

# 6<sup>th</sup> Annual Meeting of the NCCR MUST Engelberg, January 11-13, 2016

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## Highlight presentations I & II, Monday 14:10 – 16:10

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### On the Nature of the Excitonic Quasiparticles in Anatase TiO<sub>2</sub>

Edoardo Baldini<sup>1,2</sup>, Letizia Chiodo<sup>3</sup>, Adriel Dominguez<sup>4</sup>, Maurizia Palummo<sup>5</sup>, Simon Moser<sup>6</sup>, Meghdad Yazdi<sup>7</sup>, Gerald Auböck<sup>1</sup>, Arnaud Magrez<sup>8</sup>, Helmuth Berger<sup>8</sup>, Christian Bernhard<sup>7</sup>, Marco Grioni<sup>6</sup>, Angel Rubio<sup>4,9,10</sup>, and Majed Chergui<sup>1</sup> ([edoardo.baldini@epfl.ch](mailto:edoardo.baldini@epfl.ch))

<sup>1</sup> Laboratory of Ultrafast Spectroscopy, ISIC, EPFL, CH-1015 Lausanne, Switzerland

<sup>2</sup> Laboratory for Ultrafast Microscopy and Electron Scattering, ICMP, EPFL, CH-1015 Lausanne, Switzerland

<sup>3</sup> Center for Life Nano Science, Sapienza, IIT, I-00161, Rome, Italy

<sup>4</sup> Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

<sup>5</sup> Dipartimento di Fisica, Università "Tor Vergata", 00133 Roma, Italy

<sup>6</sup> Laboratory of Electron Spectroscopy, ICMP, EPFL, CH-1015 Lausanne, Switzerland

<sup>7</sup> Department of Physics, University of Fribourg, CH-1700 Fribourg, Switzerland

<sup>8</sup> Laboratory of Physics of Complex Matter Physics, ICMP, EPFL, Lausanne, Switzerland

<sup>9</sup> Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195, Berlin, Germany

<sup>10</sup> Departamento Física de Materiales, Universidad del País Vasco, E-20018, San Sebastian, Spain

The field of excitonics has gained increased attention in the last years, due to the unique properties that excitons manifest in the conversion and transport of energy. Key to these developments is the ability to exploit exciton physics in materials that are easily fabricated and widely available. A prototypical system in which excitons have been proposed theoretically [1] but never confirmed experimentally is the anatase polymorph of TiO<sub>2</sub>, which represents a superior material for a variety of challenging applications [2-4]. Here, we combine angle-resolved photoemission and optical spectroscopies, along with many-body theoretical calculations, to demonstrate that the direct optical gap of anatase TiO<sub>2</sub> is dominated by a charge-transfer exciton band rising over the continuum of indirect interband transitions. We find that the lowest exciton possesses a two-dimensional nature, with a wavefunction confined to the (001) plane, and is characterized by a giant binding energy exceeding 300 meV.

To prove the universality of these findings also in highly defective samples under the typical conditions of applications, we interrogate anatase TiO<sub>2</sub> single-crystals and nanoparticles out-of-equilibrium via ultrafast two-dimensional UV spectroscopy. Remarkably, these results demonstrate for the first time the capabilities of ultrafast two-dimensional UV spectroscopy in addressing the complex many-body dynamics resulting upon photoexcitation in wide-bandgap solids. In this regard, strong emphasis will be given to the impact that uncorrelated electron-hole pairs and coherent acoustic phonons produce on the properties of the charge-transfer excitons. Besides the fundamental interest in this exotic species, the present results can be relevant for those applications exploiting the optical properties of this material at room temperature [5].

[1] L. Chiodo *et al.*, Phys. Rev. B **82**, 045207 (2010)

[2] A. Fujishima *et al.*, Nature **238**, 37 (1972).

[3] E. Pelizzetti *et al.*, Electroch. Acta **38**, 47 (1993).

[4] B. O'Regan *et al.*, Nature **353**, 737 (1991).

[5] E. Baldini *et al.*, submitted to Science.

### Attosecond time-resolved photoelectron spectroscopy of liquids

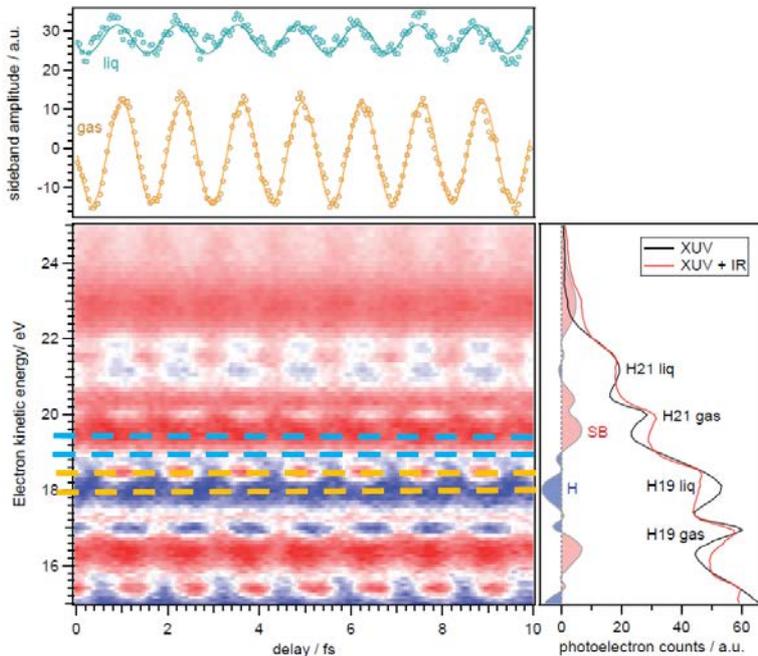
Inga Jordan<sup>1</sup>, M. Huppert<sup>1</sup>, L. Seiffert<sup>2</sup>, M. Arbeiter<sup>2</sup>, Th. Fennel<sup>2</sup> and H. J. Wörner<sup>1</sup>  
([inga.jordan@phys.chem.ethz.ch](mailto:inga.jordan@phys.chem.ethz.ch))

<sup>1</sup> ETH Zürich, Laboratory for Physical Chemistry, Ultrafast Spectroscopy, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

<sup>2</sup> Institut für Physik, Universität Rostock, Albert-Einstein-Strasse 23, 18059 Rostock, Germany

Attosecond spectroscopy in the gas phase is by now well-established and first promising results have been obtained in the solid phase. However, most chemical and biological processes take place in the liquid phase, making their analysis with attosecond temporal resolution highly desirable. Here, we report the achievement of this fundamental advance and demonstrate the measurement of attosecond photoionization delays from liquid water. We have measured relative photoionization delays between water molecules in the liquid and gas phases by applying the RABBIT-technique to a liquid microjet. Using metal filters, two spectral regions of interest were isolated. We find that the RABBIT sidebands from liquid water are delayed by ~50 as and show a substantially reduced (~15-20%) modulation contrast when compared to the gas phase. Since our measurements on solvated water molecules are referenced to isolated ones, the measured delays reflect (i) the photoionization delays caused by electron propagation through the aqueous environment and (ii) the effect of solvation on the parent molecule. The relative modulation contrast, in turn, contains information on (iii) the modification of transition amplitudes and (iv) dephasing processes. Comparison of the experiments with theory shows that the measured

delays are much smaller than the time scales of both electron transport and inelastic scattering, but comparable to the expected elastic scattering times. These results are expected to provide unprecedented insights into the nature of photoionization and electron transport in liquid water. More generally, they demonstrate the feasibility of attosecond time-resolved measurements in the liquid phase, opening a new area of research.



**Figure 1:** Attosecond interferometry using an attosecond pulse train synthesized from H15-H21 and a synchronized 800-nm laser pulse focused on a liquid-water microjet. The right-hand panel shows photoelectron spectra generated by the attosecond pulse train alone (black) and the combined XUV and IR fields (red), as well as their difference. The main panel shows the difference spectra as a function of the XUV-IR delay and the top panel shows the spectral integral over the dashed lines of the main panel, isolating the contributions from liquid and gas-phase water.

## Gaining insight into the validity of macroscopic laws on atomic scales through photoemission delays from Cu(111) surface

L. Kasmi<sup>1</sup>, L. Castiglioni<sup>2</sup>, M. Lucchini<sup>1</sup>, P. Kliuiev<sup>2</sup>, A. Ludwig<sup>1</sup>, M. Greif<sup>2</sup>, M. Hengsberger<sup>2</sup>, J. Osterwalder<sup>2</sup>, L. Gallmann<sup>1,3</sup> and U. Keller<sup>1</sup> ([kasmil@phys.ethz.ch](mailto:kasmil@phys.ethz.ch))

<sup>1</sup> Department of Physics, ETH Zürich, 8093 Zürich, Switzerland

<sup>2</sup> Institute of Physics, University of Zürich, 8057 Zürich, Switzerland

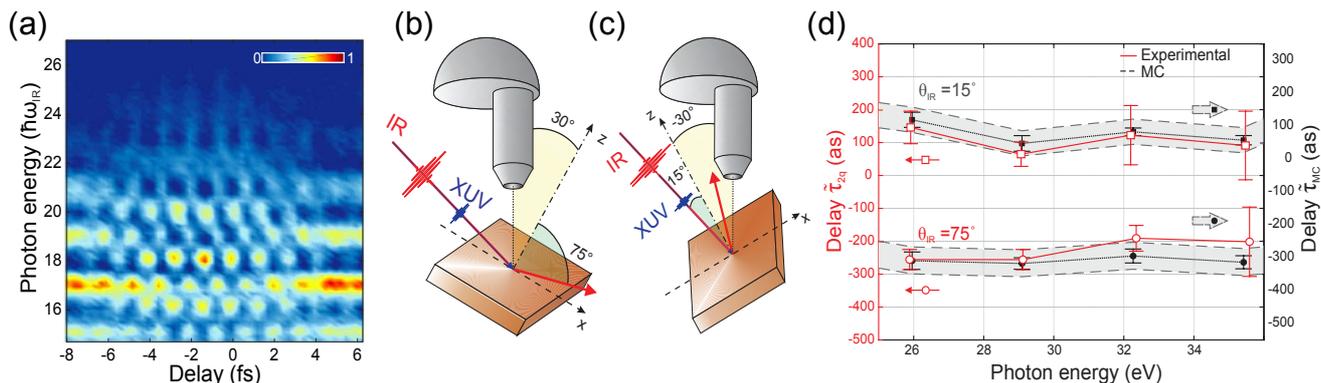
<sup>3</sup> Institute of Applied Physics, University of Bern, 3012 Bern, Switzerland

Successful extension of the study of photoemission delays to condensed matter systems (1) opened a promising route to understand electron dynamics in solids on attosecond timescales. For an improved understanding of the underlying fundamental processes an accurate measurement of photoemission delays or, equivalently, the phases of the emitted electron wave packets is essential (2).

Unlike performing pump-probe spectroscopy on a gas target, a solid target introduces a symmetry break due to the reflection of the optical beam on the surface. In this work we show that this reflection not only affects the photoemission delay but also provides insights on the electron dynamics at the surfaces. Especially, we show that the local transient grating created by interference of the incident and reflected parts of the IR (infrared) probe beam, imprints an additional phase on the photoelectron emitted from the surface after XUV (extreme ultraviolet) absorption. Given the atomic spatial and attosecond temporal scale of our experiment, it is not obvious whether this phase quantitatively reproduces the behaviour expected from the macroscopic Fresnel laws.

The experiment measures the phase of the photoemitted electron wave packets for two experimental configurations that correspond to two different incidence angles of the light on the surface, while probing at equivalent electron momenta in the reciprocal space of the solid. This enables us to uniquely assign the observed phase changes to effects from the optical fields alone. Monte Carlo simulations based on a semiclassical model describing the IR field by the Fresnel equations, quantitatively reproduce the observed phase shifts. This implies that the macroscopic optics laws still hold even on such short timescales and small length scales. Additionally, the small impact of the phase of the transmitted field on the photoemission delay shows and confirms the efficient screening of the electrons at the crystal surface for the case of Cu(111).

This important finding allows us to isolate band structure effects on photoemission delays. First results showing different photoemission delays from emission out of split valence bands will be discussed.



**Figure 1:** (Adapted from [3]) (a) RABBITT trace acquired from the Cu(111) surface obtained with the configuration in (b). (b) & (c) Experimental configuration for the two detection angles. (d) Experimental (red line) and calculated (gray line) photoemission delays between oscillating sidebands from surface and oscillating sidebands from gas, shown for detection angles of  $30^\circ$  from the surface normal (grazing light incidence) and  $-30^\circ$  from the surface normal (close to normal light incidence).

[1] A. L. Cavalieri et al, *Nature* **449**, 1029-1032 (2007)

[2] R. Locher et al., *Optica*, **2**, 405 (2015)

[3] M. Lucchini et al., *Phys. Rev. Lett.* **115**, 137404 (2015)

## Surface Enhanced Infrared Absorption of Chemisorbed CO using Plasmonic Nanoantennas

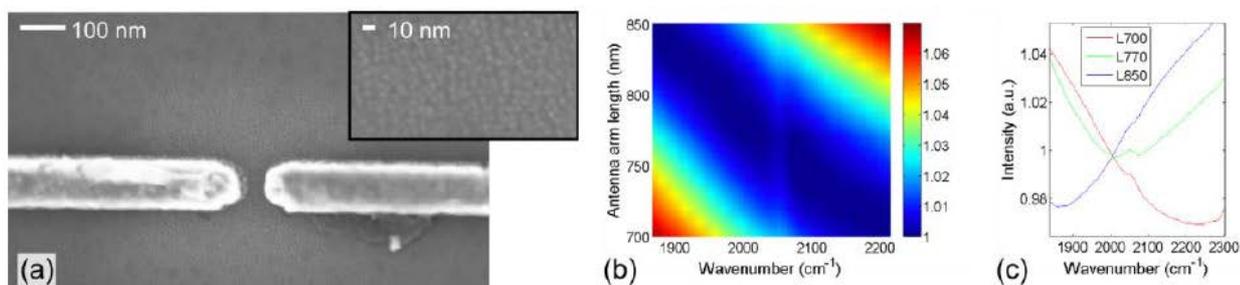
Johannes Haase<sup>1</sup>, Hans Sigg<sup>1</sup>, and Jeroen A. van Bokhoven<sup>1,2</sup> ([johannes.haase@psi.ch](mailto:johannes.haase@psi.ch))

<sup>1</sup> Paul Scherrer Institut, 5232 Villigen, Switzerland

<sup>2</sup> ETH Zurich, Institute for Chemical and Bioengineering, 8093 Zurich, Switzerland

The ultimate tool to analyze surface catalytic reactions is the X-ray free electron laser. Using X-ray absorption spectroscopy together with ultrashort X-ray pulses upon initialization of a chemical reaction, allows for the observation of the intermediate states in the reaction [1]. The insight to bond-breaking and bond-making mechanism would be of compelling interest and could significantly improve throughputs as well as efficiencies in catalysis. To initialize the reaction, a quasi-instantaneous trigger is needed. It has been proposed to use a single cycle THz pulse as a coherent source for a thermal-like excitation [2]. The low energy of THz radiation together with the high electric fields of single cycle pulses allows for an excitation of collective vibrations without the creation of hot electrons.

As a model system to validate the proposed THz excitation, we chose carbon monoxide (CO) chemisorbed on Pt and elaborate the evolution of the IR active CO stretch mode upon excitation of the low frequency wagging mode of the molecule excited by the THz pulse. For the surface sensitive detection of the adsorbed species, we developed plasmonic nanoantennas resonant to the vibronic CO stretch mode [3].



**Figure 1** (a) Nanoplasmic gold antenna resonant to the vibronic absorption of CO chemisorbed on Pt. The entire antenna is covered with 0.5 nm Pt forming particles of  $5 \pm 1$  nm in diameter (inset). (b) When tuned into resonance with the CO stretch vibration, the antenna resonance shows a Fano-like dip at a wavenumber of  $2050 \text{ cm}^{-1}$ . In figure (c) the spectra for antenna arm length  $L = 700 \text{ nm}$ ,  $770 \text{ nm}$ ,  $850 \text{ nm}$  are shown. The maximum enhancement occurs for a precise alignment of the plasmonic antenna resonance with the vibronic CO absorption.

In Figure 1 (a), a plasmonic gold-antenna processed via e-beam lithography is shown. The entire antenna is covered with 0.5 nm Pt forming particles with  $5 \pm 1$  nm in diameter to allow for the adsorption of CO without disturbing the plasmonic resonance. After reduction of the Pt at 150 °C under a continuous flow of 5 % CO in He, the Pt-surface is covered with CO. The spectra in Figure 1 (b) and (c) show the antenna enhanced absorption of the chemisorbed CO at 2050  $\text{cm}^{-1}$ . The feature appears as a transmission enhancement due to the Fano-like shape of the resonant coupling between the broadband plasmonic antenna-resonance and the narrowband vibronic molecular absorption [3]. The antenna enhancement is restricted to the regions with high electric field enhancement, i.e. the antenna tip and gap regions. Regarding the little amount of probe volume this method can be seen as ultrasensitive detection of chemisorbed molecular species [4]. To further develop our sample for THz pump IR probe experiments, we produce coupled IR THz an-tennas probing a joint sample volume.

[1] H. Öström et al., Probing the transition state region in catalytic CO oxidation on Ru, *Science* **347**, 978-982 (2015).

[2] B. D. Patterson et al., Can Energetic Terahertz Pulses Initiate Surface Catalytic Reactions on the Picosecond Time Scale?, *Chimia* **65**, 323-325 (2011).

[3] A. Pucci et al., Surface enhanced infrared spectroscopy using gold nanoantennas, *Phys. Status Solidi B* **247**, 2071-2074 (2010).

[4] O. Selig et al., Ultrasensitive Ultrafast Vibrational Spectroscopy Employing the Near Field of Gold Nanoantennas, *Phys. Rev. Lett.* **114**, 233004 (2015).

## KTT presentations, Monday 16:10 – 16:55

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### **SThAR - The physicist's approach to big data**

Marius Wehrle (CTO, [marius.wehrle@epfl.ch](mailto:marius.wehrle@epfl.ch))

*SThAR, EPFL Innovation Park, Bâtiment C, CH-1015 Lausanne*

The beauty of being a theoretician consists chiefly in the possibility to conduct countless thought experiments with impunity. Experiments, which allow to draw similarities between seemingly distant topics such as designing marketing campaigns and analyzing electronic spectra of molecules. Indeed, it turns out that these concepts are closely related since both depend on the information flow within a system, i.e., the society or molecules.

We found how crowd behavior can be modeled using laws of physics by extracting the underlying human interaction patterns from mobility and connectivity data in a systematic fashion. Using these ideas, we developed a marketing tool called DEMOGRAPHICA, which enables to identify the optimal time and place in order to spread the desired marketing message. In practical applications, it has been shown that street-marketing campaigns powered by this technology were indeed more efficient than campaigns relying solely on advertising in television.

### **Towards new polymer-based components for THz applications**

Philippe Raisin, Leandro von Werra, Adrian Ryser, and Florian Reinhard ([philippe.raisin@iap.unibe.ch](mailto:philippe.raisin@iap.unibe.ch))

*AME GmbH, Rodtmattstrasse 99, 3014 Bern*

Over the last decades, additive manufacturing has emerged as a promising way of fabrication, offering opportunities in professional research and engineering applications. Up to the present, professional 3D-printers have been deployed solely in industrial environments. More recently, desktop-sized machines have entered the market along with enhanced designs and improved reliability. The different additive manufacturing technologies offer a wide range of printable polymers. Some of these polymers happen to be transparent in the terahertz regime. Hence an opportunity to print optical elements for THz-setups presents itself. The funding received under the Industrial Project Program allows for the evaluation of these opportunities in collaboration with the Linear and Nonlinear THz Science group at University of Bern. Various prototypes have been fabricated additively and will be compared to other low-cost manufacturing techniques with a dedicated THz-instrument.

