DIET 16

BOOK OF ABSTRACTS

October 8-12, 2018
Garmisch-Partenkirchen
Eibsee-Hotel

The DIET 16 is held and supported by:

MS1P
Molecular Simulations from First Principles

We acknowledge further support by:

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WORKSHOP PROGRAMME

Monday		Tuesday		Wednesday		Thursday		Friday	
		7:00-9:00	Breakfast	7:00-9:00	Breakfast	7:00-9:00	Breakfast	7:00-9:00	Breakfast
						9:15	Photo		
		Non-Equilibrium Phenomena		Ultrafast Dynamics		Electron-Molecule Interactions		Surface Science & Plasmonics	
		9:00-9:35	Hommelhoff	9:00-9:35	Petek	9:30-10:05	Maurer	9:30-10:05	Guo
		9:35-9:55	Menzel	9:35-9:55	Mette	10:05-10:25	Fabiani	10:05-10:25	Lackner
		9:55-10:15	Coulter	09:55-10:10	Coffee	10:25-10:45	Oberhofer	10:25-10:45	Zacharias
		10:15-10:30	Coffee	10:10-10:45	Narang	10:45-11:00	Coffee	10:45-11:00	Coffee
		10:30-11:05	Dong	10:45-11:05	Deinert	11:00-11:35	Stierle	11:00-11:35	Tautz
		11:05-11:25	Dujardin	11:05-11:25	Waltar	11:35-11:55	Leung	11:35-11:55	Vasileiadis
		11:25-11:45	Mor	11:25-12:00	Gallmann	11:55-12:15	Michelitsch	12:00	Departure
		12:00-14:00	Lunch	12:00-18:00 IMPORTANT: We leave the hotel at 12:10 (sharp!), otherwise cable car will be missed!	Zugspitze Excursion (incl. Lunch)	12:30-15:30	Lunch break		
		14:00-14:35	King			14:00-15:00	DIET Committee		
		14:35-14:55	Reutzel			15:30-16:05	Christopher		
		14:55-15:15	Ghan			16:05-16:25	Dupuy		
15:00-17:00	Arrival	15:15-15:30	Coffee			16:25-16:45	Asscher		
		16:00-19:00	Poster Session			16:45-17:00	Coffee		
17:50	Welcome					17:00-17:20	Opalka		
18:00-18:35	Heinz					17:20-17:40	Noei		
18:35-19:10	Schull					17:40-18:00	Gierster		
19:15	Dinner	19:15	Dinner	19:15	Dinner	19:15	Conference Dinner		
21:30-?	Reception	21:30-?	Get-Together						

WELCOME TO THE DIET16!

We are very pleased to welcome you at the 16th edition of the *International Workshop on Dynamics, Interactions and Electronic Transitions at Surfaces*! Our outstanding invited speakers have inspired many excellent young and experienced researchers to present their latest results either in a contributed talk or poster and cover the following exciting research areas:

- Non-equilibrium phenomena
- Ultrafast dynamics
- Electron-molecule interactions
- Surface science
- Plasmonics

We look forward to stimulating presentations and discussions during sessions as well as during the informal discussion meetings.

On behalf of the international steering committee

Julia Stähler (chair)
Karsten Reuter (co-chair)

INTERNATIONAL STEERING COMMITTEE

Katharina Al-Shamery (University of Oldenburg, Germany)
Phillip N. Christopher (University of Oregon, USA)
Zhenchao Dong (University of Science and Technology, China)
Gérald Dujardin (University of Paris Sud, France)
Maki Kawai (Institute for Molecular Science, Japan)
Greg Kimmel (Pacific Northwest National Laboratory, USA)
Dietrich Menzel (Technical University Munich, Germany)
Richard Palmer (Swansea University, UK)
Julia Stähler (Fritz Haber Institute of the Max Planck Society, Germany)

DEPARTURE FROM THE EIBSEE HOTEL

EIBSEE BUS

Departure	Arrival (Garmisch-Partenkirchen)
06:48 am	07:23 am
08:10 am	8:51 am
Then hourly until...	
12:10 pm	12:51 pm
01:00 pm	01:41 pm
01:50 pm	02:31 pm
03:10 pm	03:51 pm
Then hourly until...	
07:10 pm	07:51 pm

ZUGSPITZBAHN

Departure	Arrival (Garmisch-Partenkirchen)
10:15 am	10:50 am
Then hourly until...	
05:15 pm	05:50 pm

TAXI

~ 20 mins to Garmisch-Partenkirchen

SHUTTLE

Unfortunately, no shuttle available!

GENERAL INFORMATION

WIFI: The password for internet access is “Internet”.

ORAL PRESENTATIONS: Please, bring your laptop to the conference room 10mins before your session starts (i.e. in the morning, during coffee breaks, or lunch break). In case you do not have an own laptop, please, bring a USB stick with your presentation (preferably pdf or MS Powerpoint 2010).

POSTER SESSIONS: Please, put up your poster at your earliest convenience at the poster boards in the conference room following the poster number assigned to your abstract. The posters are welcome to stay on display for the whole duration of the meeting. After dinner, informal discussions will continue in the “Kamin-Bar” of the hotel.

OUTING: Wednesday, October 10 (12:00 pm-6:00 pm)

We will leave at 12:10 pm (sharp!) from the hotel entrance and walk to the cable car station where we have to be at 12:30 pm to reach the car that leaves at 12:45 pm. Please, be on time! We cannot wait for you, as the cable car will not wait for us. The next car leaves an hour later. The ride will take 45 min. After arrival, we immediately take the “Gletscherbahn” to reach the top of the Zugspitze (15 min). We will then have a traditional Bavarian meal ("Brotzeit") for lunch. After that, there will certainly be time to stroll around and enjoy the view.

Please be aware that temperatures on the mountain will be around 0°C (32°F) and most likely there will be snow. We, therefore, strongly recommend waterproof shoes and warm clothes!

CONFERENCE PHOTO: Thursday, October 11 (9:15 am) at the hotel reception.

CONFERENCE DINNER: Thursday, October 11 (7:15 pm)

We will leave at 7:00 pm from the hotel entrance. The dinner will be held in walking distance of the hotel in the Berggasthof Eibsee-Alm (green star on the map) in very traditional Bavarian atmosphere. We would, therefore, like to encourage you to dress traditionally on that evening, either Bavarian (in Dirndl or Lederhosen) or in the tradition of your home country.

DEPARTURE: As for arrival, the transfer to Garmisch-Partenkirchen can be realized via the Blue Eibsee-Bus or the Zugspitzbahn (railway). Departure times and a map can be found on the left. Unfortunately, no shuttle service will be available. If you need a taxi, please contact the hotel reception and indicate if you are willing to share the car with other passengers. Please note that the ride to the station in Garmisch-Partenkirchen takes approximately 20 mins (ca. 25 €).

ORAL PRESENTATIONS

MONDAY, OCT 8

18:00-18:30+5
INVITED TALK

t.b.a

Tony F. Heinz

Stanford University, SLAC, California, USA

t.b.a.

18:35-19:05+5
INVITED TALK

STM-induced light emission: from molecular LED to subnanometric optical microscopy

Guillaume Schull

Centre National de la Recherche Scientifique (CNRS), Paris, France

The electric current traversing the junction of a scanning tunneling microscope (STM) may generate a local emission of light. During the last years, we have used this method to study the intrinsic luminescence properties of individual molecules. This work has progressed in two directions. On one side we have used the ability of the STM to manipulate matter with atomic-scale precision to form single-molecule light emitting devices. Composed by individual molecular wires suspended between the tip and the sample of the STM, these devices generate an emission of light whose color, intensity and bandwidth can be controlled with high precision. On the other side, we used the intrinsic resolution of the STM to performed sub-molecularly resolved vibronic spectroscopy of molecules separated from a metallic surface by a thin insulating layers. Together with other recent reports, this result constitutes an important step towards photonic measurements with atoms-scale resolution.

TUESDAY, OCT 9 – NON-EQUILIBRIUM PHENOMENA

9:00-9:30+5
INVITED TALK

Light-field controlled currents in graphene and over atomically thin interfaces

Peter Hommelhoff

Friedrich Alexander University of Erlangen-Nürnberg, Chair for Laserphysics, Erlangen, Germany

Graphene with its Dirac cone dispersion relation is ideally suited to investigate intraband currents and interband transitions driven by the optical field of phase-controlled few-cycle laser pulses. Based on the coupled nature of the intraband and interband processes, we observe repeated coherent Landau-Zener transitions between valence and conduction band separated by around half an optical period of ~1.3 fs. Because of the extremely fast dynamics, fully coherent Landau-Zener-Stückbelberg interferometry takes place. This work represents the fastest current turn-on observed in any conducting material. We will also discuss recent work on ultrafast dynamics at atomically thin Schottky junctions.

