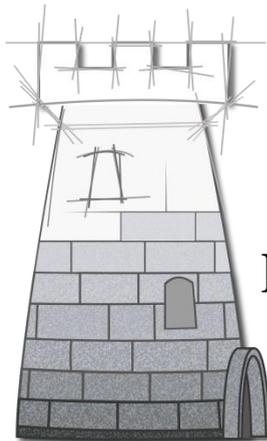


IMPRS Workshop 2018: From Models to Reality

Monday 19 February 2018 - Friday 23 February
2018

Schloss Ringberg am Tegernsee



IMPRS

From Models

To Reality

Book of Abstracts

	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
08:00–08:50		Breakfast	Breakfast	Breakfast	Breakfast
08:50–09:00		Welcome	Welcome	Welcome	Welcome
09:00–09:50		Christian Papp	Jörg Libuda	Irene Groot	Stefan Schernich
09:50–10:40		Andreas Grüneis	Angelos Michaelides	Céline Chizallet	John Uhrich
10:40–11:00		Coffee Break	Coffee Break	Coffee Break	Coffee Break & Conclusion
11:00–11:50		Sebastian Loth	Martin Sterrer	Jeroen van Bokhoven	
11:50–12:30	Arrival at Ringberg	Group Discussion	Group Discussion	Group Discussion	
12:30–14:00		Lunch	Lunch	Lunch	Lunch
14:00–14:50		Antoine Kahn		Yousoo Kim	
14:50–15:40		Maria Blanco-Rey	Social Program	Jamal Berakdar	
15:40–16:00		Coffee Break		Coffee Break	Departure
16:00–16:50		Heike Arnolds		James Lloyd-Hughes	
16:50–17:40		Group Discussion		Group Discussion	
	17:30 Castle Tour				
18:30	Dinner	Dinner	Dinner	Dinner	
20:00–20:45	Icebreaker Session	Poster Session 1		Poster Session 2 Social Evening	

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Tuesday Morning 20 Feb 2018, 09:00

Talk 50 minutes

Chemical Modification of 2D Materials

Presenter: Christian Papp

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Understanding the chemical reactivity of 2D materials such as graphene and hexagonal-boron nitride (h-BN) is of fundamental importance for obtaining flexible and tunable materials for devices and electronic applications, as well as for fundamental science to obtain concepts for the chemistry on such materials. The interaction of graphene and h-BN with oxygen and atomic hydrogen will be discussed in details and the results for the two substrates will be compared. While in the case of atomic hydrogen, graphene forms graphane, i.e. fully hydrogenated graphene, for h-BN hydrogen can bond and intercalate, depending on the exposure. Interestingly, graphene does not react with molecular oxygen, even when supplied with a high kinetic energy of 0.7 eV, while h-BN readily forms bonds to oxygen, intercalates or even reacts, depending on the substrate temperature. Further insights to the bonding and reaction mechanisms of hydrogen and oxygen are obtained from DFT calculations.

Tuesday Morning 20 Feb 2018, 09:50

Talk 50 minutes

Recent Progress in Applying Coupled Cluster Theories to Ground and Excited State Properties of Solids and Surfaces

Presenter: Andreas Grüneis

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This presentation will review recent progress in applying periodic coupled cluster theories to the study of surfaces and solids. We will briefly discuss methods that reduce the computational cost and accelerate convergence of calculated properties towards the complete basis set as well as thermodynamic limit [1-4]. These recent developments have enabled an increasing number of ab-initio studies and allowed for assessing the accuracy of coupled cluster theories by comparing to experimental findings as well as quantum Monte Carlo results. The presented applications will include phase transitions of solids [5], molecular adsorption energies [6-7], hydrogen dissociation on silicon surfaces as well as ground and excited state studies of defects in solids.

[1] A. Grüneis, Phys. Rev. Lett. 115 066402 (2015).

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Tuesday Morning 20 Feb 2018, 11:00

Talk 50 minutes

Charge and Spin Dynamics of Atoms on Surfaces

Presenter: Sebastian Loth

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Spin and charge correlations are particularly pronounced in nanoscale materials and enable new technologies that harness quantum behavior. Accessing these correlations on their intrinsic length and time scales is an important step towards a microscopic understanding of correlated-electron physics.

We combine scanning tunneling microscopy with pump probe schemes [1] to achieve ultrafast spectroscopy of spin and charge dynamics with atomic spatial resolution. Using different electronic and optical techniques it is possible to achieve time resolution between milliseconds and femtoseconds thereby matching the instrument to the dynamics of the investigated system. In this talk I will review recent advances in ultrafast scanning probe microscopy and then discuss two experiments: one in which we fabricated a few-atom spin sensor that dynamically measures minute magnetic interactions with nearby magnetic atoms [2]; and one in which we observe the ultrafast motion of a two-dimensional correlated-electron state in the vicinity of defects.

These experiments shed light onto the impact of correlations and coherences in quantum materials and highlight pathways to design and control matter at the single atom level.

[1] S. Loth, M. Etzkorn, C. P. Lutz, D. M. Eigler, A. J. Heinrich, *Science* 329, 1628 (2010).

[2] S. Yan, L. Malavolti, J. Burgess, S. Loth, *Science Adv.* 3 e1603137 (2017).

Tuesday Evening 20 Feb 2018, 14:00

Talk 50 minutes

Molecular Doping for Organic Semiconductors

Interface Engineering: Principles and Reality

Presenter: Antoine Kahn

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Molecular doping is key to controlling the electronic and electrical properties of organic semiconductors, lower contact resistance, enhance bulk conductivity and carrier mobility, and create higher performance devices. This talk reviews processes and options for interface doping in molecular and polymer semiconductors, and the roles that electron spectroscopy and carrier transport measurements have played in defining key issues. Various n- and p-type molecular dopants, their doping strength and the challenges they pose are reviewed first. Specific examples will be reviewed. First is the surface/interface doping of polymer-based devices via soft-contact lamination of highly doped interlayers [1,2]. We look at the electrical characteristics of the laminated polymer/polymer interface (with P3HT, PBDTTT-c or poly-TPD), at the problem of dopant diffusion across boundaries, and at the performance of polymer-based solar cells built with laminated hole-extraction layers [3]. We then turn to the issue of improving contacts to very low electron affinity (EA) electron transport layers (ETL), an issue critical to green and blue OLEDs. We look at the air-stable dimer of (pentamethylcyclopentadienyl)(1,3,5-trimethylbenzene)ruthenium ([RuCp*Me₅]₂) [4], and use it to n-dope phenyldi(pyren-2-yl)phosphine oxide (POPy₂) (EA = 2.1 eV). We demonstrate that photo-activation of the cleavable dimeric dopant results in kinetically stable and efficient n-doping of the host semiconductor, whose reduction potential is beyond the thermodynamic reach of the dimer's effective reducing strength [5]. We demonstrate the use of this doped ETL to fabricate high-efficiency organic light-emitting diodes. If time permit, surface n-doping of graphene to decrease its work function, shift its Fermi level and improve electron injection in organic ETLs will be described.

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[2] A. Dai, A. Shu, H. Wang, S. Barlow, S. Mohapatra, T. Sajoto, Y. Zhou, C. Fuentes-Hernandez, Y.-L. Loo, S. R. Marder, B. Kippelen, and A. Kahn, *Adv. Funct. Mat.* ****24****, 2197 (2014).

[3] A. Dai, A. Wan, C. Magee, Y. Zhang, S. Barlow, S. R. Marder and A. Kahn, *Org. Electr.* ****23****, 151 (2015)

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Tuesday Evening 20 Feb 2018, 14:50

Talk 50 minutes

Magnetocrystalline Anisotropy in Monolayer Systems: Transition-Metal-Organic Coordination Networks and Lanthanide-Metal Alloys

Presenter: Maria Blanco-Rey

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Various interactions contribute to the existence of an easy magnetization axis or plane in a system, a phenomenon known as magnetic anisotropy. Among those contributions, the so-called magnetocrystalline anisotropy (MCA) is fundamental to understand magnetism at the nanoscale, since it is intimately related to the electronic structure. MCA is due to the spin-orbit (SO) interaction and it is enhanced by reduced dimensionality. Thus, giant MCA is commonplace for single adatoms or molecules and bidimensional magnetic systems.

Since the energies associated to MCA are small (often well below the meV), perturbative models have been used to describe it [1], such as spin effective hamiltonians for isolated magnetic moments. However, these models present limitations when the ion hybridizes strongly with its surroundings. Alternatively, DFT calculations including SO terms offer a reliable description in those cases, although they might be sometimes impractical due to the accuracy needed to account for the small MCA energies.