## Multi-camera detection system for low-noise single-shot broadband detection of DUV to NIR spectra at kHz repetition rates

Egmont Rohwer, Georg Achazi, Ariana Rondi, Thomas Feurer, **Andrea Cannizzo**

([andrea.cannizzo@iap.unibe.ch](mailto:andrea.cannizzo@iap.unibe.ch))

*Institute of Applied Physics, University of Bern*

We developed a new detection system for our femtosecond stimulated Raman and transient absorption set-ups based on several compact, cost-effective and low-noise CMOS cameras. We can synchronously collect up to 8 spectra at 8 kHz, at most, spanning the spectral range from 200 nm to 1200 nm, with a signal-to-noise-ratio for each single-shot spectrum  $> 10^4$ . Remarkably each camera is a stand-alone device that can operate with any computer or laptop equipped just with an USB-2 port. The high versatility of this detector allowed us 1) to build a portable self-diffraction frequency-resolved optical gated spectrometer (SD-FROG) to characterize UV femtosecond pulses with low pulse energies ( $< 100$  nJ/pulse) and 2) to develop single shot interferometry to carry out phase sensitive measurements with conventional, not phase-stabilized set-ups.

## FAST presentations, Tuesday 14:00 – 15:00

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### DNA Inspired Assembly of Multichromophores

Robert Häner ([robert.haener@dcb.unibe.ch](mailto:robert.haener@dcb.unibe.ch))

*Department of Chemistry and Biochemistry, University of Bern, Switzerland*

The proper arrangement of multiple chromophores may lead to arrays with electronic properties that are largely different from the ones of the individual molecules. The bottom-up construction of structurally well-organized chromophore assemblies is a challenge with far-reaching implications in many scientific areas. We are exploring the assembly of multichromophores from short amphiphilic oligomers, which are structurally related to DNA. Oligo-chromophores prepared from simplified versions of the natural DNA building blocks form supramolecular aggregates via self-assembly in aqueous medium. Morphological and electronic aspects of the obtained polymers will be presented.

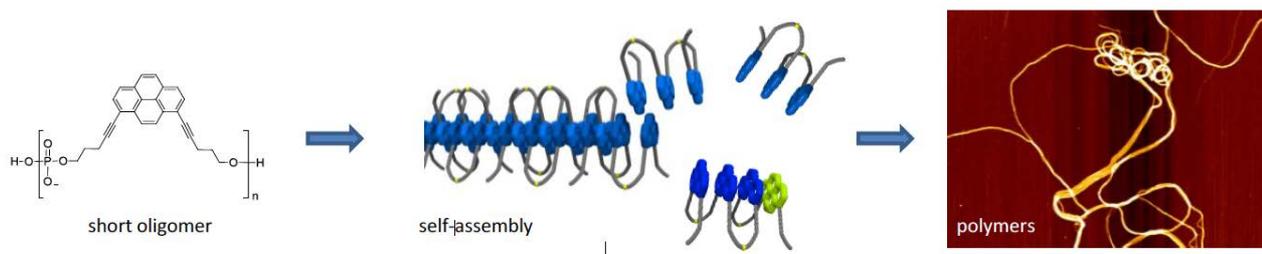


Figure 1: Schematic representation of polymerization of DNA-like oligochromophores to form supramolecular polymer fibres.

### The impact of X-ray Free Electron Lasers on membrane protein structural biology

Gebhard F.X. Schertler ([gebhard.schertler@psi.ch](mailto:gebhard.schertler@psi.ch))

*Head of Biology and Chemistry Department, Paul Scherrer Institute and Professor for Structural Biology, D-BIOL, ETH Zurich*

Free electron lasers (FELs) are highly brilliant and coherent x-ray sources. During the last years de novo structures from nanometer sized crystals as well as structures of large complexes were obtained. First room temperature structures of reaction intermediates were determined. The strongest advantage of the short x-ray pulses with extreme intensity that can be generated with a XFEL is the fact that we can observe the diffraction patterns from nano crystals before significant radiation damage can set in.

Switzerland is building its own free electron laser (SwissFEL) to support a broad range of basic research in quantum physics, material science, biology and structure based drug discovery. We will achieve major insights in quantum computing and engineering and we will gain a deeper understanding of proteins, the universal tools of life. The timing of the free electron laser pulse in the femtosecond range is coinciding with the time it takes to make or break the chemical bond. That is why XFEL free electron lasers will become the prime tools to study heterogeneous catalysis in hard matter, soft matter and enzymes. Time-resolved diffraction methods and crystallography are a major key to these questions.

The development of fast liquid jets and the sample saving viscose jets have standardized the sample application for protein crystallography with XFELs. The development of powerful software to deal with millions of diffraction patterns is enabling serial crystallography. This is interesting for dynamic crystallography. There are currently several light activatable systems where a reaction can be triggered with a short laser pulse and a variable delay time between the light pulse and the x-ray probe pulse. We can collect a series of data sets obtained at different times. This data can be analysed in a more objective way because the changing amplitudes are not influenced by radiation damage. Therefore I think free electron lasers will open a new era of dynamic crystallography, which will lead to a new level of understanding complex biological systems.

Membrane protein structural biology using X-ray free electron lasers. R Neutze, et al, *Curr. Opin. Struct. Biol.* 33, 115-125  
Lipidic cubic phase serial millisecond crystallography using synchrotron radiation, P Nogly, et al. *IUCrJ* 2 (2), 0-0

## Ultrafast manipulation of magnetism in multifunctional oxides

Manfred Fiebig ([manfred.fiebig@mat.ethz.ch](mailto:manfred.fiebig@mat.ethz.ch))

*Department of Material Sciences, ETH Zürich*

The interest in manipulating magnetic order by ultrashort laser pulses has thrived since it was observed that such pulses can alter a magnetization within picoseconds. While much interest is focused on the magnetization dynamics of ferromagnetic metals, I will discuss ultrafast dynamical processes in a variety of multifunctional oxide insulators in my talk. Examples I will include are: (i) fundamental differences between the magnetization dynamics of ferro- and antiferromagnets; (ii) Storage and recovery of an arbitrary optical polarization state in a three-sublattice antiferromagnet; (iii) non-thermal enhancement of magnetic order in the semiconducting ferromagnet EuO. A hitherto neglected topic are the dynamical properties of multiferroics, i.e., systems with coexisting magnetic and electric long-range order. This is surprising because switching the magnetic order in multiferroics by an electric field is considered a key to novel, smaller and more energy-efficient memory devices. I will propose an experiment for the all-optical ultrafast manipulation of the multiferroic state in the class of multiferroics with the strongest magnetoelectric coupling.

## Highlight presentations III, Tuesday 15:40 – 16:40

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### Emission and absorption from laser dressed states in the filamentation regime

M. Matthews<sup>1</sup>, A. Patas<sup>3</sup>, F. Morales<sup>2</sup>, M. Richter<sup>2</sup>, J. Gateau<sup>1</sup>, N. Berti<sup>1</sup>, S. Hermelin<sup>1</sup>, J. Kasparian<sup>1</sup>, A. Lindinger<sup>3</sup>, O. Smirnova<sup>2</sup>, M. Ivanov<sup>2</sup>, **J.-P. Wolf<sup>1</sup>** ([Mary.Matthews@unige.ch](mailto:Mary.Matthews@unige.ch))

1. GAP-Biophotonics, Université de Genève, 22 chemin de Pinchat, 1211 Genève 4, Switzerland

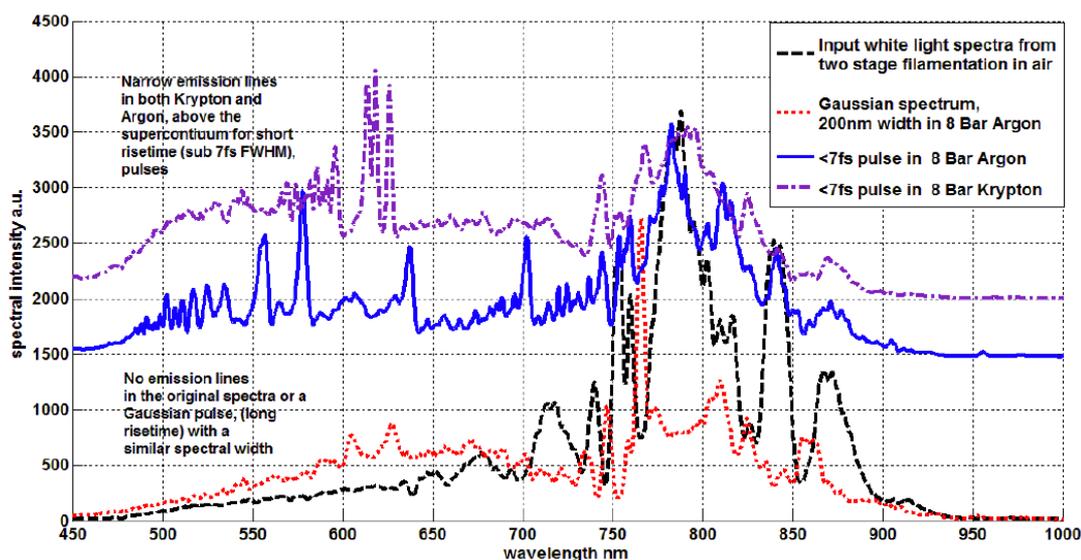
2. Max Born Institute for Nonlinear optics, Max-Born Strasse 2A, D-12489 Berlin

3. Freie Universität, 14 Arnimallee, 14195, Berlin, Germany

The pulse shape of incoming ultrashort pulses is found to profoundly modify the paradigm of laser filamentation via highly efficient coupling between upper bound states, and the field,[1][2]. At high fields,  $\sim 10^{13}$  W/cm<sup>2</sup>, at 800 nm, the electron wavefunction can occupy a 'loosely' bound state, i.e. its motion strongly driven by the field, but still weakly affected the atomic core. A small transfer of population into these dressed, Kramers-Henneberger, (KH)[3], states will contribute a significant negative Kerr response, and a defocusing effect, even while the electron remains bound. Due to their rapid decay during the laser pulse ramp, accessing these KH states requires sharp, sub-10 fs, pulse rise times, and preferably a flat top profile to preserve a constant field for the pulse duration. Using a 5 fs, 800 nm, 50  $\mu$ J laser system with a broad white light spectrum, in conjunction with a pulse shaper[4], we are able to create pulse conditions for KH states to persist. Focusing shaped pulses with 5 fs, risetimes, with 25 cm spherical mirror, in Argon or Krypton, (2-8 bar), we measure the forward super-continuum spectra, at powers close to the critical power for filamentation, and observe absorption features of transitions

between energetically high excited states. These absorption peaks become emission peaks, with increasing pulse intensity,  $\sim 10 \text{ TW/cm}^2$ . Furthermore, we note the central wavelength of these gain peaks exhibits a dependence on pulse intensity, a feature of laser dressed states, and indicative of KH states.

- [1] Morales, Felipe, et al. "Imaging the Kramers–Henneberger atom." *Proceedings of the National Academy of Sciences* 108.41 16906-16911, (2011)
- [2] Richter, M., Patchkovskii, S., Morales, F., Smirnova, O., & Ivanov, M. "The role of the Kramers–Henneberger atom in the higher-order Kerr effect". *New Journal of Physics*, 15(8), 083012, (2013).
- [3] Reed, V. C., & Burnett, K. "Ionization of atoms in intense laser pulses using the Kramers-Henneberger transformation". *Physical Review A*, 42(5), 3152, (1990).
- [4] Hagemann, F., Gause, O., Wöste, L., & Siebert, T., "Supercontinuum pulse shaping in the few-cycle regime". *Optics express*, 21(5), 5536-5549, (2013)



**Figure 1** Forward spectra from the filamentation of an ultra-short pulse, sub-7 fs, in Argon and Krypton, (blue, solid and purple, dash-dot). The red dotted line shows the forward spectra of a 200 nm width Gaussian, and the dashed black line shows the input white light spectra.

## Electro-modulated differential absorption spectroscopy: Investigating charge carrier dynamics under applied electric fields

Arun A. Paraecattil, Marine Bouduban, Jelissa De Jonghe-Risse, Ahmad Ajdar Zadeh, Joël Teuscher and Jacques-E. Moser\*

*Photochemical Dynamics Group, Institute of Chemical Sciences & Engineering, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

Ultrafast electro-modulated differential absorption (EDA) spectroscopy is based on the monitoring of the time-evolution of Stark shifts induced in a material or at a heterojunction by an externally applied electric field. Free carriers' generation following the photo-excitation of an absorber and subsequent charge separation partially screen the applied field and reduce the shift of absorption spectra. A tunable femtosecond pulsed source is used to pump the sample, while a broadband probe allows monitoring the temporal response of the Stark shift. The experimental setup and details of the technique will be presented.

Ultrafast optical probing of the electric field by means of Stark effect has proven to be a powerful tool for investigating field-induced interfacial charge transfer state dissociation and free carrier separation in OPV systems.<sup>1,2</sup> We demonstrated in particular that motions of electrons and holes can be scrutinized separately by selectively probing the Stark shift dynamics at selected wavelengths.<sup>2</sup>

High efficiency hybrid solar cells based on methylammonium lead triiodide perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) operate at maximum power with a voltage exceeding 1.0 V, implying that the material is submitted to an electric field of several  $\text{MV} \cdot \text{m}^{-1}$  in working devices. Reported studies of exciton and charge carrier dynamics in perovskite have failed so far to address field effects on charge separation processes. Applying EDA spectroscopy for the first time to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films submitted to an external electric field, we show that photogenerated carriers reach a separation of  $\sim 50 \text{ nm}$  within 3 ps, leading to a carrier mobility  $\mu = 6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ .<sup>3</sup> This separation distance

corresponds to the dimensions of grains in the active film, at boundaries of which charges get trapped. Carrier detrapping and accumulation in insulated films cause a blue shift of the perovskite absorption edge that arises with sub-nanosecond kinetics.

1) *Time-Independent, High Electron Mobility in Thin PC<sub>61</sub>BM Films: Relevance to Organic Photovoltaics*. A. Devižis, et al. *Org. Electronics* **2014**, 15, 3729–3734.

2) *Dissociation of Charge Transfer States and Carriers Separation in Bilayer Organic Solar Cells - A Time-Resolved Electroabsorption Spectroscopy Study*. A. Devižis, et al. *J. Am. Chem. Soc.* **2015**, 137, 8192-8198.

3) *Dynamics of Photogenerated Charge Carriers in Organo-Lead Iodide Perovskite Thin Films under Static Electric Field*. A. A. Paraecattil, et al. *J. Phys. Chem. Lett.* **2015** (submitted).

## LR-TDDFT Surface Hopping Simulations of the Excited State Dynamics of the Ethylene Cation

Elisa Liberatore and Ursula Röthlisberger ([elisa.liberatore@epfl.ch](mailto:elisa.liberatore@epfl.ch))

Laboratory of Computational Chemistry and Biochemistry, Federal Institute of Technology, 1015 Lausanne, Switzerland

Photochemical reactions involve highly nonadiabatic processes in which the nuclear motion is strongly coupled to electronic dynamics. Nonradiative electronic relaxation through conical intersections (CIs) is an efficient mechanism of internal conversion that is often involved in the ultrafast response of biological systems to light. In this context, ethylene - the simplest molecule containing a carbon-carbon double bond - and its cation have been intensively studied since several decades as prototypical model systems for conjugated biological chromophores. Recently, XUV-NIR pump-probe experiments were carried out in U. Keller's group at ETHZ, to investigate the nuclear excited state dynamics of the ethylene cation. The yield of charged fragments was monitored at different pump-probe time-delays and interesting features were registered. In particular, the production of C<sub>2</sub>H<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>2</sub><sup>+</sup> surprisingly increases at ~25fs time-delays. To reveal the mechanism determining the enhancement of the fragment production at these "special" times, we carried out a DFT/TDDFT based study of the system. Trajectory Surface Hopping (TSH) simulations were performed to mimic the motion of the wave packet on the excited potential energy surfaces of the ethylene cation. The trajectories were initialized on the D2 and D3 states that, according to experimental literature, are believed to be the most populated after XUV ionization of ethylene. The excited state population, the conformational changes, and the fragmentation channels were monitored during the simulations. Assuming equal initial population of the D2 and D3 states, after around ~20fs 45% of the total population is transferred to D1, while ~20% remains on each D2 and D3 and the rest is in the electronic ground state D0. In absence of a further perturbation (that is without considering the effect of the IR probe), only few trajectories lead to H or H<sub>2</sub> loss, in a ratio consistent with the experimental XUV yields. To determine the effect of the IR on the fragmentation process, we calculated the oscillator strengths between pairs of excited states for different nuclear configurations along the trajectory. In fact, re-excitation to higher excited state can cause a fragmentation enhancement. However, there are no symmetry-allowed transitions between excited states in the range of the NIR photon energy (~1.6eV). The NIR is then more likely providing the additional energy necessary to overcome barriers in the D1 excited state ultimately leads to CH bond breaking.

## Poster abstracts

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Abstracts are sorted by PI. The name of the presenting author is underlined. The names of the responsible MUST PIs, as entered in the poster submission form, are marked in **bold**.

**For presenters:** please put your poster on the poster board or wall space marked with your PI-name and the number of your poster.

### **Rafael Abela**

#### **1. Towards nonlinear time resolved X-ray spectroscopy**

Gregor Knopp, Jakub Szlachetko, Joanna Czaplá-Masztafiak, Thomas Feurer, Jeroen van Bokhoven, **Rafael Abela**, Chris Milne [gregor.knopp@psi.ch](mailto:gregor.knopp@psi.ch)

Extending the methodologies of nonlinear and quantum optics to X-ray wavelengths is a promising and exciting avenue, in the light of recent successful experiments at X-ray synchrotrons [1] and X-ray Free FELs [2,3,4]. With the development of free electron laser (FEL) radiation sources a new area of X-ray spectroscopy commenced which can have a 'comparable' impact as lasers had in nonlinear optics and spectroscopy. In nonlinear ultrafast time-resolved techniques, state specific information is often provided through multiphoton resonances with combinations of sequential photons. Theoretically, also combinations of multiple X-ray photons resonant with high frequency core transitions, characterize different excitation processes due to specific sequences of light-matter interaction. Thus particular sub-processes can be enhanced by matching the pulse frequencies to transitions between molecular eigenstates. This provides a high selectivity and flexibility due to momentum and energy conservation of the interacting photons with the material. Among other nonlinear X-ray phenomena, time resolved transient gratings (X-TG) or four wave mixing (X-FWM) spectroscopy in the XUV-region has been recently realized by Bencivenga et al.[5]. An objective goal of FEL driven ultrafast X-TG experiments is to access wave-vectors at the nm scale. Due to the spatial and temporal dependency of the signals detected and the specific resonances involved, X-TG comprises additional information compared to standard pump probe experiments. Moreover exploring the role of resonances in nonlinear-X-ray spectroscopy is an essential step towards the realization of more general X-ray FWM schemes such as Degenerate Four-Wave-Mixing and Coherent Anti-Stokes Raman Spectroscopy. We will discuss strategies and first preliminary results towards more general future nonlinear time-resolved X-ray approaches.

1. R. Rohlsberger et al., Nature 482 (2012).
2. N. Rohringer, and R. Santra, Physical Review A 76 (2007).
3. T. E. Glover et al., Nature 488 (2012).
4. K. Tamasaku et al., Nat Photon 8 (2014).
5. F. Bencivenga et al., Nature 520 (2015).

### **Natalie Banerji**

#### **2. Carrier Dynamics and Transport Properties in Few-Layer MoS<sub>2</sub> Nanoflakes**

Demetra Tsokkou, Xiaoyun Yu, Kevin Sivula and **Natalie Banerji** [dimitra.tsokkou@unifr.ch](mailto:dimitra.tsokkou@unifr.ch)

In the last few years, tremendous research interest has been focused on two-dimensional transition metal dichalcogenides, following progress in processing of layers with atomic-size thickness. Among them, molybdenum disulfide (MoS<sub>2</sub>) nanoflakes have shown unique optical and electrical properties. They are excellent absorbers, despite being ultrathin, with high exciton-binding energies that make excitonic transitions evident even at room temperature. Bulk and few-layer MoS<sub>2</sub> are indirect band gap semiconductors, while its monolayer is a direct band gap semiconductor. Also, bound trions have been reported in monolayer MoS<sub>2</sub>, due to strong interactions between excitons and charges and spatial confinement of the photoexcited species.