9:35-9:50+5
CONTRIBUTED TALK

Ultrafast charge transfer to, through, and under graphene monolayers

Dietrich Menzel

Technical University of Munich, Physic Department, Munich, Germany
Fritz Haber Institute, Berlin, Germany

For improved understanding of ultrafast dynamics of excited electrons at graphene (Gr) monolayers (ML) we use the core hole clock (CHC) method with adsorbed Ar to determine the charge transfer time constants (CTT) at and through GrML with strongly varied substrate coupling (9 systems, from decoupled to strongly bonded and corrugated GrML). Partly as expected, CTTs depend strongly on Gr-substrate coupling, but final state bandstructure, dimensionality and localisation are also important [ACSNano 7(2013)4359].
Argon intercalated and aggregated (into bubbles or blisters [ACSNano 16(2016)1808] and references therein) under GrML received considerable interest recently. Time permitting I will also describe CHC results which shed light on the state of excited states in enclosed and compressed Ar.
I thank all my coworkers (see author lists of refs.) for their excellent work and collaboration, in particular Silvano Lizzit/Trieste, Rosanna Larciprete/Rome, and Peter Feulner/Muenchen; and Elettra/Trieste for the allotment of beamtime despite lacking funds.

9:55-10:10+5
CONTRIBUTED TALK

A microscopic perspective of hydrodynamic transport in type-II Weyl semimetal WP_2

Jennifer Coulter and Prineha Narang

Harvard University, School for Engineering and Applied Sciences, Cambridge, United States

In the hydrodynamic transport regime recently studied in a set of Dirac and Weyl semimetals, momentum-relaxing processes such as Umklapp, defect, and boundary scattering are dominated by momentum-conserving scattering so that momentum is quasi-conserved and electron flow can be described using the formalism of hydrodynamics. Understanding the microscopic scattering processes in these materials therefore presents a fundamental interest. In order to provide a more comprehensive perspective of observed hydrodynamic phenomena, we present predictions of the electron-electron and electron-phonon lifetimes, and from them, calculations of the electrical and thermal conductivity with relation to the character of the electronic and phonon bandstructures, the crystal symmetry, and Fermi surface of the recently observed hydrodynamic materials such as WP_2. With these developments, a first principles approach can provide a predictive and experimentally relevant method to probe the interplay between topological physics, optical properties and ultrafast dynamics in these materials.

10:30-11:00+5
INVITED TALK

STM-based single-molecule optical spectroscopy

Zhenchao Dong

Hefei National Laboratory for Physical Sciences at the Microscale
University of Science and Technology of China, Hefei, China

Control of optical properties of single molecules by plasmonic nanostructures is an important issue in nanophotonics. In this talk, I shall demonstrate two STM-based phenomena related to plasmon-enhanced single-molecule optical spectroscopy. The first is sub-nm resolved single-molecule Raman scattering. I shall demonstrate its applications to chemically distinguish different adjacent molecules on a surface, from relatively large porphyrin molecules to small DNA-base molecules, and even to image individual chemical bonds within a molecule. The second phenomenon is single-molecule electroluminescence. I shall demonstrate the realization of electrically driven single-photon emission from an isolated single molecule, the visualization of coherent intermolecular dipole-dipole coupling in real space, and the emergence of single-photon superradiance in artificially constructed oligomers. These findings open up new routes to ultrahigh-resolution chemical imaging and intermolecular energy transfer studies.

11:05-11:20+5
CONTRIBUTED TALK

Electrically driven plasmon nanosources

Gérald Dujardin, Elizabeth Boer-Duchemin, Eric Le Moal, Shuiyan Cao

Institut des Sciences Moléculaires d'Orsay (ISMO) - The National Center for Scientific Research (CNRS), Paris, France

We report an electrical surface plasmon nanosource using radiant Inelastic Electron Tunneling (IET) from the tip of a scanning tunneling microscope (STM). The main advantages of STM induced surface plasmon excitation are (i) the very local excitation (10 nm) which enables precise localization of the excitation inside the nanometer size plasmonic devices, (ii) the low energy electrical character (≈ 3 eV) of the excitation which makes nanoplasmonics compatible with nanoelectronics, and (iii) the ability to excite both localized and propagating surface plasmons with a broadband energy distribution.

Optimization of such an electrically driven plasmon nanosource requires a carefull understanding of the radiant IET under the STM tip. In particular, the role of the local density of electromagneric states in the radiant IET process is still a puzzling problem.

11:25-11:40+5
CONTRIBUTED TALK

Photocarriers governing the ultrafast nonequilibrium dynamics of an excitonic insulator

Selene Mor[1], Marc Herzog[2], Denis Golez[3], Philipp Werner[3], Martin Eckstein[4], Takashi Mizokawa[5], Claude Monney[3], Julia Stähler[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2]University of Potsdam, Institut für Physik und Astronomie, Potsdam, Germany
[3]University of Fribourg, Physics Department, Fribourg, Switzerland
[4]University of Erlangen, Physics Department, Erlangen, Germany
[5]University of Waseda, Department of Applied Physics, Tokyo, Japan

At low temperatures, Ta_2NiSe_5 is proposed to support an excitonic insulator phase, combined with a structural distortion. Such an excitonic insulator phase stabilizes in small-gap semiconductors with strong electron-hole interaction if excitons can form spontaneously and condense into a ground state. The photoinduced ultrafast dynamics of Ta_2NiSe_5 is studied by means of coherent phonon spectroscopy and time- and angle-resolved photoelectron spectroscopy of the occupied and unoccupied electronic band structure. We show that the structural phase transition is inhibited by optical absorption saturation below the threshold for a non-thermal change. Furthermore, the electronic band gap can be transiently modulated by tuning the excitation density. The effect relies on the interplay of free-carrier-induced screening of the Coulomb interaction and photoenhancement of the exciton condensate density. Preliminary results of the conduction band dynamics further support that the screening of the Coulomb interaction plays an important role in the non-equilibrium electronic dynamics of Ta_2NiSe_5.

14:00-14:30+5
INVITED TALK

Tracing electron transfer and localization dynamics at a model electrolyte/metal interface from femtoseconds to seconds

Sarah B. King[1,2], Angelika Demling[2], Katharina Broch[2,3], Julia Stähler[2]

[1]University of Chicago, Department of Chemistry, Chicago, USA
[2]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[3]University of Tübingen, Institute for Applied Physics , Tübingen, Germany

The lifetime, coupling, and localization of electronic states in molecular films near metal electrodes fundamentally determines their propensity to act as reactants in battery chemical reactions. We investigate the formation dynamics of small polarons and their role as precursor states in thin films of dimethyl sulfoxide (DMSO) on Cu(111) using time- and angle-resolved two-photon photoemission spectroscopy. Upon photoexcitation, a delocalized and strongly-coupled DMSO electronic state is initially populated followed by a dynamic increase in binding energy and localization within 200 fs, evidence of small polaron formation. This localized state is a precursor state for a long-lived and weakly-coupled surface electronic state with a lifetime of several seconds. Moreover, experiments in oxygen atmosphere show that these trapped, long-lived electrons react with O_2 at the DMSO surface, likely forming O_2^-. This work highlights the importance of interfacial electronic states near metal surfaces as precursor states for electrochemical reactions despite their femtosecond lifetimes.

14:35-14:50+5
CONTRIBUTED TALK

Many-particle screening in metals as investigated by multidimensional coherent multi-photon photoemission spectroscopy

Marcel Reutzel, Andi Li, Hrvoje Petek

University of Pittsburgh, Department of Physics & Astronomy, Pittsburgh, USA

Light interacting with metals elicits a coherent many-body screening response on sub- to few-femtosecond time-scales making its time-domain observation challenging. However, the coherent response of a metal to an intense external light-field is evident in highly nonlinear optical interactions. Employing multi-photon photoemission (mPP), we present evidence for collective excitations, plasmons, which form through screening of the optical field.
In complementary experiments using UV and near-IR photons in 2-photon and 4-photon excitation, respectively, we tackle the screening response of Ag(111) as follows: In 2PP, tuning the photon energy through the bulk plasmon frequency causes switching in the bulk excitations from single particle to collective responses. In 4PP, we extract the coherent response of the sp-band by interferrometrically time-resolved mPP: We observe polarization beating with a period of ~10 fs modulating the mPP signal and correlate it to collective excitations of the Fermi sea.