We will discuss free-standing transition-metal-organic coordination networks. Although SO effects may seem small **a priori** here, this example nicely illustrates the complexity behind an easy magnetization axis or plane. For model Mn- and Ni-TCNQ rectangular lattices [2] we have found, using DFT calculations, how to tune the MCA upon alteration of the electronic structure by charge transfer from the substrate, lattice strain, or by symmetry breaking. Due to the latter effect in Ni-TCNQ, strong azimuthal anisotropy energy differences of up to 1.5 meV (measured with the OZ easy axis reference) are obtained.

The second example is the GdAu_2 monolayer alloy, studied both experimentally (XMCD, MOKE, and ARPES) and theoretically (DFT). In this strong SO-coupled system we have found in-plane MCA, as opposed to pure Gd surfaces, characterised by perpendicular anisotropy. Our result is a consequence of the formation of Gd(d)-Au(s) hybrid bands [3]. Further, when GdAu_2 is used as a substrate it induces a magnetization direction change in deposited Co [4].

[1] G. van der Laan, *J. Phys.: Condens. Matter* **10**, 3239 (1998).

[2] M.N. Faraggi *et al.*, *J. Phys. Chem. C* **119**, 574 (2015).

[3] M. Ormaza *et al.* *Nano Lett.* **16**, 4230-4235 (2016).

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Tuesday Evening 20 Feb 2018, 16:00

Talk 50 minutes

Surface-Enhanced Raman Spectroscopy of Molecular Electronic Junctions

Presenter: Heike Arnolds

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Metal-molecule-metal junctions are attractive for many applications such as energy harvesting and sensing and a wide variety of techniques have been developed for their creation and electrical characterization.

In particular vibrational spectroscopy of metal-molecule-metal junctions is desirable simply because it shows whether the molecule remains intact and whether any new vibrational modes in the spectrum indicate actual bond formation between a functional group and a metal layer. Moreover, in the context of molecular electronics, it permits detecting the effect of an applied electric field on the molecular structure or any coupling between electronic transport in the junction and vibrational modes.

Vibrational spectroscopy is however much less advanced due to the combined challenges of detecting a small signal whilst forming an intact sandwich system. In this talk I will show that even nonideal surfaces such as roughened gold or gold nanoparticles can be used to detect partial layer metallization by Surface-enhanced Raman spectroscopy (SERS) for the example of 4-mercaptopyridine, 4-4'-bipyridine and pyridyl-dithiocarbamates. I will also address to which degree SERS can be used to detect adsorbate charge transfer resonances, in particular on nonideal surfaces.

In the final part of the talk I will give an example of how to generate impact from even very fundamental research and explain what links rose petals, thread seal tape and CF16 gaskets.

Wednesday Morning 21 Feb 2018, 09:00

Talk 50 minutes

Electrifying Model Catalysis: Out of the Vacuum - Into the Electrolyte

Presenter: Joerg Libuda

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Electrocatalysis is the key to our future transition to a renewable energy system. Yet, our fundamental understanding of electrocatalysis lags behind classical heterogeneous catalysis, which has dominated chemical technology for a long time.

Here, we describe a new strategy to advance fundamental studies on electro-catalytic materials. We propose to “electrify” complex model catalysts made by surface science methods to explore electrocatalytic reactions in liquid environments. We demonstrate the feasibility of this concept by transferring an atomically-defined platinum/cobalt oxide model catalyst into the electrochemical environment while preserving its atomic surface structure. Combining vibrational spectroscopy, ambient photoelectron spectroscopy, and other surface science and electro-chemical methods, we explore particle size effects and identify hitherto unknown metal-support interactions that stabilize oxidized platinum at the metal-support interface. The latter effect opens a new synergistic reaction pathway that involves both metallic and oxidized platinum. Our results illustrate the potential of the concept, which makes available a systematic approach to build atomically-defined model electrodes for fundamental electrocatalytic studies.

Wednesday Morning 21 Feb 2018, 09:50

Talk 50 minutes

What we do and don't know about water at interfaces – Molecular Level Insight from Computer Simulation

Presenter: Angelos Michaelides
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There are few molecules, if any, more important than water. Yet remarkably little is known about how it interacts with solid surfaces, particularly at the all important atomic-level. This is true despite widespread general interest and compelling environmental and economic incentives. For example, water-solid interactions play a crucial role in the activity of fuel cells, the chemistry of the atmosphere, global warming, corrosion, catalysis, the operation of membranes, and so on. In this talk I will discuss some of our recent work in which we have been using classical and quantum molecular dynamics approaches as well as advanced electronic structure methods to better understand the structural and dynamical properties of water-solid interfaces. This will include work focused on understanding the formation of ice [1-3], confined water in nanocapillaries [4], and water diffusion and friction [5-7].

[1] M. Fitzner, G. C. Sosso, S. J. Cox and A. Michaelides, *J. Am. Chem. Soc.* **137**, 13658 (2015).

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[4] J. Chen, G. Schusteritsch, C. J. Pickard, C. G. Salzmann and A. Michaelides, *Phys. Rev. Lett.* **116**, 025501 (2016).

[5] G. Tocci, L. Joly and A. Michaelides, *Nano Lett.* **14**, 6872 (2014).

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[7] L. Joly, G. Tocci, S. Merabia, and A. Michaelides, *J. Phys. Chem. Lett.* **7**, 1381 (2016).

Wednesday Morning 21 Feb 2018, 11:00

Talk 50 minutes

Thin Oxide Film Based Model Catalysts - From UHV to Environmental Conditions

Presenter: Martin Sterrer

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Ultrahigh vacuum-based surface science studies of model catalysts consisting of metal nanoparticles supported by thin, single-crystalline oxide films have allowed to address catalysis-related topics (metal-substrate interaction, adsorbate-substrate interaction, catalytic active sites, etc.) on a fundamental level. This talk deals with thin oxide films applied in more applied settings. They were utilized as oxide substrate for the preparation of oxide-supported metal nanoparticle model catalysts by deposition of metal salts from aqueous solutions (Surface Science approach to catalyst preparation), and in electrochemical studies. I will present the results of combined STM and XPS studies of the preparation of oxide-supported Pd and Au nanoparticles, and in particular report on the influence of preparation parameters (e.g. solution pH, water rinsing, chloride effect) on the morphology of the model catalyst. Results about the stability of oxide films in electrolyte solutions and under applied potential, and the influence of an organic adsorbate (catechol) on the solubility will finally be discussed.

Thursday Morning 22 Feb 2018, 09:00

Talk 50 minutes

Seeing is Believing: Atomic-scale Imaging of Catalysts under Reaction Conditions

Presenter: Irene Groot

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The atomic-scale structure of a catalyst under reaction conditions determines its activity, selectivity, and stability. Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the ultra)high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra)high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts in situ under industrially relevant conditions. In this talk, I will give an overview of the in situ imaging techniques we use to study the structure of model catalysts under industrial conditions of atmospheric pressures and elevated temperatures. We have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance. Furthermore, we use other in situ imaging techniques such as transmission electron microscopy, surface X-ray diffraction, and optical microscopy, all combined with mass spectrometry.

Continued on next page

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, i.e. CO oxidation, will be shown. But additionally, results for more complex reactions such as NO oxidation and reduction, Fischer-Tropsch synthesis, and hydrodesulfurization will be discussed.

Thursday Morning 22 Feb 2018, 09:50

Talk 50 minutes

Complex Heterogeneous Catalysts in Reactive Environment: from Density Functional Theory Simulations to Predictive Kinetic Models

Presenter: Céline Chizallet

IFP Energies nouvelles

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Most efficient heterogeneous catalysts used industrially are generally very complex systems. Far away from perfect crystallinity and well-defined oriented surfaces at low coverage, they involve structural disorder, heterogeneous site distribution with variable coordination and structural dependence upon the chemical environment. Unravelling their atomic-scale structures and understanding their roles in the catalytic reaction are not easy tasks, as the respective contributions of each type of site to the spectroscopic or catalytic responses are generally convoluted. Computational chemistry is of great help to address these issues, but very often, simple structural models are proposed to understand catalytic reactions. In the present manuscript, we show how Density Functional Theory (DFT) calculations were used to provide an original information about the structure for active sites of complex catalytic systems of industrial relevance, as a function of their environment, to assign spectroscopic observations and to quantify the kinetics of multi-step reactions they can catalyze.[1] Heterogeneous catalysts involved in industrial applications such as refining, petrochemistry, biomass conversion and pollution abatement were considered. In particular, original models of imperfect aluminosilicates were developed and their Brønsted acidity unraveled.[2] The reactive environment-dependent (hydrogen and hydrocarbons) morphology of subnanometric platinum-based clusters was revealed.[3] Finally, we show how ab initio thermodynamic and kinetic information can be introduced in kinetic models, possibly integrated themselves in Computational Fluid Simulations, to access macroscopic predictions thanks to a multiscale approach.[4]

[1] C. Chizallet, P. Raybaud, *Catal. Sci. Technol.* 2014, 4, 2797.

