

Poster sessions: on January 14, from 19:30 and on January 15 during the lunch break.

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## 1. Ultrafast Processes in Organic Bioelectronics (Banerji)

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Organic biosensing and bioelectronics is a young, dynamic and exciting field. One prominent example in bioelectronics are OECTs (organic electrochemical transistors). Such devices can be integrated with living cells, tissues and organism to monitor cellular activity. However, an in-depths understanding of the underlying fundamental processes and working principles of OECTs is still lacking. The vision of our research project is to bring sophisticated spectroscopic studies into this emerging field. We expect that ion penetration strongly affect the visible absorption. To follow this evolution, we implement a voltage gate in our setups allowing a time resolution (from nanosecond to seconds). With THz spectroscopy in ATR mode, we will be able to address the nanoscale mobility of electronic charges in the OECTs (THz absorption depends both on the carrier concentration and their mobility).

## 2. Ultrafast magnetic and orbital phase transitions in a 4d correlated system (Beaud)

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In the 4d correlated material  $\text{Ca}_2\text{RuO}_4$ , the interactions between lattice, charge, orbital and magnetic degrees of freedom (DOF) form stable states differing in magnetization or conductivity, with different magnetic and electronic phase transitions that can be triggered by temperature pressure and light. To understand the elementary mechanisms associated with the magnetic and orbital changes, it is necessary to study this process on the time scale of atomic motions. In this work, we investigated the ultrafast magnetic and orbital dynamics by time resolved resonant diffraction at the Ruthenium L-edge [1]. With SwissFEL Bernina, this tender energy regime becomes accessible at an FEL diffraction instrument for the first time. In order to study the ultrafast magnetic and orbital dynamics, we followed the intensity change of (100) reflection [1] after excitation by an ultrashort IR pulse (cf. Fig.1) at 80 K. Our results show a decrease of integrated Bragg intensity (100) which is due to the Antiferromagnetic (AF) transition.

[1] Zegkinoglou, I, et al. ;Physical Review Letters, 95(13), pp. 1–4 (2005);  
<https://doi.org/10.1103/PhysRevLett.95.136401>

## 3. Ultrafast reversal of the ferroelectric polarization (Beaud)

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The macroscopic electric polarization of ferroelectric materials is formed by the shifts of oppositely charged ions at a structural phase transition. Analogue to data storage devices based on ferromagnetic materials, information can be stored in the direction of the electric polarization. Fast switching between the two states is typically induced by pulsed electric fields on sub-nanosecond time scales. Reversing the polarization with ultrashort laser pulses would be an important step toward the design of high-speed ferroelectric data storage. Here, we follow an approach, which was recently proposed in the framework of density functional theory calculations. Rather than driving the ferroelectric mode directly, we couple to it indirectly by resonant excitation of an auxiliary higher-frequency phonon mode with femtosecond mid-infrared pulses. Large-amplitude excitation of a high-frequency infrared-active lattice mode induces transient reversal of the ferroelectric polarization in  $\text{LiNbO}_3$ , forced by the anharmonic coupling between the driven and the lower-frequency ferroelectric mode.

#### **4. The Bernina Instrument at SwissFEL: Non-equilibrium physics probed by femtosecond X-rays (Beaud)**

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The Bernina instrument at the SwissFEL ARAMIS hard X-ray free-electron laser is designed for studying ultrafast phenomena in condensed matter and material science. Employing ultrashort pulses from an optical laser system covering a large wavelength range (from the ultraviolet up to the far infrared) we generate specific non-equilibrium states, whose subsequent evolution can be probed by selective X-ray scattering and emission techniques in the range from 2-12 keV. For these experiments multiple interchangeable endstations are available differing in specialization, diffractometer and X-ray analyser configuration and load capacity for specialized sample environment. We report on the status of the instrument after a series of pilot experiments realized in 2018. Regular user operation begins in 2019.

