM to perform scanning gate microscopy, pointometry as well as Kelvin probe microscopy. In this manner the high spatial resolution of SPM can be combined with sophisticated transport experiments. In a nutshell, the detailed composition of the junction can be characterized by SPM while performing transport experiments. Furthermore, SPM enables modification of the structure or adsorbed molecules with atomistic precision.

The core of this technique are electrodes which bridge the gap from mm scale patches to µm wide contacts in the center of the silicon sample. It is of particular importance that these electrodes stay intact especially after the high temperature treatment necessary for preparation of Si(100), by several short annealing steps at 1000°C or higher. Therefore, antimony, which has a low segregation speed, was ion-implanted in close proximity to the surface. Key is that the silicon host material becomes insulating at low temperature whereas the implanted electrodes stay metallic because of their high dopant density. The precise arrangement of the ion-implanted electrodes is defined by the experimental question. For example, a narrow spacing between two electrodes is desired for conductance experiments while a larger separation is favored when using them to apply an electric field for gating purposes (see Fig. 1).

For this project we have designed and set up a home-build ultra-high vacuum system optimized for semi-conductor preparation which we extended with a commercially available low-temperature SPM from Createc GmbH. Most importantly we have developed a sample holder matching the needs of high quality semi-conductor surface preparation and in-situ transport measurements: Four insulated contact are integrated into the sample clamping system of the sample holder, equipped with direct heating possibilities. Each of the four clamps will be pressed against one of the four ultra-shallow electrodes for electrical contact.

Experimental characterization of the electrodes

We tested a first set of ion-implanted electrodes by comparing their temperature dependent resistivity with and without antimony wires. To avoid out-diffusion of the dopants the thermal budget must be limited to approximately 1050°C. In contrast to a reference sample without wires the four-probe resistance of a 1 µm wide wire does not rise continuously with decreasing temperature, but reaches a plateau at roughly 0.01M Ohm (see Fig. 2a). Furthermore, a characteristic Ohmic behavior is found for the implanted wires, which is desired to rule out contributions of the contacts to the conductance measurements (see Fig. 2b). This changes when annealing the sample above 1050°C. Out-diffusion of the dopants sets in and the resistivity increases and a non-linear IV dependence is observed.

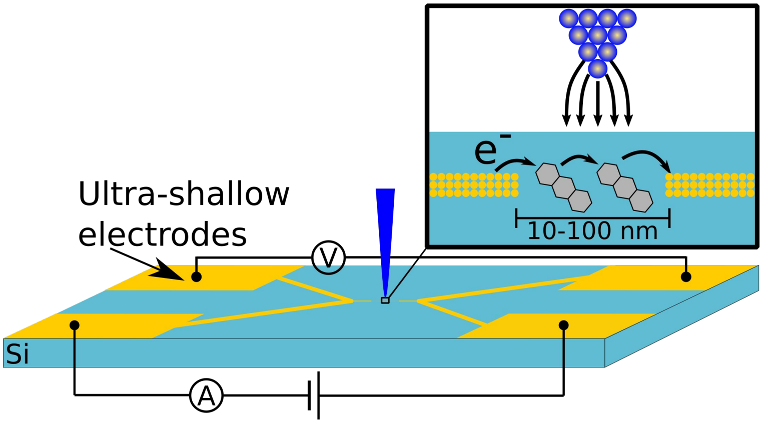

Figure 1: (a) Schematic illustration of the experimental setup: A Si(100) sample equipped with four ultra-shallow ion-implanted electrodes bridging the gap from mm to µm. These implanted electrodes can be subsequently extended with STM hydrogen resist lithography to the nm scale.

The lateral confinement of the implanted regions is confirmed by measuring the resistance of two electrodes separated by a narrow insulating region with varying width. Electrically this can be described as two p-n junctions in series, resulting in an open bipolar transistor. The IV traces are no longer Ohmic but have a large non-conducting region, which increases linearly with the separation (see Fig. 2 b and c). The narrow area between the two electrodes might limit the formation of the depletion layer and the device will be punched through. Interestingly, even when annealing the sample repeatedly to 1050°C the gap stays intact, demonstrating that lateral diffusion seems to play a minor role.

To locate the electrodes on the sample with the SPM tip a marker design, compatible with the high temperature treatment, was developed, which does not deteriorate the surface quality. The reactive ion etched markers allow us to position the SPM tip with nm-precision, even after taking the sample out of the SPM stage and growing a silicon encapsulation layer (M. Koch *et al.* 2019).

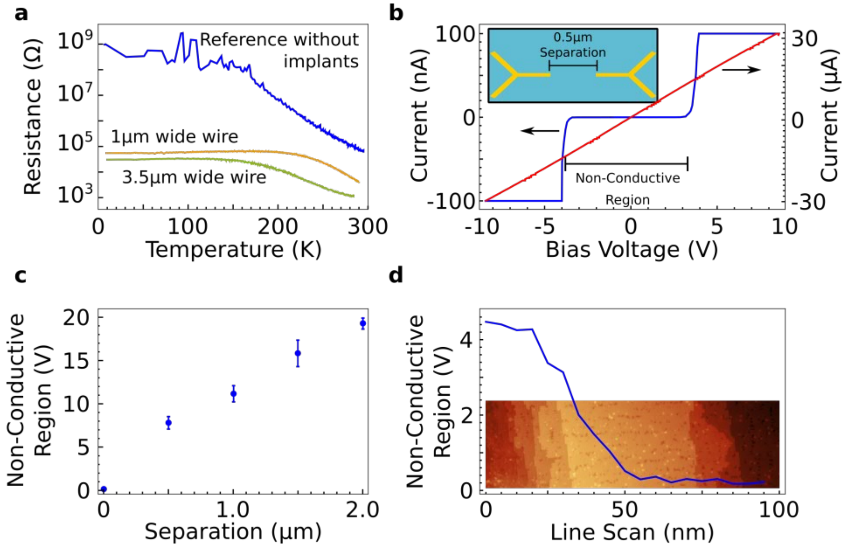

Figure 2: (a) Sample resistance as a function of temperature for a reference sample without implants and for two ion-implanted wires with a width of 1 and 3.5μm, respectively. (b) IV trace of a 1μm wide wire (red) and of two electrodes separated by 0.5μm weakly doped silicon (blue). (c) Size of the non-conductive region as a function of the electrode separation. (d) Non-conductive region extracted from STM spectroscopy. The inset shows the STM image of the same region. The sample temperature is 5K if not stated otherwise.

The enhanced conductance of the electrodes is visualized with STM spectroscopy. With increasing distance of the SPM tip to the electrodes a non-conductive gap opens which increases rapidly in size and a high bias voltage is required for STM imaging. However, we find that the presence of the electrodes does not influence the surface quality (Fig. 2 d).

Outlook

We have now successfully developed a platform with conducting electrodes on insulating Si(001), which bridge from mm length scale down to the (sub) μm scale. This versatile sample system will be used to study different scientific problems. For example, we will investigate the charge transport through organic molecules and nanostructures as well as electronic properties of nanoscopic 2D materials, like transition metal dichalcogenide (TMDC) flakes. To contact objects even down to the few nm scale we want to extend the ion-implanted ultra-shallow electrodes with STM patterned electrodes (STM hydrogen resist lithography) based on controlled phosphine adsorption. While the hydrogen passivated silicon surface is rather inert, the non-terminated (hydrogen free) Si(001) surface consists of unsaturated dangling bonds and is highly reactive. By controlling the surface passivation and removing hydrogen with atomic precision, the adsorption site of molecules can be steered. In the case of phosphine this has been perfected to pattern electronic circuits with STM. These truly nano-scale circuits will then be used to electrically contact for example organic assemblies to study their transport behavior.

By applying oscillating electric fields we intend to induce motion on the molecular level which will be studied by SPM. For this purpose we have designed a double-decker molecule with an integrated dipole moment, isolated from the substrate. SPM manipulation will allow to control the environment of the molecular rotor so that we can address the steric interaction between individual molecules.