[2] C. Chizallet, P. Raybaud, *Angew. Chem. Int. Ed.* 2009, 48, 2891 ; F. Leydier, C. Chizallet, D. Costa, P. Raybaud, *J. Catal.* 2015, 325 ; M.-C. Silaghi, C. Chizallet, J. Sauer, P. Raybaud, *J. Catal.* 2016, 339, 242.

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Thursday Morning 22 Feb 2018, 11:00

Talk 50 minutes

About Catalytically Active Sites

Presenter: Jeroen A. van Bokhoven

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Catalysts often consist of nano-sized catalyst particles on an support. It has been recognized since long that the role of the support is not only to stabilize the catalytically active particles of particular size, shape and composition, but that they may actively participate in the catalytic reaction. Specific reaction steps may occur completely on the support or at the metal-support interface. In other cases, the support may be responsible for the communication between different catalytic entities by stabilizing and facilitating transport of species over its surface, a process called spillover.

In my talk, I will describe some of our contributions in this field. Ceria is an often-used catalyst support and catalytic material because of its ability to reversibly store oxygen. Thus, in oxidation reactions, oxygen activation may occur on ceria and the reaction at the interface of metal and support. The role of Ce^{3+} is often invoked to explain catalytic activity, however, a quantitative understanding of its role is lacking. Using transient X-ray emission and absorption spectroscopy, we were able to distinguish between Ce^{3+} that participates in a catalytic cycle, oxidation of carbon monoxide over Pt/CeO₂, and Ce^{3+} that does not contribute to catalytic conversion and is thus a spectator. The reaction takes place at the metal-support interface and the rate of reaction correlates to the rate of ceria reduction, not the oxygen storage capacity.

Spillover of hydrogen over reducible and non-reducible supports is often suggested to be responsible for a catalytic action at a distance. To quantify the phenomenon of hydrogen spillover, we designed a supported metal catalyst, which contains platinum and iron oxide particles with a distance that is controlled to a nanometer. The further development of single-particle spectroscopy enabled visualization of the phenomenon of hydrogen spillover. As expected, hydrogen atoms can freely move over a titania surface as electron-proton pair. On alumina, the situation is more complex and a gradient of hydrogen coverage away from the platinum particle is observed. The strong competition of water with the same adsorption sites, make the occurrence of hydrogen spillover over an alumina surface much less likely.

Thursday Evening 22 Feb 2018, 14:00

Talk 50 minutes

Real-space Observation of Energy Transfer between Two Molecules by Single-molecule Emission/Absorption Spectroscopy with an STM

Presenter: Yousoo Kim

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Excitation of molecules by light irradiation triggers various important processes including luminescence, photovoltaic effect and photochemical reactions, and detailed understanding of the molecular excited states is crucial to improve organic opto-electronic devices. Absorption spectroscopy is a powerful tool to describe the molecular excitations and the combination with emission (luminescence) spectroscopy which deals with deexcitation processes is effective to investigate the excited states. Single-molecule luminescence detection has progressed rapidly and become indispensable in quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, absorption spectroscopy is far behind; numbers of molecules are still necessary to obtain an absorption spectrum. A difficulty lies in the difference between the diffraction limit of excitation light and absorption cross section of a single molecule.

Here I introduce our recent progress in measurement of the single molecule luminescence and absorption spectra of a single molecule using a scanning tunnelling microscope (STM) equipped with optical detection facilities. I will discuss about the single molecule reaction of a single metal-free phthalocyanine molecule on the NaCl ultrathin film on Ag(111) with tunneling electrons and accompanied optical property changes in a single-molecule optical spectra. Application of the single-molecule emission/absorption spectroscopy to the real-space investigation of energy transfer between molecules will be also introduced.

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[2] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura and Y. Kim, *Phys. Rev. Lett.* 119 (2017) 013901.

Thursday Evening 22 Feb 2018, 14:50

Talk 50 minutes

Multifunctionality Through Interfacial Multiferroicity

Presenter: Jamal Berakdar

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Interfacing materials results a wealth of emergent physical properties that can be exploited for new functionalities of the coupled sample. This contribution will concentrate on the interfaces of two ferroic materials such as ferroelectric/ferromagnetic/or ferroelastic compounds. Thereby, the ferroic order itself can be an emergent one due to interfacial proximity effects. After a discussion of the underlying physics, emphasis is put on prospect applications of such composite systems in (opto)electronics as well as in energy saving and conversion devices, such as four-point and non-volatile memories, electrically-driven ultrafast magnetism, thermal diodes, and multiferroic nanoscale heat engines.

Thursday Evening 22 Feb 2018, 16:00

Talk 50 minutes

Colossal Terahertz Magnetoresistance in Oxide Nanocomposites

Presenter: James Lloyd-Hughes

University of Warwick

Contact: j.lloyd-hughes@warwick.ac.uk

Conventional materials have magnetoresistances $\Delta R/R=[R(B)-R(0)]/R(0)$ of a few percent, and the giant magnetoresistance of metal heterostructures approaches 30% for dc fields and at THz frequencies [1]. In contrast, in colossal magnetoresistance (CMR) oxides the resistance can change by orders of magnitude in a magnetic field. Here we report for the first time that colossal magnetoresistance persists to THz frequencies, with magnetoresistances above -99% at 1THz and at room temperature [2].

The THz magneto-optical conductivity of the colossal magnetoresistance compound $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ was investigated by THz time-domain spectroscopy. The response of vertically-aligned nanocolumns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ in a ZnO matrix [3] was compared with that of pure $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films. This is particularly important as it allows the comparison of the intrinsic CMR effect, witnessed in pure single crystals around room temperature, with the extrinsic CMR effect, which is controlled by grain boundaries. Extrinsic CMR requires lower applied magnetic fields than the intrinsic effect, desirable for applications, but works below room temperature. Surprisingly, and in contrast to the dc CMR effect, we demonstrate that the THz magneto-optical response in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanocolumns is an intrinsic effect. The THz CMR is large at the Curie temperature, when core Mn spins begin to align ferromagnetically, but decreases at lower temperatures.

Continued on next page

At temperatures below the metal-insulator transition (when samples are metallic) the frequency-dependent conductivity is well described by the Drude model of free-carrier absorption. The application of a magnetic field perpendicular to the samples was found to enhance the Drude spectral weight, which can be understood within the double-exchange picture of charge transport in the CMR manganites. At the Curie temperature (300K) the THz conductivity of the nanocolumn film was dramatically enhanced by the application of a magnetic field, creating a non-Drude conductivity that increases with frequency. We discuss possible origins of this trend, including the prevalent picture in the literature of bipolarons destruction under a magnetic field into single polarons. The observed colossal THz magnetoresistance suggests that the magnetoresistance can be large for ac motion on nanometre length scales, even when the magnetoresistance is negligible on the macroscopic length scales probed by dc transport. Colossal THz magnetoresistance at THz frequencies may find use in active THz optical and electronic components controlled by magnetic fields.

[1] Z. Jin et al., Nat. Phys. 11, 761 (2015).

[2] J. Lloyd-Hughes et al., Nano Letters 17, 2506 (2017).

[3] A. Chen et al., Adv. Funct. Mater. 21, 2423 (2011).

Friday Morning 23 Feb 2018, 09:00

Talk 50 minutes

A Transition from Academia to Industry: How Model Surfaces and Catalysts turned to Tablets, Optics Technology, and Project Management

Presenter: Stefan Schernich

Carl Zeiss SMT GmbH

Contact: stefan.schernich@gmail.com

With the final months of the PhD coming closer, every graduate needs to make a decision about his or her future: pursue a career in science or in the private sector?

While graduates are familiar with the academic environment after several years of research at universities or other scientific institutions, the private sector remains a big unknown to many. So, how do you make a sound choice? Which is more suiting to your interests, personality, goals, and way of life?