#### **5. High sensitive Deep UV Raman spectroscopy for online water analysis (Borgschulte)**

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During the last decades the scientific interest in the waste water analysis has been growing due to the appearance of new harmful contaminants in treatment plants. Agriculture-derived organic compounds as Sodium Nitrate and Pharmaceutical ingredients (APIs) such as Amisulpride and Carbamazepine have been reported with typical concentrations of  $\mu\text{g/l}$  or lower [1, 2, 3]. The standard chemical analysis is commonly performed in analytical chemistry laboratories by means of gas and liquid chromatography (GC and LC) and Mass spectroscopy (MS) [4]. However, at present an alternative online technique to perform quantitative analysis and detection is missing.

Raman spectroscopy in the visible range is a promising online technique, but its maximum sensitivity is still limited [4,5] due to overlap of fluorescence and Raman emission. By changing the excitation energy is theoretically possible to vary the relative intensity of the Raman and fluorescence signal but the final result strongly depends on the sample under investigation.

We demonstrated the proof of concept using an Optical Parametric Oscillator (OPO) as excitation source for Deep UV radiation. We achieve limits of detection (LOD) for nitrate better by a factor of ten than 25mg/L as required for an online water analysis method [6,7,8]. Similar values were obtained for organic pollutants.

On this poster, we want to address the challenge to overcome for commercial applications. This is mainly related to the excitation source as the most expensive part. We also discuss potential future design and key parameters.

[1] M. Decrem et al., *Agron. Sustain. Dev.* 27, 243 (2007)

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[3] J. L. Martinez et al., *Environmental Pollution* 157, 11 (2009)

[4] P. Burchill et al., *Water Research* 17, 12 (1983)

[5] G. Persichetti, R. Bernini, *Talanta* 155, 145–152 (2016)

[6] Gewässerschutzverordnung (CH), <https://www.admin.ch/opc/de/classified-compilation/19983281/index.html>

[7] Water Framework Directive (EU), <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:l28002b>

[8] T.H. Kauffmann et al., *Sensor and Actuators B: Chemical* 209, 154-161 (2015)

## 6. The SwissFEL endstation for AMO sciences (Bostedt)

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A new endstation for atomic, molecular and optical (AMO) sciences is planned for one of the soft X-ray branches of ATHOS at SwissFEL. The ATHOS undulator section will have small chicanes in between every undulator segment and tuneable undulators, enabling novel and advanced FEL operation modes. Specifically, a mode to generate ultrashort pulses from a few femtoseconds down to hundreds of attoseconds, high power operation with up to 8 mJ pulse energy at 250 eV, two color X-ray pump-probe or the combination of these schemes will be available. Exploiting these capabilities opens new exciting opportunities for the field of AMO sciences. For example, charge transfer and migration in molecules shall be investigated on the few femtosecond time scales with site selectivity employing X-ray pump-probe schemes with pulses tuned to specific absorption edges. With a photon energy range from 250 to 1800 eV, ATHOS covers essential absorption K-edges, such as C, N and O and L-edges of 3d transition metal elements, like Ti, Mn, Fe, and Cu to allow for a broad spectrum of targets. In addition to a synchronized optical pump-probe laser, which is intended to cover the wavelength regime from THz to UV radiation using secondary sources, a high harmonic generation source will be implemented into the AMO endstation, to extend the available photon energies into the XUV regime. Thus, optical light driven valence processes as well as XUV-initiated valence and inner-valence dynamics can be probed with soft X-rays or vice versa. The endstation for AMO science is planned to provide the capabilities of electron- and ion-spectroscopy, absorption spectroscopy and X-ray scattering.

## 7. X-ray pump/ X-ray probe photoelectron spectroscopy (Bostedt)

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Applications for intense X-ray pulses from XFELs span a broad spectrum from atomic and molecular physics to chemical, materials and biological sciences [1]. Several methods have been developed in the recent years enabling XFELs to deliver two collinear intense femtosecond x-ray pulses with high control on the time delay and color (energy). This opened the possibility of carrying out time-resolved studies of complex x-ray induced phenomena with x-ray pump / x-ray probe schemes [4].

The combination of this unique capability with X-ray photoelectron spectroscopy (XPS), a powerful tool for extracting chemical information of a specific site by measuring the binding energy of core electrons, enables time-resolved XPS experiments with chemical or even site specificity and femtosecond time resolution. This allows us to observe electronic and nuclear dynamics out of equilibrium and to see how a local excitation travels over molecule in real time.