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Interfacial Molecular Spectroscopy

Much of the work performed in our group is done in collaboration with the Nonlinear Spectro-Electrochemistry Group of Dr. Yujin Tong, who was a post-doc with us until 2017. While there is substantial overlap of the interests of both groups, he has focussed to a larger extent on the steady-state characterization of other catalytically interesting systems. As of the winter of 2019/20 the activities of both groups will move to the University of Duisburg-Essen where Dr. Campen has been appointed as a W3 Professor and Dr. Tong will take up a senior scientist position.

The Goal: Mechanistic Insight into (Photo)electrocatalysis

(Photo-)electrocatalytic chemistry holds out hope for mitigating human effects on the climate system, more efficiently producing value-added chemicals and helping clean up polluted environments. Building the best possible catalysts for reactions of interest requires understanding the *mechanism* of the relevant heterogeneous chemistry and its change with catalyst material, solution composition and surface structure. Despite the clear need for this sort of insight there are very few catalytic systems where the mechanism of the relevant chemistry is well understood.

The absence of such insight can be largely attributed to three factors: (1) particularly for buried, solid/liquid, interfaces characterizing interfacial molecular structure is experimentally challenging, (2) most candidate catalytic materials have significant spatial structural heterogeneity and thus presumably strong spatial heterogeneity in reactivity, and (3) assuming the first two hurdles can be overcome, experimental characterization of interfaces under steady-state reactive conditions cannot unambiguously probe mechanism: one cannot know whether a particular species observed at an interface is an intermediate in the desired chemistry or an unwanted side product.

In the *Interfacial Molecular Spectroscopy Group* we focus on addressing these challenges for prototypical electrode/electrolyte and solid/gas systems. We are doing so by developing nonlinear optical, vibrationally resonant sum frequency generation (VSFG), and mixed optical/current measurements that allow the characterization of the solid/gas and electrified solid/liquid interface with *interfacial specificity*; by performing second harmonic generation (SHG) microscopy *to spatially characterize chemical reactivity operando* and *by performing femtosecond perturbation experiments* to overcome the limits of steady-state characterization of reactivity.

Building Interface-Specific Tools

From 2017-2019 we invested much effort in developing VSFG spectroscopy for application to (thin-film) spectro-electrochemistry. It was necessary to overcome a substantial number of technical obstacles (e.g. identifying materials that are suitable for both optics and electrochemistry, compensating for distortion of fs pulses, etc). In many of these we were largely successful: *e.g.* we have characterized the potential dependent structure of water and of sulfate on an Au and Pt electrodes and of ClO_4^- at the air/water interface [Tong 2017][Zwaschka 2018][Tong 2018].

Because we are interested in (photo)electrocatalytic systems with semi-conductor electrodes, and a central issue in such systems is the role of surface states, we have invested much effort in developing optical surface phonon spectroscopy by extending VSFG to MIR wavelengths. Part of the challenge here is relating this novel observable to microscopic surface structure. We have done so on α-Alumina single crystals, where, in collaboration with theory from Prof. Peter Saalfrank (University Potsdam) we have quantified the manner in which increasing coverages of water (from UHV to ambient) induce surface reconstruction.

Finally, conventional VSFG spectroscopy detects the intensity of the emitted sum frequency light, not the field. However, accurate extraction of the interface's nonlinear optical response, and in particular the separation of surface and possible bulk contributions, requires high precision measurements of both the amplitude and phase of the emitted sum frequency field. Performing this measurement, particularly for interfaces between two condensed phases, is extremely challenging. In this period we have developed a novel, collinear, time domain, balance detected heterodyned spectrometer [Thämer 2018] and demonstrated its application to the quantitative separation of surface and bulk signals in α-quartz [Thämer 2019], and for the characterization of the optical response of the metal electrode/ electrolyte interface.

Resolving the Spatial Heterogeneity of Reactivity

To address the challenge in understanding the *spatial heterogeneity* of electro-catalytic reactivity we initiated a collaboration with Prof. Sylvie Roke (at EPFL Lausanne). In proof-of-principle experiments we constructed in electrochemical cell inside an existing second harmonic generation (SHG) microscope and imaged the electrooxidation and oxygen evolution reactions on several Au electrodes *operando*. The exceptional signal-to-noise of this microscope made it possible to resolve the growth and detachment of O_2 bubbles, under mildly anodic conditions, in real-time. Given this capacity, we demonstrated that the reactivity of the surface is controlled by active sites that are 3-11 % of the surface area, as shown in Fig. 1, and are of least two different structural types. This is a new approach to electrocatalytic systems and is, to our knowledge, the first study to spatially resolve product formation in water splitting on an electrocatalyst.

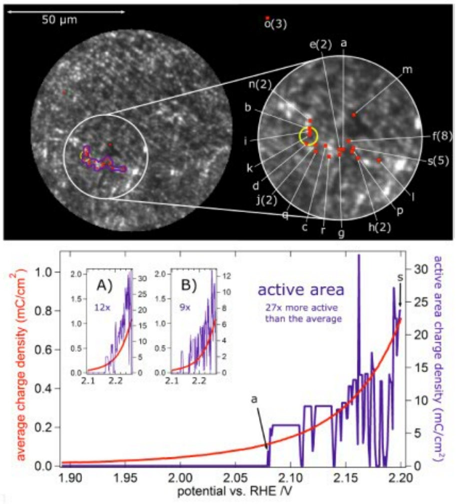

Figure 3: top left panel: circular FOV of the electrode at 1.8 V vs. RHE. Red dots are sites at which bubbles nucleate during the linear potential sweep shown in the bottom panel. Top right: magnification of active area showing the order of bubble appearance. Bottom panel: comparison of measured electrode charge density and bubble derived charge density for three different fields of view.

Moving Beyond Steady-State Reactive Conditions

We are currently moving beyond steady-state nonequilibrium characterization for the hydrogen evolution reaction (HER) on Pt and Au. We do so by performing perturbation experiments triggered, using fs optical pulses, on the fs timescale of electron transfer. As an initial step on Pt single crystal working electrodes we demonstrated the detection of photocurrents induced by femtosecond optical excitation as a function of bias [Zwaschka 2019]. This approach allows separation of current induced by the femtosecond duration elementary step of charge transfer from that induced by slower, picosecond, electrolyte structural dynamics. The results of its application to the HER on Pt suggest that ease of electron

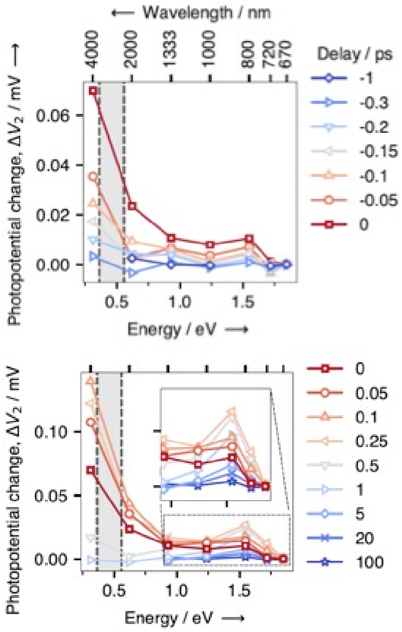

Figure 4: Photovoltage induced by a 4.56 eV UV pulse and a second pulse of variable photon energy plotted as a function of photon energy and delay between the two femtosecond pulses. The presence of a photoinjected conduction band electron near 0 fs Is clear (adsorption in the far infrared) and its localization over 200 fs (shift of spectral position towards 800 nm). The resulting localized solvated electron is long-lived and its spectral response, which is 200 meV red shifted from its bulk value, reflects the electrons partial desolvation at the interface.

transfer may control previously observed trends in H_2 generation activity with change of Pt crystal face[5]. Current work is devoted towards spectroscopic characterization of the interface after excitation using VSFG.

Using a similar approach, we also characterized the mechanism of H_2 generation at the Au electrode/water interface. In contrast to Pt, hydrogen adsorbs very weakly on Au and thus we initiate adiabatic electron transfer by forming an interfacial solvated electron (which reduces water forming H_2 over longer timescales). We have observed this solvated electron in a novel two pulse photovoltage scheme in which we form the solvated electron with an initial femtosecond UV pulse, illuminate the interface with a second fs pulse, and measure the photovoltage as a function of delay between the two pulses and the wavelength of the second pulse. This scheme, some results from the application of which are shown in Fig. 2, in conjunction with more conventional UV pump – VSFG probe measurements, allows us to extract the spectrum of the solvated electron at a metal water interface and show how the surface bias alters its local structure.