In my talk I will provide you with my personal point of view: why I chose to work in industry, how things turned out as an industrial researcher, and how my career has developed ever since. An introduction to the technological problems that I faced trying to improve the performance of potassium hyperoxide based respiratory protection systems as well as optical coating technology will be given.

More importantly, I want to share my experience related to the way of working in industry and how it has shaped my thinking.

Friday Morning 23 Feb 2018, 09:50

Talk 50 minutes

What Do Editors Do All Day?

Presenter: John Uhrlich

Wiley-VCH

Contact: jjuhrlich@wiley.com

From the perspective of an editor, John Uhrlich (Editor-in-Chief, *Energy Technology*), will present on the current state of publishing in the physical sciences and energy research, including chemistry, materials science, and engineering, by outlining the roles, responsibilities, and ethical obligations of authors, editors, and reviewers. The talk will include offer tangible examples and how-to's related to publishing in journals and communication between authors, editors, and reviewers. An introduction to the Wiley-VCH journals will be presented along with some tips for preparing scientific publications and how to achieve the highest possible impact after publication.

Poster Session I

Poster 15 minutes

Messenger Atom Action Spectroscopy of Solid Surfaces

Presenter: Agata Plucienik

Fritz-Haber-Institut

Contact: plucienik@fhi-berlin.mpg.de

Vibrational action spectroscopy employing infrared radiation from a free electron laser is successfully used since many years for the vibrational and structural characterization of gas phase aggregates. Despite the high sensitivity of this method, no relevant studies have yet been conducted for solid samples. An ultra-high vacuum (UHV), chamber incorporating surface science techniques, has been constructed at the free electron laser of the Fritz Haber Institute (FHI FEL). An aim is to apply this method to solid surfaces in order to learn about their vibrational, electronic and structural properties. As central components of heterogeneous catalysts, deposited metal clusters on oxide surfaces have been intensively investigated; yet in most cases little is known about their atomic structure, since it is experimentally not easily accessible. With messenger atom action spectroscopy, the vibrational modes of clusters are detected via infrared heating induced desorption of rare gas atoms attached to the clusters. A quadrupole mass spectrometer and a low temperature scanning probe microscope are available for the detection of the desorption process. Comparison of the experimental vibrational spectrum with quantum chemical calculations provides structural information and information about electronic properties. As the preliminary topics, we studied the action spectroscopy of rutile $\text{TiO}_2(110)$, as well as $\text{V}_2\text{O}_3(0001)/\text{Au}(111)$ in the middle infrared range at liquid helium temperature. The results of the former sample surface revealed a series of defect independent bulk vibrational states of $\text{TiO}_2(110)$, which were not well recognized before. The results of the latter sample surface clearly demonstrated that our method is surface sensitive and capable of investigating a wide range of scientific topics.

Motivation:

Incorporating the high sensitivity action spectroscopy method with surface science techniques to study the structural and electronic properties of the oxide film supported metal clusters model catalysts, in order to broaden our understanding of structure-reactivity relation of heterogeneous.

Poster Session I

Poster 15 minutes

Ab Initio Prediction of Co-adsorption of Gases by GCMC Simulations on a Lattice of Sites

Presenter: Arpan Kundu

Humboldt-Universität zu Berlin

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The metal-organic frameworks (MOF) are a new class of porous materials that have high potential for carbon capture and storage (CCS). CPO-27-Mg (Mg-MOF-74) is one such MOF that has under-coordinated Mg²⁺ sites where CO₂ gas molecules can bind selectively at low partial pressure (below 1 bar). Prerequisite to a rational design of improved material with optimized separation conditions is the reliable prediction of co-adsorption equilibria. Generic force fields, which have often been employed in classical Grand Canonical Monte Carlo (GCMC) simulations to forecast co-adsorption of gas mixtures, are found to be inadequate in describing the molecule-surface interactions in MOFs with open metal sites. Although the tedious *ab initio* parametrization of force fields improve the description, these standard GCMC simulations still neglect the zero point vibrations (ZPV) and framework relaxation (FR) effects on adsorption.

We developed an alternative GCMC simulation methodology [1], which utilizes Gibbs free energies of adsorption of individual sites and the lateral (adsorbate–adsorbate) interaction energies obtained from *ab initio* calculations, which define the Hamiltonian of the coarse-grained lattice-gas description of the adsorbent surface. The former includes the ZPV and FR effects, whereas the latter can be treated exactly in the proposed scheme, which avoids cumbersome fitting of the force field parameters. The possibility of applying very accurate quantum chemical methods for lateral interactions or Gibbs free energies of the individual sites makes it a powerful tool for benchmarking standard GCMC simulations.

Hybrid MP2:(PBE+D2)+ Δ CCSD(T) schemes, which were shown to produce accurate Gibbs free energies (within 1 kJ/mol) [2-4], are used for each individual sites, whereas CCSD(T) lateral interaction energies are employed in this work. Together, they yield pure gas isotherms that are in close agreement with experiment. Our simulations reveal the importance of lateral interactions on co-adsorption of gas mixtures that are relevant to CCS.

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- [2] A. Kundu, G. Piccini, K. Sillar, J. Sauer, *J. Am. Chem. Soc.* 138, 14047 (2016).
- [3] K. Sillar, A. Kundu, J. Sauer, *J. Phys. Chem. C.* 121, 12789 (2017).
- [4] K. Sillar, J. Sauer, *J. Am. Chem. Soc.* 134, 18354 (2012).

Poster Session I

Poster 15 minutes

Cold-Ion Infrared Spectroscopy using Helium Nanodroplets – from Biomolecules to Surface Science?

Presenter: Eike Mucha

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The combination of mass spectrometry (MS) and infrared (IR) spectroscopy is a powerful tool to elucidate the structure of isolated ions in the unique clean-room environment of the gas-phase. To avoid line broadening due to thermal contributions during the measurement, cryogenic ion spectroscopy can be employed. In our experimental setup we use helium nanodroplets as a matrix to cool ions to their extremely low equilibrium temperature of 0.4 K. This experimental approach can be utilized to capture both cationic and anionic molecules ranging in size from tens of Da to several kDa and subsequently probe their structure using infrared radiation produced by the FHI-FEL. In the past, we used this method for the structural analysis of biomolecules such as peptides and proteins as well as complex oligosaccharides. Using a different MS/IR spectroscopy method at room temperature, the analysis of ionic molybdenum oxide clusters failed to unambiguously assign the molecular structure, which is mainly attributed to thermal peak broadening. This system will provide an excellent benchmark to evaluate our cryogenic spectroscopy towards the analysis of ionic metal clusters.

Poster Session I

Poster 15 minutes

Rotational Dynamics of Rigid Rotor Molecules under the Combined Influence of Permanent and Induced Dipole Interactions with a Half- Cycle Pulse (HCP)

Presenter: Mallikarjun Karra

Fritz-Haber-Institut

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Advances in generating intense unipolar half-cycle pulses have led to their use in efficient schemes to align and orient molecules as well as to engineer non-equilibrium states of matter. Herein we present preliminary results of a combined analytical and numerical study on the interactions of a 3D rigid rotor with half-cycle pulses efficiently modelled as narrow-width Gaussians. The added effect of the induced dipole interaction term is found to be non-negligible, and the resulting excitation dynamics of the combined interactions quite non-trivial. While the combination of the two interactions does not automatically result in a greater alignment or orientation, we discuss certain cases in which the two quantities may be enhanced when compared to a single interaction. Investigations of the time evolution of the probability densities (visualised as quantum carpets) and the concomitant orientation and alignment provide insights into the non-adiabatic — adiabatic threshold. Onset of adiabaticity is marked by the appearance of ‘resonances’ in the kinetic energy for specific values of the pulse width, a striking feature that is accounted for by considering a two-level analytic model in the weak-excitation limit.