Here we present x-ray pump / x-ray probe XPS experiments aimed at studying energy flow and relaxation dynamics in CO, i.e., small heteronuclear molecules, in the gas phase. We used two x-ray pulses to first excited a core-electron resonantly at the oxygen K-edge and then probed the molecular response with photoemission from the carbon core levels with a second x-ray pulse. The data gives a glimpse of electronic and nuclear relaxation pathways proceeding on time scales <40 fs upon x-ray excitation on the oxygen site.

## 8. Investigating Long Range Electron Transfers and Intramolecular Electrostatic Fields with Multidimensional Transient Stark Shift Spectroscopy (Cannizzo)

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We recently proved the feasibility of phase-sensitive measurements with conventional, non phase-stabilized set-ups based on single shot interferometry (SSI) of broad, fs pulses. This approach has the potential to allow Fourier-transform four-wave mixing (FT-FWM) spectroscopy (also 2D photon echo) without wavelength limitations and working with conventional optics only. The unique advantage to adopt non-phase stabilized designed allows the implementation of very compact schemes which make concrete the possibility to combine FT-FWM spectroscopy with other techniques and unexplored spectral ranges.

In my project I will pursue this goal with the specific aim of combining a complete non collinear 2D UV-Vis experiment with intense THz pulses to investigate the role of local intramolecular electrostatics and of the polar properties of the intermediate states on the charge transfer in photo-catalysts.

G. Achazi, A. Cannizzo. Fourier transform spectral interferometry with non-phase stable setups by broadband single shot detection of fs and ps pulses. *Review of Scientific Instruments*, 88(8):083110, 2017.

## 9. Ultrafast photo-induced enhancement of oxidation catalysis at Mo(VI) centers of Ru(II)-Mo(VI) dyads (Cannizzo)

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In this work, we have studied biomimetic molybdenum (Mo) complexes [1] with ruthenium (Ru) appended photoactive units, namely a bridged Ru(II)-Mo(VI) dyad, synthesized with the aim of facilitating oxidation catalysis at the Mo moiety via photo-triggered electron transfer (PeT) towards the Ru center.

The previously proposed model for the photo-induced oxidation-enhancing effect in Ru(II)-Mo(VI) complexes [2] is described in three steps: (a) Photo-oxidation of the Ru(II) into Ru(III) and reduction of one of the Ru ligands (a bpy or a phen) upon formation of the Ru(III)-bpy/phen(-3) metal-to-ligand charge-transfer (MLCT) excited state, (b) neutralization of the charge on the ligand by means of an oxidizing agent and (c) finally, the activation of the Mo complex upon back-reduction of Ru(II/III). Since the second step is diffusion-limited, the last step, which corresponds to the production of a highly reactive one-electron oxidized Mo unit, occurs on  $\mu\text{s}$  time scales.

To verify this model and to shed new light on ultrafast photo-induced processes within the Ru(II)-Mo(VI) dyad relevant to the proposed intramolecular electron transfer mechanism, we carried out ultrafast transient absorption (TA) spectroscopic measurements of these complexes. We succeeded to track down the oxidation of the Mo unit and, surprisingly, we found multi-exponential dynamics spanning from 2 ps to 60 ps, with ca. half of the oxidation events happening within 2 ps. This result implies an intramolecular process which is in contrast with a diffusion-limited process. Based on this evidence, we propose a completely new explanation of the photo-induced oxidation-enhancing effect due to an electron transfer from Mo unit towards the bridging groups immediately after photo-oxidation of Ru(II) to Ru(III).

[1] Ducrot, A. B; Scattergood, B.; Coulson, B. A.; Perutz, R. N.; Duhme-Klair, A.-K. Electronic Fine Tuning of Oxygen Atom Transfer Reactivity of cis-Dioxomolybdenum(VI) Complexes with Thiosemicarbazone Ligands *Eur. J. Inorg. Chem.*, 2015, 3562.