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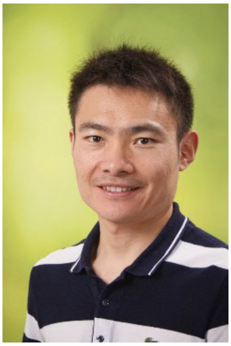

Nonlinear Spectro-Electrochemistry Group

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Nonlinear Optical Spectro-Electrochemistry

A deep understanding of electrochemical processes generally requires a combination of electrochemical and spectroscopic methods. While electrochemical analysis can provide the potential, current and charge information, the spectroscopies can reveal the electronic and vibrational properties of the reaction intermediates or products. The combination is referred to as *spectro-electrochemistry*. Among the modern spectro-electrochemical techniques, vibrational spectrsocopy such as Infrared absorption and Raman scattering are powerful in terms of providing structural and chemical information of interfacial species and have thus been widely employed for *in situ* spectro-electrochemical characterization. However, IR and Raman spectroscopies are not surface specific. When the surface and the bulk have similar chemical compositions, i.e. bulk solvents and anions adsorb to the electrode surface, it is very challenging to selectively probe the adsorbed species and discriminate from those of the bulk. Vibrational sum frequency spectroscopy (VSFS), based on the 2nd order nonlinear optical process, is intrinsically surface specific hence an excellent tool in probing buried interfaces. Our group employs VSFG to study fundamental processes in electrochemistry, whereby a majority of work has been done in collaboration with Interfacial molecular spectroscopy group of Dr. R. Kramer Campen.

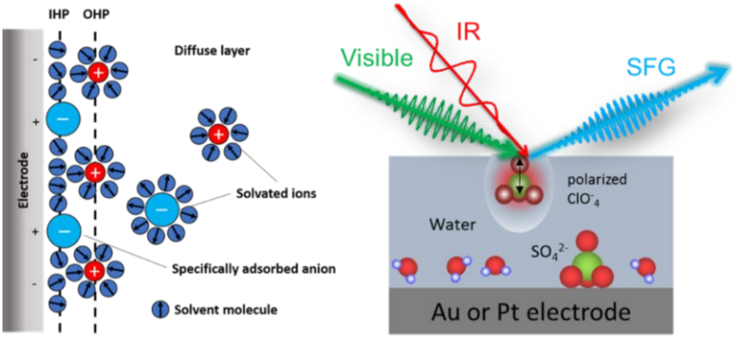

Figure 5: Left panel: Electric double layer structure according to the Gouy–Chapman–Stern model. Right panel: Example systems studied with VSFS in our group: hydrophobic water on gold; sulfate adsorbed on a Pt(111) single crystal electrode and solvated perchlorate at the air/water interface.

Structure of the electric double layer

Electric double layer is the key component of electrochemistry, where reactants, products, ions and solvents follow certain spatial distribution at the interface. Currently the most accepted model is the Gouy-Chapman-Stern model (Fig. 1 left), in which the interface has been divided into three regions: the inner Helmholtz plane, where solvent and specific anions adsorb directly to the electrode; the outer Helmholtz plane, where solvated cations present; and the diffuse layer, where ions follow Poisson- Boltzmann distribution. However, this model is depicted based essentially on the thermodynamic measurements, i.e. the electro-capillary curve, surface excess, differential capacitance, etc. The molecular level information is still insufficient and many of the recent observations cannot be explained by this qualitative model. For example, why different ions can affect the efficiency and selectivity of CO_2 reduction? To gain such information, we have to directly probe the molecules and ions in the electric double layer. This is what we are doing in our group. A few examples are shown in the right panel of Fig. 1. With VSFS, we have successfully probed the bias dependent structure of water on gold electrode, the chemical and physical nature of sulfate anions on Pt(111) surface, and also the anisotropic properties of the polarizability of perchlorate at the air/solution interface where weak electric double layer present.

Structure and chemistry of adsorbates under potential control

Electrochemistry is about the chemical reaction under bias control. In the ideal case, one would like to follow the evolution of all the structure and chemistry of the reactants and products during the reaction. Here we demonstrate with a model system of pyridine derivative (Dimethylaminopyridine) to monitor the deprotonation and phase transition processes with VSFS. As demonstrated in Fig. 2, the spectroelectrochemical approach can provide fruitful information to reveal the detailed physical chemistry actions that happen as a function of bias.

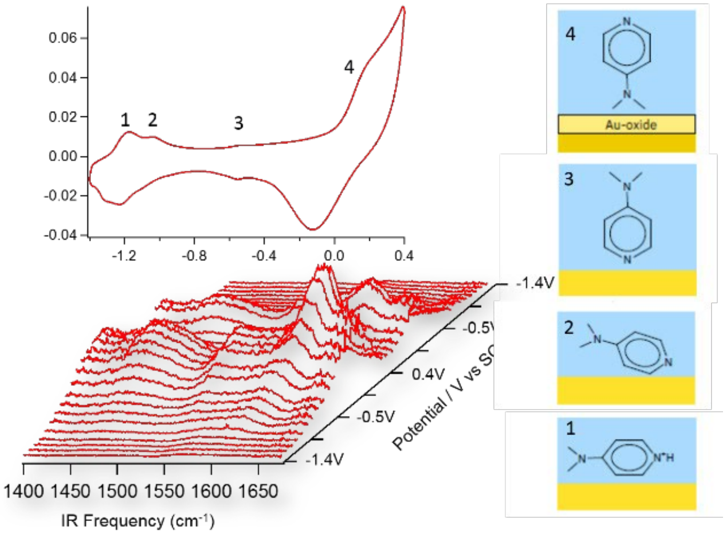

Figure 6: Top left: Cyclic voltammetry of gold electrode in 0.1M $NaClO_4$ solution containing 1mM Dimethylaminopyridine (DMAP). The Numbers indicate features related to the interaction of DMAP with the gold electrode; Bottom left: potential dependent VSFG spectra of DMAP; Right panel: The corresponding chemical and structural changes as suggested from the spectroelectrochemical measurements.

Toward ultrafast electrochemistry

Many electrochemical and photo-electrochemical related processes take place on pico- or even femtosecond time scales. However, a three electrode system coupled to a conventional potentiostat has a rather poor time resolution of, at best, 10 ns. To overcome this resolution problem, we have combined the photocurrent or photovoltage detection with ultrafast laser excitation. As demonstrated in Fig. 3 left, using a sequence of two ultrashort laser pulses of different photon energies and detecting the laser induced change in photovoltage as a function of time delay between the two incident pulses, ultrafast electrochemical processes on femtosecond timescales can be resolved.

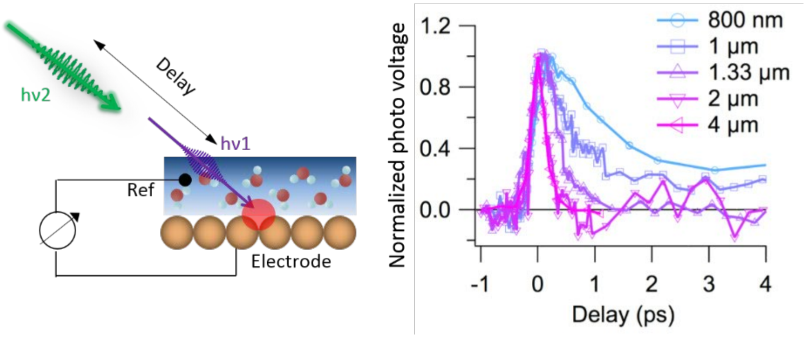

Figure 7: Left panel: scheme for newly developed photo voltage detection scheme to follow ultrafast processes at electrochemical interfaces. Right panel: time dependent photo voltage measured for gold solution interface as trigger by a UV laser (267 nm) followed by a second layer pulse with the indicated energies. The dynamics consistent with the evolution of solvated electron at the interface.