Ultrafast spectroscopy has brought important clarification to the aforementioned properties in MoS<sub>2</sub> nanoflakes and has unraveled their carrier dynamics and transport properties. We have used complementary techniques of time-resolved absorption and THz transmission spectroscopy to shed new light on the photophysical properties of solution-processed, few-layer MoS<sub>2</sub> nanoflakes. The combination of these methods and experiments at different excitation photon energies and fluences allowed us to distinguish between carrier and exciton relaxation/recombination processes and the corresponding time scales. Also, we have used the spectrum of the complex photoconductivity in the THz region to study the carrier transport properties in the nanoflakes.

**Paul Beaud**

### **3. Insulator-to-metal transition induced by coherent lattice excitation in a manganite**

V. Esposito, R. Mankowsky, H. Lemke, M. Chollet, M. Nakamura, U. Staub, **P. Beaud** and M. Först  
[vincent.esposito@psi.ch](mailto:vincent.esposito@psi.ch)

The strong coupling between the lattice and the electronic degrees of freedom makes strongly correlated systems a very nice playground to create new ways of controlling its properties. We have studied in detail the dynamics of the metal-insulator type of phase transition induced by photoexcitation of an electronic transition in manganite compounds (Beaud et al. Nature Material 2014, Caviezel et al. Phys. Rev. B 2012).

In parallel, the MPI/CFEL group has demonstrated the possibility of using selective lattice excitation to induce phase transitions in solids, introducing non-linear phononics as a new framework to describe phonon interaction (Först et al. Nature Physics 2012, Mankowsky et al. Nature 2014, Först et al. Account of Chemical Research 2015). This new tool in hand, Subedi et al. (Phys. Rev. B 2014) predicted that excitation of an infrared-active mode could induce a metal-insulator transition in PrMnO<sub>3</sub> via non-linear phonon coupling.

Joining our efforts, we recently performed a time-resolved resonant X-ray diffraction experiment at the XPP beamline in LCLS. We observed that, following coherent excitation of an IR-active mode in Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>, an insulator-to-metal transition is launched. Interestingly, the observed dynamics are very similar to those upon photoexcitation of an electronic transition. Indeed, a fast melting of charge order triggering the rearrangement of the unit cell was observed, even though the excitation mechanism is completely different than in earlier experiments. The main difference lies in the behavior as a function of the absorbed energy density. Comparison of the charge-ordering dynamics is expected to unravel the role of the electron-lattice coupling. Moreover, this gives us a unique opportunity to test the ultrafast order parameter concept for photo-induced phase transition.

### **4. Structural dynamics of the single-layered manganite Pr<sub>0.5</sub>Ca<sub>1.5</sub>MnO<sub>4</sub> following optical excitation of the charge and orbital ordered phase**

M. Porer, V. Esposito, L. Rettig, E. Bothschafter, J. Rittmann, M. Savoini, M. Kubli, G. Lantz, R. Versteeg, P. van Loosdrecht, S. Johnson, **U. Staub**, P. Beaud  
[michael.porer@psi.ch](mailto:michael.porer@psi.ch)

Three-dimensional manganites have stimulated considerable interest in the recent past due to the discovery of colossal magnetoresistance and metal-insulator transitions in these materials. Lattice distortions, especially the Jahn-Teller effect, play a crucial role in the phase transitions and are closely linked to charge and orbital order. The study of the structural dynamics associated with the photoinduced phase transition in manganites is an important step towards their understanding. As critical exponents in adiabatic theory of continuous phase transitions are known to depend on the dimensionality of the system the question arises whether this applies also to the non-thermal case. Comparing the result on the single layer Pr<sub>0.5</sub>Ca<sub>1.5</sub>MnO<sub>4</sub> to our previous results on the 3-D manganites addresses this fundamental question. The compound under study shows a CE-type charge and orbital order in the antiferromagnetic insulating ground state. The charge and orbital order sets in at a temperature of T = 308 K and coincides with a metal-insulator like transition. Using the ultrafast 800 nm pump - X-ray probe setup at the Micro-XAS beamline at the SLS, we study a superlattice reflection that is sensitive to charge and orbital order. We photoexcite the system in the ground state via intersite 'd-d' excitations and monitor the ultrafast dynamics of the structural superlattice systematically for a series of pump fluences and temperatures.

**Andreas Borgschulte**

### **5. Electron-Transfer reactions by time-resolved Magneto-Optics**

Andreas Borgschulte, Sue Yun Oh, Bruce Patterson, Davide Bleiner  
[andreas.borgschulte@empa.ch](mailto:andreas.borgschulte@empa.ch)

On this poster, we propose a novel method to unravel mechanisms during elementary (photon-induced) charge transfer reactions. Combining recent developments in ultra-fast spectroscopy with established magneto-optical techniques, we have a probe to study the dynamics of short living species generated by photo-excitation. This includes the investigation of excited states, fluorescence and electron transfer in organic dyes and change of the oxidation state in photo-catalysts. The data will be used to improve materials for organic photovoltaics and solar-water splitting and will contribute to answer fundamental questions, i.e. the modelling of electron transfer reactions in electrochemistry. The flexibility of the proposed photo-induced Magneto-Optics method makes it

possible to study homogeneous (molecular) systems as well as heterogeneous systems, and is therefore suited to bridge the scientific gap between the Marcus theory of molecular systems and electron transfer reaction with metallic electrodes. We present first preliminary results."

**Andrea Cannizzo**

## **6. Single Shot detection for UV-Spectroscopy**

Georg Achazi, Maryam Nazari Haghighi Pashaki, Egmont Rohwer, Ariana Rondi, Thomas Feurer, **Andrea Cannizzo** [georg.achazi@iap.unibe.ch](mailto:georg.achazi@iap.unibe.ch)

We present new concepts based on our novel single shot broadband detection to characterize UV pulses for diagnostics and spectroscopy. In this contribution we report on two examples: 1) a portable self-diffraction frequency-resolved optical gated spectrometer (SD-FROG) for the characterisation of 100 nJ UV femtosecond pulses and 2) a new concept for single shot Fourier transform spectral interferometry that allows heterodyne detection without phase stabilisation. Both methods are a huge step towards the goal of our project to extend the 2D-photon-echo-spectroscopy into the deep-UV.

## **7. Ultrafast energy transfer dynamics in DNA-hosted multichromophoric systems investigated by DUV-to-Vis femtosecond pump-probe spectroscopy**

M. Nazari, M. Akbarimoosavi, M. Gazzetto, A. Rondi, T. Feurer, **A. Cannizzo**, C. D. Bösch, S. M. Langenegger, R. Häner [maryam.nazari@iap.unibe.ch](mailto:maryam.nazari@iap.unibe.ch)

"During the last year, we improved our femtosecond Transient Absorption (TA) set-up by increasing the spectral region covered in excitation (down to 250 nm) and detection (from 270 to 750 nm), achieving a signal-to-noise ratio of  $10^5$  and a time resolution of 40 fs (standard deviation). This allowed us to investigate a family of multichromophoric systems designed for light-harvesting in supramolecular photocatalysers. In these systems, several phenanthrenes (the light-harvesters) and one pyrene (the energy acceptor) are pi-stacked in a DNA scaffold and experience a robust coupling, which gives rise to an energy transfer (EnT) with unitary quantum yield over several nm. Excited state dynamics of these systems are investigated by DUV-to-Vis femtosecond TA to clarify their photophysics, the relevant times and dynamics of EnT as well as the role of molecular environment on the EnT mechanism.

We found that EnT takes place within our time resolution (i.e.  $<40$  fs) over a 1 nm distance, accounting for the unitary quantum yield. We observed the formation upon excitation of transient delocalized states that last from a few 10s to 100s of fs depending on the presence of the energy acceptor, suggesting that these states could mediate the EnT. To our knowledge, such a mechanism has never been proposed before, and violates the common opinion that efficient energy and charge transfers need long-lived states. These systems are ideal models to investigate the effect of fs shaped pulses and ps THz fields (sub-ps Stark spectroscopy) on transfer phenomena over long distances ( $\geq$ nm).

## **8. Ultrafast energy and charge transfer dynamics in functional materials investigated with femtosecond DUV-to-Vis transient absorption and resonant stimulated Raman spectroscopies**

M. Gazzetto, M. Akbarimoosavi, M. Nazari, A. Rondi, E. Rohwer, T. Feurer, **A. Cannizzo**, J. Kübel, M. Wächtler, B. Dietzek, L. Sciortino, F. Messina (IAP, Bern), J. Kübel, M. Wächtler, B. Dietzek (Leibniz Institute of Photonic Technology, Jena) [michela.gazzetto@iap.unibe.ch](mailto:michela.gazzetto@iap.unibe.ch)

With the goal to study electronic and vibrational dynamics in new emerging materials for photonics and photocatalysis, we have developed a versatile time-resolved femtosecond spectrometer, which can easily operate in different configurations as stimulated Raman or transient absorption (TA), with or without referencing of the probe spectrum and of pump and Raman pulse intensities. The setup is designed to achieve single-shot detection with a signal-to-noise ratio  $>10^4$  on each spectrum detected. The probed range covers more than one octave from 270 nm to 760 nm, with a time resolution of 40 fs (standard deviation). Here we present our first studies on an emerging family of carbon-based nanomaterials and on a prototypical H<sub>2</sub>-evolving supramolecular photocatalyst for artificial photosynthesis (RuPd). The latter hosts Ru- and Pd-containing moieties, which play the role of light harvester and catalytic center, respectively. Stimulated resonant Raman measurements with a spectral resolution

of  $<20 \text{ cm}^{-1}$  revealed signature modes of the Pd units, corresponding to the conversion of 4-coordinated Pd into 3-coordinated Pd, upon excitation of the electron donor Ru-unit. These results shine new light on the much-debated fundamental mechanisms responsible for the catalytic activity. Carbon nanodots (CDs) are a novel family of carbon-based nanomaterials synthesized only a few years ago. They have the potential to complement or even replace semiconductor nanoparticles in several applications and domains, in particular where bio-toxicity is an issue. From a more fundamental point of view, they show unique optical properties currently debated in literature, and whose understanding is crucial to move towards applications. We carried out an extensive study with our setup in TA configuration to achieve a deeper understanding of the photo-physical properties of CDs. To the best of our knowledge, we report here for the first time on a detailed photocycle of CDs, which also includes higher excited states. We observed rotational diffusion dynamics of the transition dipole moments on timescales faster than the rotational diffusion of the entire CD. A tentative model is presented to rationalize such an unexpected behaviour.

**Fabrizio Carbone**

## **9. Simultaneous Experimental Observation of the Quantization and the Interference Pattern of a Plasmonic Near-Field**

Tom T. A. Lummen, L. Piazza, E. Quiñonez, Y. Murooka, B. W. Reed, B. Barwick and **F. Carbone**

[tom.lummen@epfl.ch](mailto:tom.lummen@epfl.ch)

Miniaturized plasmonic and photonic integrated circuits are generally considered as the core of future generations of optoelectronic devices, due to their potential to bridge the size-compatibility gap between photonics and electronics. However, as the nanoscale is approached in increasingly small plasmonic and photonic systems, the need to experimentally observe and characterize their behavior in detail faces increasingly stringent requirements in terms of spatial and temporal resolution, field of view, and acquisition time. This work focuses on a specific electron microscopy technique, Photon-Induced Near-Field Electron Microscopy (PINEM), which is capable of imaging optical evanescent fields and surface plasmon polaritons (SPPs) in nanoplasmonic structures with both nanometer and femtosecond resolution. To do so, an advanced electron energy filter is used to analyze the quantized energy exchange between a photo-induced SPP and an ultra-short bunch of probing electrons. In electron energy loss/gain spectroscopy mode, the exchange of up to 30 photon quanta with the photo-induced SPPs in silver nanoantennae is observed. In PINEM imaging mode, the spatial properties of the photo-induced standing SPP wave on a single silver nanoresonator are shown to be controlled by the polarization of the optical pump pulse. These results are guided and corroborated by extensive 3D finite-element modeling. Moreover, in a novel hybrid acquisition mode - which synchronously characterizes the electron-SPP interaction along both a spatial coordinate and energy - both the characteristic spatial interference and the energy quantization of the SPP are obtained in the same experiment, providing a unique visualization of the wave-particle duality of its electromagnetic near-field.

## **10. Signatures of Low-Temperature Charge-Density-Wave Order in Photoexcited High-Temperature Magnetite**

S. Borroni, E. Baldini, A. Mann, C. Arrell, F. van Mourik, J. Teyssier, J. Lorenzana, and **F. Carbone**

[simone.borroni@epfl.ch](mailto:simone.borroni@epfl.ch)

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is the earliest discovered magnetic material. Below  $T_V \sim 120 \text{ K}$ , magnetite undergoes a structural phase transition, concomitant to a metal-insulator transition, between a cubic half-metallic and a monoclinic insulating phase. Here, we show that, above  $T_V$ , the impulsive photoexcitation of the charge-transfer between O 2p and Fe 3d states transiently promotes the low-temperature charge-ordered state. The coherent superposition of the charge fluctuations associated with the charge order and the phonon modes responsible for the structural transition is excited via impulsive stimulated Raman scattering. The consequent coherent oscillations of the optical constants are detected via ultrafast broadband reflectivity. We reveal that the primary order parameters of the structural transition are strongly coupled to the charge-density-wave and undergo softening in the critical region, revealing the involvement of the structure in the metal-insulator transition.

## 11. Real-space and real-time imaging and control of plasmonic fields

L. Piazza, T.T.A. Lummen, Erik Quinonez, Y. Murooka, B.W. Reed, B. Barwick, **F. Carbone**

[fabrizio.carbone@epfl.ch](mailto:fabrizio.carbone@epfl.ch)

Electromagnetic excitations called surface plasmon polaritons (SPP) can be found at the interface between a metal and a dielectric. The definition refers to the coupling between a collective motion of charges in the metal, the surface plasmon, and the radiated electromagnetic field, the polariton, which is evanescently confined in the direction perpendicular to the surface. The term polariton is used to define a field that is strongly coupled to a dipolar excitation, which in this case is provided by the distribution of electrons in the metal. SPPs can be induced at the surface of metallic nanostructures, guiding the electromagnetic field in bends, corners or any arbitrary shape thanks to their ability to spatially confine it. In novel materials which exhibit exotic electronic properties due to dimensional confinement, SPPs have been reported to be very sensitive to applied electric or magnetic fields, to have low loss propagation and an unusually high refractive index. Such phenomena are widely investigated because of their potential application in photonic circuits, where sub-wavelength guiding of the electromagnetic field is crucial to miniaturization. Here, we show that a plasmonic standing wave can be induced on an isolated metallic nanowire with an intense fs laser pulse, and demonstrate the possibility to control its spatial interference pattern by tuning the properties of light excitation, such as its polarization. A fs snapshot of the interaction between the imaging electrons and the SPPs is taken by a new ultrafast-imaging methodology that uses an electron imaging filter to form a 2D projection of one spatial coordinate and energy. These space- energy resolved images simultaneously show the quantization of the photo-induced SPP field and an interference pattern in its spatial distribution, providing an interesting perspective on the quantum properties of plasmonic fields.

## 12. Evidence for Pre-Formed Cooper Pairs in the Pseudogap Phase of Slightly Underdoped $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$

Edoardo Baldini, Andreas Mann, Benjamin Mallett, Christopher Arrell, Frank Van Mourik, Thomas Wolf, Dragan Mihailovic, Jeff Tallon, Christian Bernhard, José Lorenzana, **Fabrizio Carbone** [edoardo.baldini@epfl.ch](mailto:edoardo.baldini@epfl.ch)

In the last years ultrafast experiments have contributed to shed new light on high-temperature superconductivity. In particular, tailored excitation in the mid-infrared spectral range was demonstrated to suppress competing structural and electronic orders and to promote a highly coherent state in several underdoped cuprates [1 - 4]. In  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  this transient state was found to persist up to room temperature, evidenced by the enhancement of the superfluid strength in the THz response. The question whether the high coherence is the signature of a perfect conducting or of an exotic superconducting state at nonequilibrium still remains open. Here, we address this problem from a spectroscopic point of view, by investigating a slightly underdoped sample of  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  through ultrafast spectroscopy in the optical regime. The use of a broadband detection scheme enables us to reveal evidence for quasiparticle (QP) excitation up to a temperature  $T_{\text{ons}}$ , which is higher than the superconducting critical temperature  $T_c$  but lower than the pseudogap temperature  $T^*$ . The existence of a QP spectral signature in the pseudogap phase, together with its peculiar temporal evolution and temperature dependence, can be directly related to the presence of a pairing gap for QP excitation. In the same experiments, we also track the temperature evolution of the coherent Ba mode, which represents a sensitive probe of pairing correlations, and we observe an anomaly of its intensity also at  $T_{\text{ons}}$ . The pump-probe experiments are complemented by equilibrium spectroscopic ellipsometry measurements, covering a wide spectral range from the far-infrared to optical frequencies, which confirm the existence of such temperature scale  $T_{\text{ons}}$  between  $T_c$  and  $T^*$ . The observation of preformed pairs under nonequilibrium conditions not only provides important spectroscopic information on the dynamics of the local pairing correlations above  $T_c$ , but also opens new exciting perspectives towards the ultrafast control of these incoherent pairs.

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### 13. Filming the formation and fluctuation of skyrmion domains by cryo-Lorentz transmission electron microscopy

J. Rajeswari, P. Huang, G. F. Mancini, Y. Murooka, T. Latychevskaia, D. McGrouther, M. Cantoni, E. Baldini, J. S. White, A. Magrez, T. Giamarchi, H. M. Ronnow, **F. Carbone** [rajeswari.jayaraman@epfl.ch](mailto:rajeswari.jayaraman@epfl.ch)

Skyrmions are rotationally symmetric nano-scale spin structures, observed in materials with chiral space-groups and possessing an intrinsic Dzyaloshinskii-Moriya interaction. Magnetic skyrmions are promising candidates as information carriers in logic or storage devices thanks to their robustness, guaranteed by the topological protection, and their nanometric size. Currently, little is known about the influence of parameters such as disorder, defects, or external stimuli on the long-range spatial distribution and temporal evolution of the skyrmion lattice. Utilising the Fresnel mode of a 200keV cold field emission gun cryo-Lorentz transmission electron microscope, we image up to 70,000 skyrmions in a large ( $7.3 \times 7.3 \mu\text{m}^2$ ) single-crystal nanoslice of  $\text{Cu}_2\text{OseO}_3$ . Images were recorded as a function of the applied magnetic field. The emergence of the skyrmion lattice from the helimagnetic phase is monitored, revealing the existence of a glassy skyrmion phase at the phase transition field, where patches of an octagonally distorted skyrmion lattice are also discovered. In the skyrmion phase, dislocations are shown to cause the emergence and switching between domains with different lattice orientations. The temporal fluctuation of these domains is filmed as a movie for 50 s, where each frame is exposed for 100 ms, and an image is acquired every 500 ms. These results demonstrate the importance of direct-space and real-time imaging of skyrmion domains for addressing both their long-range topology and stability.