14:55-15:10+5

CONTRIBUTED TALK

Mechanism of ultrafast electron transfer on ferromagnetic interfaces: theory and application

Simiam Ghan, Harald Oberhofer, Karsten Reuter

Technical University of Munich, Chair of Theoretical Chemistry, Munich, Germany

Self-assembled monolayers of organic molecules (SAMs) on surfaces show great promise in the emerging field of molecular electronics due to tunable charge transport properties, long-range 2-dimensional order and ease of manufacture. Growth of SAMs on ferromagnetic surfaces offers the additional possibility of spin-dependent transport for molecular spintronics in e.g. spin-valves and magnetic tunneling junctions. To establish design principles for such applications, a thorough understanding of charge transport mechanisms over SAM-metal interfaces is of great importance.

As an initial benchmark, we report calculations of spin-dependent electron transport in model systems of Argon monolayers on ferromagnetic Fe(110), Co(0001) and Ni(111) substrates. Spin-polarized charge transfer rates are calculated from the Fermi Golden Rule and explicit time propagation using first-principles-parametrized model Hamiltonians. Results are compared to ultrafast core-hole-clock spectroscopy measurements, which found faster transport for minority electrons. The benchmarked protocol is applied to thiol-based model SAMs with an aim towards predicting tunable spin-transport behavior.

WEDNESDAY, OCT 10 – ULTRAFAST DYNAMICS

9:00-9:30+5

INVITED TALK

Coherent ultrafast hot electron generation at plasmonic heterojunctions

Shijing Tan and Hrvoje Petek

The University of Pittsburgh, Department of Physics and Astronomy, Pittsburgh, USA

We study the plasmonic enhancement of hot electron generation, by measuring ultrafast time-resolved multiphoton photoemission (mPP) spectroscopy of Ag nanocluster-decorated graphite and TiO_2 surfaces. Hot electrons have been implicated in enhanced photo-physical and photochemical processes at metal plasmon-semiconductor heterojunctions, but their activation mechanisms remain obscure. Deposition of Ag onto the substrates produces small (5 nm dia., 1 nm high) Ag nanoparticles that support Mie plasmon resonances of the metal nanoparticle-support system. Excitation of the plasmonic modes greatly enhances the mPP yields over the bare substrates [1-3]. Analysis of the mPP spectra and hot electron relaxation rates show that hot electrons are generated directly in the substrates by dephasing of the plasmon resonances. This is possible because the plasmon resonances are electronically, optically, and chemically coupled with the substrates. We also find coherent photoinduced electron transfer from Ag nanoclusters to graphite via dipole transitions [4]. The probing of ultrafast polarization and hot electron dynamics reveals the energy and charge coupling at plasmonic heterojunctions.

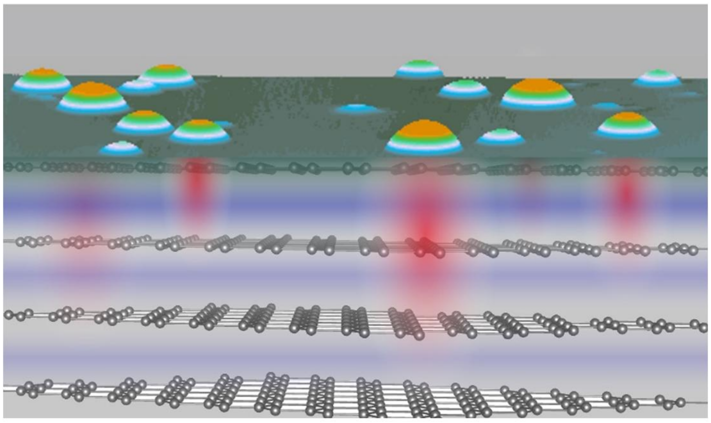

Fig. 1. The coupling of surface plasmons with single particle excitations at the Ag/graphite interface. STM image of the Ag nanoparticle covered graphite surface is shown.

[1]Tan, S., Argondizzo, A., Wang, C., Cui, X., & Petek, H. Ultrafast Multiphoton Thermionic Photoemission from Graphite. Phys. Rev. X 7, 011004 (2017).

[2]Tan, S., Liu, L., Dai, Y., Ren, J., Zhao, J., & Petek, H. Ultrafast Plasmon-Enhanced Hot Electron Generation at Ag Nanocluster/Graphite Heterojunctions. J. Am. Chem. Soc. 139, 6160-6168 (2017).

[3]Tan, S., Argondizzo, A., Ren, J., Liu, L., Zhao, J., & Petek, H. Plasmonic coupling at a metal/semiconductor interface. Nature Photon 11, 806-812 (2017).

[4]Tan, S., Dai, Y., Zhang, S., Liu, L., Zhao, J., & Petek, H. Photoinduced Coherent Electron Transfer at Ag/Graphite Heterojunctions. Phys. Rev. Lett. 120, 126801 (2018).

9:35-9:50+5
CONTRIBUTED TALK

Time-resolved SHG imaging microscopy on TMDC monolayers and heterostructures

Gerson Mette, Jonas Zimmermann, Ulrich Höfer

Philipps-Universität Marburg, Department of Physics, Marburg, Germany

2D transition-metal dichalcogenides (TMDC) have been intensively investigated since the discovery of extraordinary luminescence of MoS_2. In particular, TMDC heterostructures attract attention due to their possible application in optoelectronics. As the efficiency of such devices is expected to depend strongly on the relative orientation of individual layers, experimental techniques to characterize the charge-transfer dynamics with dependence on stacking angle are required.

Here, we show that optical second-harmonic generation (SHG) in imaging mode is a versatile tool for systematic time-resolved investigations of TMDC monolayers and heterostructures. It allows us to quantify the crystal orientation and at the same time provides access to the charge-carrier dynamics by femtosecond pump-probe experiments. Measurements performed on MoS_2 mono- and multilayers reveal strong pump-induced features assigned to exciton generation in the material. In contrast, a delayed build-up and longer lifetime of the SH response is observed for a $MoSe_2$/WSe_2 heterostructure, suggesting the existence of charge-transfer excitons.

10:10-10:40+5
INVITED TALK

Light-matter interaction in quantum materials, excited-state nanophotonics, and quantum plasmonics

Prineha Narang

Harvard University, John A. Paulson School of Engineering and Applied Sciences, Cambridge, USA

Recently, research at the interface of chemistry, material science, and quantum optics has surged and opened new possibilities to study strong light-matter interactions at thermodynamic and quantum limits. Light-matter interactions and electronic excited-state phenomena require high-level electronic structure methods beyond the all-pervasive density-functional theory. Simultaneously, the properties of interest are fundamentally non-equilibrium and require techniques that are reliable beyond small perturbations from equilibrium. Electron-photon, electron-electron as well as electron-phonon dynamics and far-from-equilibrium transport are critical to describe ultrafast and excited-state optoelectronic interactions in materials. In this talk, I will show recent results using a new theory method we have developed to calculate arbitrary electron-phonon and electron-optical interactions in a Feynman diagram many-body framework integrated with a nonequilibrium carrier transport method. I will present a new formalism at the intersection of cavity quantum-electrodynamics and electronic structure, quantum-electrodynamical density functional theory, to treat electrons and photons on the same quantized footing.

10:45-11:00+5

CONTRIBUTED TALK

THz-induced nonlinear electron dynamics: High harmonics in graphene and the pursuit of photoelectron probing

Jan-Christoph Deinert[1], Sergey Kovalev[1], Hassan Hafez[2], Bertram Green[1], Dmitry Turchinovich[3], Michael Gensch[1]

[1]Helmholtz-Zentrum Dresden-Rossendorf, High-field THz-driven Phenomena, Dresden, Germany
[2]Max Planck Institute for Polymer Research, Department of Molecular Spectroscopy, Mainz, Germany
[3]Universität Duisburg-Essen, Faculty of Physics, Duisburg, Germany

Low-energy Terahertz (THz) excitation at surfaces offers resonant access to a multitude of fundamental modes, e.g. the motion of free electrons. In this twofold contribution, we demonstrate how this can be utilized to drive strong nonlinear effects, such as THz high harmonic generation in the model 2D material graphene. Here, the response of free background electrons near the Dirac point enables efficient generation of harmonics in the technologically relevant THz frequency range. These findings make graphene a promising model system for a novel experimental approach to study low-energy surface excitations: THz pump – photoelectron spectroscopy (ARPES) probe. In the second part of our contribution we present our concept for this method which is currently being implemented at the high-field high-repetition-rate THz facility TELBE. Once established, this technique may offer a *direct* view on THz-induced changes of the electronic structure in highly relevant processes from metal-insulator-transitions to superconductivity and catalytic activity.