This method can be employed to study the evolution of the interfacial charge carriers which are directly relevant to photo-electrochemistry. Since the measured quantity is the charge/voltage instead of photons, the experimental geometry will be less restricted by the spectroscopic requirement, hence this method can be directly used for *in situ* characterization of the photovoltaic devices. The right panel of Fig. 3 shows as an example of such study, whereby photoinjected solvated electrons at the gold/solution interface are monitored. The excitation laser was chosen at 267nm, whicle the probe laser (2nd pulse) was tuned from mid infrared to the visible frequency region. The induced photovoltage induced by the 2nd pulse is plotted as a function of delay in Fig. 3, right panel. The wavelength dependence is attributed to the different degrees of localization of solvated electrons at the interface. The results suggest that with such ultrafast laser excitation, sub picosecond time resolution could be achieved at the electrochemical interface.

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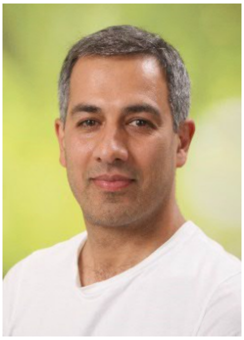

THz-Driven Molecular Dynamics Group
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Terahertz Spectroscopy of Molecular Systems

Collective and cooperative molecular motions are decisive to the physical and chemical properties of molecular systems. The spectral fingerprint of these dynamics lies in the low-frequency terahertz (THz) and sub-THz frequency range. We aimed to develop novel spectroscopic techniques by which the entire THz dynamics of liquids can be obtained and further gain microscopic insights on intermolecular interactions.

Ultra-Broadband THz time-domain spectroscopy

We have employed THz time-domain spectroscopy (THz-TDS) to obtain the dielectric loss and permittivity spectra of liquids. In our approach the THz spectra of liquids in the 0.5 THz - 16 THz range are obtained, using an inherent property of the newly developed spintronic emitter. As shown in Fig. 1, upon femtosecond excitation, the spintronic emitter radiates a THz pulse inversely proportional to the complex refractive indices of the surrounding materials (namely diamond and a liquid). Relative to the refractive index of air, the ultra-broadband complex refractive index of liquids is obtained with unprecedented accuracy[1].

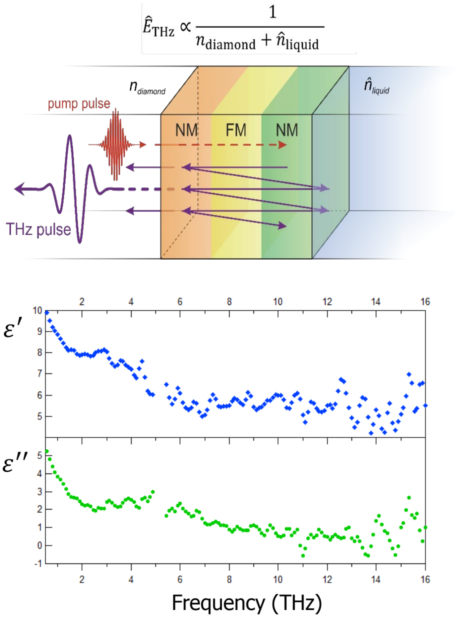

Figure 1: Top) The radiated THz pulse from a few nm thick spintronic emitter is inversely proportional to the refractive indices of the materials sandwiching the metallic stack. We used this feature to obtain the complex refractive index $\hat{n}_{\mathrm{liquid}}$ of liquids. When a liquid is in contact with the metallic stack, its $\hat{n}_{\mathrm{liquid}}$ is printed on the radiated THz pulse due to the Fabry–Pérot effect. Below) The ultra-broadband dielectric permittivity ε' and loss ε'' spectra of liquid water are obtained by the spintronic emitter approach. The covered bandwidth of the measured response depends only on temporal duration and the stability of the laser pulse that pumps the spintronic emitter.

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[1] To keep the novelty of the spintronic THz spectrometer for a patent application, we appreciate if this information is treated as confidential.

Time resolved nonlinear THz spectroscopy

To overcome the limitations of linear THz spectroscopy to characterize the intermolecular interactions and dynamics we employ nonlinear THz spectroscopy by which the intermolecular degrees of freedom are resonantly driven with intense THz pulses.

THz Kerr Effect (TKE). Here, we measure the THz-pump induced ellipticity of an optical pulse traversing the liquid samples as function of the time delay between the THz pump and the optical probe pulses. The third-order nonlinear response of the TKE signal, scales with the square of the permanent dipoles of the liquid at the THz pump frequency and its polarizability anisotropy at the probe frequency. The latter relation was directly corroborated in our TKE studies of molecular gases.

Ultrafast Energy Dissipation in Water. Due to its ability to form hydrogen bonds, water exhibits rich low-frequency intermolecular dynamics within a spectral bandwidth of more than 1000 cm^{-1} (~30 THz). The different intermolecular degrees of freedom associated with the H-bonding network of water facilitate ultrafast and efficient dissipation. Using the TKE approach, we resolved the real-

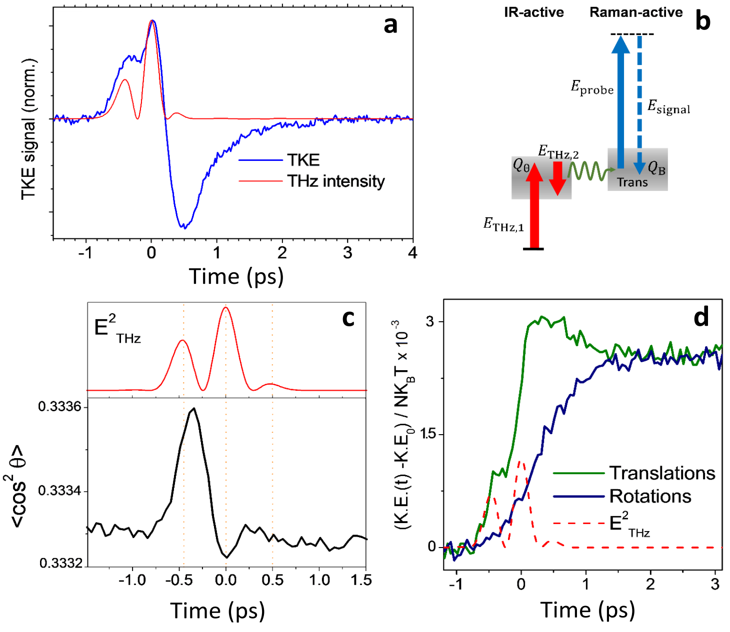

Figure 2: a) Water has a peculiar bipolar THz Kerr effect (TKE) signal with a feature resembling the THz field squared around time zero followed by a relaxation tale with flipped polarity. b) Two-field interaction changes the rotational distribution of molecules (coordinate Q_θ) from a disordered into a partially aligned molecular system. The energy/momentum of this interaction is transferred into the restricted translational motion (coordinate Q_B) of the neighboring molecules, shown as a wavy arrow. The relaxation of the latter mode is observed in the TKE signal via a Raman interaction. c) MD simulations reveal a significant molecular alignment due to the THz electric field torque on the molecular dipoles however, with no relaxation tail. d) Dynamics of the kinetic energy declare relaxation of the molecular translational degrees of freedom (green line) analogous to the TKE signal relaxation tail. The step-like increase of the kinetic energy exhibits the 100 mK temperature rise due to THz absorption.

time energy fellow within the H-bonding network of water. As shown in Fig. 2, the bipolar TKE signal of water manifests intermolecular energy transfer between the rotational and the translational degrees of freedom. MD simulations[2] corroborate the experimental findings. A significant THz field induced molecular alignment is found, but no relaxation is resolved. However, we observe a relaxation tail resembling the tail of the TKE signal of water, in the translational degrees of freedom of water molecules.

Nonlinear THz spectroscopy of aqueous ionic solutions. The symbiotic relation of water and ions is vital to the bio-functionality of both partners. Water shields the giant electric field of ions which otherwise strongly polarizes their surrounding and in return its H-bonding network is disrupted. However, the extent of this co-operativity and mechanism of ionic solvation are not exactly known. To this end, we measured the TKE response of a large series of aqueous ionic solutions. Notably, as the TKE response of aqueous solutions originates from a water-water interaction, it can directly probe the structural deformation of water around ions. In general, relative to the pure water signal, we observe a reduction (enhancement) of the TKE signal amplitude for anions (cations) which signifies the different cationic versus anionic solvation mechanisms. Cations are repelled by the H-bonding network and interact electrostatically with the water electron lone pairs, resulting in stronger H-bonding between water molecules. In contrast, negatively charged anions accommodate themselves in the H-bonding network, disrupting the water-water coupling.