Poster Session I

Poster 15 minutes

The Order-Disorder Transition in $\text{Cu}_2\text{ZnSnS}_4$: A Theoretical and Experimental Study

Presenter: Tim Küllmey

Freie Universität Berlin

Contact: tim.kuellmey@fu-berlin.de

In this work the Cu/Zn order-disorder transition in $\text{Cu}_2\text{ZnSnS}_4$ kesterites on Wyckoff positions 2c and 2d was investigated by a structural and electronic analysis in theory and experiment. For experimental investigations stoichiometric samples with different Cu/Zn order, annealed in the temperature range of 473-623 K and afterwards quenched, were used. The optical gaps were determined using the Derivation of Absorption Spectrum Fitting (DASF) method. Furthermore, the order-disorder transition was examined by DFT calculations for a closer analysis of the origins of the reduced band gap, showing a good agreement with experimental data with respect to structural and electronic properties. Our studies show a slight increase of lattice parameter *c* in the kesterite lattice with increasing disorder. Additionally, a reduced band gap was observed with increasing disorder, which is an effect of newly occurring binding motifs in the disordered kesterite structure. DOI: 10.1016/j.jssc.2017.03.018

[1] M. Quennet, A. Ritscher, M. Lerch and B. Paulus, *J. Solid State Chem.* 250, 140-144 (2017)

Poster Session I

Poster 15 minutes

From 2D to 1D – Tb Silicide Nanowires on Si(hhk)

Presenter: Stephan Appelfeller

Technische Universität Berlin

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The deposition and annealing of Tb on Si surfaces leads to a variety of fascinating nanostructures from zero-dimensional clusters on Si(111) over one-dimensional nanowires on Si(001) to well ordered two- and three-dimensional Tb silicide layers on Si(111). The metallic Tb disilide monolayer on Si(111) is especially interesting since its formation pins the Fermi level near the Si conduction band minimum making it interesting for ohmic contacts on n -type Si. Its electronic structure near the Fermi level is characterized by sharp bands forming a hole pocket at $\bar{\Gamma}$ and strongly anisotropic electron pockets at the \bar{M} points. For monolayer depositions on Si(hhk) surfaces being vicinal to Si(111), the formation of nanowires with widths depending on the offcut angle is expected.

In this work, the growth and the electronic structure of such Tb disilicide nanowires on vicinal Si(111) surfaces were studied with scanning tunneling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). In general, narrower Tb disilicide structures are observed for larger offcut angles, but the morphology of these structures strongly depends on the offcut direction. For Si(hhk) surfaces with $h < k$, the silicide forms well defined nanowires with sharp edges while only irregular stripes are formed for $h > k$.

Nevertheless, the characteristic two-dimensional electronic structure of the disilicide monolayer is observed with ARPES on all vicinal surfaces. Thereby, the bands, which were sharp for the extended monolayer on planar Si(111), broaden in the direction perpendicular to the step edges due to the confinement of the silicide structures to finite widths. This effect is quantified by an analysis of the electron pockets at the \bar{M} points.

Furthermore, electronically purely one-dimensional bands emerge for low Tb coverage on Si(335). Tb silicide structures possibly corresponding to these bands are discussed.

Poster Session I

Poster 15 minutes

Enantioselective Reactions on Chirally-Modified Model Surfaces: A New Molecular Beam/Surface Spectroscopy Apparatus

Presenter: Smadar Attia

Fritz-Haber-Institut

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A molecular-level understanding of enantioselective processes on chirally modified surfaces is an important prerequisite for the rational design of new enantiospecific catalysts. Therefore, in this study, the reaction mechanisms, kinetics and dynamics of surface reactions were investigated using multi-molecular beam techniques and in-situ surface spectroscopic and microscopic tools on well-defined model surfaces in UHV.

A new UHV apparatus consisting of two independent vacuum systems for preparation and characterization of chirally modified model catalysts as well as investigations of their reactivity behavior has been designed and built. This apparatus comprises three molecular beams (two effusive and one supersonic molecular beam), infrared reflection absorption spectroscopy (IRAS) as well as a number of standard tools for preparation and characterization of model surfaces, both single crystals and nano-structured surfaces consisting of metal nano-particles supported on thin oxide films. Additionally, the sample can be transferred to an independent unit containing scanning tunneling microscope (STM), as well as to high pressure cell, where the reactivity of the chirally modified model catalysts can be investigated under ambient pressure conditions.

First experiments were carried out at the newly UHV setup to investigate adsorption and reactivity behavior of a chiral modifier (R)-(+)-1-(1-Naphthyl)ethylamine (NEA) and a prochiral molecule acetophenone over Pt(111). These processes were investigated over a broad range of coverage and temperature conditions. Acetophenone was observed to strongly interact with the pristine Pt(111) surface resulting in strong changes of the IR spectra as compared to the unperturbed molecules in multilayers.

Continued on next page

NEA was found to homogeneously distribute over Pt(111) surface at room temperature, and to build self-assembled structures at 180K. Spectroscopically, it was found that NEA adopts a tilted geometry at sub-monolayer coverages. Lastly, CO was used as a first proxy to probe the interactions of carbonyl compounds with the chiral modifier and was found to strongly interact with the NEA.

Currently, co-adsorption of NEA with acetophenone is investigated with STM to follow the formation of NEA-acetophenone complexes on this chirally modified surface.

Poster Session I

Poster 15 minutes

Driving Hydrogen Evolution and Oxidation on Pt with Femtosecond Laser Pulses

Presenter: Gregor Zwaschka

Fritz-Haber-Institut

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The Hydrogen Evolution and Oxidation Reactions (HER/HOR) on Pt have been studied for decades due to their fundamental interest and importance in applications such as electrolyzers and fuel cells. Despite much effort there is no clear view of the mechanism of these reactions that can explain the large dependence of their rates on surface structure, pH and electrolyte. Because the HER/HOR on Pt are fast, one possible explanation for the challenge in obtaining such mechanistic insight is that intermediates exist on the Pt electrode surface at very low concentrations under steady state reactive conditions. In principle such a limit can be overcome by rapidly and transiently increasing the amount of reactants present and characterizing their effect. Here we present our efforts to trigger the HER/HOR on Pt using femtosecond laser pulses. The resulting, laser-induced voltammogram clearly shows that the femtosecond pulse train induces HER/HOR and that the magnitude of this effect depends on crystal face in a manner rationalizable by the surface electronic structure. Control experiments varying pulse lengths, energies and the frequencies of the incident field suggest that we induce the HER/HOR by creating a population of hot electrons. These results offer a novel experimental window on the HER/HOR and are a first step in experimentally characterizing the mechanisms of these important reactions.

Poster Session I

Poster 15 minutes

Vibrational Spectroscopy and Dynamics of the Hydroxylated α -Al₂O₃(0001) Surface with (and without) Water: Insights from ab initio Molecular Dynamics

Presenter: Giacomo Melani

Universität Potsdam

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Understanding water interactions with metal oxide surfaces [1] (such as aluminum oxide, Al₂O₃) is of importance both for fundamental reasons and for technological applications.

To unravel the details of such interactions, spectroscopic methods in the form of vibrational (IR) spectroscopy or, as surface-sensitive tool, Vibrational Sum Frequency (VSF) generation spectroscopy [2,3] are powerful experimental techniques which have been applied with great success. However, the interpretation of vibrational spectra is typically hard and requires theoretical support. On the simplest level of theory, simple Normal Mode Analysis (NMA) is performed in order to do so. This approach lacks inclusion of anharmonicities, thermal motion, and spectroscopic selection rules, however, which can be decisive. These features are accessible, in principle, by (classical) correlation function approaches [4] which can be evaluated by Ab Initio Molecular Dynamics (AIMD).

Here we apply recently proposed, efficient methods based on velocity-velocity autocorrelation functions (VVACFs) [5] to compute vibrational spectra (IR and VSF) of hydroxylated α -Al₂O₃(0001) surfaces with and without additional water [6]. We compare the validity of NMA and of Vibrational Density of States (VDOS) curves to predict / interpret IR and VSF spectra at finite temperature which we determine by VVACF-based AIMD. Further, a detailed assignment of vibrational signals is given, with special emphasis on the key role played by surface OH bonds, their dynamical behaviour and the effects brought in by H₂O adsorption. When possible, a connection to recent experiments [7,8] is made.

Continued on next page

Further theoretical efforts are spent to address the vibrational relaxation and lifetimes of surface OH-species, whose dynamics is followed by pump-probe VSF-measurements. We again employ AIMD simulations to investigate the structural properties of hydroxylated α -alumina surface which can influence the energy pathways of excited OH-bonds. We then propose lifetimes in qualitative agreement with time-resolved experiments [9].

- [1] Olle Bjørneholm et al, Chem. Rev., 116(13):7698, 2016.
- [2] Fivos Perakis et al, Chem. Rev., 116(13):7590, 2016.
- [3] Paul A. Covert et al, Ann. Rev. Phys. Chem., 67(1):233, 2016.
- [4] B. J. Berne et al, Adv. Chem. Phys., 27:64, 1970.
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- [9] Aashis Tuladhar et al, J. Phys. Chem. C, 121:5168, 2017.