11:05-11:20+5

CONTRIBUTED TALK

Effective THz fields on thin-film metal catalyst surfaces

Kay Waltar[1], Johannes Haase[2], Torsten Golz[3], Ekaterina Zapolnova[3], Rui Pan[3], Nikola Stojanovic[3], Sasa Bajt[3], Jürg Osterwalder[1], Matthias Hengsberger[1], Luca Castiglioni[1]

[1]University of Zurich, Physic Institute, Zurich, Switzerland
[2]Paul Scherrer Institute, Villigen, Switzerland
[3]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany

The study of elementary catalytic reaction steps in time-resolved experiments requires knowledge on the character of the exciting electric field that controls amplitude and orientation of excited molecular vibrational modes. Here, we investigate the spatio-temporal behavior of the electric field on nanostructured Pt(111) thin film samples that are exposed to few-cycle, low-frequency THz pulses (1.5-2 THz). A THz-pump/XUV-probe experiment was performed at the free electron laser facility FLASH at DESY (Hamburg). XUV-emitted photoelectrons were subject to streaking by a strong THz pulse, i. e. an electron momentum gain proportional to the instantaneous vector potential of the THz field. Our 2D electron analyzer, capable of probing both the kinetic energy and emission angle of the photoelectrons, allowed us to follow modifications in the electron momentum distribution and to reconstruct the effective electric field in terms of amplitude and polarization in close surface proximity.

11:25-11:55+5
INVITED TALK

The effective mass in attosecond photoemission from solids

Lukas Gallmann[1], Lamia Kasmi[1], Matteo Lucchini[1], Luca Castiglioni[2], Pavel Kliuiev[2], Jürg Osterwalder[2], Matthias Hengsberger[2], Peter Krüger[3], Ursula Keller[1]

[1]Eidgenössische Technische Hochschule (ETH) Zürich, Institute of Quantum Electronics, Zurich, Switzerland
[2]University of Zurich, Department of Surface Physics, Zurich, Switzerland
[3]Chiba University, Department of Materials Science, Chiba, Japan

The motion of electrons in solids is governed by the electronic band structure, which defines the effective mass or group velocity of an electronic wave packet. Recent experimental and theoretical work suggests that electrons may need a finite time to acquire their effective mass after a sudden perturbation. We present our recent studies probing the dynamics of photoemission on attosecond time scales and atomic length scales, which yield an upper limit for the time an electron needs to assume its effective mass after excitation with an attosecond extreme-ultraviolet pulse. Probing the photoemission from a Cu(111) surface, we found the final state Bloch wave packet to form within a travel distance of 5-7 Å and the effective mass to remain a valid concept even on the few hundred attosecond scale of the experiment. We will review the current state and open questions in the field of attosecond photoemission from solids.

THURSDAY, OCT 11 – ELECTRON-MOLECULE INTERACTIONS

9:30-10:00+5
INVITED TALK

Ab initio simulation of hot-electron induced chemistry at metal surfaces

Reinhard Maurer

University of Warwick, Department of Chemistry, Coventry, UK

Low-lying electronic excitations in metals, so-called hot electrons, efficiently mediate molecule-metal energy transfer during molecular reactions at surfaces. In doing so, they give rise to a number of curious experimental observations. This includes pico-second-scale energy loss of molecular adsorbate vibration, highly inelastic atomic and molecular scattering from metal surfaces, and light-assisted molecular desorption and chemical transformations, so-called "hot-electron chemistry". I will present our efforts to develop a first-principles treatment of hot-electron effects in molecular dynamics based on Density Functional Theory. Using our efficient implementation of hot-electron-induced frictional forces based on Time-Dependent Perturbation Theory, I will show how we correctly capture vibrational relaxation in large-scale metal-mounted molecular catalysts as well as the energy loss and coupled electronuclear dynamics of small molecular adsorbates. We compare our simulations to recent Sum-Frequency Generation (SFG) spectroscopy and molecular beam scattering experiments. I will conclude with an outlook of applying these methods to light-driven hot-electron chemistry.

10:05-10:20+5
CONTRIBUTED TALK

Femtosecond laser-induced associative desorption of molecular hydrogen from graphite

Lorenzo Maddii Fabiani, Robert Frigge, John D. Thrower, Helmut Zacharias

Center for Nanotechnology (CeNTech), Münster, Germany

The formation of molecular hydrogen via radiation-induced associative desorption from carbonaceous dust particles plays an important role in the interstellar medium. We investigate the desorption of molecular hydrogen from graphite following surface excitation with fs-laser pulses, λ=400 nm. Desorbed species are analyzed by internal state selective (1+1) REMPI in the XUV region.
The desorbing hydrogen molecules show a strong non-equilibrium behavior. The vibrational ground state is less populated than the first excited and possesses a significantly higher kinetic energy: E_{kin}=170 meV for v''=0 and E_{kin}=100 meV for v''=1. The rotational populations present a non-thermal distribution that can be fitted by two temperatures for low and high J''. Equivalent studies for higher vibrational states are ongoing. A nonlinear fluence dependence of the desorption yield allows two-pulse correlation measurements. The 450 fs FWHM of the correlated desorption peak suggests an electron induced desorption mechanism. Measurements for molecular deuterium reveal similar results.

10:25-10:40+5
CONTRIBUTED TALK

Modelling (photo-)electrochemistry beyond the computational hydrogen electrode

Harald Oberhofer

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

In (photo-)electrochemistry, state of the art simulation approaches tend to rely on a number of assumptions and simplifications which---especially on oxide surfaces---may not be fully justified. For example, simulation of water splitting is mainly based on idealised surfaces and the computational hydrogen electrode approach, which evaluates the thermodynamic feasibility of a catalyst looking at pathways where each hydrogen abstraction is coupled to the removal of one electron.
In my presentation I will outline some of the steps necessary to augment theoretical approaches that so far have been geared towards the simulation of metal surfaces under ideal conditions to oxides under realistic conditions.
There, I focus on the nature of the reactive site---considering e.g. defects---and the appearance of free energy barriers and their influence on reaction kinetics. Finally, for a realistic model of photo-electrochemical reactions occurring on the solid-liquid interface I will examine the role the solvent itself.

11:00-11:30+5
INVITED TALK

Operando investigations of heterogeneous catalysts: overcoming the spatio-temporal average

Andreas Stierle

Deutsches Elektronen-Synchrotron (Desy) and University of Hamburg, Hamburg, Germany

Heterogeneous catalysts are composed of oxide supported catalytically active 4d and 5d transition metal nanoparticles, which are exposed to gas mixtures at atmospheric pressures and elevated temperatures under reaction conditions. The catalytic reactions involve spatio-temporal patterns with mesoscopic to nanoscopic spatial heterogeneities and slow reaction kinetics to ultrafast dynamics during chemical bond making and breaking.
One important ingredient of catalytic reactions are nanoparticle shape changes under reaction conditions, since they may have implications on the activity and selectivity of the catalyst. Nanoparticle shape changes involve atomic surface diffusion, which is a process with typical time constants from 1 s at room temperature to 100 fs at 1200 K. In the presence of gases, surface self-diffusion may be further enhanced.
In my presentation, I will highlight our recent attempts to overcome the complexity of a real catalyst under working conditions by operando surface x-ray diffraction experiments [1]. I will present operando studies of surface restructuring of PtRh nanoparticles under CO oxidation conditions [2] and MgO supported Pd nanoparticle shape changes [3]. Further on, I will address possibilities for future time resolved surface structure characterization using x-rays during fast kinetic processes or during photo-induced reaction dynamics.

[1] A. Stierle, J. Gustafson, E. Lundgren in "Operando Research in Heterogeneous Catalysis" Springer Series in Chemical Physics, Vol. 114 (2017).

[2] U. Hejral, D. Franz, S. Volkov, S. Francoual, J. Strempfer, A. Stierle, Phys. Rev. Lett. 120, 126101 (2018).
[3] P. Nolte, A. Stierle, N. Kasper, N. Jeutter, H. Dosch, Nano Lett., 11, 4697 (2011).

11:35-11:50+5
CONTRIBUTED TALK

Surface-molecular-beams give reaction at selected impact parameters

Kelvin Angarra, Lydia Leung, Matthew Timm, Zhixin Hu, John Polanyi

University of Toronto, Department of Chemistry, Toronto, Canada

Crossed molecular beams of gases have yielded important information concerning the dynamics of chemical reactions under single-collision conditions. The results have of necessity been averaged over collisions with impact parameters ('miss-distances') ranging from zero to infinity, obscuring the effect of this important parameter. Here we describe a method by which this averaging is suppressed in surface reaction by aiming a highly-collimated reactive 'projectile' molecule along a surface at a stationary adsorbed 'target' molecule, both located by STM. The projectile was CF_2 recoiling from electron-induced bond-breaking in chemisorbed CF_3 on Cu(110) at 4.6 K. The collimation of the resulting CF_2 in what we term a 'surface-molecular-beam' restricted it to a lateral spread of ±1° by its chemical interaction with the underlying surface. This collimation effect was successfully modelled by Molecular Dynamics. Collimated surface-molecular-beams could aim molecular projectiles with selected impact parameters at the wide range of target species identified by STM.