[2] Ducrot, A. B; Coulson, B. A.; Perutz, R. N.; Duhme-Klair, A.-K. Light-induced Activation of a Molybdenum Oxotransferase Model within a Ru(II)-Mo(VI) Dyad, *Inorg. Chem.*, 55, 2016, 12583-12594.

## 10. Ultrafast study of a novel family of nanomaterials (Cannizzo)

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Carbon nanodots (CDs) are a novel family of carbon-based nanomaterials synthesized only 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. They show indeed excellent solubility in aqueous environments and photo and chemical stability. Here we investigate nitrogen-rich CDs, showing, from a fundamental point of view, unique optical properties currently debated in literature, such as tunable strong fluorescence in the visible, provided that the CDs' surface is properly passivated; emission sensitive to perturbations like the presence of metal cations; capability of behaving as efficient photo-activated acceptors or donors for electrons and protons. Understanding their optical properties is crucial to move toward applications such as optoelectronic, bio-imaging, physicochemical sensors and markers.

We carried out an extensive study to characterize CDs with  $\beta$ -C<sub>3</sub>N<sub>4</sub> nanocrystalline structure, developing a versatile DUV-to-Vis femtosecond time-resolved transient absorption spectrometer with time resolution of 40 fs (standard deviation). We present here the detailed photocycle of nitrogen-rich CDs. Our study included varying pump wavelength, polarization and solvents to gain a deeper understanding of the photophysical properties of CDs and of the relaxation dynamics of the higher excited state. Moreover, we addressed size-dependent effects on optical and physical properties. We observed rotational diffusion dynamics of the transition dipole moments on timescales (10s ps) faster than the rotational diffusion of the entire CD (10s ns). Our results point to a diffusional energy transfer occurring through surface states of the nanodots assisted by solvent fluctuations, making them appealing for chemical sensing or as light harvester antennas. Modelling and further experimental evidences are underway to rationalize such an unexpected behavior.

## 11. New insights into the Verwey Transition in magnetite via Inelastic Neutron Scattering and Time-Resolved Spectroscopy and Electron Diffraction (Carbone)

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Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is the first magnetic material discovered and utilized by mankind. Despite thousands of years of applications, it remains among the most fascinating materials for physicists due to the occurrence of discontinuous changes in its ground state around 120 K, the so-called Verwey transition, which presents intertwined structural, electronic and magnetic alterations.

The remarkable complexity of the transformation process still leaves open fundamental problems in the understanding of the microscopic mechanism of the Verwey transition. To have further insights in this open problem, we combine together the potentials of steady-state and time-resolved spectroscopy and diffraction to study the critical dynamics of the lattice vibrations, and the fluctuations of electronic and structural order across the Verwey transition. Their signatures are identified in the coherent response of the optical functions to ultrashort laser pulses, and the inelastic scattering of light and neutrons, which provide complementary information, with selective sensitivity to different types of elementary excitations. Among the most important results, we manage to observe in the energy and time domain critical modes with different interplay of charge distribution and atomic displacements typical of an order-disorder process. In addition, Ultrafast Electron Diffraction studies unveiled phase segregation intermediate states during the phase transformation and disclosed structural differences between the photoinduced and the thermal phase transition mechanism.

## 12. Electron-light interaction for coherent polariton imaging, and electron wave-function control (Carbone)

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We present recent achievements in control and utilization of electron-light interaction in ultrafast electron microscopy. Utilization of the inverse-transition radiation with multiple optical pulses has allowed us to provide the experimental evidence for long temporal coherence of photo-electrons in UEM, and develop a temporal holographic imaging technique. Additionally, we present first observation of momentum and angular momentum transfer from light to electrons in coherent interaction.

## 13. Revealing picosecond dynamics of myoglobin's tertiary structure with ultrafast polarization spectroscopy in the deep-ultraviolet (Chergui)

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A major aim of biophysical studies of proteins is the resolution of the dynamical relationship between their structure and function. Here, the observation of sub-nanosecond conformational changes under physiological conditions is particularly challenging, because popular techniques such as solution-phase NMR or X-Ray scattering are limited in their time- or spatial resolution, respectively. In this context we propose polarization-controlled transient absorption spectroscopy in the deep-UV (250 – 370 nm) as an alternative technique to resolve structural changes of the tertiary structure of proteins on a picosecond timescale, by monitoring the response of amino-acid residues, such as tryptophans.