Poster Session I

Poster 15 minutes

Multi-dimensional Femtosecond-Laser Induced Dynamics of CO on Metals: Accounting for Electronic Friction and Surface Motion with Combined Models

Presenter: Robert Scholz

Universität Potsdam

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Understanding how adsorbates bind to and behave on metal substrates is crucial for advancements in heterogeneous catalysis. Ultrashort laser pulses open up new ways to investigate such systems and may also allow for future applications (so-called femtochemistry).

We employ two potential energy surfaces, that were recently developed for the well-known model systems CO on Ru(0001) and CO on Cu(100), to simulate hot-electron driven dynamics induced by femtosecond-laser irradiation. The potentials account for all six molecular degrees of freedom and via the Generalized Langevin Oscillator (GLO) model, surface phonons are included as well. The coupling of the molecule to electron-hole pairs is included by a quasiclassical Langevin approach using electronic friction coefficients derived from the Local Density Friction Approximation (LDFA). The action of ultrashort laser pulses enters through a substrate-mediated, hot-electron mechanism via a time-dependent electronic temperature (derived from a Two-Temperature Model (2TM)), and random forces acting on the molecule.

The model is applied to laser-induced lateral diffusion of CO on the surfaces, "hot adsorbate" formation, and laser-induced desorption. Furthermore, for CO on Cu a vibrational analysis was performed to compare with recent time-resolved Sum Frequency Generation (SFG) experiments.

Our effectively parameter-free simulations allow for good statistics and treatment of long-time dynamics, giving generally good agreement with experimental data where available and detailed mechanistic insight in addition. A recently proposed laser-induced population of physisorbed precursor states for CO on Ru could not be observed with the present low-coverage model.

Poster Session I

Poster 15 minutes

Electronic and Optical Properties of Group-IV Transition Metal Dichalcogenides Monolayers and Their Heterostructures

Presenter: Ka Wai Lau

Humboldt-Universität zu Berlin

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The interest in transition-metal dichalcogenides (TMDs) monolayers as promising materials for opto-electronics has rapidly increased in the last few years [1]. The majority of studies has been devoted so far to group-VI TMDs, with MoS₂ and WS₂ as the most relevant examples of this material class [1]. Here, we study monolayers of group-IV TMDs focusing on ZrS₂ and HfS₂. We investigate their electronic and optical properties in the framework of many-body perturbation theory (GW and the Bethe-Salpeter equation) as implemented in the all-electron full-potential code exciting [2]. The optical response of these systems is characterized by intense peaks in the visible region due to tightlybound excitons with binding energies of the order of hundreds of meV. The degeneracy of the hole state at the Γ point with different dispersion along the M- Γ -K direction and the strong spin-orbit coupling in the valence band leads to several distinct excitonic states around Γ . Finally we study van-der-Waals heterostructures obtained by combining ZrS₂ and HfS₂ monolayers in view of understanding how different stacking patterns influence band alignment and optical excitations.

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Poster Session I

Poster 15 minutes

Effects of Oxygen, Water, and Air Exposure on the Electronic Structure of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Mixed Halide Perovskite Film Surfaces

Presenter: Maryline Ralairisoa
Humboldt-Universität zu Berlin
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In the past few years, organic-inorganic metal halide perovskites employed as light absorber have achieved an impressive breakthrough in the field of photovoltaics, particularly due to a rapid improvement of the power conversion efficiencies of up to 22 % obtained from perovskite-based solar cells. However, perovskite solar cells are confronted with air stability and reproducibility issues, which represent a serious obstacle for establishing reliable property-function relationships and long-term applications. Thus, the understanding of the processes underlying these issues is indispensable and it is equally important to gain information that best possibly reflects the perovskite material behavior in an actual device-operation environment.

Here, by means of photoelectron spectroscopy (PES), we investigated (i), the influence of pure oxygen and water exposure on the electronic structure of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ mixed halide perovskite film surfaces, and (ii), that of ambient air exposure, where both oxygen and water act in combination.

While the perovskite surfaces were originally n-type, pure oxygen exposure leads to a shift of the Fermi-level towards a mid-gap position, i.e., the surface became significantly less n-type. Upon water vapor exposure, the n-type character of the surface was accentuated. This change is mostly reversible after mild heating in ultra-high vacuum. We further discuss the impact of water on the perovskite thin films by monitoring structural changes in-situ at high relative humidity levels above 80 % by means of grazing-incidence X-ray diffraction. We find indications for the formation of a monohydrate phase before severe material degradation sets in.

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Importantly, after air exposure we observe the prevailing effect of oxygen over water on the electronic properties of the perovskite films. Such variations of the electronic structure of perovskite film surfaces will certainly affect the energy-level alignment at the interface between the perovskite and typical charge-transport materials.

Poster Session I

Poster 15 minutes

Core Spectroscopy from *ab initio* Many-Body Theory

Presenter: Christian Vorwerk

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X-ray absorption near-edge structure (XANES) spectroscopy is a widely used tool to determine structural, chemical, and electronic properties of finite and crystalline systems alike. Due to the localization of the excited core states, XANES is an element- and site-specific probe of the electronic environment of the absorbing atom. Complementing these experiments with accurate first-principles studies offers a comprehensive picture of the electronic structure of materials.

Here, we present an all-electron, many-body approach to describe core excitations in solids from first principles, which is implemented in the open-source, all-electron full-potential code exciting [1,2]. Starting from the electronic structure obtained from density-functional theory, which includes an explicit treatment of core states, we obtain absorption spectra in the framework of many-body perturbation theory through the solution of the Bethe-Salpeter equation [3]. In this approach, the effects of the interaction between the excited electron and the core hole, screened by the surrounding many-electron system, are included.

As exemplary cases, we present core spectra of the oxides CaO and TiO₂, where we consider excitations from the Ca **2p** and Ti **1s** states. In both examples, we discuss the role of the electron-core hole correlation and analyze the excitations, revealing the contributions of specific bands and regions of the Brillouin zone to the final states. Our results are in good agreement with available experimental data.

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Poster Session I

Poster 15 minutes

Alkyne Semi-Hydrogenation on CeO₂(111): The Role of O Vacancies

Presenter: Kristin Werner

Fritz-Haber-Institut

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Ceria (CeO₂) was recently identified as a promising catalyst in the selective hydrogenation of alkynes to alkenes[1]. This reaction occurs primarily on highly dispersed metal catalysts, such as Pd, but rarely on oxide surfaces. The origin of the outstanding activity and selectivity observed on CeO₂ remains unclear. In this work, we show that one key aspect of the hydrogenation reaction – the interaction of H₂ with the oxide – depends strongly on the presence of O vacancies within CeO₂. [2] By infrared reflection absorption spectroscopy (IRAS) on well-ordered CeO₂(111) thin films and density functional theory (DFT) calculations, we show that the preferred heterolytic dissociation of molecular hydrogen on CeO₂(111) requires H₂ pressures in the mbar regime. Hydrogen depth profiling with nuclear reaction analysis (NRA) indicates that H species stay on the surface of stoichiometric CeO₂(111) films, whereas H incorporates as a volatile species into the volume of partially reduced CeO_{2-x}(111) thin films (x ~ 1.8-1.9). Complementary DFT calculations suggest that oxygen vacancies facilitate H incorporation below the surface and that they are the key to the stabilization of hydridic H species in the volume of reduced ceria. Finally, we currently assess the role of O vacancies in the selective semi-hydrogenation of alkynes by gas chromatography (GC) reactivity studies.

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Poster Session II

Poster 15 minutes

Nonlinear Response and Strong Coupling of Surface Phonon Polaritons

Presenter: Nikolai Paßler

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Surface Phonon Polaritons (SPhP) are recently investigated as an alternative building block for mid-infrared (MIR) nanophotonic applications, promising to possibly solve the intrinsic loss problem of plasmonics [1]. SPhPs arise in polar dielectrics due to IR-active phonon resonances leading to negative permittivity between transverse and longitudinal optical phonon frequencies, a region called the Reststrahlen band. SPhPs exhibit tremendous field enhancements [2,3], driving the lattice ions into a strongly non-linear regime. Hence, SPhPs might grant a frequency-tunable access to vibrational-driven transient material phases.

In contrast to surface plasmon polaritons in metals, the strong dispersion of the SPhPs in the Reststrahlen region provides a natural way for tailoring SPhP resonances. Multilayers composed of different polar dielectrics with overlapping Reststrahlen bands exhibit a variety of novel phenomena such as mode-splitting, index-sensing, and wave-guiding [4], thus allowing for the engineering of novel hybrid materials with custom-designed polaritonic response.