### Majed Chergui

#### 14. The elaborate simplicity of PTPOP: beyond the harmonic oscillator model.

G. Capano, R. Monni, G. Aubock, **M. Chergui**, I. Tavernelli [gloria.capano@epfl.ch](mailto:gloria.capano@epfl.ch)

The biplatinum complex PtPOP, short name for  $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ , is one of the most studied face-to-face binuclear d8-d8 transition complexes. Due to the rigidity of the external cage, formed by phosphorus atoms linked by bridge oxygen, the system can be considered as an harmonic oscillator along the Pt-Pt direction [1]. In solution, upon photo-excitation into the optical allowed  $1A_{2u}$  state, it relaxes, non-adiabatically, into the lowest triplet state  $3A_{2u}$ , through intersystem crossing (ISC). The quantum yield of the process is  $\sim 1$  and, surprisingly, the rate of this transition is strongly solvent dependent, varying from 1 ps in acetonitrile to 30 ps in ethanol. Despite several spectroscopic studies, the ISC mechanism and the role of the solvent in modifying its rate are still elusive [1,2]. Linear response TD-DFT calculations combined with QM/MM molecular dynamics were performed in order to shed light on the ISC process and the mutual influence of geometry, electronic structure and solvent interactions. Notably, we found that the harmonic oscillator model, although it well depicts some aspects of the photo-relaxation pathway, is not suitable to describe the ISC mechanism and the solvent dependency of its rate.

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#### 15. Polarization dependent, vibrationally resolved transient absorption spectroscopy of single crystalline pentacene.

Lars Mewes, André Al Haddad, Paul Gratia, Philippe Bugnon, Frank Van Mourik, and **Majed Chergui** [lars.mewes@epfl.ch](mailto:lars.mewes@epfl.ch)

The physics of organic semiconductors remain unclear even though they are now widely being used in electronics [1,2], and light harvesting [3]. Their molecular structure clearly separates them from inorganic semiconductors, and unraveling their behavior involves understanding both, their crystal effects and molecular properties, and the interplay thereof.

We present time-resolved transient absorption measurements that have been performed on 400 nm thin slices of single crystalline pentacene and observe a clear polarization dependence when changing the relative polarization between the pump- and the probe laser pulses. This dependence is observable in ellipsometry [4,5], and is a result of Davydov splitting inside the crystal.

Our results yield insight into the widely discussed singlet fission mechanism [6,7,8], as well as the subsequent exciton, and charge-carrier dynamics in single crystalline pentacene. This will add to the current understanding of the physics in organic semiconducting materials.

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## 16. Ultrafast ligand-to-metal charge transfer dynamics in aqueous ferricyanide

José Ojeda, Christopher Arrell, Jakob Grilj, Lars Mewes, Frank van Mourik and **Majed Chergui**

[jose.ojeda@epfl.ch](mailto:jose.ojeda@epfl.ch)

The ultrafast ligand to metal charge transfer (LMCT) process in aqueous ferricyanide is studied by means of photoelectron spectroscopy (PES) and transient absorption (TA). The LMCT band centered at about 415 nm [1] is excited by the 395 nm second harmonic of a 40 fs Ti:sapphire laser running at 10 kHz. Extreme ultra violet (EUV) probe pulses created by high harmonic generation (HHG) in argon are monochromatized using a single-grating time-preserving monochromator [2], and focused onto a 15 micrometer liquid jet [3] by an ellipsoidal mirror in a 4:1 configuration. Photoreduction of the Fe(III) center is observed within 200 fs after excitation with subsequent relaxation in the order of 1 ps. TA measurements (395 nm pump, 430-700 nm probe) of the same complex in dilute aqueous and ethylene glycol solutions are also presented. As previously reported [4], solvent dependent relaxation mechanisms are present. By combining the interpretation of the PES and TA results, possible reaction pathways are discussed.

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## 17. Ultrafast optical spectroscopy of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> hybrid perovskites

Tania Palmieri, Andre Al Haddad, **Majed Chergui**

[tania.plmr@gmail.com](mailto:tania.plmr@gmail.com)

Organometallic halide perovskite-based solar cells have witnessed an incredibly fast emergence in the last years. This success is primarily due to the increasing conversion efficiency, now approaching 21% [1], and to the low manufacturing costs that make perovskite materials an attractive alternative to silicon. Moreover, the high photoluminescence quantum efficiency, as well as the narrow and tunable emission band that characterizes these materials, make them the perfect candidate for high-performance optoelectronic devices [2]. In order to optimise these unique features, detailed understanding of the photophysics of organometallic halide perovskites, especially fundamental studies on charge carrier dynamics, are needed in order to assist the efforts of material scientists. In particular, one of the most controversial issue regards the interplay between photoexcited species, which can be excitons or free carriers. We investigate carrier- and exciton dynamics in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> polycrystalline films by means of ultrafast broadband optical spectroscopy, to observe in real time the effects of these elementary excitations on the optical absorption spectrum. The femtosecond transient absorption experiment reveals that the dynamics is occurring exclusively at the onset of the band gap absorption, in correspondance with an excitonic feature observed in the steady-state spectrum at low temperatures [3]. We will present our progress in the study of brominated perovskites, in order to elucidate the excited-state behavior and discuss the processes involved of charge separation, diffusion and recombination, as well as the definition of the timescales on which they manifest.

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**Claudio Cirelli**

## **18. Suitability of a table-top cold-cathode XUV-source for high energy-resolution off-resonance spectrometry (HEROS)**

Francesco Barbato, Yunieski Arbelo, Bruce Patterson, **Claudio Cirelli** and Davide Bleiner

[francesco.barbato@empa.ch](mailto:francesco.barbato@empa.ch)

X-ray absorption spectroscopy (XAS) is a powerful method to study the local electronic and geometric structures of matter. High-brightness, short pulses X-ray sources have opened the possibility to perform time-resolved XAS studies of photo-active species. However the need to scan the incident beam energy across the investigated absorption edge puts severe constraints on the feasibility of such time resolved studies. Recently it has been demonstrated with the new high energy resolution off-resonance spectroscopy (HEROS) technique [1,2] that a high resolution XAS spectrum can be reconstructed by collecting an X-ray fluorescence (XES) spectrum at a single excitation energy far below the absorption edge. To date, these measurements have been performed solely at advanced radiation sources, e.g. synchrotron and XFEL.

Here, we present the characteristics of a table-top XUV-source based on cold-cathode plasma-emission aimed to the implementation of soft X-ray absorption and emission spectroscopy as well as imaging experiments in a lab-scale system. The source performances are tested with different working gases (argon, nitrogen and oxygen), pressures and input voltages and the dependence of these parameters on the source repetition rate and XUV flux is analyzed between 12 and 30 nm.

Our results demonstrate that an increase of working gas pressure or input voltage from the power supply induce an increment of the repetition rate up to about 30 Hz and a decrement of the emitted XUV flux ( $\lambda$  between 7 nm and 16 nm) by about one order of magnitude. However, a total flux of 1013 photons/(2 $\pi$ sr pulse) can be recovered when the working gas is mixed with helium. Stability measurements and determination of optimal sample position for XUV-irradiation are also presented. Fluctuations lower than 6% are observed, demonstrating the feasibility of the experiments.

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**Thomas Feurer**

## **19. Linear and nonlinear time domain THz spectroscopy of VO<sub>2</sub> thin films**

Gregory Gäumann, Nagla Numan, **Thomas Feurer**

[gregory.gaeumann@iap.unibe.ch](mailto:gregory.gaeumann@iap.unibe.ch)

Vanadium dioxide (VO<sub>2</sub>) exhibits a reversible first order phase transition from a monoclinic insulator to a metallic tetragonal (rutile) structure when the sample temperature is increased above the critical value of 68°C. VO<sub>2</sub> thin films of different thickness were deposited via pulsed laser deposition on sapphire and silica substrates. These samples are measured in different terahertz (THz) spectroscopy setups including THz near-field, low- and high-field spectrometers and a THz time-domain spectroscopic ellipsometer (THz-TDSE). Thereby the complete dielectric properties of the VO<sub>2</sub> films above and below the phase transition in the frequency range of 0.1-2.5 THz can be determined. The novel technique of THz-TDSE is operating in reflection mode and can be used to extract the complex dielectric properties of nontransparent materials. In addition, we investigated the THz induced phase transition of VO<sub>2</sub> layers deposited in gold nanoslits with widths in the range of tens of nanometers.

## **20. Femtosecond Transient Absorption Spectroscopy of VO<sub>2</sub> Thin Films**

N. Numan, G. Gäumann, M. Maaza, **T. Feurer**, M. Akbarimoosavi, R. Egmont

[nagla.numan@iap.unibe.ch](mailto:nagla.numan@iap.unibe.ch)

The optical properties of VO<sub>2</sub> thin films are investigated across the metal-insulator phase transition. The VO<sub>2</sub> thin films on sapphire (Al<sub>2</sub>O<sub>3</sub>) substrates were synthesized by the pulsed laser deposition (PLD) technique. Their properties and composition were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). First, we performed transmission spectroscopy measurements across the metal-insulator transition and determined the optical properties, such as transmission and absorption coefficients, at temperatures below and above the phase transition temperature. The spectral range covered extended from the visible to the infrared part of the spectrum. Next, we measured the first time resolved 800 nm pump white light probe transient absorption

spectra with 50 femtosecond resolution. These measurements reveal the ultrafast dynamics of the charge carriers and the phonon system.

## 21. Femtosecond time-resolved Stark spectroscopy: project status

Egmont Rohwer, Maryam Akbarimoosavi, Andrea Cannizzo, **Thomas Feurer** [egmont.rohwer@iap.unibe.ch](mailto:egmont.rohwer@iap.unibe.ch)

The latest developments in the combined transient absorption- and THz field-induced Stark spectroscopy project are presented. The results include; a solvato-chromic effect observed in transient absorption measurements done on organic donor-acceptor molecules. Varying the solvent simulates the effect of a local electric field of different magnitude while the solvent molecules re-orientate with respect to the changed dipole moment of the molecule in the photo-excited state. These results provide a litmus test for selecting suitable candidates for eventual experiments measuring changes in excited state absorption due to an electric field applied by THz pulse. The same molecules were measured in a low temperature Stark spectroscopy setup with an electric field applied by a capacitor in an RLC circuit. The presented results show that a Stark effect was observed in all samples with field strengths around 100 kV/cm, and with a signal-to-noise ratio in the  $10^{(-5)} - 10^{(-6)}$  regime ( $\mu$ OD). On both counts this is comparable to what has been achieved in our setup; peak fields achieved by THz generation routinely exceed 100 kV/cm and the sensitivity of our TA detection setup has achieved  $10^{(-5)}$  in other experiments. These molecules are therefore excellent candidates to show a ground state Stark effect due to the application of a single-cycle THz pulse. First results of a ground state Stark effect observed in a polymer thin film using a THz-supercontinuum pump-probe configuration are shown and confirm the field strengths and detection sensitivity that the setup is already capable of.

## 22. Extreme localisation of electromagnetic THz pulses in Ångström-slit arrays

Salvatore Bagiante, Yannik Waeber, Justyna Fabiaska, Florian Enderli, Hans Sigg, **Thomas Feurer** [yannik.waeber@iap.unibe.ch](mailto:yannik.waeber@iap.unibe.ch)

Over the past decades our ability to fabricate and manipulate structures on the nanoscale has continuously grown and has resulted in numerous advances in nano-science and nano-optics. For example, in 1998 Ebbesen et al. [1] demonstrated that nanoscale metallic antennas can couple incident optical beams to length scales much smaller than the diffraction limit. This scheme has recently been extended to the THz regime. Using suitable structures that act as nanoantennas, the electric field generated by THz light can be enhanced and localised to a scale well beyond the diffraction limit. Due to the planar geometry of almost all structures the electric field component, which is enhanced, is the in-plane component; see for example reference [2]. Here, we demonstrate an out-of-plane field enhancement by using multilayer vertical nano-slit arrays. Through simulations and experiments we demonstrate that the field enhancement factor and the transmission coefficient are comparable to those observed in planar slit arrays. The corresponding structures are fabricated using standard thin film technology and will pave the way for experiments where strong out-of-plane THz electric fields are required. Our planar multilayer fabrication process is easy to implement, and allows fabrication of slits with less than one nanometer gap size.

## 23. Multidimensional coherent electronic spectroscopy with shaped pulses

Y. Rodriguez, A. Cannizzo, **T. Feurer** [yuseff.rodriguez@iap.unibe.ch](mailto:yuseff.rodriguez@iap.unibe.ch)

In the last year we have started to explore the capability of our high fidelity two-dimensional electronic spectroscopy setup to modulate amplitude and phase of the individual exciting and probing pulses. In this contribution we present different examples of non-standard schemes in order to track down processes such as solvation and intramolecular dynamics in several reference molecular systems in solution. We also discuss future experimental developments and possible implementations of further detection schemes solely possible with a pulse shaping apparatus being an integral part of the setup.

## 24. New transient in the rotational DFWM spectrum of Difluorobenzene

Takuya Den, Hans-Martin Frey, **Thomas Feurer** and Samuel Leutwyler [hans-martin.frey@iap.unibe.ch](mailto:hans-martin.frey@iap.unibe.ch)

Femtosecond Degenerate Four-Wave Mixing (DFWM) rotational coherence spectroscopy (RCS) is a background-free method that yields accurate gas-phase rotational constants of non-polar molecules that exhibit no microwave

spectrum. The transients of nonpolar asymmetric tops show a large number of RCS transient types and require a ~100 times larger computational effort to simulate and fit the experiment. We present RCS spectra of nonpolar 1,4-difluorobenzene (p-DFB), an asymmetric top, measured in supersonic jet and in a gas cell. A novel transient (S-type) that has not been characterized so far is characterized besides the well known J-, K-, A-, and C-type transients. The jet and gas cell RCS measurements were fully analyzed and yield the ground-state ( $v = 0$ ) rotational constants  $A_0 = 5637.68(20)$  MHz,  $B_0 = 1428.23(37)$  MHz, and  $C_0 = 1138.90(48)$  MHz ( $1\sigma$  uncertainties).

## Manfred Fiebig

### 25. Ultrafast all-optical manipulation and probing of a multiferroic state

Christian Tzschaschel, Stefan Günter, Takuya Satoh, **Manfred Fiebig** [christian.tzschaschel@mat.ethz.ch](mailto:christian.tzschaschel@mat.ethz.ch)

Manipulating and probing of magnetic order with light is both interesting for future energy-efficient applications and provides deep insight on the fundamental level of light-matter interaction. Recently, in the context of all-optical switching, ultrafast magnetization dynamics attracted significant interest. On the other hand, multiferroic materials offer manifold features that could be interesting for future applications, e.g. data storage. These arise especially due to the coupling of magnetization and electric polarization. In our poster, we will present an enhancement of magnetization in EuO on a few-picosecond timescale. We employed non-linear optics, especially second-harmonic generation, as a probe to study the magnetization dynamics with femtosecond time resolution. The dynamics are beyond the well-established three-temperature model, but show a striking agreement with the RKKY theory. Based on this, we propose an extended experiment to probe and manipulate a multiferroic state in the class of multiferroics with the strongest magnetoelectric coupling in order to investigate the coupling and hitherto almost neglected dynamical properties of multiferroics.

## Peter Hamm

### 26. Surface-Sensitive Spectro-Electrochemistry Using Ultrafast 2D ATR IR Spectroscopy

Davide Lotti, **Peter Hamm**, Jan Philip Kraack [philip.kraack@uzh.ch](mailto:philip.kraack@uzh.ch)

A new method is presented for the combination of spectro-electrochemistry and femtosecond 2D IR spectroscopy. The key-concept is based on ultrathin (~nm) conductive layers of noble metals as well as Indium-Tin-Oxide (ITO) as working electrodes on a single reflection Attenuated Total Reflectance (ATR) element in conjunction with ultrafast, multi-dimensional ATR spectroscopy. The ATR geometry offers prominent benefits as compared to transmission or external reflection experiments in ultrafast spectro-electrochemistry, i.e. surface-sensitivity for studying electrochemical processes directly at the solvent-electrode interface as well as the application of strongly IR-absorbing solvents such as water due to a very short effective path-length of the evanescent wave at the interface. We present 2D ATR IR spectra of carbon monoxide (CO) adsorbed to platinum-coated, ultrathin ITO electrodes with the electrochemical performance being demonstrated by vibrational Stark-shift spectroscopy of the CO stretching mode and oxidative desorption together with redox-chemistry of metal complexes. Ultrafast vibrational relaxation and spectral diffusion of the stretching mode from surface-bound CO is determined as mildly dependent on the applied potential to the working electrode. Finally, we discuss experimental challenges and benefits and the scope for ultrafast 2D ATR IR spectroscopy along with relevant ongoing investigations in the field of electrocatalysis.

### 27. Quantifying Equilibrium Protein-Ligand Interactions with Unnatural Amino Acids and Two-Dimensional Infrared Spectroscopy

Klemens L. Koziol, Philip J. M. Johnson, **Peter Hamm** [klemens.koziol@chem.uzh.ch](mailto:klemens.koziol@chem.uzh.ch)

Azidohomoalanine (Aha) is a very versatile label that can be incorporated into proteins. It absorbs in the non-congested part of protein IR spectra and the center frequency is sensitive to the environment [1]. The combination of ultrasensitive 2D IR spectroscopy and Aha labelling of proteins gives rise to new possibilities of investigating biological structures and their dynamics with very low sample demands [2]. With voice coil flexure guided delay stages and automated exchange of buffer and protein samples it is possible to measure Aha labelled proteins down to a concentration of 0.5 mM with good signal to noise ratio. This is demonstrated with equilibrium binding studies of Aha-labelled peptide with its associated wild-type protein binding domain PDZ2. Upon binding, the Aha band redshifts by ~ 15  $1/\text{cm}$  and can clearly be resolved from the unbound fraction. For a fixed ligand

concentration of 0.5 mM, analysis of fractional binding recovered from 2D IR spectra collected at various protein concentrations allows for the direct observation of the binding affinity.

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## 28. Charge transfer processes in a molecular pentad

Margherita Oraziatti, Martin Kuss-Petermann, Oliver S. Wenger and **Peter Hamm**

[margherita.oraziatti@chem.uzh.ch](mailto:margherita.oraziatti@chem.uzh.ch)

A better understanding of single and multiple electron transfer is needed in order design systems able to mimic natural photosynthesis. For this purpose, triad systems capable of forming photoinduced charge-separated state with single electron transfer, have been extensively studied.

We decided to focus our research on a different system, a new linear pentad, formed by two triaryl amines, which act as electron donors (D), two ruthenium trisbipyridine as photosensitizers (PS) and anthraquinone as electron acceptor (AQ). Due to its design and to the ability of AQ of accommodating two electrons, it has the unique capability of performing a double intramolecular electron transfer, thus forming a long-living charge-separated state where two negative charges are located in the final electron acceptor.

Using Vis-pump IR-probe ultrafast spectroscopy, we are following the formation of the charge-separated state and the charge-recombination processes, and we are discriminating between the different intermediates. Preliminary data show the presence of a band in the transient spectrum corresponding to AQ<sup>•-</sup> (1490 cm<sup>-1</sup>). Furthermore, if we compare the spectrum to the one of the reference triad (D-PS-AQ), where the second electron transfer cannot occur, one more band (1366 cm<sup>-1</sup>), corresponding to the AQ=, can be clearly distinguished, thus confirming the double electron transfer. The kinetics of the AQ<sup>•-</sup> show that both the pentad and the triad form a photoinduced charge-separated state that lives for few microseconds and that if an acid is also present in the solution, it stabilizes the charge-separated state via protonation of the reduced AQ, leading to shorter AQ<sup>•-</sup> and AQ= kinetics.

## 29. Intrinsic phasing of oversampled heterodyne-detected multidimensional infrared spectra

Philip J. M. Johnson, Klemens L. Koziol, and **Peter Hamm**

[philip.johnson@uzh.ch](mailto:philip.johnson@uzh.ch)

Here, we show that it is possible to phase 2D spectra generated by a boxcars geometry 2D IR spectrometer directly from the coherence time interferograms (i.e. without the need of any additional reference measurement) when the sampling rate exceeds the Nyquist frequency of the mid-IR interference. This is achieved using flexure-guided voice coil translation stages and interferometric tracking of the coherence time delay. As a proof of principle, the 2154 wavenumber stretch vibration of MeSCN in DMF, which exhibits anharmonicity such that the 0-1 and 1-2 transitions are fully spectrally resolved, allows for direct phasing from the ground and excited state response separately. The general applicability of this approach is discussed.