In this prototype study we investigate the photolysis reaction of carboxymyoglobin (MbCO), a small heme protein with near unity ligand photodissociation quantum yield and little geminate recombination [1]. Upon photoexcitation of the heme's Q-band, centered at about 550 nm, CO is dissociated in approximately 50 fs creating a vibrationally hot, unligated form, deoxymyoglobin (deoxyMb), with a domed heme. The doming occurs on an ultrafast time scale and triggers conformational changes of the tertiary structure in the vicinity of the heme. We thus performed pump-probe experiments [2] with a polarization-controlled, linearly polarized visible pump and a linearly polarized broadband deep-UV probe pulse, thereby recording transient absorption spectra for parallel and perpendicular pump-probe polarization geometries. We then extract the population kinetics at magic angle and the transient anisotropy of the aromatic side chains (< 300 nm) and the heme's N-band (> 350 nm) with a time-resolution of 200 fs. We observe rich multi-exponential kinetics on a picosecond timescale in both regions and identify anisotropy changes that indicate an ultrafast response of the protein's tertiary structure. It is worth noting that this addresses a gap in heme protein research as the picosecond response of the amino acids to ligand dissociation has not yet been reported in detail [3].

Our results demonstrate the rich information content provided by the aromatic absorption bands and their role as structural reporter groups in proteins. Furthermore, this study is paving the way for a systematic comparison with the more complex and less established photolysis reaction of the nitric oxide ligand in MbNO.

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[2] G. Auböck, C. Consani, R. Monni, A. Cannizzo, F. v. Mourik and M. Chergui Femtosecond pump-supercontinuum-probe setup with 20 kHz repetition rate, *Rev. Sci. Instrum.* 83, 093105–6 (2012).

[3] Subpicosecond UV spectroscopy of carbonmonoxy-myoglobin: absorption and circular dichroism studies, *Phys. Chem. Chem. Phys.* 9, 1611 (2007).

## 14. Time-resolved element selective probing of photo-induced charge carriers in inorganic lead perovskites (Chergui)

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Lead halide perovskites represent promising candidates for the next generation of solar materials, due to their low-cost fabrication and outstanding optoelectronic performances. Despite the large research efforts in recent years, microscopic details of the charge carrier formation and relaxation are still missing. In this perspective, time-resolved X-ray absorption spectroscopy (TR-XAS) represents an ideal tool to investigate this multi-element material.

Previous time-resolved experiments performed at the Swiss Light Source (SLS) on the Br K-, the Pb L3- and the Cs L2-edges of CsPbBr<sub>3</sub> nanocrystals in toluene (optical pump 355 nm) have pointed out to localization of the holes at Br sites, which leads to formation of a small polaron in the valence band (VB) within 100 ps. The results also suggested that the electrons remain either delocalized or form large polarons in the conduction band (CB). [1,2]

Recently, these investigations were pursued at the Advanced Photon Source (APS, Chicago). The Br K-edge energy spectra at different time delays have been recorded to probe the local structural modification in the EXAFS region and kinetic traces at the pre-edge, edge and post-edge were collected, in order to determine the relationship between the electronic dynamic at Br sites and the structural changes of the local environment. Furthermore, high energy resolution fluorescence detection (HERFD) was implemented at the Pb L3-edge XANES, yielding finer details of the broad featureless absorption. The study allows to obtain further insights about the charge carrier relaxation process and to relate the spectral features at the Pb centers with the nuclear and electronic changes of the Br sites.

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## 15. Exciton dynamics in DNA oligomers studied by broadband deep-UV transient absorption spectroscopy (Chergui)

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Exciton dynamics in DNA oligomers plays a crucial role in photo protection. Using ultrafast broadband deep-UV transient absorption spectroscopy [1] on Deoxyadenosine monophosphate oligomers of various lengths, we observe the effect of  $\pi$ - $\pi$  stacking. In the monomer sample we observe ground state bleach (GSB), stimulated emission (SE) and excited state absorption (ESA), resulting from a hot ground state, which experiences vibrational cooling on the few picosecond time scale.