11:55-12:10+5
CONTRIBUTED TALK

Approximate methodologies in the simulation of core-level spectroscopies

Georg Michelitsch and Karsten Reuter

Technical University of Munich, Chair of Theoretical Chemistry, Munich, Germany

Spectroscopies based on core-hole excitations, such as X-ray photoelectron spectroscopy (XPS) and Near-Edge X-ray Absorption Fine-Structure (NEXAFS), are nowadays routinely used to characterize a material's composition. The state-of-the-art protocols to simulate experimental signatures correspond to multi-parameter fitting procedures and effective model Hamiltonians. Although theory has made a huge leap forward by introducing quasiparticle formalisms, high computational cost presently restricts them to small systems. There is thus a need of approximate schemes, accurate enough to allow for an unambiguous and reliable interpretation of the experimental spectra, and at a tractable computational cost for realistic system sizes. A careful validation and gauging of the various conceptual approximations and numerical settings is, however, mandatory for their successful deployment. To this end, we present a systematic DFT study using occupational core-hole constraining approaches, where we highlight important boundary conditions apart from the multifacetted choice of DFT functional and basis set, such as a proper localization of the core-hole.

15:30-16:00+5
INVITED TALK

How adsorbates influence plasmon dephasing and relationships to photocatalysis

Phillip Christopher

University of California, Santa Barbara, Department of Chemical Engineering, Santa Barbara, USA

Recently, evidence has been reported in literature that catalytic reactions can be facilitated on the surface of coinage metal nanoparticles through the excitation of localized surface plasmon resonances. Measurements made using low intensity continuous wave sources to excite plasmon-mediated catalysis, in addition to wavelength and isotope dependent photocatalytic rate measurements, suggest that plasmons facilitate catalytic reactions through non-thermal processes. However, details of how the energy stored in surface plasmons flows into the promotion of bond-making and bond-breaking steps are not known. A prevailing theory is that plasmons dephase through Landau damping to form “hot” electrons and holes in the metal and subsequently, hot carriers transport to the adsorbate-metal interface and transiently localize in adsorbate resonance states, thereby depositing energy into potential energy surfaces as described in the original DIET model. Another possibility is that adsorbate resonance states act as scatterers that induce the dephasing of plasmons, thereby directly populating adsorbate resonances in localized electron-hole pairs across the metal-adsorbate interface – this process is known as chemical interface damping (CID). Here we will discuss experimental evidence suggesting that the second mechanism is most likely responsible for plasmon-facilitated catalytic processes on metal nanoparticle surfaces.

16:05-16:20+5
CONTRIBUTED TALK

Desorption of neutrals, cations and anions induced by core-excitation of water ice

Rémy Dupuy[1], Jean-hugues Fillion[1], Mathieu Bertin[1], Géraldine Féraud[1], Maud Hassenfratz, Xavier Michaut[1], Thomas Putaud[1], Laurent Philippe[1], Roberto Cimino[2], Vincent Baglin[3], Claire Romanzin[4], Pascal Jeseck[1], Marco Angelucci[2]

[1]Sorbonne Université, Laboratoire d'étude du rayonnement et de la matière en astrophysique et atmosphères (LERMA), Paris, France
[2]LNF,[3]CERN
[4]LCP

Water ice plays an important role in many different fields of physical sciences. In particular, it is ubiquitous in the interstellar medium, where interaction with high energy radiation, such as X-ray photons, is a key process in the balance between gas phase and solid phase. The study of core excitation of water ice has yielded information on ice structure, relaxation processes and fragmentation dynamics as well.

We studied X-ray induced desorption from water ice in the O1s range using synchrotron radiation from the SOLEIL facility. The approach combines neutral and ion quantitative detection as a function of photon energy, with for the first time detection of anions. Neutral species are by far the most abundant species desorbed, and the process is dominated by secondary electrons. The spectral signature of many ions deviates from the absorption spectrum of the ice, showing processes resulting directly from core excitation rather than secondary electrons.

16:25-16:40+5
CONTRIBUTED TALK

Temperature effect on charging and transmission of electrons through amorphous solid water films

Micha Asscher and Roey Sagi

Hebrew University of Jerusalem, Department of Physical Chemistry, Jerusalem, Israel

The charging of solid water films is an important phenomenon in astrochemistry and environmental studies. Temperature effect on both the conductivity and capacitance of Amorphous Solid Water (ASW) films in UHV will be presented, following interaction with 5 eV electrons in the range 50-120 K. Their charging was detected via Contact Potential Difference (CPD) utilizing a Kelvin probe. It was found that ASW conducts and stores electrons with “memory” of the film's thermal history. Furthermore, we propose that trapped electrons discharge during substrate annealing in a process driven by the formation and propagation of cracks within the molecular layer at lower temperatures than the onset of crystallization. Thermal binding energies of the electrons are obtained from the discharge measurements, in the energy range of 0.26±0.08 eV. These values are an order of magnitude smaller than the photoemission numbers. The reactivity of embedded methane molecules in ASW will be discussed.

17:00-17:15+5
CONTRIBUTED TALK

Photocatalytic water splitting by heptazine units in graphitic carbon nitride

Johannes Ehrmaier, Wolfgang Domcke, Daniel Opalka

Technical University of Munich, Department of Chemistry, Garching, Germany

Graphitic carbon nitrides (CN) represent an inexpensive and highly flexible class of materials. Since the discovery of their photocatalytic activity for the production of hydrogen from liquid water [1], the production of hydroxyl radicals and hydrogen by CN catalysts after irradiation has been reported in several studies. The photochemical properties of graphitic CN materials are largely determined by heptazine units, the primary molecular building blocks of graphitic CNs.

In this contribution results from recent theoretical work on the photochemistry of CN for photochemical water splitting are presented. Density functional theory (DFT) was applied to study structural and optical properties of a representative heptazine unit in the gas phase and in solution [2,3]. Based on the specific nature of the frontier orbitals and their energy levels with respect to the valence band of water, we developed a coherent picture of the photochemical oxidation of liquid water via hydrogen atom transfer from water to heptazine. The role of solvent molecules for the absorption properties and photocatalytic cycle was examined by ab initio molecular dynamics calculations and the calculation of optical properties at selected snapshots. The simulations demonstrate the critical role of the bulk water phase for the efficient absorption of light by a local $\pi \rightarrow \pi^*$ excitation, which is symmetry-forbidden in gas phase heptazine. The mechanism of water splitting by CNs is discussed in the context of recent high-level ab initio calculations for molecular clusters and the band structure in aqueous solution.

[1] Wang, X. et al. Nat. Mater. 2009, 8, 76.
[2] Ehrmaier, J. et al. J. Phys. Chem. Lett. 2018, 9, 4695-4699.
[3] Ehrmaier, J. et al. J. Phys. Chem. A 2017, 121, 4754–4764.

17:20-17:35+5
CONTRIBUTED TALK

Time-resolved photoemission study of the charge transfer dynamics in anatase TiO_2 for CO photooxidation to CO_2

Heshmat Noei[1], Michael Wagstaffe[1], Simon Chung[1], Lukas Wenthaus[1], Guilherme Semione[1,2], Steffen Palutke[1], Giuseppe Mercurio[3], Siarhei Dziarzhytski[1], Harald Redlin[1], Nicolai Klemke[4], Yudong Yang[4], Anne-Laure Calendron[4,5], Franz Kärtner[4,6], Wilfried Wurth[1,2,4], Andreas Stierle[1,2]

[1]Deutsches Elektronen-Synchrotron (DESY), X-ray Physics and Nanoscience, Hamburg, Germany
[2]University of Hamburg, Institute of Experimental Physics, Hamburg, Germany
[3]XFEL
[4]Center for Free-Electron Laser Science (CFEL), Hamburg, Germany
[5]The Hamburg Centre for Ultrafast Imaging (CUI), University of Hamburg, Hamburg, Germany
[6]Massachusetts Institute of Technology (MIT), Massachusetts, United States

TiO_2 is widely regarded as the most active photocatalyst and solar energy converter. Nanocrystalline anatase TiO_2 is photoactive for CO oxidation to CO_2, but only during exposure to UV light. A key factor in understanding the activity of TiO_2 is to gain information about the transport of the photogenerated electrons. Here, we obtained the first insight into the activation mechanism of light induced CO oxidation on TiO_2 surfaces by applying ultra-fast optical pump-soft x-ray photoelectron probe experiments at the free-electron laser FLASH at DESY in Hamburg under CO and O_2 co-exposure. An optical laser of 800 nm and a FEL energy of 647.8 eV were utilized to follow changes of the Ti and O core levels on picosecond timescales resulting from the formation of photogenerated electrons and holes in anatase TiO_2 and the subsequent oxidation of CO to CO_2.