THz-Magnetic-field induced Faraday Rotation in Molecular Liquids. Upon copropagation of a THz pulse, with ~1T magnetic field strength and 0.5ps duration, and a short optical pulse through molecular liquids, we resolved an ultrafast Faraday rotation of the optical pulse. Analog to the electric Hall effect, the polarization rotation is explained by the deflection of an optically induced instantaneous electric polarization by the Lorentz force originated from the THz magnetic field. The resolved effect scales linearly with the THz magnetic field and quadratically with the molecular polarizability. Nonpolar liquids (e.g. n-hexane) and long chain alcohols (e.g. 1-hexanol) show strongest Faraday rotation.

Rotational dynamics of encapsulated water molecules. Fullerene based molecular cages provide a unique opportunity to study the dynamics of confined molecules. For example, the dynamics of different spin isomers of water can be accessed in H2O@C60. To this end, as shown in Fig. 3 we obtained the THz transmission spectra of H2O@C60 at 8K and remarkably resolved the onset of ortho (total spin I=1) to para (total spin I=0) conversion of water spin isomers[3]. We have also measured the THz pump/THz probe response of H2O@C60 at 220K. The latter signal shows the real-time dynamics of the encapsulated molecule. Further measurements are underway to capture the entire spin conversion dynamics of H2O@C60 and resolve the non-saturated rotational transition line shapes. The latter information will enable us to realize the impact of the highly polarizable C60 cage structure on water dynamics. Moreover, we will perform THz pump/THz

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[2] In collaboration with Thomas Kühne, Paderborn University and Roland Netz, Free University Berlin.

[3] In collaboration with Richard Whitby and Malcolm Levitt, University of Southampton and Boris Gorshunov, Moscow Institute of Physics and Technology.

probe experiment at 77K to resolve both the coherent and the non-coherent dynamics of ortho and para spin isomers of water.

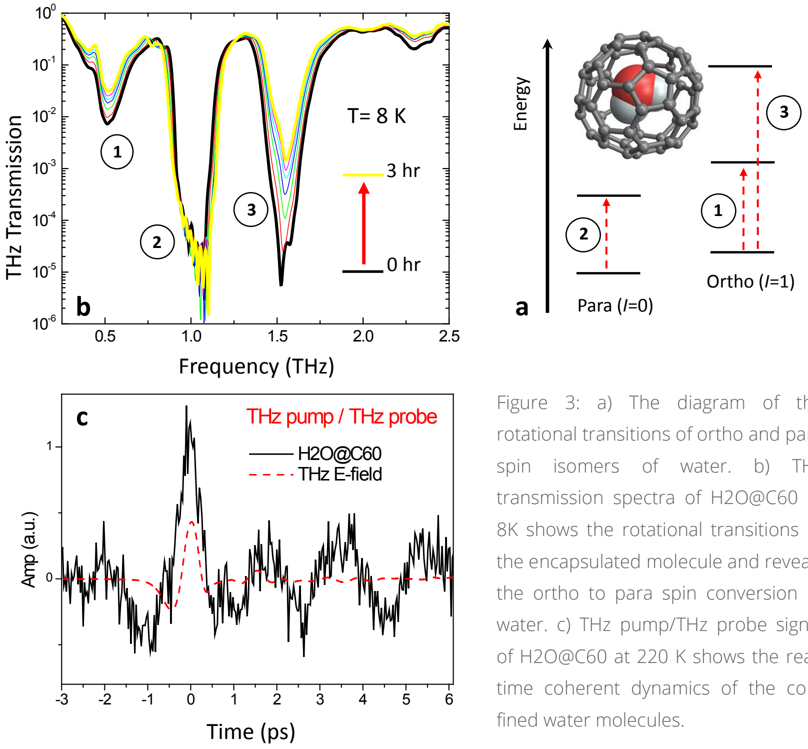

Figure 3: a) The diagram of the rotational transitions of ortho and para spin isomers of water. b) THz transmission spectra of H2O@C60 at 8K shows the rotational transitions of the encapsulated molecule and reveals the ortho to para spin conversion of water. c) THz pump/THz probe signal of H2O@C60 at 220 K shows the real-time coherent dynamics of the confined water molecules.

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Scientific Scope of the Electron Dynamiχ Group

The group's research focus lies on the non-equilibrium dynamics in materials and at their surfaces as well as interfaces launched by ultrafast optical excitation. Using a broad selection of femtosecond time-resolved (TR) spectroscopic techniques, we investigate how particles, quasiparticles, and the electronic structure of matter react to photoexcitation on an ultrafast timescale. With this approach, we do not only characterize elementary relaxation mechanisms and determine how different subsystems interact; the research is consciously tailored to identify and understand the differences in bulk and interface properties of materials and, ultimately, create transient functionality at interfaces by the exploitation of the evanescent properties of so-called "hidden" or "unconventional" states of matter.

Ultrafast Quasiparticle Dynamics in (Quasi-)2D Systems

Exciton dynamics in monolayer WS_2

In WS_2, multiparticle states like excitons or trions are present even at room temperature and dominate the optical response. Optical excitation of a transition metal dichalcogentite (TMDC) and the resulting transient change of quasiparticle density in the system strongly affects the screening of the Coulomb interaction, reducing the binding energy E_B of the multiparticle states and, simultaneously, decreasing the quasiparticle band gap leading to red and/or blue shifts of optical resonances (Fig. 1b) that are unpredictable *a priori*.

We investigated the photoinduced change of the optical response of a pristine monolayer of WS_2 on SiO_2 under different excitation conditions. The broadband reflectivity contrast (RC, Fig1a) shows two overlapping optical resonances, the A exciton (X_A) at 1.95 eV and the trion (T^-) at 1.91 eV. The non-equilibrium dynamics of their energy position, width, and intensity after (i) resonant (hv_{pump} = 1.96 eV) and (ii) above-resonant (hv_{pumo} = 3.1 eV) expose a complex multi-exponential character. While (i) resonant excitation, which solely generates excitons in the material, leads to an overall *blue* shift of the X_A resonance, (ii) above-resonance excitation, which initially primarily excites quasi-free carriers in the system, first results in a *red* shift that later emerges to a blue shift (Fig. 1c). We conclude that the E_B reduction induced by exciton screening is stronger than the excitons' impact on the quasiparticle band gap, while the free carrier screening of the Coulomb interaction leads to a stronger band gap renormalization than E_B decrease. Based on a very simple rate equation model, we find - in agreement with literature - that exciton formation occurs within τ_F = 0.9 ps, competing with quasi-free electron-hole recombination with a time constant of τ_D = 1.6 ps. The initial exciton population decay happens within τ_X = 5.9 ps, likely *via* an Auger process.

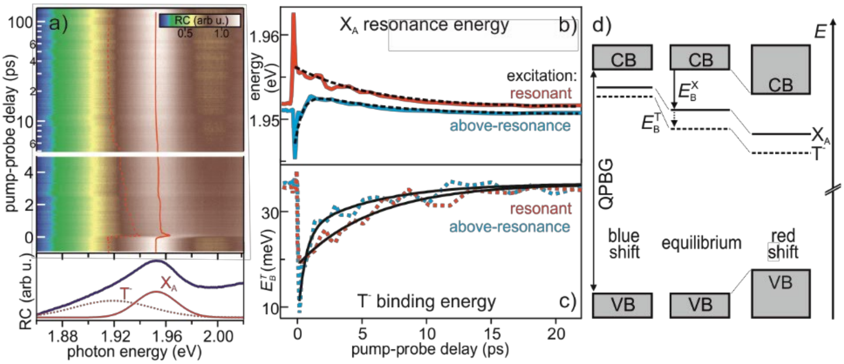

Figure 8: a) Top: Reflectivity contrast (RC) in false colors as a function of photon energy and pump-probe time delay, solid and dashed red curves indicate the peak position of the X_A and T^- resonance position respectively. Bottom: Spectrum at $t < 0$ (blue) and corresponding X_A and T^- fits. Time-dependent evolution of b) the X_A resonance energy and c) the trion binding energy for resonant and above-resonance excitation. d) illustrates how screening of the CIA can lead to red and blue shifts of optical resonances

This work demonstrates the fragile balance of free carrier and exciton screening of the Coulomb interaction that determine the complex non-equilibrium optical properties of TMDC monolayers and highlights the different interactions of excitons and trions with photogenerated quasiparticles [Calati *et al.*, in prep.].