## 30. Towards site-selective IR spectroscopy of a photoswitchable allosteric protein

Brigitte Stucki-Buchli, Philip J. M. Johnson, Klemens L. Koziol, Olga R. Bozovic, Claudio Zanobini, Steven A. Waldauer, Rolf Pfister, **Peter Hamm**

[olga.bozovic@chem.uzh.ch](mailto:olga.bozovic@chem.uzh.ch)

Allostery has long been an intense research topic, and much about the underlying mechanism allowing a signal to propagate across a protein still must be investigated. By covalently linking an azobenzene photoswitch across the binding groove of an allosteric protein domain, a conformational transition can be initiated by a laser pulse. This transition mimics the conformational change of the unmodified domain upon ligand binding. We have studied this light induced transition by ultrafast IR spectroscopy. So far, we have probed two IR absorption bands: First, the amide I band which arises from the carbonyl stretch vibration of all amide groups in the protein and is sensitive to overall structural changes, and second, a vibration localized on the photoswitch, which is sensitive to the local environment of the photoswitch, namely the opening of the binding groove. To gain more site-specific resolution, we are now incorporating IR labels that will allow us to observe structural changes at different positions close and far away of the binding groove of the protein.

### 31. 2D Infrared Spectroscopy of High Pressure Phases of Ice

Halina Tran, Andrey Shalit, Peter Hamm

[halina.tran@chem.uzh.ch](mailto:halina.tran@chem.uzh.ch)

The spectroscopic signature of the OH-stretch vibration of ice is complex. It has been studied with 2D spectroscopy before. However the assignment of the distinct peaks of the OH-band remains controversial [1].

In part this is due to the involvement of hydrogen bonds, but also because the hydrogen atoms in ice Ih are unordered. By studying other phases of ice which are hydrogen ordered (like ice II, for which we present the first 2D infrared spectra here) we try to simplify the problem. Measuring solid samples and especially powders is challenging in 2D spectroscopy due to the sensitivity of this technique to unwanted scattering. A new preparation method for high pressure phases of ice was developed by us in order to obtain samples that scatter significantly less than established methods.

[1] F. Perakis, P. Hamm: Two-dimensional infrared spectroscopy of neat ice Ih, Phys. Chem. Chem. Phys., 2012, 14, 6250-6256

### 32. Transient Terahertz spectroscopy of UV photoionized water

Arian Berger, Saima Ahmed, Janne Savolainen, Peter Hamm

[arian.berger@chem.uzh.ch](mailto:arian.berger@chem.uzh.ch)

The kinetics of the hydrated electron in its generation were studied by transient terahertz spectroscopy by Savolainen et al. (Nature Chemistry, 6(8): 697-701, 2014). There the photoionization of the water was achieved by the use of 800 nm, 400 nm and 267 nm pulses. To paint a more complete picture, this series was extended to a wavelength of 200 nm, where the photoionization of water by two photon absorption, has been explored more extensively.

### 33. Parametrization of Ion Force Fields for Polarizable Water Models

David Sidler, Peter Hamm

[david.sidler@uzh.ch](mailto:david.sidler@uzh.ch)

The experimental 2D-Raman-THz response of water was published recently [1]. With this method it is possible to measure the dynamics of the extended hydrogen bonding network in water. Recently, these measurements have been extended to salt solutions and showed a significant change in the response for strongly hydrated cations.

Since the signals measured are very complex, we need MD simulations to support interpretation. In order to simulate the 2D-Raman-THz response of aqueous salt solutions, a force field is needed which can describe both the dynamics of the system as well as the dipole moment. The TL4P water model [2] qualitatively reproduces features of the bulk response of water. For that reason, polarizable force field parameters for ions are developed for the use in the TL4P water model.

[1] J. Savolainen, S. Ahmed, and P. Hamm, Proc. Natl. Acad. Sci. U. S. A. 110, 20402 (2013)

[2] P. Tröster, K. Lorenzen, M. Schwörer, P. Tavan, J. Phys. Chem. B, 117, 9486 (2013)

### 34. 2D Raman-THz Spectroscopy of Aqueous Salt Solutions

Andrey Shalit, Saima Ahmed, Peter Hamm

[andrey.shalit@chem.uzh.ch](mailto:andrey.shalit@chem.uzh.ch)

The change in the viscosity ( $\eta$ ) of water upon addition of simple inorganic salt is described fairly well by the semiempirical Jones-Dole equation  $\eta/\eta_0 = 1 + Ac/2 + Bc$  when  $\eta_0$  is viscosity of water,  $c$  is a concentration and  $A$  and  $B$  are empirical coefficients. Based on the sign of the  $B$ -coefficient the ions are usually classified as “structure maker” ( $B > 0$ ) or “structure breakers” ( $B < 0$ ) based on their ability to increase/decrease viscosity upon solvation. However the consistent molecular level picture beyond this classification, namely how and to what extent ions perturbed the water structure, is still missing. The intensive experimental and computational studies applied for the these systems suggesting a very diverse interpretation of the obtained data to the point that Alan Soper noticed that “the range of statements on the effect of ions perturbing the local structure of water is so wide that it can be equally concluded that either most or almost none of the water molecules in solutions are influenced by the presence of the ions...”. Here we apply a recently developed 2D Raman-THz spectroscopy to investigate the effect of ions on the structural and dynamical properties of water. Unlike common two-dimensional spectroscopies in IR regime, this method interrogates the hydrogen-bond stretching and bending modes of liquid water in the low frequency range, thus allowing to observation of the dynamics of the collective intermolecular motion directly. We demonstrate that direct comparison of the 2D Raman-THz response of pure water with the series of chloride salts reveal the extended relaxation component along the  $t_1 = t_2$  diagonal in the 2D plot as the “structure making” ability

of the cations are increased. As in case of conceptually similar 2D Raman spectroscopy the signal along  $t_1=t_2$  reflects the degree of the inhomogeneity of the intermolecular motion. The observed trend of the increasing of the relaxation times (relative to water) qualitatively correlates with the empirical Jones-Dole B-coefficients allowing to connect the macroscopic observable (viscosity) to microscopic hydrogen bond networks dynamics.

## Christoph Hauri

### 35. Large optical spectral broadening triggered by intense THz field

Carlo Vicario, Mostafa Shalaby and Christoph Hauri

[carlo.vicario@psi.ch](mailto:carlo.vicario@psi.ch)

According to the field strength, THz radiation can drive linear and nonlinear response of the matter. We present nonlinear electro-optical interaction and strong cross-phase modulation (XPM) on an optical pulse driven by intense single-cycle terahertz (THz) field. THz pulses carrying energy up to 50  $\mu$ J and frequency contents in the range between 0.1 and 5 THz are realized by optical rectification in organic crystal DSTMS. The radiation is focused to diffraction-limited waist for the realization of field strength up to 10 MV/cm. The time-dependent evolution of the THz electric field induces transient XPM leading to significant spectral modification and broadening of a co-propagating 60 fs, 800 nm probe pulse. At the maximum amplitude, the THz field strongly changes the optical index of refraction of the EO crystal resulting in large spectral broadening and shift of the central wavelength. At the positive and negative THz peaks the optical spectrum is enlarged by more than a factor 3. The THz-induced XPM effect presented here can be used to control the spectral and temporal properties of an optical pulse on femtoseconds time scale.

### 36. Development of 83 MV/cm $\lambda$ 3 THz bullets / Anomalous THz imaging with CCD

Mostafa Shalaby, Carlo Vicario, Christoph Hauri

[mostafa.shalaby@psi.ch](mailto:mostafa.shalaby@psi.ch)

Recent developments in pulsed Terahertz sources opened new perspective for controlling optical and electronic properties of matter on a sub-cycle timescale. Intense THz pulses are of particular interest for the future THz-pump/X-ray-probe experiments at the SwissFEL. In the first part of the talk, I will present the high-power single-cycle THz laser developments pursued at the SwissFEL laser group [1] and discuss a scheme to reach the physical limits of pulse energy confinement (3D THz bullets), in space (diffraction limit) and time (transform limit) [2]. This regime allowed us to reach low frequency THz fields as high as 8 GV/m and 26 T (that is an order of magnitude more intense than the state-of-the-art).

In the second part, I will present various preliminary experiments with the THz bullets:

- (1) Imaging: next-generation 2-dimensional THz detectors based on CCD technology which provides significantly higher spatial resolution, a larger chip area and faster readout compared to the conventional bolometric detectors [3].
- (2) Gas photonics: Assessment of THz induced nonlinearities in the propagation (ambient air) medium [4].
- (3) Solid state: Ultrafast THz-induced demagnetization and damage of common magnetic materials [5].
- (4) Nonlinear optics: octave-spanning spectral broadening by cross-phase-modulation [6].

[1] C. Vicario, et al, Opt. Lett. **39**, 6632 (2014)

[2] M. Shalaby, C. Vicario, C.P. Hauri, Nature Commun. **6**, 8439 (2015).

[3] M. Shalaby, C.P. Hauri, Appl. Phys. Lett. **106**, 181108 (2015).

[4] M. Shalaby, C.P. Hauri, Nature Commun. **6**, 5976 (2015).

[5] M. Shalaby, C. Vicario, and C.P. Hauri, arXiv:1506.05397.

[6] C. Vicario, M. Shalaby, and C.P. Hauri (in preparation).

## Matthias Hengsberger – Jürg Osterwalder

### 37. Phase retrieval problem in molecular orbital imaging

P. Kliuiev, T. Latychevskaia, H.-W. Fink, J. Osterwalder, M. Hengsberger, L. Castiglioni [kliuiev@physik.uzh.ch](mailto:kliuiev@physik.uzh.ch)

We present a technique for the complete reconstruction of molecular electronic wave functions including the phase, from angular resolved photoelectron spectroscopy (ARPES) data. ARPES of oriented molecules on single-crystalline metal substrates was shown to provide rich information on the molecular orbital structure [1,2]. If the photoelectron final state can be treated as a plane wave, then the ARPES intensity is proportional to the squared

modulus of the Fourier transform of the initial state wave function [1]. The phase of the complex-valued photoelectron distribution in the detector plane is lost in the measurement, but can be found by adapting iterative phase retrieval methods known in optics [3,4], provided the intensity in the detector plane is measured at so-called oversampling condition and some a priori knowledge about the object is known [3,4]. In this work, we draw an analogy between the molecular orbital imaging via ARPES and optical coherent diffractive imaging of microstructures and discuss the main problems of related phase retrieval.

We present molecular orbital reconstructions from simulated and experimental ARPES data and address the limitations of the plane wave approximation for the final state [5].

[1] Puschnig, P. et al. Reconstruction of Molecular Orbital Densities from Photoemission Data. *Science* 2009, 326, 702-706.

[2] Lueftner, D. et al. Imaging the wave functions of adsorbed molecules. *PNAS* 2014, 111, 2, 605-610.

[3] Fienup, J. R. Reconstruction of an Object from the Modulus of Its Fourier Transform. *Optics letters* 1978, 3, 27-29.

[4] Fienup, J. R. Phase Retrieval Algorithms: A Comparison. *Applied optics* 1982, 21, 2758-69.

[5] Bradshaw A. et al. Molecular orbital tomography for adsorbed molecules: is a correct description of the final state really important? *New Journal of Physics* 2015, 17, 013033."

### 38. Following the molecular motion of THz excited CO on Pt(111)

Kay Waltar, Luca Castiglioni, Johannes Haase, Michael Greif, Tibor Nagy, Maksym Soloviov, Markus Meuwly, Jeroen A. van Bokhoven, Jürg Osterwalder and **Matthias Hengsberger** [waltar@physik.uzh.ch](mailto:waltar@physik.uzh.ch)

Due to the pressing need for better catalysts a strong research effort is put into time-resolved investigations of the geometrical structure of adsorbates. The overall structural dynamics of surface catalytic systems is found to be on the (sub-)picosecond timescale with typical bond lengths in the 100 pm range. Attempts to resolve these dynamics by optical means require wavelengths and pulse durations on a similar length- and timescale. X-ray photoelectron diffraction (XPD) is a technique that provides possibilities to elucidate the molecular adsorption geometry. Combining a suitable trigger for the adsorbate mode of interest and XPD (excited by a short XUV pulse) into a pump-probe scheme may therefore yield time-resolved information about the geometrical orientation of adsorbates. In the present study we investigate the feasibility of employing XPD to follow the molecular motion of near-resonant excited CO on Pt(111). A THz-pump and x-ray-probe experiment is simulated in which a 2 THz-pump pulse coherently excites a frustrated translational mode of an ensemble of CO molecules. The momentary alignment of the CO molecule is then directly probed by XPD. The XPD pattern is governed by a pronounced forward scattering of the C1s core level along the C-O bond. From this study, important conclusions on the timescale of the triggered adsorbate motion can be drawn. THz fields are typically strongly screened at metal surfaces and the effective field at the surface is close to zero. We hence design specifically tailored surface structures to reduce such screening effects and have a sufficiently strong field at the surface to excite the adsorbed molecules. Static XPD experiments to investigate the C 1s forward scattering peak of CO on thin Pt(111) films are currently underway and will be discussed.

### Steve Johnson

### 39. THz near-field enhancement by means of isolated dipolar antennas: the effect of finite sample size

Matteo Savoini, Sebastian Grübel, Salvatore Bagiante, Hans Sigg, Thomas Feurer, Paul Beaud and **Steven L. Johnson** [matteo.savoini@psi.ch](mailto:matteo.savoini@psi.ch)

Generation of high intensity Terahertz radiation in the low frequency region ( $f < 5$  THz) is still a challenging task and only few experimental demonstrations exceeding 1 MV/cm have been reported so far [1-5]. One viable option is the use of resonant metallic structures which act as amplifiers for the impinging radiation. Here with the aid of finite difference time domain simulations, we design and realize a set of isolated resonant elements which allow us to reach a 28-fold enhancement of freely propagating THz radiation at  $f \approx 1$  THz. This enhancement is measured directly with a simple setup, based on electro-optical measurements. Interestingly, we experimentally show strong modifications of the antennas resonance, which can be interpreted in terms of interference effects. These are particularly important in samples thinner than half the spatial pulse length [6]. We will also present preliminary data in the coherent control of the ferroelectric polarization of Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> using antennas-enhanced THz pulses.

[1] M. Liu, et al., *Nature* 487, 345-348 (2012).

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[3] A. J. L. Adam, *J. Infrared Milli. Terahz. Waves*, 32, 976-1019 (2011).

[4] C. Schaafsma, et al., *New Journal of Physics* 15 015006 (2013).

- [5] M. Shalaby, and C. P. Hauri, Nat. Comm. 6, 5976 (2014).  
[6] M. Savoini et al., Opt. Express, submitted (2015).

## 40. Reflection mode THz time domain spectroscopy

Martin Kubli, Lucas Huber and **Steve Johnson**

[Kublim@phys.ethz.ch](mailto:Kublim@phys.ethz.ch)

THz time-domain spectroscopy uses coherent pulses of electromagnetic radiation to obtain information about the frequency range typically between 0.1 and 5 THz. One unique feature is that the phase information can be measured directly, which eliminates the need for calculating the complex conjugate via the Kramer-Kronig relationship. So far, most THz-based spectrometers work in transmission mode, which requires that the sample thickness be comparable to or less than an absorption length of the THz radiation. For some samples where this is not the case the ability to measure in reflection would be preferable. Reflection geometry measurements would have the added benefit of circumventing limitations due to the etalon effect. [1]

The biggest drawback of working in reflection is the need for high precision (< 1 micron) in positioning the sample and reference. We report on the design and implementation of a spectrometer that uses a white light interferometer to measure the relative position of the sample and reference. Current work is proceeding on characterizing the impact of the remaining positioning uncertainty and comparing the results to transmission measurements.

- [1] P. U. Jepsen and B. M. Fischer, OPTICS LETTERS, Vol. 30, No. 1 (2005)

## 41. Structural dynamics in a prototypical shape memory alloy

Gabriel Lantz, Martin Kubli, Matteo Savoini, Vincent Esposito, Elsa Abreu, Kelin Tasca, Paul Beaud, **Steven L. Johnson**

[lantzg@phys.ethz.ch](mailto:lantzg@phys.ethz.ch)

Magnetic memory shape alloys with magnetically induced strain up to 10% have already several technological applications [1]. The Heusler alloy Ni<sub>2</sub>MnGa is the model system for these compounds. The phase transition between the high temperature phase, austenitic phase, and the low temperature, martensitic phase occurs simultaneously with the appearance of a superlattice modulation preceding the phase transition [2]. In order to understand this, a charge density wave (CDW) scenario was suggested [3-4]. Time-resolved techniques have been able to identify the amplitude mode of the CDW in the low temperature phase [5-6]. However, the pre-martensitic phase had not yet been fully explored. Here, we report a structural dynamic study in the pre-martensitic phase using time-resolved X-ray diffraction. The fluence dependence shows a complex behavior showing a modification of the underlining CDW potential.

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[2] S. O. Mariager, et al., Acta Mater. 66, 192–198 (2014).  
[3] S. M. Shapiro, et al., Europhys. Lett. 77, 56004 (2007).  
[4] C. P. Opeil, et al., Phys. Rev. Lett. 165703, 1–4 (2008).  
[5] S. O. Mariager, et al., Appl. Phys. Lett. 100, 261911 (2012).  
[6] M. Schubert, et al., Phys. Rev. Lett. 115, 076402 (2015).

## 42. Ultrafast dynamics of TbMnO<sub>3</sub> seen via broadband reflectivity changes

T. Kubacka, E. Baldini, B.P.P. Mallett, A. Mann, M. Yazdi-Rizi, S.M. Koohpayeh, C. Bernhard, F. Carbone, **S.L. Johnson**

[tkubacka@phys.ethz.ch](mailto:tkubacka@phys.ethz.ch)

Excitation of the d-d transitions of the multiferroic TbMnO<sub>3</sub> results in sublattice demagnetization over several tens of picoseconds, as has been shown using time-resolved resonant x-ray diffraction [1]. Here we look at the dynamics of TbMnO<sub>3</sub> upon 800nm excitation probing it over a wide range of wavelengths in the visible region of the spectrum. First, we see that the time-resolved changes in the optical spectrum resemble the changes seen upon thermal heating, and that the timescale of the process roughly matches the timescale of the demagnetization dynamics. Second, superimposed on the long-timescale dynamics we observe oscillations which we interpret as multiple coherent phonon modes excited via the ISRS mechanism. Up to three modes can be distinguished in the part of the spectrum associated with the peak of the main d-d absorption feature, while no clear oscillations can be seen in other parts of the spectrum. The data suggest that the sample reacts to the excitation in a complex way, which can be compared to behavior of prototypical magnetoelectric Cr<sub>2</sub>O<sub>3</sub> on one hand, and to a parent manganite LaMnO<sub>3</sub> on the other.

\*TK and EB contribute equally to this work

[1] J. A. Johnson et al., Magnetic order dynamics in optically excited multiferroic TbMnO<sub>3</sub>, Phys. Rev. B 92, 184429 (2015)

### 43. Ultrafast polarization dynamics in TbMnO<sub>3</sub>, induced by high THz field transients

Elsa Abreu, Teresa Kubacka, **Steven L. Johnson**

[elsabreu@phys.ethz.ch](mailto:elsabreu@phys.ethz.ch)

Quantum materials are characterized by a strong interplay of charge, lattice, orbital and spin degrees of freedom. Of particular interest is the coupling between spin and charge order through the magnetoelectric effect, which can lead to electric field control of magnetic properties. Multiferroics are ideal candidates for this type of application due to the coexistence of electric and magnetic order they exhibit.

TbMnO<sub>3</sub> is a well-studied rare earth manganite which becomes multiferroic at low temperatures. Below 41K it orders antiferromagnetically. Below 27K the magnetic order changes from sinusoidal (almost along the b-axis) to cycloidal (in the bc-plane) and a ferroelectric polarization arises along c. In the multiferroic phase electromagnons are detected in the 0.5-2THz range using electromagnetic fields polarized along the a-axis. These electric-dipole active magnetic excitations can be used as a tool to investigate the dynamics of the multiferroic state, and help reach the ultimate goal of tailoring and controlling the magnetoelectric interaction.