17:40-17:55+5
CONTRIBUTED TALK

Disassembling a hybrid exciton in the time domain

Lukas Gierster[1], Sesha Vempati[1,2], Jan-Christoph Deinert[3], Niklas Mutz[4], Anton Zykov[4], Stefan Kowarik[4], Yves Garmshausen[5], Stefan Hecht[5], Julia Stähler[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2] Indian Institute of Technology, Bhilai, India
[3]Helmholtz-Zentrum Dresden-Rossendorf, High-field THz-driven Phenomena, Dresden, Germany
[4]Humboldt-Universität zu Berlin, Department of Physics, Berlin, Germany
[5]Humboldt-Universität zu Berlin, Department of Chemistry, Berlin, Germany

Charge separation at inorganic/organic interfaces is essential for the function of hybrid solar cells. The notoriously low charge separation efficiency at ZnO-organic interfaces was suggested to result from hybrid charge transfer exciton (CTX) formation, which favors recombination at the interface [1]. However, direct observation of the CTX, its formation and decay dynamics on ultrafast timescales remained elusive. Here we use time-resolved photoelectron spectroscopy to elucidate the CTX formation at the ZnO/p-quinquephenyl pyridine (5P-Py) interface. We show that after intramolecular excitation the electrons decay from the LUMO to the conduction band within a short time span of 350 fs, consistent with [2]. Following this decay, we observe the rise of a spectral feature located about 0.5 eV below the Fermi level on a 100 ps timescale with a lifetime exceeding the inverse laser repetition rate (5 µs), indicative of CTX formation and decay.

[1] M. Eyer et al., J. Phys. Chem. C 121, 21955-21961 (2017).
[2] C. Strothkämper et al., J. Phys. Chem. C 117, 17901–17908 (2013).

FRIDAY, OCT 12 – SURFACE SCIENCE & PLASMONICS

9:30-10:00+5
INVITED TALK

Supported metal-organic clusters: stability, mobility and orientational polymorphism

Quanmin Guo

University of Birmingham, School of Physics and Astronomy, Birmingham, UK

We have recently investigated a Fullerene-metal coordinated system and produced magic number, hybrid (C60)m-Aun clusters on the Au(111) surface. The smallest magic number cluster, (C60)7-Au19, consists of a hexagonal 19-Au atom island capped by seven C60 molecules. The 19-Au island on its own is not stable beyond 200 K, a (C60)7 cluster on its own is not stable beyond 240 K. The hybrid cluster, however, is stable up to 400 K. The hybrid clusters are held together by neither directional H-bonding nor covalently bonding. Instead, the collective interaction among all the constituents within the cluster is responsible for the stability of the cluster. The nature of such globally optimized interaction gives the clusters some interesting properties: i) Ripening into magic sizes. ii) The ability of the cluster to self-repair and re-shape. iii) Anomalous diffusion via a break-transition-settle route which could be a more general phenomenon for loosely assembled clusters.

10:05-10:20+5
CONTRIBUTED TALK

Helium droplet synthesis as a new route to plasmonic nanoparticles and nanostructures

Florian Lackner[1], Alexander Schiffmann[1], Roman Messner[1], Maximillian Lasserus[1], Martin Schnedlitz[1], Harald Fitzek[2], Peter Pölt[2], Daniel Knez[2], Gerald Kothleitner[2], Wolfgang E. Ernst[1]

[1]Graz University of Technology, Institute of Experimental Physics, Graz, Austria
[2]Graz University of Technology, Institute of Electron Microscopy and Nanoanalysis & Graz Centre for Electron Microscopy, Graz, Austria

Helium nanodroplet synthesis is introduced as a novel method for the production of plasmonic nanostructures, assembled by the deposition of nanoparticles formed in the inert low-temperature helium environment. Sub-10 nm core@shell nanoparticles can be formed, where core and shell materials can be chosen independently from a large variety of different dopants. The deposition process of the formed nanoparticles is very soft, enabling, for example, the decoration of ultra-thin hexagonal boron-nitride with Ag@Au nanoparticles, which we employed for plasmon spectroscopy in a transmission electron microscope. Using Ag@Au nanoparticles we demonstrate that the synthesis approach allows to tune the spectral position of the localized surface plasmon resonance by adjusting the Ag:Au ratio and that the resulting substrates are suitable for surface enhanced Raman spectroscopy (SERS). In general, a large variety of materials can be doped to helium nanodroplets, our current efforts are geared towards potassium clusters, vanadium oxide and Ag@ZnO nanoparticles.

10:25-10:40+5
CONTRIBUTED TALK

Electronic spin filtering by helical molecules

Daniel Nürenberg, Paul Möllers, Helmut Zacharias

Center for Soft Nanoscience, University of Münster, Münster, Germany

Helical molecules adsorbed in monolayers on various substrates preferentially transmit one longitudinal spin component of electrons emitted by the substrate. First shown for natural biomolecules, like oligo-DNA with a spin polarization up to 60%, bacteriorhodopsin, and oligo-peptides, which only appear in their natural enantiomeric form, this effect has recently also been observed for hepta-helicene molecules adsorbed on precious metal surfaces Cu(332), Ag(110), and Au(111). Using both pure enantiomers it could be shown that the sign of the electrons spin polarization is directly connected with the chiral sense of the helicene. Further, this conjugated organic molecule is conducting, different from the hopping conduction of the biomolecules. An extension to chiral inorganic thin films will be discussed.

11:00-11:30+5
INVITED TALK

Nanoscale engineering with molecules at surfaces

F. Stefan Tautz

Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany
Jülich Aachen Research Alliance (JARA), Fundamental of Future Information Technology, Jülich, Germany

The study of molecular adsorption at surfaces has long been a focus of surface science. With increasing molecular complexity, new properties and phenomena emerge, and the design of functional single-molecule devices becomes possible. I will present recent examples from our research that illustrate the intriguing physics of complex molecules at surfaces.

First, I will demonstrate the emergence of a topologically protected quantum critical point in a spin-carrying molecular structure [1]. Among many others, this example may serve as motivation to develop a methodology for crafting molecular "designer structures". Next, I will report our recent advances towards such a methodology [2]. Finally, I will demonstrate that even relatively simple designer structures show intriguing functionalities, including quantum dot behaviour [3], electrostatic potential sensing [4], and coherent single-electron field emission [5].

[1] Nature Physics 12, 867 (2016); PRB 91, 144415 (2015).
[2] Beilstein J Nanotechnol. 5, 1926 (2014); Nat. Comm. 5, 5568 (2014); Beilstein J of Nanotechnol. 6, 2148 (2015); Perspectives of Molecular Manipulation and Fabrication. In *Molecular Architectonics, Advances in Atom and Single Molecule Machines*, Ogawa, T., Ed. Springer 2017.
[3] PRL 120, 206801 (2018).
[4] PRL 115, 026101 (2015).
[5] Nature 558, 573 (2018).

11:35-11:50+5

CONTRIBUTED TALK

Ultrafast energy flow and atomic disordering of size-selected Au nanoclusters

Thomas Vasileiadis[1], Lutz Waldecker[1], Dawn Foster[2], Alessandra Da Silva[2], Daniela Zahn[1],
Roman Bertoni[1], Richard E. Palmer[3], Ralph Ernstorfer[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2]University of Birmingham, School of Physics and Astronomy, Birmingham, United Kingdom
[3]Swansea University, College of Engineering, Wales, United Kingdom

Ultrafast electronic excitation can initiate ultrafast motion of adsorbates on metallic surfaces. The underlying mechanisms involve efficient coupling of electronic degrees of freedom, of the metal substrate, to the degrees of freedom of the adsorbed molecule [1]. However, the response of surface atoms of the metal itself and its effect on femtosecond chemical reactions remain largely unexplored. Laser-induced, structural changes of metallic nanostructures with large surface-to-volume ratio can be studied using femtosecond electron diffraction (FED). Applying FED to size-selected Au nanoclusters, we observe an ultrafast broadening of diffraction peaks, indicative of deteriorated crystallinity. This effect arises only during strong non-equilibrium between electrons and the lattice [2]. We attribute the effect to disordering of surface atoms and discuss its implications to surface chemical reactions.