Here, we use linear and nonlinear MIR spectroscopy [5] for studying SPhPs in SiC and AlN, employing Otto-type prism coupling. The air gap in the Otto geometry is actively steered, as monitored by the white light interferometry, granting extrinsic control over the critical conditions of the SPhP excitation [6]. Employing intense, tunable and narrowband MIR pulses from the FHI free-electron laser, our experiments reveal prominent increase of the resonant second harmonic generation (SHG), arising from the optical field enhancement that is associated with propagating SPhPs at the SiC/air interface [3].

Continued on next page

Further, a nanoscale thin layer of AlN is grown on SiC, leading to the strong coupling and mode-splitting of the SiC SPhP and the AlN ultrathin film polariton. Specifically, we show that the coupling strength can be tuned both intrinsically (using different AlN layer thicknesses) and extrinsically, by modulation of the SPhP radiative losses through variation of the air gap width. These experimental observations are corroborated by a specifically developed matrix formalism for anisotropic multilayer wave propagation [4], in order to achieve precise understanding and predictability of the linear and non-linear properties of SPhPs in polar dielectric heterostructures.

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Poster Session II

Poster 15 minutes

First Principles Simulations of Small Polarons in Ionic Crystals

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A small polaron can be modeled by a supercell with a hole or an electron in periodic boundary conditions. In order to correctly cover long-range contribution, very large supercells are often needed, which makes advanced first-principles simulations prohibitively expensive to run. In this work, we propose a corrected model to efficiently describe the lattice distortion due to the long-range contribution in a reasonably small supercell model [1]. In this approach the electronic structure close to the center is treated accurately, on the theoretical levels of semilocal PBE, hybrid HSE06, and second-order many-body perturbation theory, but taking into account the contribution of elastic distortion of the distant atoms by lower level methods.

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Poster Session II

Poster 15 minutes

The Importance of Meta-Stable Structures and High Spin States for Oxygen Activation on Small Gas-Phase Silver Clusters from First Principles

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At finite temperature, the silver-cluster catalysts could have transient meta-stable structures with spin states higher than those of zero kelvin stable structures (singlets for an even number of silver atoms). These transient structures could be crucial in activating adsorbed species like O₂. In this work, the temperature-dependent relative stability of Ag_n and Ag_nO₂ (n=4,8) systems are simulated at different finite temperatures, by means of replica-exchange *ab initio* molecular dynamics (REMD) and efficient Boltzmann-reweighting based methods (e.g., Weighted Histogram Analysis Method, WHAM, and multi-state Bennett acceptance ratio estimator, MBAR). The multi-spin-state free energy surfaces are visualized with the help of Sketch-Map [1]. The results show that meta-stable structures and the spin-polarized states can synergistically influence the activation of the adsorbed O₂ molecule.

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Poster Session II

Poster 15 minutes

Resolving Dynamic Processes in Real Space with Variable-Temperature High-Speed Scanning Tunneling Microscopy

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Scanning Tunneling Microscopy (STM) atomically resolved 2D-silica in both, the amorphous [1] and the crystalline state, leading to a structural comparison of the two phases [2]. Resolving dynamic changes in 2D network structures can give indications for the fundamental processes at the atomic scale occurring during glass-transformation.

With the aim of monitoring dynamic processes during the temperature induced change of the network structure, we design a variable temperature high-speed STM. A temperature ramp from 4 to 1500 K is enabled by a continuous-flow cryostat and a sample stage heated by electron bombardment. Thermal drift is reduced due to the symmetric setup of the microscope.

For higher frame rates, a spiral scan geometry will be applied, which represents a monotonic continuous function of the angle for the radius without points of inflection nor crossing of lines. The scan is realized with a combination of a conventional STM control unit and custom made high-speed electronics.

Due to the high data throughput, programs are needed, which automatically detect atom and ring-center positions in the recorded STM images. We hope to clarify important structural steps in oxide network structures at so far with STM unrivaled time scales.

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Poster Session II

Poster 15 minutes

Coupling of Yu-Shiba-Rusinov States in a Molecular Lattice

Presenter: Laëtitia Farinacci

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Magnetic impurities on a superconductor act as scattering centers for the Cooper pairs of the latter and thereby induce a bound state, called Yu-Shiba-Rusinov state, in their vicinity. The spatial extent of these Yu-Shiba-Rusinov states is of several nanometers which allows for hybridization between them.

Here, we observe the formation of a Kagome lattice after deposition of iron(III)-porphine-chloride molecules on Pb(111) and subsequent annealing. The lattice is composed of triangular units made of three iron-porphine molecules and one Cl adatom. By investigating small structures made of a few of these triangular units we can prove that the Yu-Shiba-Rusinov states induced by the molecules hybridize with one another within these structures. We are thus able to produce a two-dimensional coupled network by molecular self-assembly

Poster Session II

Poster 15 minutes

Thin Film Thermoelectric Materials made from Earth Abundant Materials

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With the improvement of efficiency and lower cost, thermoelectric devices make their way into more commercial applications. [1] They have been used to improve efficiency of cars [2], steam turbines[3] and to generate electricity in deep space exploration. [4] One of the strategies to improve the efficiency is lowering the thermal conductivity of the thermoelectric device. [5] The cost can be lowered by using earth abundant materials and switching to thin film materials. [6-8] In this work the thermal conductivity of thin films on carrier materials are investigated by the finite element method. The results show that the supporting material plays a crucial role in the devices thermal conductivity. [5] Samples of copper oxide doped with gold and samples of Titanium dioxide doped with Niobium are investigated for their electrical resistance and their Seebeck coefficient. For the TiO_x samples Seebeck coefficients of $-80 \mu\text{V/K}$ and electrical resistivities of less than $1.1 \times 10^{-3} \Omega \text{ cm}$ are measured. For the CuO_x Samples Seebeck coefficients in excess of $300 \mu\text{V/K}$ and resistivities of less than $100 \text{ k}\Omega \text{ cm}$ are measured.

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Poster Session II

Poster 15 minutes

Driving Ultrafast Magnetization Dynamics of Gd with 1300 nm Laser Pulses

Presenter: Kamil Bobowski

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We have studied the laser-induced magnetization dynamics of single-crystalline Gd(0001) thin films with time- and angle-resolved photoemission spectroscopy (tr-ARPES). Our earlier measurements showed a magnetic non-equilibrium in the valence bands [1,2], between the valence band and the 4f systems [3], and in the surface state [4]. All these measurements share a common excitation energy of 1.55 eV.

In a recent study performed at the Artemis Facility at the Rutherford Appleton Laboratory, we used a 0.95 eV pump and 36 eV probe pulse to record the band structure of single-crystalline Gd during laser-induced demagnetization.

We find an initial increase of the exchange splitting within the first 200 fs after excitation, which was also observed in MOKE experiments. The exchange splitting then decreases on the same time scale (0.8 ps) as in our previous experiments [2] despite the lower pump energy. In addition, we observe oscillations in the energetic position of the valence bands and the surface state before excitation. This effect was attributed to ponderomotive acceleration by a transient grating formed by the interference of the incoming and outgoing pump pulses [5].

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Poster Session II

Poster 15 minutes

Ultrafast magnetization and spin dynamics driven by terahertz radiation pulses

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Magnetization reversal, spin transfer torque, giant magnetoresistance [1] and the emission of terahertz (THz) radiation [2] are intriguing spintronic applications. They all require controlled generation and manipulation of spin currents. Promising candidates to generate spin currents for high speed spin information processing are the anomalous and spin Hall effects (AHE, SHE), whose inverse were demonstrated recently up to THz frequencies [3]. However, no direct observation of AHE-related ultrafast spin accumulation at sample interfaces has been reported so far.

In this contribution, the interaction of ultrashort intense Pulses of THz radiation with metallic thin film samples is studied. A strong THz electric field (up to ~0.5 MV/cm) is used to drive ultrafast charge currents in the plane of the sample. By means of the magneto-optic Kerr effect, we investigate the ultrafast spin and charge redistribution in thin films due to such excitation and the AHE currents.

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Poster Session II

Poster 15 minutes

Hybrid QM:QM Methods for Extended Periodic Systems

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We rely on hybrid QM:QM methods that combine high-level MP2 on cluster models with low-level DFT+D2 on periodic models to obtain accurate potential energy surfaces (PESs) for even extended and complex periodic systems. The hybrid MP2:(DFT+D2) PESs are counterpoise corrected (CPC) for the basis set superposition error (BSSE) and extrapolated to the complete basis set (CBS) limit. A posteriori, CCSD(T) coupled-cluster correlation effects are estimated as CCSD(T)-MP2 energy differences. The *multi-level* hybrid MP2/CPC-CBS:(DFT+D2) + Δ CCSD(T) PESs are designed by using the new MonaLisa program [1].