Our approach relies on using high THz field pulses to drive the electromagnons, and on detecting the subsequent dynamics with magnetic and electric order probes. An initial THz pump experiment was performed at the Linac Coherent Light Source (LCLS) [1]. The THz pulse was seen to resonantly excite the spin cycloid, whose dynamic response was tracked using time-resolved resonant x-ray diffraction sensitive to the Mn magnetic order, thereby demonstrating that THz pulses can drive electromagnon excitations.

In this poster we present our ongoing efforts to address the precise coupling mechanism that follows the THz excitation and leads to magnetic order disruption. One possibility, discussed in [1], is that the THz field induces a rotation of the Mn spin cycloid away from the bc-plane. This can be tested by following the static ferroelectric polarization, which acts as a signature of the cycloid strength and structural orientation. Our experimental setup enables time resolved reflectivity measurements of the bulk sample birefringence following THz excitation.

[1] T. Kubacka et al., Science 343, 1333–1336 (2014).

### 44. Time resolved differential time domain spectroscopy of phonons in the range of 1-10 THz

Lucas Huber, **Steven Johnson**

[huberluc@phys.ethz.ch](mailto:huberluc@phys.ethz.ch)

We report on our recent progress in the development of a gas based time domain spectrometer measuring pump induced changes in reflectivity in the frequency range between 1-15 THz. In our current implementation we typically reach signal to noise ratios of 200 at a spectral resolution of 70 GHz in the range between 1-5 THz, while the SNR drops below 20 above 10 THz. Being fully gas based, the spectral resolution is only limited by window thickness and optical drift. However, achieving high resolution requires extensive time traces, which increases acquisition times and limits the temporal resolution of the pump-probe experiment. Preliminary results on Si, CuO and SrMnO<sub>3</sub> are given to show the potential and limitations of the device in the current state.

**Ursula Keller**

### 45. Thin-Disk-Laser-Driven High-Harmonic Generation at MHz Repetition Rate

Andreas Diebold, Florian Emaury, Clara J. Saraceno, **Ursula Keller**

[diebold@phys.ethz.ch](mailto:diebold@phys.ethz.ch)

We demonstrate, for the first time to the best of our knowledge, a compact XUV source based on high harmonic generation (HHG) at 2.4 MHz repetition rate from the compressed output of a modelocked thin disk laser oscillator. The SESAM modelocked Yb:YAG thin disk laser delivers, after compression in a simple single-stage Kagome-type hollow-core photonic crystal fiber, an average power of up to 46 W in 108 fs pulses at 2.4 MHz repetition rate, which corresponds to a peak power of 105 MW. The overall layout of this infrared driving source for HHG is very compact with a footprint of approximately 1.2 m x 1.6 m and possesses low-noise performance comparable to standard ultrafast low-power oscillators. Focusing into a high-pressure Xenon gas jet with a peak intensity of  $5.5 \times 10^{13}$  W/cm<sup>2</sup> we generate XUV radiation with up to  $>5 \times 10^7$  photons/s on the 19th harmonic (23 eV). This result opens the path towards the next generation of compact high-repetition rate coherent XUV sources

driven solely by low noise passively modelocked diode-pumped solid-state laser oscillators. Such sources would be beneficial for a broad range of applications in which high-repetition-rate low noise XUV pulses are crucial, including ultrafast photoemission studies on solid surfaces or coincidence detection schemes in atomic and molecular physics.

#### **46. Attosecond transient absorption spectroscopy of silicon dioxide nanofilm**

Mikhail Volkov, F. Schlöpfer, M. Lucchini, A. Ludwig, L. Gallmann and **U. Keller** [volkovm@phys.ethz.ch](mailto:volkovm@phys.ethz.ch)

We report on the observation of sub-femtosecond electron dynamics in SiO<sub>2</sub> in a transient absorption experiment. We probe with XUV attosecond pulses the transient changes in the valence-to-conduction band transitions induced by strong NIR femtosecond laser radiation. The time- and energy-resolved absorption dynamics exhibits a complex oscillatory behavior with a periodicity of twice the NIR pump carrier frequency. We show, by varying the pump and probe sources, that the observed transient absorption features are characteristic of the material and do not depend on the measurement technique. We probe the lower (20-30 eV) and higher (30-50 eV) energy parts of the XUV absorption spectrum with attosecond pulses generated in Xe and Ar, respectively. Additionally, changing the parameters of the NIR nonlinear pulse compression allows us to investigate the effect of the pump carrier frequency. We suggest an interpretation based on a dynamical above-band-gap Franz-Keldysh effect.

#### **47. Asymmetric Wigner time delay in CO photoionization**

Jannie Vos, L. Cattaneo, S. Heuser, M. Lucchini, C. Cirelli and **U. Keller** [jvos@phys.ethz.ch](mailto:jvos@phys.ethz.ch)

Here, we report on the asymmetric Wigner time delay in the photo-ionization of CO-molecules excited by an XUV-APT using the RABBITT measurement technique. Our angularly resolved detection of the fragment ions and photoelectron in coincidence allows for the reconstruction of the molecular recoil axis after ionization without pre-orientation. From this we are able to extract photoelectron angular distributions in the recoil frame, thereby distinguish between electrons emitted towards the C- or the O-fragment. Time delays are extracted for each electron ejected in the asymmetric Coulomb potential of the molecule and we observe an asymmetric relative time delay in the photoionization.

#### **48. Comparison between attosecond streak camera and RABBITT techniques**

S. Heuser, M. Sabbar, J. Vos, Laura Cattaneo, M. Lucchini, R. Boge, L. Gallmann, C. Cirelli and **U. Keller** [claura@phys.ethz.ch](mailto:claura@phys.ethz.ch)

The recent progress in the generation of ultra-short light pulses has enabled the determination of photoionization time delays with attosecond precision. The two dominating techniques used to investigate these electron dynamics are the attosecond streak camera or Streaking, and the reconstruction of attosecond beating by interference of two photon transitions or RABBITT. Both techniques are based on a pump-probe scheme, employing an extreme ultraviolet (XUV) single attosecond pulse (Streaking) or attosecond pulse train (RABBITT) as pump, and an infrared (IR) pulse as probe. In both cases only relative timing information between electrons originating from different states within the same atom or different atoms can be extracted. Here it may arise the question whether the two methods give the same answer. In this work we present a complete study, supported by both experiments and simulations, about the comparison of these two techniques when the photoemission time delay between valence electrons emitted from Ne2p and Ar3p ground states is investigated. We highlight not only their differences and similarities but also critically investigate the robustness and reliability of the calculations used to extract the timing information.

#### **49. Non-Dipole Effects on Rescattered Photoelectrons from Strong-Field Ionization with Elliptical Polarization**

Benjamin Willenberg, Jochen Maurer, Benedikt W. Mayer, Christopher R. Phillips, Lukas Gallmann, **Ursula Keller** [bwillenb@phys.ethz.ch](mailto:bwillenb@phys.ethz.ch)

We study strong-field ionization of rare gases beyond the long wavelength limit of the dipole approximation using elliptically polarized mid-IR laser pulses. Rescattering of the released photoelectrons with the parent ion leads to a sharp line-like structure along the major polarization axis in the 3D photoelectron momentum distribution (PMD), which is significantly influenced by the non-dipole effects. For linear polarization, a shift of the maximum of the

projected PMD opposite to the beam propagation direction was recently reported in [1]. This observation can be explained by the combined action of the magnetic field of the driving laser pulse and the Coulomb field of the parent ion. When scanning the ellipticity from linear to circular polarization the shift changes from opposite to the beam propagation direction to a shift in beam propagation direction.

[1] A. Ludwig et al., Breakdown of the Dipole Approximation in Strong-Field Ionization, Phys. Rev. Lett. 113, 243001 (2014)

## Markus Meuwly

### 50. Computational study of state-resolved collisions between $N_2^+(X)$ cations and Ar atoms

Juan Carlos Castro-Palacio, Oliver T. Unke, Raymond J. Bemish and **Markus Meuwly** [oliver.unke@unibas.ch](mailto:oliver.unke@unibas.ch)

The collisional dynamics of  $N_2^+(X)$  cations and Ar atoms is studied by using molecular dynamics (MD) simulations.  $N_2^+-Ar$  is a proxy to study cooling of molecular ions and interesting in its own right for molecule-to-atom charge transfer reactions. An accurate potential energy surface (PES) is constructed from a reproducing kernel Hilbert space (RKHS) interpolation based on high-level ab initio data. The global PES including the asymptotics is fully treated within the realm of RKHS. From several ten thousand reactive trajectories, the final state distribution of the rotational quantum number of  $N_2^+$  after collision with Ar is determined. Contrary to the interpretation of previous experiments which indicate that 98 % of collisions are elastic and conserve the quantum state, the present simulations find a considerably larger number of inelastic collisions. This has important consequences for future experiments which capitalize on the cooling of quantum state-defined ions.

### 51. A Force Field Approach to Reproduce Grothuss Mechanism in Reactive Systems

Zhen-Hao Xu and **Markus Meuwly**

[z.xu@unibas.ch](mailto:z.xu@unibas.ch)

Theoretical studies of Grothuss mechanism in the bulk phase, which involves with fundamental charge transport processes in biochemical systems, is a long-standing problem in computational chemistry. The MMPT force field in CHARMM is proven trustful in simulating proton transfer processes in the gas and condensed phases. In this work, the extensive developments of MMPT force field shows new advances in delocalizing the reactive sites in multi-molecular systems. By introducing global potential energies with mixed multi-surfaces, which corresponds to combinatorial recognition of donor-proton-acceptor (D-H-A) motifs, it is feasible for all hydrogen atoms to complete transfer moves in the water bulk with excess protons. Meanwhile, a transferable point charge model is employed to improve the diffusibility of positive charges throughout all water molecules in the system."

### 52. Modelling of Benzonitrile as a Spectroscopic Probe in Lysozyme

Padmabati Mondal, Pierre-Andre Cazade and **Markus Meuwly**

[padmabati.mondal@unibas.ch](mailto:padmabati.mondal@unibas.ch)

Being in the spectral window of proteins and peptides, nitrile group has been extensively studied theoretically and experimentally as infrared spectroscopic probe for proteins. Benzene in the active site of a specific mutant (L99A) of T4 phase lysozyme was found to stabilize the enzyme [1]. Combining benzene and nitrile group, herein, we focus on the modelling of benzonitrile as a spectroscopic probe in T4 phase lysozyme with the aim of speeding up the protein-ligand interactions. Different models of CN bond (Harmonic/Morse) and electrostatics (Fixed/Fluctuating point charge) are explored to find the best to reproduce the experimental results of benzonitrile using a recent spectroscopic implementation [2] in CHARMM molecular dynamics simulation package. The forcefield parameters are extracted from the fitting of ab initio data obtained using MP2/aug-cc-pvDZ method/basis-sets and by reproducing gas phase experimental peak of nitrile group in benzonitrile at 2242  $cm^{-1}$ . The peak is found to be redshifted in presence of water. Lineshape function is calculated using the parameters obtained by the tri-exponential fitting of frequency fluctuation correlation function. After accounting for the lifetime of the excited state, the FWHM of the calculated 1D-IR spectrum is 4  $cm^{-1}$  which compares with the experimental value of 9  $cm^{-1}$  [3]. 2D-IR spectra of benzonitrile in water are calculated by the fourier transformation of the response functions which were obtained using the lineshape function and with the cumulant expansion truncated after second order. Using the results of benzonitrile in water as reference, the peak shift, intensity changes, time scale of spectral diffusion of benzonitrile in different mutants of T4 lysozyme are calculated and compared to investigate the effect of protein-ligand interaction (especially the electrostatics) on the vibrational spectra benzonitrile.

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### **53. The sigma-hole is larger than the halogen alone: solvent dynamics around halogenated benzenes**

Krystel El Hage, Tristan Bereau, Sofie Jakobsen and **Markus Meuwly**

[krystel.elhage@unibas.ch](mailto:krystel.elhage@unibas.ch)

The considerable interest of halogen bonding in medicinal chemistry motivated the development of empirical force fields to capture the sigma-hole in order to accurately compute ligand binding free energies. The present work provides a systematic investigation of the importance of higher order MTPs on specific sites of halobenzenes for dynamical properties in condensed-phase simulations. Solute-solvent interactions using PC, MTP and mixed PC/MTP electrostatic models have been analyzed in regions of halogen bonding and p-orbitals of phenyl carbons, where commonly used PC force fields fail in providing an accurate ESP representation of the sigma-hole feature. Using molecular dynamics simulations and quantum chemical methods it is found that the sigma-hole does not only affect the halogen or the CX bond but it extends to the carbon atoms linked to it and to the carbons adjacent to the CX carbon; In addition, when passing to the water phase, the sigma-hole affects also the organization of the water network and the water-residence time around the halogen and around the compound, which also depends on the type of the halogen and the size of the sigma-hole. The established computational approaches for accurate solvation free energies of halogenated benzenes, provides a microscopic explanation why point charge-based representations fail in doing so. Hence, halogenation is one of the cases for which advanced molecular simulation methods are mandatory for quantitative and predictive studies. In addition, computationally efficient hybrid PC/MTP models are proposed which capture most of the important energetic and solvent exchange dynamical properties."

### **54. Nitrogen monoxide rebinding to wild-type and mutant myoglobins**

Polydefkis Diamantis, **Markus Meuwly**

[polydefkis.diamantis@unibas.ch](mailto:polydefkis.diamantis@unibas.ch)

The interaction of diatomic gas-phase molecules with myoglobin is of high importance for the physiological function of living organisms. Under this scope, the interaction of oxygen (O<sub>2</sub>), nitrogen monoxide (NO) and carbon monoxide (CO) with myoglobin has been extensively investigated from a physico-chemical perspective. Here, we aim at studying the kinetics of geminate rebinding of NO to wild-type (wt) and 12 mutant myoglobins, using multisurface adiabatic reactive molecular dynamics (ARMD) simulations [1]. Different mutations were considered for leucine 29, histidine 64 and valine 68. These three amino acids are all involved in myoglobin's binding site. Rebinding events were recorded for up to 200 picoseconds for each system. Our results show that depending on the mutation, the effect on the rebinding kinetics and on the rebinding fraction varies. For example, replacement of small amino acids (leucine, valine) with larger ones (phenylalanine, tryptophan) leads to an increase of the rebinding fraction, as well as to an overall acceleration of the rebinding process. Depending on the system, the rebinding fractions observed in the simulations range from 40% to almost 100% within 200 ps. In agreement with experimental findings [2]-[3], our results indicate that for all 13 myoglobins investigated here, the overall NO rebinding process can be divided to a fast and a slow sub-process. Amongst the 13 myoglobins, the decay time for the fast rebinding sub-process varies between 5 ps and 30 ps. The decay time of the slower sub-process is found to be in the range of hundreds of picoseconds.

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### **55. Mechanistic Study of Denitrification Reaction in Truncated Hemoglobin using Adiabatic Reactive Molecular Dynamics**

Akshaya Kumar Das, Tibor Nagy and **Markus Meuwly**

[akshaya.das@unibas.ch](mailto:akshaya.das@unibas.ch)

Proteins such as truncated hemoglobin (trHbN) binds oxygen cooperatively with very high affinity and a slow dissociation rate. Understanding the kinetics of binding of nitric oxide (NO) to the oxygenated hemoglobin (trHbN) gains increased interest as it plays an important role in bacterial detoxification and nitrosative stress[1,2]. Many studies have been carried out on trHbN but it is not clear how the denitrification reaction takes place in trHbN

(reaction sequence shown below). Mechanistic details of binding of NO to the oxygenated trHbN was studied here using force field based multi surface adiabatic reactive molecular dynamics (MS-ARMD) as implemented in CHARMM[3]. Although {it ab initio} MD or hybrid QM/MM can be used to study such process. However, they do not allow to sample the phase space exhaustively because of high computational cost. On the other hand we successfully parametrized the force field for the above process with sufficient accuracy, which allow to exhaustively sample the phase space and in turn offers meaning full energetics and rate constant for the NO replacement reaction (Expt. rate constant  $4.36 \times 10^7 \text{ M}^{-1}\text{S}^{-1}$ ) [4,5].



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## 56. A new toolkit for fitting forcefield parameters used for Permanent Multipoles molecular simulations

Florent Hédin, Krystel El Hage, Markus Meuwly

[florent.hedin@unibas.ch](mailto:florent.hedin@unibas.ch)

Permanent atomic multipoles (MTPs) are an extension to common point-charge (PC) representations in atomistic simulations[1][2][3]. MTPs are commonly fitted from an ab initio electrostatic potential, and the ability of simultaneously fitting several molecules and/or conformations usually increases parameters' transferability. In a second time when PCs or MTPs have been fitted, it is also possible if required to optimise Lennard-Jones (LJ) parameters by using a Molecular Dynamics (MD) package [3][4]. Here we present a unified toolkit gathering in one package all the scripts and processing steps ([3][4]), required for the MTPs fitting procedure.

It provides:

- (1) ability to load coordinate files in several formats (XYZ, PDB, ...),
- (2) setting and execution of the ab initio simulation (Gaussian 09),
- (3) preparation of the fitting step (like custom atom typing),
- (4) execution of the fit and visualisation of results (JMOL, VMD).
- (5) MTPs parameters are used for setting up and running a MD simulation. Several target thermodynamic properties of interest, such as density, enthalpy of vaporization, free energy of hydration, are chosen, and the LJ parameters are scaled until the desired properties of interest are reproduced with a sufficient accuracy.

The software also includes a connection to a database of compounds where the user can find, for a given molecule, reference values for the mass, density, and a few thermodynamic observable. Built on a collaborative model, this database will grow in size as users submit new compounds or edit existing ones. This software will be available under an open-source license, facilitating a possible extension to other ab initio or MD packages.

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[3] C. Kramer et al, Journal of Chemical Information and Modeling, 2013 53 (12), 3410-3417

[4] K. El Hage et al., Journal of Chemical Theory and Computation, submitted.

## 57. Reactive molecular dynamics simulations of photodissociation processes of small molecules

Sebastian Brickel, Markus Meuwly

[sebastian.brickel@unibas.ch](mailto:sebastian.brickel@unibas.ch)

Photodissociation dynamics of small molecules in gas and condensed phase give insight in intermolecular interactions. Those electronic excitation processes can be characterized as immediate; when dissociation occurs directly from the Franck-Condon region; or as delayed; when the molecule has a specific lifetime on the excited electronic state before dissociating [1]. The latter is the case for the vibrationally induced photodissociation of HSO<sub>3</sub>Cl. This molecule, which can be used as a prototype system for experimental analysis of the atmospheric processes of H<sub>2</sub>SO<sub>4</sub> [2]. Dissociates after excitation of the OH-stretch mode. Reactive molecular dynamic simulations[3] of HSO<sub>3</sub>Cl reveal that two processes, HCl elimination proceed by intramolecular H-transfer and direct HCl elimination, compete with one another on the ns time scale [4]. A prototype system for studying immediate photodissociation is ClCN. Simulations of ClCN in water can give insight into the dynamical role of the

solvent, which is particular important for biochemical reactions [5]. Final state energy distribution of internal degrees of freedom can be predicted from the MD simulations, which should be observable in experimental measurements.

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## 58. Oxygen-Atom Diffusion on Amorphous Solid Water in Interstellar media

Marco Pezzella, Markus Meuwly

[marco.pezzella@unibas.ch](mailto:marco.pezzella@unibas.ch)

The presence of O<sub>2</sub> in interstellar media is considered important for understanding the origins of the interstellar clouds. This molecule is found only in two clouds, characterized high temperatures and low concentrations of N<sub>2</sub> [1]. Due to a lack of information, the formation mechanism of this molecule remains unclear. The surface of dust particles are considered catalyst for this reaction. For this study Amorphous Solid Water is chosen, due to its high concentration in space. The rough nature of the water surface allows the O-atoms to be stored inside cavities; a second atom, diffusing on the surface can interact with the first one and form O<sub>2</sub>.