Inhibition of a photoinduced structural phase transition in TNS

We used fs TR mid-IR reflectivity to investigate the electron and phonon dynamics occurring at the direct band gap of the excitonic insulator Ta_2NiSe_5 (TNS) below the critical temperature of its structural phase transition from a monoclinic to an orthorhombic high-*T* phase. The phonon dynamics show a strong coupling to the excitation of free carriers at the Γ point of the Brillouin zone. The optical response saturates at a critical fluence of 0.3 mJ/cm^2 due to optical absorption saturation. This limits the excitation density such that the system cannot be pumped sufficiently strongly to undergo the structural phase transition [Mor 2018].

Complex Non-Equilibrium Dynamics in Transition Metal Oxides

Ultrafast generation and decay of a surface metal in ZnO

Photoinduced phase transitions occur in strongly correlated systems due to coupling between electronic, lattice, and spin degrees of freedom. Also, semiconductor-to-metal transitions occur in many "conventional" semiconductors upon doping, e.g. in phosphorous-doped Silicon. ZnO undergoes a such a transition, too, when the surface is "doped" with hydrogen resulting in downward surface band bending causing a partially filled conduction band (CB).

We succeeded in driving an ultrafast semiconductor-to-metal transition at the ZnO(10$\bar{1}$0) surface [publication in preparation]. A first laser pulse ($h\nu_{pump}$) generates holes in the valence band (VB) and depletes deep-lying in-gap states caused by surface defects, which induces downward surface band bending (Fig. 2a). The resulting dynamics near the Fermi energy (E_F) are probed by a time-delayed second fs laser pulse $h\nu_{probe}$ by angle-resolved photoelectron spectroscopy (ARPES). Photoexcitation causes the generation of density of states (DOS) below E_F (Fig. 2b, top) and, simultaneously, to a downward shift of the VB (bottom), indicative of a photoinduced downward surface band bending. This is an *inverse* surface photovoltage effect due to a transient increase of surface charge by photodepletion of defect states.

The non-equilibrium state of ZnO exposes all footprints of a transient metal: DOS below E_F (Fig. 2b) of a partially filled dispersive band (m_{eff} = 1.6(4) m_e), showing the same build-up (20 fs and 1.25 ps) and decay dynamics (224 ps) as the up- and downward shifting of the VB (Fig. 2c), respectively, and an electron distribution following Fermi-Dirac statistics that thermalizes with the lattice within 200 fs (not shown). This work demonstrates that ultrafast semiconductor-to-metal transition can be photoinduced in "ordinary" semiconductors in the absence of strong correlation effects. Complementary to previous studies, which showed the ultrafast formation of *metal-like semiconductors* (e.g. Si or GaAs) after strong photoexcitation with quasi-Fermi energies in the CB and VB through photoexcited carriers at densities exceeding the Mott density of the respective material, our results reveal the formation of a *transient metal* with a Fermi-Dirac distribution centered at the equilibrium E_F of the ground state semiconductor [Gierster *et al.*, submitted to *Nature*]. This finding is of great relevance for industrial applications, in particular combined with the ultrafast back-switching to the semiconducting ground state, which could not be demonstrated for photoinduced phase transitions in strongly correlated systems so far.

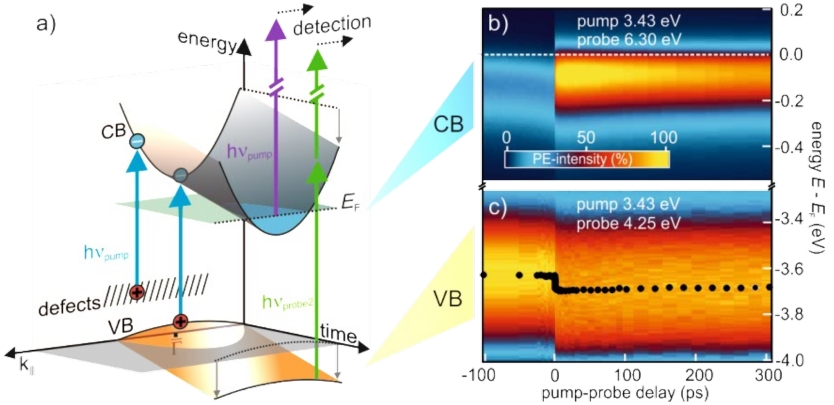

Figure 9: a) Experimental scheme and observed processes. Photodepletion of defect states causes a transient downward surface band bending via an inverse surface photovoltage effect. The resulting time-dependent population of the CB, which is shifted below E_F, and the down-shift of the VB are depicted in b) and c), respectively. Build-up and decay of both effects occur on coinciding timescales and behave similar to the formation and relaxation of the nearly-free electron mass of the transient surface electron signal (not shown).

First TR photoemission experiments of Hematite (1$\bar{1}$02) surfaces

Up to date, all measurements of excited states in hematite (α-Fe_2O_3), which is the most stable iron oxide in nature, lack an absolute energy scale. We are conducting TR-ARPES of (i) the bulk-like (1x1) and (ii) the oxygen-deficient (2x1) surface termination of the (1$\bar{1}$02) surface. In good agreement with previous UPS work, the equilibrium VB maximum lies at (i) 1.58(5) and (ii) 1.77(5) eV below E_F and an occupied state attributed to Fe^{2+}-like cations of the (2x1) structure is found at 1.13(5) eV. We observe a fluence-*independent* reduction in surface potential, presumably caused by adsorption of residual hydrogen gas or oxygen defect formation, and an additional fluence-*dependent* component of surface potential decrease which is interpreted as a reduction of intrinsic upward surface band bending owing to a surface photovoltage effect.

Interfacial Electronic Structure & Elementary Excitations in Hybrid Systems

Disentanglement of a hybrid exciton in the time domain

The notoriously low charge separation efficiency at ZnO-organic interfaces was suggested to result from weak electronic coupling of the LUMO to the ZnO CB or from the formation of a hybrid charge transfer state, which favors recombination at the interface. Using TR–ARPES, we disentangled the key processes in the charge separation sequence at the interface of a ZnO single crystal and *p*-quinquephenyl-pyridine (5PPy, inset in Fig. 3a). Characterization and comparison of the interfacial electronic structure of pyridine/ZnO(10-10) with the one of 5PPy/ZnO(10-10) reveals an occupied in-gap state directly below E_F, an extraordinarily strong work function reduction >2 eV, and a 5PPy LUMO around 2 eV above E_F [Vempati 2019]. In order to disentangle the contributions of pure electronic coupling of the LUMO to the ZnO CB and to reveal the influence of the electron-hole interaction on the charge separation dynamics at this inorganic/organic interface, we used two different excitation schemes to transiently populate the LUMO: Interfacial excitation from the in-gap state (Fig. 3b) causes population decay due to pure wave function overlap with the ZnO CB within only 70 fs (Fig. 3a, green), while intramolecular excitation (Fig. 3c) results in a lifetime increase by a factor of five (Fig. 3a, blue) as a result of the on-site electron-hole interaction in the molecule.