[1] Frischkorn, C. et al., Chem. Rev. 2006, 106, 4207–4233.
[2] Vasileiadis, Th. et al., ACS Nano 2018, 12 (8), pp 7710–7720.

POSTER PRESENTATIONS

TUESDAY, OCT 9 – 16:00-19:00

POSTER #1

Wavelength-resolved UV photodesorption from pure and binary molecular ices: mechanisms and absolute efficiencies

Mathieu Bertin[1], Rémi Dupuy[1], Claire Romanzin[2], Géraldine Féraud[1], Laurent Philippe[1], Thomas Putaud[1], Xavier Michaut[1], Jean-hugues Fillion[1]

[1]Sorbonne University, Laboratoire d'étude du rayonnement et de la matière en astrophysique et atmosphères (LERMA), Paris, France
[2]Laboratoire de Chimie Physique (LCP), Orsay, France

In the colder regions (~ 10 – 100 K) of space, the matter is predominantly molecular, physisorbed at the surface of dust grains. These icy mantles are the main reservoir of molecules: they can act as catalysts for further chemical complexity, and enrich the gas phase by means of non-thermal desorption processes. Desorption of neutral species induced by vacuum UV radiation is considered one of the main process that accounts for the gas-to-ice molecular balance in such regions of space. We have developed these last years a new approach to quantitatively study the photodesorption from astrophysically relevant ices using the tunable and monochromatized output of the synchrotron SOLEIL. I will summarize the main findings of our studies, i.e. the critical influence of several physical parameters, such as ice composition, and the identification of competing processes - non-dissociative energy transfer, photodissociation and exothermic chemistry - at the origin of the photodesorption.

POSTER #2

Coherence measurements of multiphoton-photoemitted electrons from tungsten nano tips

Stefan Meier, Takuya Higuchi, Peter Hommelhoff

Friedrich Alexander University Erlangen-Nürnberg (FAU), Institute of Physics of Condensed Matter, Chair of Laserphysics, Erlangen, Germany

Highly coherent electron emitters are essential for various applications such as electron microscopy, electron diffraction or electron holography. We show our results on investigations of the spatial coherence of pulsed electrons emitted in a multiphoton-photoemission process induced by few-cycle laser pulses with a duration of ~ 6 femtoseconds focused on a tungsten nanotip, an excellent electron source when operated in DC field emission mode. We measured the effective source size of these photoemitted electrons, which is a measure for the spatial coherence, and compare it with that of the DC-field emitted electrons, which have been already well investigated. Despite of the different emission mechanisms, we can show that electrons emitted by multiphoton photoemission are as coherent as DC-field emitted ones. This study marks an important step for various applications as it demonstrates the possibility of strong spatiotemporal electron confinement without the loss of spatial coherence.

POSTER #3

Bulk defect dependent adsorption of acetone on rutile TiO_2(110)

Jessica Kräuter and Katharina Al-Shamery

University of Oldenburg, Department of Chemistry, Oldenburg, Germany

In chemical industry acetone is produced by the Cumene Process using homogenous catalysis. We want to elucidate the potential of TiO_2 as alternative heterogeneous photo-catalyst. An important part of the reaction is the interaction of acetone with titania itself.

In previous coverage dependent studies on acetone and coadsorbed molecular oxygen the occurrence of a diolate species has been identified on a medium reduced single crystal by Henderson and coworkers.[1,2] We considered the adsorption of acetone and coadsorption with molecular oxygen and oxygen adatoms on differently reduced rutile TiO_2(110) single crystals by Temperature Programmed Reaction Spectroscopy (TPRS) and polarized FT-Infrared Reflection Absorption Spectroscopy (FT-IRRAS). Besides diolate a possible β-hydroxy ketone formation enhanced by oxygen adatom coadsorption is found at stronger reduced single crystals.

[1] M. A. Henderson, J. Phys. Chem. B 108, 18932 (2008).
[2] N. G. Petrik et al., J. Phys. Chem. C. 119, 12273 (2015).

POSTER #4

Molecular photoreaction dynamics and 2PP spectroscopy of acetone on TiO_2(110)

Evelyn Artmann, Florian Knall, Thorsten Bernhardt

University of Ulm, Institute of Surface Chemistry and Catalysis, Ulm, Germany

Titanium dioxide is a widely used material in photochemistry and -catalysis. Since surface defects and co-adsorbates like, e.g. molecular oxygen, have a huge influence on the photoreaction dynamics of organic molecules at the surface, we employ two-photon-photoemission (2PP) spectroscopy as well as surface pump-probe femtosecond-laser mass spectrometry to investigate both the electronic structure of the adsorbate covered TiO_2(110) and the photoreaction dynamics of acetone following UV-light excitation.

The 2PP spectra of acetone on TiO_2(110) exhibited a polarization dependent excitation of an electronic state above the Fermi level. This state can only be occupied with p-polarized light and we assign it to a 'wet-electron' state. Interestingly, if molecular oxygen is co-adsorbed on the surface, this state disappears.

Our single-color (266/266 nm) surface pump-probe femtosecond-laser mass spectrometry experiments revealed a transient signal for the CH_3^+- and CH_3CO^+-fragments, which, however, did not depend on the pre-adsorption of molecular oxygen.

POSTER #5

Defect density dependence of partial oxidation and deoxygenation reactions of small organic compounds on rutile TiO_2 (110) surfaces

Lars Mohrhusen, Milena Osmić, Katharina Al-Shamery

University of Oldenburg, Department of Chemistry, Oldenburg, Germany

Though titanium dioxide is an important photocatalyst, many structural details of the occurring reactions remain unclear, particularly with respect to point defects.[1-2] We investigate the reaction of small organic molecules on rutile TiO_2 (110) single crystals with respect to the defect density. [1,3] Defect states like bridging oxygen vacancies as well as $Ti^{+\mathit{III}}$ interstitials (which can start to diffuse towards the surface at elevated temperatures) can easily be introduced to this material. We present our latest results illustrating the importance of such defects and different oxygen surface species for thermal and photostimulated reactions of organic molecules such as deoxygenation reactions or partial oxidation in different temperature regimes for oxygenates, for instance, methanol.

[1] P. Clawin, C. Friend, K. Al-Shamery, Chem. Eur. J. 20, 7665 (2014).
[2] E. Lira, S. Wendt, P. Huo et al., J. Am. Chem. Soc.133, 6529 (2011).
[3] M. Osmić, L. Mohrhusen, K. Al-Shamery, under revision.

POSTER #6

Embedded-cluster calculations of surface oxygen vacancies at TiO_2 with Hubbard-corrected DFT

Matthias Kick, Karsten Reuter, Harald Oberhofer

Technical University Munich, Chair of Theoretical Chemistry, Munich, Germany

Surface oxygen vacancies, in particular their nature as charge trapping centers, play an important role for the (photo-)chemical properties of many oxide materials. However, addressing them with first-principles density-functional theory (DFT) computations remains a challenge. At least DFT+U is required to achieve an appropriate electron localization. At the same time, the large dielectric constant of polarizable oxides like TiO_2 leads to a strong polarization response. As a result supercells of increasing size are necessary in order to avoid spurious interactions between periodic images in case of charged defects, rendering the conventional periodic boundary conditions approach impractical.

Full DFT+U functionality has been implemented in the all-electron electronic structure code FHI-aims. Combined with the solid state embedding functionality in FHI-aims, this yields a numerically most efficient approach to treat aperiodic aspects at oxide surfaces. We illustrate this by calculating neutral and charged states of the surface oxygen vacancy at rutile TiO_2 (110).

POSTER #7

Dynamics of oxygen-induced shape changes of supported Palladium nanoparticles

Simon Chung[1], Vedran Vonk[1], Jan-Christian Schober[1], Andreas Stierle[1,2]

[1]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
[2]University of Hamburg, Solid State and Nanostructure Physics, Hamburg, Germany

Understanding the dynamics, such as shape changes observed in oxidation and reduction reactions of metal nanoparticles remains elusive. These processes occur at high temperatures and under gas exposure on ultrafast time scales of femtoseconds to nanoseconds, and are crucial for understanding of fundamental processes in heterogeneous catalytic reactions. Pd nanoparticles exhibit reversible shape changes in oxidizing and reducing environments. We plan to investigate oxygen induced shape changes of Pd nanoparticles supported by MgO(001). It has been shown that, 8nm-sized Pd nanoparticles with truncated octahedral shape form (112) facets under oxygen exposure. Time-resolved diffraction experiments deliver information about the time and length scales involved in the shape change as a function of sample temperature and oxygen pressure. In addition, transient laser heating processes of oxide supported metal nanoparticles will be elucidated, which is valuable for future experiments involving ultrafast lasers and reaction triggering in these systems.