The first step is to understand how the O-atom diffuses. In order to obtain this data, Monte Carlo Simulations are run on a water surface. Due to the lower temperature, only translation of the O-atom is considered. This information is stored in a two dimensional grid, obtaining the Maxwell Boltzmann Distribution at equilibrium conditions and in Free Energy Surface (FES). Barriers (1-1.6 kcal/mol) and pathways between different regions of the surface are obtained. The FES is interpolated and used to analyze how the distributions evolve in time. The probability for each distribution is then calculated for each cavity. It corresponds to an atom that arrives in one cavity and then diffuses on the surface [2]. The timing of the diffusion is heavily influenced by the cavities: the morphology of the surface remains unaltered for 300 ps. If the atom is trapped inside a cavity of height 1.2 kcal/mol, it will be trapped inside for nanosecond time scale. The results are compared with Molecular Dynamics simulations, presents in literature [3] and ad hoc calculations. The model is showed valid.

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## 59. Vibrational excitation/relaxation of NO (2Π) in collision with O(3P).

Otoniel Denis Alpizar, Markus Meuwly

[otonieldenisalpizar@gmail.com](mailto:otonieldenisalpizar@gmail.com)

The reactions involving N and O atoms plays a major role in the energetics of the reactive air flow around spacecraft during the atmospheric reentry. A recent potential energy surface of NO<sub>2</sub> computed at the multireference configuration interaction level [1, 2] is used. Quasiclassical trajectory calculations are performed on this surface. From the initial vibrational states  $v = 5$  and  $v = 10$  of NO, the final states for each possible channel are investigated. This analysis showed that higher vibrational excitation facilitates the reaction, which is in agreement with the Polanyi's rule [3]. The dependence of the vibrational relaxation time with the temperature for the exchange channel is also studied. This behaviour is compared with the experimental results for other systems [4]. Finally, the non-equilibrium rate coefficients up to 2000 K for the exchange channel are reported.

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**Chris Milne**

## **60. Ultrafast photochemistry and photobiology at SwissFEL's Experimental Station A: A Status Report**

**Chris Milne**, Jakub Szlachetko, Joerg Schneider, Gregor Knopp, Joanna Czaplá-Masztafiak, Julien Réhault, Tadej Humar, Rafael Abela [chris.milne@psi.ch](mailto:chris.milne@psi.ch)

X-ray free electron lasers (XFELs) are 4th-generation X-ray sources, which produce very large numbers of X-ray photons ( $10^{11}$ - $10^{12}$ ) in very short pulse durations (1-100 femtoseconds). This makes them ideal for certain types of experiments, including time-resolved pump-probe experiments, single-shot experiments, and nonlinear x-ray experiments. The Swiss hard X-ray free electron laser SwissFEL started construction at the Paul Scherrer Institute in late 2012, with a planned startup date of 2017 for the ARAMIS hard x-ray undulator section. This poster will present an overview of the design and current status of Experimental Station A (ESA), which will be the first experimental station to come online in mid-2017. This instrument is designed to investigate ultrafast photochemical and photobiological processes using a range of X-ray techniques, including both scattering and spectroscopy. The poster will also present examples of our recent research where we have applied these techniques to investigate a variety of photophysics, including applying X-ray spectroscopy to probe DNA damage mechanisms, nonlinear X-ray optics, and ultrafast dynamics of functional materials. The poster will provide NCCR-MUST scientists with a vision as to how we expect ESA to allow researchers to perform investigations into a variety of fields.

**Jacques-E. Moser**

## **61. Photoinduced charge transfer mechanism in Diketopyrrolopyrrole(DPP) dye-sensitized solar cell**

Heewon Bahng, **Jacques-E. Moser**

[heewon.bahng@epfl.ch](mailto:heewon.bahng@epfl.ch)

Dye-sensitized solar cell (DSSC) has been reported as powerful alternative energy source since its potential for high conversion efficiency and low cost of production.[1] Especially, the use of organic sensitizer such as blue DPP-based dyes which is synthetically accessible, with high photostability, starts to receive attention as DSSC sensitizer by using donor-chromophore-anchor(D-C-A) concept.[2] Here, we explore photoinduced charge transfer pathways in blue-colored DPP based sensitizer adsorbed onto mesoporous wide-bandgap semiconductor, titanium oxide.

As kinetic competition between forward charge transfer and recombination processes greatly influences efficiency in DSSC, it is crucial to reveal the dynamics of holes and electrons following light excitation. By using time-resolved transient absorption spectroscopy, we monitor charge separation such as electron and hole injection at the sensitizer-semiconductor heterojunction probing the fs-ps time domain, and reveal the pathway of charge recombination at longer timescale up to the ms.

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## **62. Ultrafast electro-modulated differential absorption spectroscopy and THz spectroscopic investigation of carrier dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films**

Arun Paraecattil, Jelissa Risse, Joel Teuscher, Ahmad Zadeh, **Jacques E. Moser**

[arun.paraecattil@epfl.ch](mailto:arun.paraecattil@epfl.ch)

In ultrafast electro-modulated differential absorption (EDA) spectroscopy, we investigate the picosecond screening of the electric field induced (Stark) shift of a materials absorption spectrum by photo-generated carriers. The technique was employed to investigate the separation distance between photo-generated charge carriers of opposite sign upon drifting in illuminated methylammonium lead triiodide perovskite ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) insulated thin films. In addition we investigate the fluence dependent carrier formation and recombination dynamics. Our results highlight the importance of midgap and interfacial trap states in mediating the nature and rate of carrier recombination and transport across the perovskite thin film.

### 63. Ultrafast Stark Spectroscopy of Microstructures in $\text{CH}_3\text{NH}_3\text{PbI}_3$

Marine E. F. Bouduban, Arun A. Paraecattil, Amita Ummadisingu, Fabrizio Giordano, Joël Teuscher and **Jacques-E. Moser** [marine.bouduban@epfl.ch](mailto:marine.bouduban@epfl.ch)

Ever since their birth, hybrid lead-halide perovskite solar cells have kept their promises and proven an always more valid alternative to current solar cell technologies, with efficiencies rising above 20%. At this point however, a fundamental understanding of the key properties yielding such record efficiencies is still lacking. Similarly, it is known that the quality of the final device varies strongly upon : (i) the preparation method, (ii) the constituents of the perovskite material itself, (iii) the interface with electron-accepting and hole-accepting layers.

Herein, we aim at clarifying at the material level what are the limiting parameters towards maximized perovskite solar cells efficiencies. Observables in such a framework are the charge carriers mobilities within the perovskite layer and their extraction at the interfaces with selective transporting materials. Both properties are accessible via Electromodulated Differential Absorption spectroscopy (EDA). An external field is applied on a sample yielding an electroabsorption signal (EA, quadratic with the field). Then, upon pumping with an ultrafast laser pulse, charge carriers are generated that will move towards the electrodes, screening the external field. As a consequence, probing the dynamics of the EA signal (EDA, transient Stark effect) is a direct measurement of the charge carriers transport and extraction.

In this study, perovskite films yielding cells of drastically different qualities have been studied by ultrafast Electromodulated Differential Absorption (EDA) and Transient Absorption (TA) spectroscopy. We show that the material composition itself is not as much of a limiting factor as its interface with charge extracting layers.

**Ursula Röthlisberger**

### 64. LR-TDDFT Surface Hopping Simulations of the Excited State Dynamics of the Ethylene Cation

Elisa Liberatore, **Ursula Röthlisberger**

[elisa.liberatore@gmail.com](mailto:elisa.liberatore@gmail.com)

Ethylene and its cation have been intensively studied since several decades as model systems for photochemical reactions. Motivated by recent XUV-NIR pump-probe experiments performed in U. Keller's group at ETHZ, we carried out a DFT/TDDFT study of the ethylene cation. In these experiments the yield of charged fragments was monitored at different pump-probe time-delays and interesting features were registered. In particular, the production of  $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_2^+$  surprisingly increases at  $\sim 25$  fs time-delays. Trajectory Surface Hopping (TSH) simulations were performed to mimic the motion of the wave packet on the excited potential energy surfaces of the ethylene cation. The trajectories were initialized on the D1, D2 and D3 states that according to older experiments are believed to be the most populated after XUV ionization. Higher excitations, up to the D6 state were also considered for comparison. The excited state population, the conformational changes, and the fragmentation channels were monitored during the simulations. In absence of external perturbation (the NIR probe), only a few of the trajectories initialized on the lower excited states lead to H or  $\text{H}_2$  loss in the ground state. More fragmentation events, also in excited states, were instead observed for the other trajectories. Assuming equal initial population of the D2 and D3 states, after around  $\sim 25$  fs 45% of the total population is transferred to D1, while D2, D3 and D0 are almost equally populated. Further excitation from D1 to dissociative states could explain the observed enhanced fragmentation. However, we found no symmetry-allowed transition at energies corresponding to a NIR photon absorption. The NIR field is then more likely to give the system additional energy, that can be used to overcome dissociative barriers in the D1 or D0 states.

**Urs Staub**

### 65. Ultrafast all-optical switching of a multiferroic

E.M. Bothschafter, M.Savoini, M. Porer, M. Buzzi, Y.Windsor, C. Dornes, L. Rettig, M. Ramakrishnan, A. Alberca, S.R.V. Avula, D. Schick, N. Pontius, C. Schuessler-Langeheine, C. Piamonteze, S. L. Johnson, **U. Staub**

[elisabeth.bothschafter@psi.ch](mailto:elisabeth.bothschafter@psi.ch)

All-optical switching of ferromagnets has attracted tremendous interests as it opens up the possibility of ultrafast writing of magnetic bits for data storage applications. After its observation in simple ferrimagnetic GdCoFe [1], investigations showed that also other stacked ferromagnets do switch after excitation with an ultrashort laser pulse. The understanding of the origin of this effect remains highly controversial though. In improper multiferroic

materials the magnetic order can be directly coupled to a ferroelectric polarization. We investigate the possibility of switching this ferroelectric polarization by manipulation of the magnetic order using femtosecond light pulses. Such ultrafast magnetization and polarization switching is of fundamental interest for future light-based control of magnetic memory or data processing. One way of manipulating both the magnetic structure and the polarization state of a multiferroic is to directly address an electromagnon resonance via THz excitation [2]. Another scenario for ultrafast polarization switching is based on magnetization reversal. Here, we demonstrate that the ferromagnetic component of the strongly correlated multiferroic  $\text{CoCr}_2\text{O}_4$  can indeed be switched on ultrafast timescales by excitation of the material above the bandgap. This reverses both the Cr and Co sublattice magnetization as seen by a very recent optical-pump x-ray-probe experiment (Fig. 1). The observed switching of the magnetization in the multiferroic state will not only strongly impact models describing all-optical magnetization switching but also opens up a completely new way for simultaneous reversal of electric polarization on ultrafast time scales. Another interesting aspect of our study is that we can show that the switching process is x-ray assisted, as the switching occurs only after immediate irradiation with x-rays. This hints to a switching process related to a change in conductivity created by the x-ray absorption. The simultaneous reversal of magnetization and polarization will enable us to take advantage of the full strength of multiferroic materials for ultrafast applications through the coupling of their magnetic and electric order.

**André Stefanov**

## 66. Quantum tomography inspired pulse reconstruction

Stefan Lerch, **André Stefanov**

[andre.stefanov@iap.unibe.ch](mailto:andre.stefanov@iap.unibe.ch)

Quantum state tomography allows to reconstruct the density matrix of a system from the results of a well chosen set of projective measurements. By decomposition of a short laser pulse into a basis set of orthogonal functions, the pulse spectrum can be described by a complex vector, thus formally equivalent to a quantum state. The respective projections are realized by pulse shaping combined with sum frequency generation in a long crystal. We achieve faithful reconstruction of the even part of the spectrum and compare the reconstruction quality for different basis sets.

**Thomas Südmeyer**

## 67. Toward intracavity high harmonic generation with thin disk lasers.

Loïc Merceron, François Labaye, Clément Paradis, Maxim Gaponenko, Norbert Modsching, Andreas Diebold, Florian Emaury, Clara Saraceno, Valentin Wittwer, Ursula Keller and **Thomas Südmeyer**

[loic.merceron@unine.ch](mailto:loic.merceron@unine.ch)

High-order harmonic generation is very attractive for time-resolved studies due to its small size, low cost, good spatial coherence, brightness, tunability and ultrashort pulse duration. This extremely non-linear process finds a large number of applications in atomic[1], molecular[2], surface and solid state time-resolved spectroscopy. Unfortunately, intensities in the order of  $10^{13} \text{ W/cm}^2$  are required for energy conversion. State of the art sub-100 fs thin disk oscillators deliver pulses of only few watts of average power [4]. In order to reach higher intensities, the intracavity power can be used enhancing the intensity by a ratio of one over the output coupling rate. In this contribution, we present a study of thin disk laser SESAM mode-locked based on CALGO material that delivers pulses as short as 49fs, reaching intracavity peak power of 35 MW. In this regime, a sufficiently tight focus would lead to intensities high enough to enable high harmonic generation.

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## 68. Multi-megahertz repetition rate high power THz spectroscopy

Clément Paradis, Norbert Modsching, Loïc Merceron, François Labaye, Maxim Gaponenko, **Thomas Südmeyer**

[clement.paradis@unine.ch](mailto:clement.paradis@unine.ch)

Terahertz time domain spectroscopy is an excellent tool to gain insight into electron dynamics of numerous systems. In the NCCR MUST, it helps to understand processes in a wide range of materials as diverse as superconductors excited around their bandgap, ferroelectric materials, organic dyes for sensitized solar cells, or novel organic crystals. The University of Neuchatel advances these studies by providing a novel source of THz radiation, which operates at multi-megahertz repetition rates and is based on a high-power ultrafast thin-disk laser. This allows one to drive THz generation at average powers which are several orders of magnitude higher compared to standard femtosecond laser systems.

For the proof-of-principle experiment we built a mode-locked Yb:LuO thin-disk laser oscillator which operates at a wavelength of 1030-nm and produces pulses with energy of ~1-uJ and duration of 400-fs at a repetition rate of 43-MHz. The average output power of the laser exceeds 20-W. The first results of THz-radiation generation via optical rectification in GaP and ZnTe nonlinear crystals as well as further steps for power scaling will be presented.

## Jeroen van Bokhoven

### 69. Dissociation dynamics of dissolved halogenated methanes studied with time-resolved spectroscopy.

R. Bohinc, A. Schneider, G. Smolentsev, M. Nachtegaal, and **J. A. van Bokhoven**

[rok.bohinc@psi.ch](mailto:rok.bohinc@psi.ch)

The understanding of the carbon-halogen bond breakage in dissolved halogenated methanes is important because it can provide useful information for commercialized catalytic reactions, such as the Monsanto process. In the later reaction, the C-I bond breakage in CH<sub>3</sub>I and the subsequent reaction with an active metal (Rh or Ir) represents a fundamental reaction step in the synthesis of acetic acid from carbon monoxide and methanol. In our study we investigate dissociation dynamics of CH<sub>3</sub>I and CBr<sub>4</sub> on the ns-us time scale via transient optical and X-ray spectroscopies. By a comparison with theoretical simulation employing quantum mechanical molecular dynamics simulations and the transition potential approach to calculate liquid-phase X-ray absorption spectra the kinetics of transition states and final decay products are extracted.

### 70. Intermediate states of cobaloxime-based multicomponent and supramolecular photocatalysts are caught by time-resolved X-ray absorption spectroscopy

Grigory Smolentsev, Alexander Guda, Flavio Zamponi, Murielle Chavarot-Kerlidou, Vincent Artero, Maarten Nachtegaal, and **Jeroen A. van Bokhoven**

[grigory.smolentsev@psi.ch](mailto:grigory.smolentsev@psi.ch)

Time-resolved X-ray absorption spectroscopy in the nanosecond-microsecond time range has been used to investigate the charge transfer from photosensitizer to the catalysts in multicomponent and supramolecular photocatalytic systems. We demonstrate how this method allows to obtain the solution structure of the Co (I) intermediate of cobaloxime, which is a non-noble metal catalyst for solar hydrogen production from water. Distances between cobalt and the nearest ligands including two solvent molecules and displacement of the cobalt atom out of plane formed by the planar ligands were determined. In the supramolecular system with a ruthenium photosensitizer and a cobaloxime catalyst, the charge transfer was observed only in the presence of a sacrificial electron donor. This suggests that reductive quenching of the photosensitizer is the dominant charge transfer mechanism in this system. A slight modification of the catalyst structure lead to the formation of a catalytically inactive Co(I) state. Possible deactivation mechanisms that lead to the formation of inactive state will be discussed.

### 71. Optical Pump/Terahertz Probe Studies on Gold-on-Titania Nanoparticles

Arno Schneider, Ahmad Ajdar Zadeh, Jacques-E. Moser, **Jeroen A. van Bokhoven**

[arno.schneider@psi.ch](mailto:arno.schneider@psi.ch)

The generation of hydrogen gas through photocatalytic or photoelectrolytic water splitting on titania (TiO<sub>2</sub>) using sunlight is often considered to be a key technology for the sustainable production of a storable fuel. However, because of the large bandgap of titania (~3.2 eV), only the ultraviolet part of the solar spectrum can be used.

Recently it was shown that the addition of noble metal nanoparticles may extend the range of usable photon energies into the visible, thus enhancing the overall efficiency. This is mainly attributed to the existence of localized surface plasmons with a resonant energy typically in the 2-3 eV range.

It is often assumed that the fast decaying plasmon transfers its energy to a single "hot" electron which can then drift into the conduction band of titania, where it is available for the reduction of hydrogen. We tested this theory using terahertz time-domain spectroscopy, which is sensitive to the presence of free charge carriers. Pellets of anatase-TiO<sub>2</sub> nanoparticles, with and without 0.3 wt% of gold nanoparticles, were excited with femtosecond laser pulses at two different wavelengths, (i) 360 nm (UV) sufficient for the intraband excitation within titania and (ii) 550 nm (green) at the maximum of the plasmon resonance. As expected, the UV excitation lead to free electrons in titania. Their lifetimes exceeded the maximum detectable time delay of 1 ns by far, which shows that some of the electrons are effectively separated from the holes.

In the second experiment with green light excitation, we did not observe any change in THz transmission in the sample containing gold. This is evidence that the hot electrons are not in the conduction band of the titania particles. Comparing this result to other studies that have observed a transient infrared absorption with a picosecond lifetime, we conclude that this was most probably caused by the hot electrons occupying shallow traps near the gold-titania interface."

## 72. Time-resolved structures for catalysis and photo-catalysis

**Jeroen A. van Bokhoven**

[j.a.vanbokhoven@chem.ethz.ch](mailto:j.a.vanbokhoven@chem.ethz.ch)

Pump-probe measurements hold great promise to help understand the processes that occur in catalysis and photo-catalysis. The processes that occur cover many time scales, from the ultrafast of the bond breaking / making and charge separation to the second time range of the macrokinetics of chemical reactions. Since our participation in MUST, we have started a research program to be able to capture fundamental process at these time-scales. We have optimized the treatment of titania that leads to optimal water splitting activity. The presence of nano-sized metal particles greatly improves its water splitting performance. Using optical pump / terahertz probe, we determine the ability of plasmon excitation of the supporting metal in generating electrons in the conduction band of titania that are active in hydrogen formation during water splitting in collaboration with the group of Moser. Observing bond breaking and bond making reactions in real time requires developing new tools to coherently excite the catalytic system on the one hand and spectroscopic methods to detect the structural change using a free electron laser on the other. At PSI, we analyze the ability of using THz radiation to coherently excite adsorbates to initiate the chemical reaction. Detection of excitation is done by infrared spectroscopy respectively x-ray photoelectron diffraction, the latter in collaboration with the group of Hengsberger and Osterwalder. Finally, molecular structures have the advantage of structural control and because they are non-noble metal active water-splitting photo-catalysts, they hold promise of application. At the Swiss Light Source, we develop novel tools to measure in the time domain the mechanism of charge transfer and the identification of the reaction paths that lead to active respectively inactive intermediates.