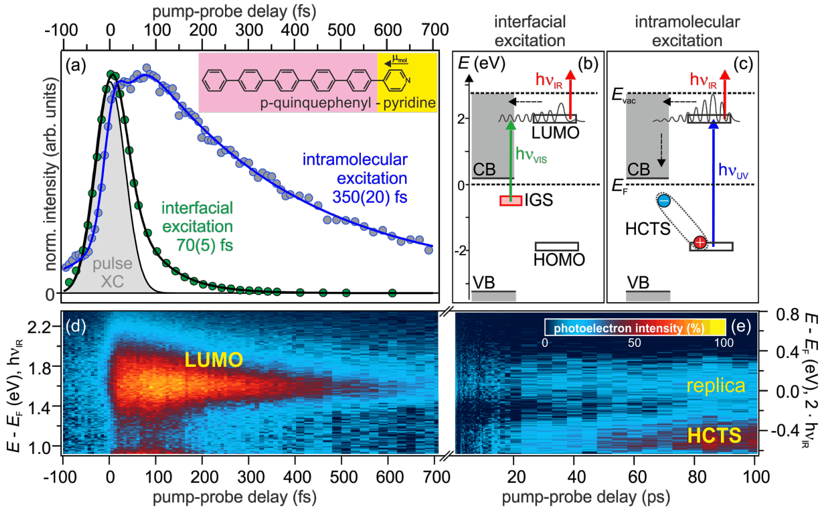

Figure 10: a) Comparison of LUMO population decay for interfacial (scheme in b) and intramolecular photoexcitation (scheme in c). (d) Exemplary time-resolved 2PPE experiment for intramolecular excitation. (e) Build-up of the hybrid charge transfer exciton on ps timescales. The replica of the hybrid charge transfer exciton is probed by pump photons.

Note that this lifetime enhancement by the local Coulomb interaction in the molecule is not sufficient to explain the comparably low charge separation efficiency of ZnO-based inorganic/organic hybrid systems, as lifetimes on the order of only few hundreds of fs are clearly resulting from strong electronic coupling. The origin of the low charge separation efficiency phenomenon lies in the build-up of the hybrid charge transfer exciton 0.5 eV below E_F (Fig. 3e), which builds up on a 100 ps timescale, exhibiting a lifetime that exceeds 5 µs. In this work, we do not only provide a comprehensive understanding of the structural, electronic, and non-equilibrium properties of a model inorganic/organic interface and the first observation of a hybrid charge transfer exciton at a buried interface in the time domain [Gierster *et al.*, in prep.], but also offer – by the selective interfacial and intramolecular excitation – a unique tool to disentangle elementary processes at buried inorganic/organic interfaces [Vempati 2019].

Terrylene – a textbook dye

TR investigations of charge and energy transfer processes across organic-TMDC interfaces require organic dye molecules with appropriate HOMO-LUMO gaps and sufficiently long excited state lifetimes to allow for interfacial phenomena to take place. We characterized the optical properties of terrylene molecules in para-xylene solution. The combination of polychromatic transient absorption spectroscopy with time-correlated single photon counting experiments shows that excitation at the absorption maximum leads to photoluminescence and ground state bleaching that decays within 3.7 ns. Above resonance excitation is followed by internal vibrational relaxation on a 100 ps timescale [Tanda Bonkano *et al.*, in preparation]. Without any surprising or ground-breaking new properties terrylene may not attract significant research interest on its own. However, the complete absence of any unexpected behavior and the simplicity of its non-equilibrium properties make this unpretentious molecule an ideal species for the study of complex charge and energy transfer studies at organic/inorganic interfaces.

Further studies

- Development of the first comprehensive picture of intrinsic and defect-related charge carrier and exciton dynamics in ZnO [Foglia 2019]
- Revelation of the elementary steps of charge injection, localization, and solvation across the electrochemically relevant DMSO/Cu(111) interface [King 2019]
- Triplet-triplet annihilation through autoionization on microsecond timescales in an organic chromophore [Vempati *et al.*, submitted to JCP]

Future Perspectives

The Electron Dynamiχ Group is – after the laboratory move and maternity leave in the previous evaluation period – growing again and preparing for future challenges. These will likely involve our move to the Department of Chemistry at the Humboldt University Berlin following a call to a W3 professorship.

One major strength of the group is the complementarity of its femtosecond time-resolved experimental techniques (photoemission, transient transmission and reflection, photoluminescence, electronic sum frequency generation) that allows the disentanglement of the bulk, surface, and interface properties of a given material system. This sets the basis for the study of very diverse research questions, ranging from strong correlation phenomena in condensed matter physics to electrochemistry, as the respective fundamental interactions and elementary processes in these areas are strongly related and in some cases even similar. Our curiosity-driven, complementary approach will be continued in the future and is reflected in the breadth of the forthcoming research topics in the fields of Physics, Chemistry, and Material Science. In order to even extend the access of the group's experimental suite to spatio-temporal dynamics relevant for nano science and most applications, capabilities will be expanded by a novel femtosecond time-resolved scanning probe technique.

Toward TR interferometric optical nanoscopy

The femtosecond electron dynamics in 2D materials and at surfaces can exhibit significant variation at the nanometer scale. We are developing TR interferometric optical nanoscopy (TRION), where a scattering-type scanning near-field optical microscope (s-SNOM) is used for TR optical spectroscopy. This technique will exploit near-field enhancement close to a metallic tip to achieve spatial resolution (<40 nm), while the temporal resolution is obtained using femtosecond laser pulses in a pump-probe scheme (~40 fs). This technique has yet to be demonstrated in the visible spectral range, while it has been used in the IR region previously by other groups. Using TRION, we will investigate the spatial dependence of the relaxation rates and spectral dynamics in TMDC monolayers as well as in TMDC/organic lateral heterojunctions.

Forthcoming research topics

- The susceptibility of 2D materials (e.g. TMDCs) to local changes of the dielectric function through the substrate or adsorbates will be used to manipulate the electronic structure and optical response on the nm scale and on ultrafast timescales.
- Charge and energy transfer processes across TMDC-based inorganic/organic hybrid interfaces and along nano-structures on dielectric templates will be studied and exploited for advanced opto-electronic or light-harvesting functionalities.
- Transient phenomena at catalyst surfaces (e.g. ZnO) like charge accumulation or metallization may be used to trigger or enhance desired chemical processes and to study their – often stochastic – dynamics on the relevant ultrafast timescales.
- The injection of charges into electrolytes near oxide surfaces is a key process in (photo-) electrochemistry. We will bridge the gap between what is known for ultrafast charge carrier dynamics across well-defined solid/frozen solvent interfaces under UHV conditions and solid/liquid systems.

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Max Planck Research Group Transient X-ray Spectroscopy & Diffraction
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Ultrafast Carrier and Spin Dynamics Probed by Transient X-ray Spectroscopy and Diffraction

The Max Planck Research Group Transient X-ray Spectroscopy and Diffraction experimentally explores structural, carrier and spin dynamics in novel quantum materials, heterostructures and on surfaces and at interfaces to answer current questions in materials science and physical chemistry. For this we pursue a multidisciplinary research program that combines the exquisite possibilities that ultrafast X-ray spectroscopy and nanoimaging offers and closely interface with material synthesis and theory groups. In the lab, we develop and employ attosecond XUV and soft X-ray sources to perform transient absorption spectroscopy and time-resolved X-ray diffraction experiments. We further develop novel nonlinear X-ray spectroscopies at large-scale facilities with the goal to gain interfacial and surface sensitivity combined with the material specificity provided by X-rays on femtosecond time scales. We are interested in experimentally studying and controlling material properties on time scales down to the sub-femtosecond regime and on nanometer length scales to tackle challenging problems in quantum electronics, information storage and solar energy conversion. The Max Planck Research Group Transient X-ray Spectroscopy and Diffraction officially started in March 2019 after a 3-month preparational phase beginning in December 2018. The group is currently moving to the University of California at Berkeley, where Dr. Michael Zürch has been appointed as assistant professor with tenure-track and new labs will be set up in early 2020.

Attosecond diffraction spectroscopy

In our group we develop a new scheme that we refer to as attosecond diffraction spectroscopy, which is a multimodal approach to probe the long-range spin order and the electronic and lattice dynamics in magnetic thin films. For this, we generate isolated attosecond pulses in a broad spectral range covering several absorption edges present in the multilayer thin films and interrogate the spin order by resonant magnetic diffraction, while the electronic-structural response is simultaneously measured with atomic specificity by transient absorption spectroscopy (Fig. 1a). Using this scheme enables us following the ultrafast optical excitation of the carriers out of equilibrium and the subsequent demagnetization. This provides insights into the complex correlation between magnetism and electronic excitation. With this we seek to contribute to the experimental and theoretical efforts to understand and control this phenomenon, acknowledging the prospects ultrafast spin control has for novel fast and efficient memories and spintronic devices.