Within this computational strategy we reached chemical accuracy limits (± 4 kJ/mol on the electronic energy) and extended the benchmark data available for periodic systems to experimentally well-known processes from the field of heterogeneous catalysis: (i) adsorption of light alkane molecules in the H-chabazite zeolite [2], (ii) adsorption of methane and ethane monolayers on the MgO(001) surface [3] and (iii) methylation reactions via methanol of light alkene molecules in the H-ZSM-5 zeolite [4].

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Poster Session II

Poster 15 minutes

Kinetic Studies of Partial Oxidation Reactions on Single Crystalline Au Surfaces

Presenter: Christoph David Feldt

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Nanoporous gold has emerged as a promising, highly selective catalyst material for a variety of partial oxidation reactions at low temperatures. Structural aspects and admixtures with other metals, for example copper and silver have been investigated to gain insight in the catalytic properties of this material system. Single crystal surfaces, studied under ultra-high vacuum conditions, can serve as model systems, which allow to investigate a variety of surface properties including reaction kinetics on a molecular level under well-defined conditions.

Employing pulsed molecular beam techniques, combined with in-situ IR spectroscopy and mass spectrometry, we have investigated the kinetics of oxidation reactions on the stepped Au(332) surface. Since molecular oxygen does not dissociate on Au surfaces under UHV conditions, atomic oxygen was provided by a thermal cracker, operated as an effusive beam source. The oxidation of carbon monoxide has been studied as an initial test reaction. Beside the nature of the adsorption sites on the Au(332) surface, the reaction kinetics of the gold surface was investigated in dependence of various parameters, e.g. temperature and oxygen partial pressure. In particular, the influence of water on the activity of the gold catalyst was tested, showing that water can prevent the deactivation of the system, which is in line with results found for the np-Au catalyst. In addition, oxidative coupling of methanol was studied under isothermal conditions. The pulsed molecular beam approach provides access to transient as well as steady state kinetics, which can be studied as a function of various parameters such as temperature or educt flux and can be combined with in-situ IR spectroscopic data, to elucidate the nature of possible surface species. These results will be discussed in terms of activity and selectivity of the reaction and compared to the results on nanoporous gold.

Poster Session II

Poster 15 minutes

Germania Ultrathin Films: From Crystalline to Amorphous

Presenter: Adrian Leandro Lewandowski

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The difficulty to reveal the atomic structure of bulk amorphous materials can be overcome using a thin film approach. The development of an amorphous 2D silica bilayer has recently allowed deriving the atomic positions by using scanning tunnelling microscopy (STM) [1], atomic force microscopy (AFM) [2] and transmission electron microscopy (TEM) [3].

In order to establish a general understanding of amorphous networks more structural characterization of glass-former materials, such as germanium oxide, must be done. Germania ultrathin films were grown on Ru(0001) and Pt(111) by physical vapor deposition and subsequent annealing in oxygen. The atomically flat films were characterized by combining intensity-voltage low energy electron diffraction (I/V-LEED) and *ab initio* density functional theory (DFT) analysis with high-resolution STM imaging.

The film-substrate interaction plays a decisive role in the film structure. On Ru(0001) a crystalline hexagonal monolayer film is obtained. Structural defects introduce ring-sizes that vary from the ideal six-membered rings. Highly resolved STM images allow classifying the different boundary structures according to their ring distribution. At higher coverage disordered phases are revealed, displaying similar features observed for silica bilayer films before. However, the connectivity rules seem to be different.

On Pt(111) many different phases can be identified after annealing in a narrow range of temperatures. Monolayers have shown either hexagonal or rectangular symmetry and also coexisting phases. The second layer grows atomically flat and amorphous, being an optimum model system to study and characterize glass properties.

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Poster Session II

Poster 15 minutes

Analysis of Electron Correlation Effects in Strongly Correlated Systems

Presenter: Christian Stemmlé

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Strong correlation refers to electron correlation effects inadequately described by DFT and single-reference methods like Coupled-Clusters. Examples for such systems are dissociation fragments (chemical bond breaking)[1] and partially occupied close-degenerate orbitals, for example in transition metals. Accurate treatment is possible by wave function based multi-reference methods, but computationally demanding.

With the aim of systematic improvement of existing method, strong correlation effects are investigated by application of Quantum Information Theory (QIT), which is able to quantify contributions of orbitals to electron correlation. Calculations are performed using the *ab initio* Density Matrix Renormalization Group (DMRG), which allows of large, strongly correlated systems.

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Poster Session II

Poster 15 minutes

The influence of Oxygen Deficiency on the Rectifying Behavior of Pt/ZTO Interfaces

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In search of a replacement for the expensive and scarce indium in indium-tin oxide (ITO), which is mostly used in transparent electrodes nowadays, zinc-tin oxide (ZTO) has proven to be a promising candidate.

In this study we present the effect of aging and oxygen content of the PtO_x contact on the efficiency of ZTO diodes. It is found that a high oxygen content in the sputter gas (>70%) is needed to produce functional devices with an on/off ratio of 10². It was also found that this further improves over time by a factor of 100 after 30 days. This is due to a strong reduction of current flow in backward direction, whereas the forward characteristics of the diodes stay the same. This indicates that the bulk of the ZTO remains unchanged and effects take place at the interface between PtO_x and ZTO, which reduce the leaking current.

It was found by depth resolved x-ray photoelectron spectroscopy measurements that at the interface a reduction of the PtO_x to Pt takes place. This effect was found to be more pronounced after aging of 30 days. This results suggest that the oxygen from the PtO_x contact diffuses into the ZTO and leads to a reduction of oxygen vacancies. This is assumed to yield a lower doping concentration in the vicinity of the interface and with this results in a spatially extended depletion region at the Schottky-contact compared to contacts with lower amounts of oxygen during deposition. This yields a reduction in tunneling current, which is responsible for the conducting behavior in backward direction for Pt contacts deposited without additional oxygen.

Poster Session II

Poster 15 minutes

Asymmetric Electron and Hole Dynamics in the Rashba Material BiTeI

Presenter: Sophia Ketterl

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Due to strong spin-orbit coupling and non-centrosymmetric crystal structure, the narrow band-gap semiconductor BiTeI hosts Rashba-split surface and bulk bands. This makes BiTeI a promising material for the generation of spin-polarized currents. It is intrinsically n-doped and exhibits additional strong band-bending at its polar surfaces, leading to partially occupied electron- and hole-like surface states for Te and I termination, respectively.

We studied the electron and hole dynamics in the surface state and bulk conduction band on the Te-surface with time-resolved ARPES and observed a strong asymmetry for carriers close to the Fermi level. Electrons behave according to Fermi-liquid theory, while hole lifetimes decrease towards the Fermi level. We attribute this behavior to drift currents due to the surface band bending and the influence of a plasmon decay channel as predicted by Eremeev *et al.* in *JETP Lett.* **96**, 437 (2012).

Poster Session II

Poster 15 minutes

Efficient Metallic Spintronic Emitters of Ultrabroadband Terahertz Radiation

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Terahertz spectroscopy is a powerful tool to probe numerous low energy excitations. However, there are still challenges regarding broadband, gap-free and efficient sources of terahertz radiation driven by a compact femtosecond oscillator.

In our experiments, we employ laser pulses (duration 10 fs, center wavelength 800 nm, repetition rate 80 MHz, pulse energy 2.5 nJ) from a laser oscillator to launch spin currents in magnetic heterostructures (see Fig. 1). The dynamics of these ultrafast currents are monitored by taking advantage of the inverse spin Hall effect [1] and broadband terahertz emission spectroscopy [2].

In particular, we study THz emission from multilayers consisting of ferromagnetic and nonmagnetic metallic layers. The emission data can be evaluated to give an estimate of the strength of the spin Hall Effect. Spintronic emitters can be developed to provide an efficient and scalable THz electromagnetic pulses that fully cover the range from 1 to 30 THz without gap [3]. This THz source outperforms standard emitters such as zinc telluride in terms of bandwidth while having a comparable conversion efficiency.

The results shown here were obtained in close collaborations with the research groups of L.M. Hayden, M. Kläui, Y. Mokrousov, M. Münzenberg, P.M. Oppeneer, I. Radu and D. Turchinovich.

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