## Jiri Vanicek

### 73. Dynamically consistent method for mixed quantum-classical simulations: a semiclassical approach

**Sergey V. Antipov**, Ziyu Ye, Nandini Ananth and **Jiri Vanicek**

[sergey.antipov@epfl.ch](mailto:sergey.antipov@epfl.ch)

We introduce a new semiclassical approach, the Mixed Quantum-Classical Initial Value Representation (MQC-IVR), for calculation of real time-correlation functions [1], which is based on combination of the modified Filinov transformation [2] and the Double Herman-Kluk Initial Value Representation (DHK-IVR) method [3].

The key feature of MQC-IVR is the ability to control the net action of pairs of trajectories incorporated in describing the dynamics of a given degree of freedom by varying the corresponding Filinov parameter. It can be shown analytically that the presented approach can continuously tune between full semiclassical and classical limits of Initial Value Representation. Thus, the described methodology allows to use different levels of theory for different modes of a complex system without introducing approximations at the quantum-classical boundary and provides a uniform framework for mixed "quantum-classical" molecular dynamics simulations. We demonstrate its numerical accuracy in the calculation of real-time correlation functions for a model 1-D and 2-D systems over the full range of quantum- to classical-limit behaviors.

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[3] W. H. Miller, J. Chem. Phys., 125, 132305 (2006).

## 74. Accelerating Quantum Instanton Calculations of Kinetic Isotope Effects

K. V. Karandashev, J. Vanicek

[konstantin.karandashev@epfl.ch](mailto:konstantin.karandashev@epfl.ch)

Path integral implementation of the quantum instanton approximation currently belongs among the most accurate methods for computing quantum rate constants [1] and kinetic isotope effects [2], but its use has been limited due to the rather high computational cost. Here we demonstrate that the efficiency of quantum instanton calculations of the kinetic isotope effects can be increased by orders of magnitude by combining two approaches: The convergence to the quantum limit is accelerated by employing high-order path integral factorizations of the Boltzmann operator [3], while the statistical convergence is improved by implementing virial estimators for relevant quantities [4,5]. After deriving several new virial estimators for the high-order factorization and evaluating the resulting increase in efficiency, using H+H<sub>2</sub> model exchange as an example, we apply the proposed method to obtain several kinetic isotope effects on CH<sub>4</sub>+H=CH<sub>3</sub>+H<sub>2</sub> forward and backward reactions [6].

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5. Jiri Vanicek and William H. Miller, J. Chem. Phys. 2007, 127, 114309.

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## 75. On-the-Fly ab Initio Semiclassical Dynamics of Floppy Molecules: Absorption and Photoelectron Spectra of Ammonia

Marius Wehrle, Solene Oberli, and Jiri Vanicek

[marius.wehrle@epfl.ch](mailto:marius.wehrle@epfl.ch)

We investigate the performance of on-the-fly ab initio (OTF-AI) semiclassical dynamics combined with the thawed Gaussian approximation (TGA) for computing vibrationally resolved absorption and photoelectron spectra. Ammonia is used as a prototype of floppy molecules, whose potential energy surfaces display strong anharmonicity. We show that despite complications due to the presence of large amplitude motion, the main features of the spectra are captured by the OTF-AI-TGA, which --\_by definition --\_does not require any a priori knowledge of the potential energy surface. Moreover, the computed spectra are significantly better than those based on the popular global harmonic approximation. Finally, we probe the limit of the TGA to describe higher-resolution spectra, where long time dynamics is required [1].

[1] Marius Wehrle, Solene Oberli, and Jiri Vanicek, J. Phys. Chem. A, 2015, 119 (22), pp 5685–5690

## 76. Nonadiabatic quantum dynamics of iodomethane (CH<sub>3</sub>I) induced by the interaction with ultrashort laser pulses

Aurelien Patoz and Jiri Vanicek

[aurelien.patoz@epfl.ch](mailto:aurelien.patoz@epfl.ch)

Photodissociation dynamics of iodomethane (CH<sub>3</sub>I) following the excitation to the A band has been studied since the discovery of the first laser relying on photodissociation. More recently, this chemical reaction has been explored with time-resolved high-harmonic spectroscopy by the NCCR MUST Werner group. While some of the results of these experiments have been explained qualitatively by a one-dimensional theoretical model of CH<sub>3</sub>I, in an on-going collaboration the NCCR MUST Vanicek group attempts to describe these results in a more quantitative detail by simulating the photodissociation dynamics using a higher-dimensional model that also includes nonadiabatic couplings. To do so, we have implemented general split-operator and partitioned Runge-Kutta algorithms of arbitrary order of accuracy for exact nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. In order to test the effect on various degrees of freedom and of the nonadiabatic dynamics, we have applied these algorithms to one-, two-, and three dimensional models of iodomethane both in the presence and in the absence of nonadiabatic couplings.

## Jean-Pierre Wolf

### 77. A dive into the Cytochrome b6f complex via ultrafast spectroscopy

Adrien Chauvet, André Al Haddad, Rachna Agarwal, William Cramer, Majed Chergui, **Jean-Pierre Wolf**

[adrien.chauvet@unige.ch](mailto:adrien.chauvet@unige.ch)

The Cytochrome (Cyt) b6f complex is a key element of the photosynthetic apparatus in plants. It serves as the mediator of electrons between Photosystem II and Photosystem I and as a result, participates in the creating of an electrochemical potential across the membrane. It is therefore one of the driving force of ATP synthesis. As a dimer, it is comprised of pair of heme f and two pairs of b-hemes (bh and bl), therefore structurally similar to its homologue Cyt bc1. However the Cyt b6f has the particularity of having additional constituents such as a Chlorophyl (Chl) and a Caroten (Car) molecule that have up to now no known function in the physiological mechanisms of this Cyt. Their presence in the Cyt b6f will be discussed.

The ferrous ( $\text{Fe}^{2+}$ ) centers of the heme f is shown to photo-dissociate with its tyrosine ligand after excitation by a short laser pulse (~50 fs). This "instantaneous" cleavage is then followed by the ligand recombination within 6 ps. Interestingly, via the heme's transient signal, we can follow the structural rearrangement of the heme binding pocket with a time constant of 2 ps. The b-hemes give rise to signals that differs drastically from the Cyt bc1 signals, certainly due to their proximity with the Chl and Car molecule. Their interaction is here discussed.

The effects of molecular oxygen on the different relaxation mechanisms of Chl and Car have also been investigated. In the light of our data, oxygen seems to only have affected the spectral signatures while leaving the early fs-ps dynamics of the chromophores unchanged. To our knowledge, this is the first ultrafast heme-analysis of the Cyt b6f. Such unique behaviors shine light on the still intriguing electron-coupled-proton transfer mechanism of the complex.

### 78. Optimally Shaped Pulses To Control Cell Poration

S. Courvoisier, L. Bonacina, , N. Götte, B. Zielinski, , T. Baumert, **J. P. Wolf**

[sebastien.courvoisier@unige.ch](mailto:sebastien.courvoisier@unige.ch)

In opto-transfection the cell survival is related to phototoxicity. For example, direct DNA damages can occur. It is therefore of primary importance to optimize the laser-cell interaction in order to increase the membrane perforation yield while reducing collateral cell damage. Very interestingly, it was demonstrated that the use of third order phase control of ultrashort pulses leading to Airy temporal profiles (Abdollahpour, D. et al. Physical Review Letters 2010) could manipulate the interaction with a glass substrate and lead to holes of smaller sizes, compared to damages produced by bandwidth limited pulses (Englert, L. et al. Journal of Laser Application 2012). We show here that optimally shaped temporal Airy pulses can control the poration of cell membranes, with variable hole sizes and even hole-less poration (small fractures), and significantly reduce the peak intensity and deposited energy as compared to Gaussian pulses.

### 79. Simultaneous characterization and use for multiphoton imaging of second and third order responses of metal oxide harmonic nanoparticles.

Cédric Schmidt, Aline Uldry, Andrii Rogov, Luigi Bonacina, **Jean-Pierre Wolf**

[cedric.schmidt@unige.ch](mailto:cedric.schmidt@unige.ch)

We use Hyper Rayleigh Scattering and polarization resolved multiphoton microscopy to investigate simultaneously the second- and third-order nonlinear response of Potassium Niobate and Bismuth Ferrite harmonic nanoparticles. We derive the second-to-third harmonic intensity ratio for colloidal ensembles and successively explore the tensorial response of individual nanoparticles. We investigate the use of bismuth ferrite (BFO) nanoparticles for tumor tissue labeling in combination with infrared multiphoton excitation. On this basis, we set up a novel imaging protocol based on the co-localization of the two harmonic signals and demonstrate its benefits in terms of increased selectivity against endogenous background sources in tissue samples.

### 80. Nonlinear THz spectroscopy on single layer graphene

Iris Crassee, Gregory Gaumann, Nagla Numan, Jean-Marie Poumirol, Michele Tamagnone, **Jean-Pierre Wolf** and Thomas Feurer

[iris.crassee@unige.ch](mailto:iris.crassee@unige.ch)

Recently several groups explored the nonlinear terahertz response of single layer graphene, both experimentally and theoretically. Strong generation of third order harmonics in the THz, even at moderate fields as low as ~10

kW/cm<sup>2</sup> [1-4] were predicted. However the predominated nonlinear observed experimentally is a strong saturable absorption [5-8]. The saturable absorption is generally explained by the creation of hot carriers, which might renormalize the carrier distribution in the graphene sheet upon excitation with the THz [7,8]. However direct experimental evidence is lacking due to a restriction of previous experiments to room temperature. We show experimental results of THz nonlinear spectroscopy of single layer CVD graphene performed at various temperatures and doping levels and explore directly the effect of carrier temperature and concentration on the nonlinear THz response. The THz field strength was varied between about 10kV/cm and 130 kV/cm, the temperature from 20 to 300K and the doping level in the sample from the Dirac point (charge neutrality) to a hole doping of about 330 meV (~80THz). Importantly, by varying the doping level from the Dirac point to a high hole concentration, we were able to actively tune the system such that interband transitions excited by the THz light become allowed or forbidden due to the Pauli blocking principle.

## 81. Real-time monitoring of atmospheric aerosols by fluorescence and pump-probe techniques

G. Sousa, A. Rogov, D. Kiselev, L. Bonacina and J.-P. Wolf

[gustavo.sousa@unige.ch](mailto:gustavo.sousa@unige.ch)

In the quest of fast identifying aerosol particles in air, considerable efforts have been dedicated to the development of real time, compact and field capable optical detectors [1]. Most of them rely on optical scattering and fluorescence detection from individual particles. In our system, we measure the time of flight between two scattering lasers in order to get both the velocity and the aerodynamic size of the flowing particles. UV-visible fluorescence is used for addressing aerosol composition, mainly through the emissions from biological and organic chromophores (e.g. tryptophan). The major drawback of this approach is that some of the fluorescence spectra between bio and non-bio species are similar, therefore we are implementing an optical interrogation involving fluorescence depletion spectroscopy [2] using a nanosecond pulsed laser.

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## Hans Jakob Wörner

### 82. Attosecond time-resolved photoelectron spectroscopy of liquids

Inga Jordan, M. Huppert, L. Seiffert, M. Arbeiter, Th. Fennel and H. J. Wörner

[jordani@ethz.ch](mailto:jordani@ethz.ch)

Attosecond spectroscopy has offered promising insights into ultrafast dynamics in solid and gas phase systems, but has not approached the liquid phase yet, where most of chemical and biological processes occur. Here, we report the achievement of this fundamental advance and demonstrate the measurement of attosecond photoionization delays from liquid water. We have measured relative photoionization delays between water molecules in the liquid and gas phases by applying the RABBIT-technique to a liquid microjet. In combination with theory, the photoionization delays reveal propagation effects on the electron wave packet in the aqueous environment, the effect of solvation on the parent ion and dephasing processes. These results are expected to provide unprecedented insights into the nature of photoionization and electron transport in liquid water.

### 83. Photodissociation dynamics of NO<sub>2</sub> probed with single harmonics from an XUV monochromator

Aaron von Conta and Hans Jakob Wörner

[aaron.v conta@gmail.com](mailto:aaron.v conta@gmail.com)

A time-preserving XUV/VUV monochromator for HHG is used to investigate the photodissociation dynamics of NO<sub>2</sub> by photo-electron kinetic energy measurements in a magnetic-bottle time-of-flight spectrometer. Upon pumping the system optically with 3.1 eV (400 nm) pulses of ~40fs duration the molecule is excited to the  $\tilde{A}^1 2B_2$  state of the neutral followed by internal conversion and dissociation into NO and O fragments. A defined time delay after the pump pulse the molecule is ionized with 26.3 eV radiation of ~30 fs duration. This experiment reveals the evolution of the electronic structure during the conical-intersection dynamics and the subsequent photodissociation.

## 84. Time-Resolved High-Harmonic Spectroscopy of Pericyclic Reaction Dynamics

A. Tehlar, N. Thiré, P. M. Kraus, Y. Pertot, J. Gateau, J. P. Wolf, F. Légaré, and H. J. Wörner

[andres.tehlar@phys.chem.ethz.ch](mailto:andres.tehlar@phys.chem.ethz.ch)

The dynamics during the ring-opening of 1,3-cyclohexadiene after photo-excitation in the deep UV (267 nm, 40 fs FWHM) was researched using time-resolved high-harmonic spectroscopy with 1420 nm driving wavelength. The two conical intersections, 1B to 2A and 2A to 1A, lead to distinct features in the pump probe signal, allowing the assignment of maxima in the populations of the 1B state after 20 fs and of the 2A state after 60 fs. After 350 fs, the signal stays constant, signifying the end of the reaction.

## 85. Dynamical symmetries of atoms and molecules probed by bicircular high-harmonic spectroscopy

Denitsa Baykusheva, Md Sabbir Ahsan, Nan Lin and Hans Jakob Wörner

[denitsa.baykusheva@phys.chem.ethz.ch](mailto:denitsa.baykusheva@phys.chem.ethz.ch)

High-harmonic spectroscopy (HHS) is a well-established probe of the structure and dynamics of matter on the sub-femtosecond and sub-Ångström scales. A hitherto unexplored aspect of this technique is its ability to probe the symmetry of the underlying medium on these scales. High-harmonic generation from linearly polarized fields enables the characterization of the electronic asymmetry of the sample under study by manipulating the inversion symmetry of the system. Here we present bicircular high-harmonic spectroscopy (BHHS) - an approach aimed at extending the sensitivity of HHS to general rotational symmetries and their time-dependent breaking by employing a circularly polarized fundamental field (800 nm) and its counter-rotating co-propagating second harmonic (400 nm) [1, 2]. We first demonstrate that BHHS is able to distinguish between s- and p- angular-momentum symmetries of atomic orbitals. Breaking the three-fold rotational symmetry of a medium-either on a macroscopic scale or on the single-atom level results in the emission of otherwise parity-forbidden harmonic orders that provide a background-free probe of dynamical molecular symmetries and their time evolution [3].

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## 86. A beamline for attosecond streaking on liquids

A. Jain, I. Jordan, M. Huppert and H.J. Wörner

[arohi.jain@phys.chem.ethz.ch](mailto:arohi.jain@phys.chem.ethz.ch)

We describe the design of a beamline for the demonstration of attosecond streaking in liquids. It consists of a high-harmonic-generation chamber for generation of isolated attosecond extreme-ultraviolet (XUV) pulses. A diagnostics chamber hosts the metallic filters for filtering the XUV pulse and an aperture to control the intensity of the NIR beam at the liquid jet. The co-propagating XUV and NIR beams are reflected by a two-component mirror. It consists of an inner multilayer mirror for spectral filtering and focusing of the XUV attosecond pulses and an outer mirror for focusing the IR few-cycle pulses. The advantage of using multilayer mirrors over the current setup in our lab [1] is to accurately compensate the attochirp to create near-Fourier-limited isolated attosecond pulses while still maintaining a high XUV flux. An XUV spectrometer positioned after the double-mirror setup can be accessed for optimization of the XUV spectra. An imaging system is implemented for spatial and temporal overlap of the two beams. To this end, a pick-up mirror in the diagnostics chamber images the beam onto a CCD camera outside the experimental chamber. The two beams focus are focused onto a liquid microjet in the interaction chamber coupled to a field-free time-of-flight spectrometer. The laminar region of the liquid jet can be positioned with respect to the focus of the beams using the imaging system.

[1] M. Huppert et. al., Rev. of Sci. Ins. 86, xxx, (2015).

## 87. Near L-edge absorption spectroscopy of SF<sub>6</sub> with high-harmonic-generation sources: towards water-window transient absorption

Y. Pertot, C. Schmidt, M. R. Matthews, A. Chauvet, L. Bonacina, M. Huppert, A. von Conta, J. P. Wolf, H. J. Wörner

[yoann.pertot@phys.chem.ethz.ch](mailto:yoann.pertot@phys.chem.ethz.ch)

In the past few years, the development of intense optical sources between 1.2 and 2 micrometer wavelength have led to the generation of bright soft-X-ray (SXR) femtosecond and attosecond pulses in the water window range.

This opens up the study of ultrafast dynamics by well-established spectroscopic techniques like X-ray Absorption Near Edge Structure (XANES) and in the future, Extended X-ray Absorption Fine Structure (EXAFS). In the present study, we demonstrated the ability to generate photons at energies above the K-edge of carbon (285 eV) and recorded absorption spectra near the L-edge of SF<sub>6</sub> (170 eV) and Argon (250 eV) compatible with the flux required for time-resolved experiments.

The experimental setup consists of a high-harmonic source followed by a carbon-coated toroidal mirror focusing the SXR beam into a gas cell filled with SF<sub>6</sub> or argon and then sent in a SXR spectrometer where absorption spectra are recorded. The high-order harmonics are generated by focusing an 1800 nm, 2.3 mJ, 1 kHz beam into a 6.5 mm long gas cell filled with 150 mbar of neon. The fundamental beam is generated by parametric amplification in a white-light TOPAS. SXR photons with energies up to 350 eV were observed. Absorption spectra near the L-edge of SF<sub>6</sub> (170 eV) and Argon (250 eV) were recorded with an integration time of 5 seconds or less, with very good signal to noise ratio. A first attempt to study strong field ionization dynamics in SF<sub>6</sub> has been done by ionizing SF<sub>6</sub> with an 800 nm pulse and recording the spectra as a function of delay between pump (800 nm pulse) and probe (SXR pulse). Theoretically expected results have not been observed during our first campaign. However, we believe that these preliminary results are very encouraging for further development of this joint project.

This table-top experimental setup leading to transient absorption measurement at the L-edge of sulfur or argon, and in a near future in the water window, is of great interest for the study of femtosecond and attosecond dynamics in molecules. Indeed, valence electronic dynamics as well as structural information become available in a single spectrum at a femtosecond time scale and possibly at the attosecond time scale with further development."

## 88. Spin-orbit resolved relative photoionization delays in noble gases

M. Huppert, I. Jordan, S. Pabst and H. J. Wörner

[huppertm@ethz.ch](mailto:huppertm@ethz.ch)

Attosecond time-resolved photoelectron experiments have been performed by combining an actively-stabilized pump-probe setup with a magnetic-bottle time-of-flight spectrometer. We have measured the relative ionization delays between photoelectrons associated with the two spin-orbit components (2P<sub>3/2</sub> and 2P<sub>1/2</sub>) of the electronic ground states of Xe<sup>+</sup> and Kr<sup>+</sup> by using the RABBIT technique. The delays vary between -20 and +20 as a function of the XUV-photon energy (20-30 eV) for xenon. In contrary, in krypton the measured delay is zero within the error margins, which is in good agreement with calculations based on the recently-developed time-dependent configuration-interaction singles (TDCIS) approach.