A first experiment was conducted in collaboration with the group of Prof. Leone at the University of California at Berkeley and evaluated during the first few months of the MPRG. In the experiment, 4-fs optical pump pulses and extreme ultraviolet (XUV) attosecond probe pulses covering the core-level absorption edges of cobalt and platinum, the constituents of the magnetic multilayer under investigation, between 50 and 75 eV are employed (Fig. 1b, top). The two pulses are collinearly focused onto a Co-Pt multilayer thin film with stripe-like oriented magnetic domains (domain size ~160 nm, inset Fig. 1a). The observed transient absorption spectra (Fib 1b, bottom) feature photo-induced red-shifts of the absorption edges indicating out-of-equilibrium excitation of the electrons (Fig. 1c, black and red curves for Co and Pt, respectively). The demagnetization, i.e. loss of magnetization M, observed in the diffraction signal peaks after ~200 fs and slowly recovers over a time scale of ~100 ps (not shown here), consistent with previous observations in Co-Pt multilayers. Intriguingly, it is observed that the onset of the demagnetization (Fig. 1c, blue curve) is delayed by approximately 4 fs with respect to time zero. To understand this observation, we initiated a collaboration with a theory group from the Max Born Institute. The observation can be explained by the fact that in the ground state the cobalt layers are responsible for the magnetization and the platinum layers become weakly magnetized at the interface. The optical excitation then drives a spin current from the cobalt into the platinum layers through a mechanism known in literature as optically induced spin and orbital momentum transfer causing a brief increase of the magnetization in the platinum layers, while cobalt demagnetizes. It is found that the total observed magnetization is nearly constant in this case. The observed time scale thus manifests the time scale before many body effects and scattering events disturb the coherence in this process.

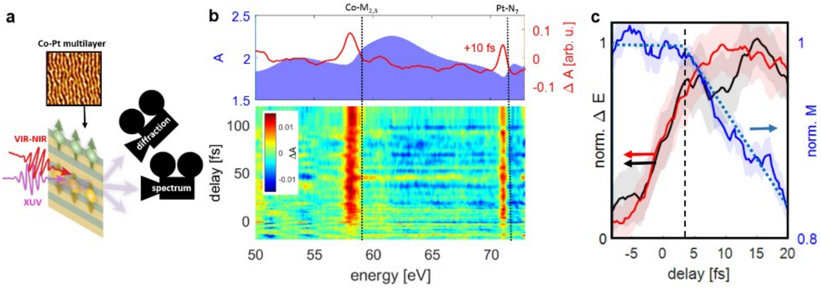

Figure 1: Scheme and application of attosecond diffraction spectroscopy to study ultrafast demagnetization. (a) Experimental scheme of attosecond diffraction spectroscopy. (b) Static absorbance and photo-induced absorption change (top) and transient absorption signal depending on the time delay (bottom). (c) Normalized absorption edge shift in Co (black) and Pt (red) upon laser excitation. The onset of demagnetization (blue) measured by resonant magnetic diffraction is observed at approximately 4 fs delay.

In the near future we hope to expand the analysis further as we have strong indication that we can separate the cobalt and platinum response in the diffraction data and, thus, gain a better insight into these complex dynamics. Following this first demonstration, we plan expanding this scheme to different physical problems that are of interest to research groups in the Department, for instance for quantifying charge density wave (CDW) dynamics where our scheme will allow to acquire structural and electronic details during the first femtosecond of CDW melting.

Nonlinear X-ray spectroscopy at Free-electron lasers

While our table-top studies are restricted to either study the bulk response of a system or investigate spatially confined, e.g. 2D, materials, for many application-relevant aspects the electronic structure at the surface is relevant and should be studied ideally with all advantages that X-ray spectroscopy offers. Unfortunately, access to surface spectra cannot be easily gained due to the relatively large penetration depth of X-rays. In optical spectroscopy, nonlinear techniques, such as SHG and sum-frequency generation, can overcome this limitation by exploiting the breaking of the symmetry at interfaces and surfaces as mastered by other groups in the Department. The challenge for transferring these techniques to the X-ray regime lies in the inherent need for high intensities to induce a nonlinear response. Attosecond sources are currently not powerful enough to push into a relevant intensity regime. Free-electron lasers in turn can achieve sufficient intensities as has been very recently demonstrated in a first surface-sensitive SHG measurement.

In our group we collaborate with various research groups from Japan and the USA and successfully apply for beamtime at Free-electron laser facilities around the world to perform proof-of-concept experiments concerning nonlinear spectroscopies and material responses in the X-ray regime and their application to surface/interface dynamics. During 2019 experiments were performed at FERMI (Triest, Italy; twice) and FLASH in Hamburg. For 2020 beamtimes have been scheduled at SACLA (Japan) and several proposals are currently under evaluation.

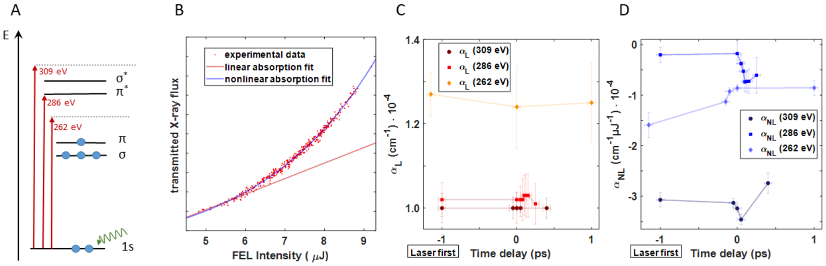

Figure 2: FEL-induced nonlinear absorption in graphite thin foils. (a) Three possible electronic excitations of the 1s electrons. Depending on the FEL wavelength the 1s electrons can be resonantly excited to the π* orbital, virtual below-edge states or higher-lying conductions band states. (b) Plot of the transmitted X-ray flux versus the FEL intensity. The data (red circles) shows clear nonlinear behavior (blue curve). Graphite becomes more transmissive as expected from a linear Beer-Lambert law (red curve). Extracted linear absorption coefficients αL (d) and nonlinear absorption coefficients αNL (d) are shown for different time delays of the optical laser to the FEL for three different photon energies. While αL shows only a wavelength dependence, αNL varies also with time delay.

At FERMI we conducted a first experiment studying the nonlinear absorption of carbon under the influence of an ultrashort melting laser pulse. Graphite thin foils were placed in the overlap of the FEL beam and an optical laser. The transmitted light was measured for three different photon energies under (262 eV), at (286 eV) and above (309 eV) the K-edge of carbon. Additionally, the time-delay between the two light sources were varied to probe different states of carbon. As stated by Beer-Lambert law, the absorption coefficient is independent of the intensity of the incoming light. Due to the high intensity of the X-ray beam the graphite gets partially depleted of the 1s electrons and the transmission is higher than expected from Beer-Lambert law (Fig 2B). The absorption coefficient α is not sufficient to describe the behavior and is replaced by a linear absorption coefficient α_L and an intensity-dependent nonlinear absorption coefficient α_{NL}. These two absorption coefficients were extracted from the experimental data and are plotted versus the time delay. Measurements were taken from -1 ps, at which the optical laser hit the sample first, up to +1 ps, at which the FEL hit the sample first. The linear absorption coefficient α_L shows wavelength dependence but no variations with time delay (Fig 2C). The nonlinear absorption coefficient (Fig 2D), however, shows additionally to the wavelength dependence a sensitivity for the time delay. This information is expected to lead to further understanding of different carbon states, including liquid carbon, which we currently model using time-dependent density functional theory.

Transition to the University of California at Berkeley

During the start-up phase of the MPRG and implementation of the new laboratory at FHI, the group leader received an offer to join the Faculty at the University of California at Berkeley within the College of Chemistry as Assistant Professor with tenure track. Following the successful negotiation and acceptance of the offer in May 2019, the appointment at Berkeley started in July 2019, which started a one-year transition phase of the MPRG effectively ending the MPRG in June 2020.

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