POSTER #8

C K-edge Selective Probing Ultrafast Surface Chemistry in Catalytic CO Oxidation on Ru (0001)

Boyang Liu[1], Simon Schreck[1], Matthew Weston[1], Martina Dell'Angela[2], Flavio Capotondi[2], Emanuele Pedersoli[2], Denys Naumenko[2], Hirohito Ogasawara[3], Martin Beye[4], Jerry LaRue[5], Anders Nilsson[1]

[1]Stockholm University, Department for Physics, Stockholm, Sweden
[2]Elettra Sincrotrone Trieste S.C.p.A., Trieste, Italy
[3]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Stanford, United States
[4]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
[5]Chapman University, Schmid College of Science and Technology, California, United States

In order to understand the reaction mechanism, it is essential to unveil and characterize the transient short-lived intermediates and transition states under ultrafast time scales. In previous LCLS experiments, we demonstrated the transient precursor state that weakly interacts with the surface from CO desorption and the transition state region in CO oxidation on Ru, both at the O K-edge. Recently we brought the selective probing of ultrafast chemistry in CO oxidation on Ru (0001) surface to the C K-edge, adding complementary knowledge to its previous O K-edge counterpart. The experiments were performed at DiProI beamline at FERMI in Elettra. The endstation used in the current experiment were transferred from Stockholm to FERMI, which equips with X-ray absorption (XAS), allowing the record of reaction products by mass spectrometry. For XAS measurements, both linear horizontal and vertical polarized FEL pulses were applied. Detailed results will be present during DIET16 conference.

POSTER #9

Second harmonic studies on the electrode/electrolyte interface of hematite photoanodes

Julius M. Plescher, R. Kramer Campen, Martin Wolf

Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany

So far, slow water oxidation kinetics at hematite (α-Fe_2O_3) photoanodes have been attributed to charge accumulation, hole trapping and the formation of electronic states at the electrode/electrolyte interface.[1,2] However, intense disagreement remains on the mechanism of charge accumulation and the role and nature of intragap states.[1]

Our studies focus on charge transfer processes at the hematite/electrolyte junction by means of electronically resonant second harmonic generation spectroscopy (eSFG). This technique allows to optically probe electronic processes *in situ* with high interfacial specificity.[3] The effects of electrolyte, photoexcitation and external bias potential on eSFG spectra are presented and discussed in the context of other findings from optical[4] and AC-photoelectrochemical[2] spectroscopies.

[1] D. A. Grave et al., Adv. Mat., 2018, 0, 1706577.
[2] Z. Wang et al., RSC Advances, 2016, 6, 85582.
[3] B. Doughty et al., J. Phys. Chem. C, 2015, 119, 2752.
[4] M. Barroso et al., PNAS, 2012, 109, 15640.

POSTER #10

Modified optical properties and structural dynamics of Au-decorated WSe_2

Thomas Vasileiadis, Daniela Zahn, Sang Eun Lee, Maciej Dendzik, Laurenz Rettig, Ralph Ernstorfer

Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany

We use femtosecond electron diffraction (FED) to study ultrafast energy flow and the resulting structural changes in low-dimensional metal / semiconductor heterostructures. The dynamics of Au nanostructures can be significantly modified by the optical and thermal properties of a thin-film substrate [1]. In this work we demonstrate the inverse effect: a discernible change in the optical properties and structural dynamics of multilayer WSe_2 flakes, induced by decoration with Au. The deposited Au is ultrathin and epitaxial and hence we can complement our FED studies with angle-resolved photoemission measurements to obtain a momentum resolved picture of the electronic levels alignment. This allows to identify the electronic states that are involved in the energy transfer processes.

[1] Vasileiadis, Th. et al., ACS NANO 2018, 12 (8), pp 7710–7720.

POSTER #11

Towards ultrafast exciton dynamics in monolayer WS_2 probed by femtosecond time-resolved broadband electronic sum frequency generation (eSFG)

Stefano Calati[1], Selene Mor[1], Sarah B. King[1,2], Julia Stähler[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2]University of Chicago, Department of Chemistry, Chicago, USA

Ultrafast processes involving energy and charge transfer at interfaces determine the functionality of opto-electronic devices. Our aim is to unveil the exciton dynamics of transition metal dichalcogenides (TMDCs) which are enhanced in these 2D crystals due to the reduced dielectric screening and resulting strong Coulomb interaction.

We present our preparational work on pristine monolayer WS_2 using femtosecond time-resolved electronic sum frequency generation (eSFG) based on a white light supercontinuum [1].

We show the first preliminary time-resolved eSFG measurements of monolayer WS_2, thereby demonstrating remarkably intense eSFG generation from a monolayer sample. We observe a resonant contribution assigned to the WS_2 A exciton. Transient spectral changes of this resonance are measured and the different ultrafast processes responsible for the observed dynamics are discussed. Further investigations will provide the basic framework for future studies on exciton dynamics in heterostructures, and energy and charge transfer at TMDC-based HIOS interfaces.

[1] L. Foglia, M. Wolf and J. Stähler, Appl. Phys. Lett. 109, 202106 (2016).

POSTER #12

Development of femtosecond time-resolved photoluminescence spectroscopy for the study of TMDCs

Boubacar Tanda Bonkano[1], Sesha Vempati[1,2], Lukas Gierster[1], Mohsen Sajadi[1], Julia Stähler[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2] Indian Institute of Technology, Bhilai, India

Time-resolved photoluminescence (tr-PL) is a technique used to address the relaxation pathways in photoexcited samples. Our work aims at the understanding of the exciton dynamics in transition metal dichalcogenides (TMDC) monolayer systems. Although these are intensely investigated, the temporal resolution given by the commonly used instruments, for instance TCSPC or streak camera, is of the picosecond order. We are developing a tr-PL setup based on optical up-/down conversion of the emitted light in order to resolve faster dynamics, down to 100 fs. However, the PL emitted from the monolayer is weak. This naturally reduces the conversion efficiency and raises the level of difficulty of the experiment. In addition to this method, we also perform TCSPC experiments. The latter is a good tool to study relatively weak intensities, but provides only a temporal resolution of 50 ps limited by the photodetector used. In future studies, we aim at investigating the properties of TMDC-organic hybrid systems.

POSTER #13

Trapped electrons and their impact on oxygen reactivity in a DMSO/Cu(111) model system

Angelika Demling[1], Sarah B. King[1,2], Katharina Broch[1,3], Julia Stähler[1]

[1]Fritz Haber Institute, Department of Physical Chemistry, Berlin, Germany
[2]University of Chicago, Department of Chemistry, Chicago, USA
[3]University of Tübingen, Institute for Applied Physics , Tübingen, Germany

DMSO is a common non-aqueous solvent with the potential to be used in lithium-oxygen batteries due to its ability to catalyze the superoxide formation and to stabilize the products. Here we investigate the electron dynamics in DMSO films on Cu(111) using time- and angle-resolved two-photon photoemission. We show that films of a thickness > 2 monolayers exhibit a surface-bound electronic state at 2.35 ± 0.05 eV above the Fermi level with a lifetime on the order of several seconds. Further static and time-resolved experiments provide evidence that it is most likely formed from a small polaron on the second monolayer/vacuum interface. Due to its long lifetime and binding location on the DMSO surface, we assign the surface state to electrons residing in deep traps at the DMSO/vacuum interface. These surface-bound electrons react with oxygen, making these findings relevant for the understanding of the formation of superoxide in lithium-oxygen batteries.

POSTER #14

STM-induced fluorescence of charged single-molecules

Shuiyan CAO, Benjamin Doppagne, Michael C. Chong, Hervé Bulou, Alex Boeglin, Fabrice Scheurer, Guillaume Schull

Université de Strasbourg, CNRS, IPCMS, UMR 7504, Strasbourg, France

The spectroscopic properties of neutral, oxidized and reduced states of fluorescent molecules are important because they lay the foundation for building photovoltaic and optoelectronic organic devices. While generally addressed for large ensembles of molecules within an electrochemical cell, the luminescence properties of organic compounds are hard to probe at the single-molecule limit. Here we show that the tip of a scanning tunnelling microscope can be advantageously used to simultaneously control the charge state and excite the fluorescence of a single Phthalocyanine molecule. Our data reveal that the color of the emission and the respective intensity of vibronic features in the spectra crucially depend on the redox state of the probed molecule. The excitation and charging mechanisms are discussed in the light of the current, voltage and tip-molecule distance dependencies of the emission.