In the dimer, an additional decay component with a 1 eV (FWHM) broad plateau-like ESA spectrum and a time constant of 385 ps is present. Suppressing stacking with a methanol solution makes this signature vanish, confirming that this decay and the associated broad ESA feature are due to  $\pi$ - $\pi$  stacking and thus a signature of a two-base exciton. In the 20-mer the excitonic ESA signature is significantly broader and decays twice as fast as in the dimer. We assign these spectral and temporal differences to the contributions of excitons spanning more than two bases [2, 3]. The ESA signal in the 20-mer, in contrast to the dimer, broadens on the 100 ps time scale, which may come from conformational changes and/or exciton migration.

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## 16. Valence band mapping of CsPbBr<sub>3</sub> perovskite single crystals by angle-resolved photoemission spectroscopy (Chergui)

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CsPbBr<sub>3</sub> is a perovskite semiconductor with outstanding optoelectronic properties. Nonetheless, the material's band structure was not yet experimentally measured. By applying angle-resolved photoemission spectroscopy utilizing an extreme-UV light, a direct view of the electronic structure in the whole surface Brillouin zone has been achieved. The mapped valence band is in agreement with ab-initio DFT calculations. The measured band dispersion is related to the hole effective mass, a key optoelectronic property, and compared with the theory and previous experiments. The larger measured quasi-particle mass, as compared to the calculations, hints at many-body effects, compatible with a polaron model.

## 17. X-ray Absorption Linear Dichroism at the Ti K-edge of TiO<sub>2</sub> Anatase Single Crystal (Chergui)

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Titanium dioxide (TiO<sub>2</sub>) is one of the most studied large-gap semiconductor due to its present and potential applications in photovoltaics and photocatalysis. The increasingly strict requirements of modern devices call for sensitive material characterization techniques which can provide insights at the atomic level. Experiment support to the assignment of the pre-edge transitions at the Ti K-edge of the anatase TiO<sub>2</sub> XAS spectrum is still lacking while it provides a deep insight into the electronic structure and geometry around Ti atoms. We show that the peak A1 is mainly due to dipolar transitions to on-site hybridized px,y-(dxz,dyz,dx<sup>2</sup>-y<sup>2</sup>) orbitals in the final state with an excellent agreement between ab-initio calculations and spherical harmonic analysis. Peaks A3 and B have off-site dipolar components from which the electronic structure of Ti nearest neighbors can be explored. Finally, we experimentally observe a quadrupolar evolution of the A2 peak amplitude in qualitative agreement with finite difference method calculations. We argue that the amplitude of this transition may strongly depend on atomic vacancies which allow orbital mixing via lowered symmetries. This explains the relatively intense peak A2 in amorphous TiO<sub>2</sub> or after photoexcitation of anatase or rutile TiO<sub>2</sub>.

## 18. Ultrafast photoinduced dynamics in solvated molecules probed by VUV photoelectron spectroscopy (Chergui)

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We aim to study ultrafast charge and structural dynamics of solvated and photoexcited molecular complexes by means of VUV photoelectron spectroscopy (PES) on liquid micro jet. Time-resolved PES can unfold the complete ultrafast relaxation process along any electronic configuration by probing the system through ionization by means of ultrashort vacuum-ultraviolet (VUV) laser pulses from High-harmonic generation (HHG). The rough element selectivity of valence PES can be pushed towards the shallow core-levels of certain elements (<100 eV) to follow all-round electronic and structural dynamics in molecular complexes. It also paves the way to the study of the interaction between the molecule and its environment and a characterization of the solvent effect on the electronic dynamics and photochemical reactions.

## 19. Ultrafast core level dynamics in lead halide perovskite semiconductors (Chergui)

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Lead halide perovskites (LHP) are remarkable optoelectronic materials with unusually long carrier diffusion lengths, despite being grown by low-temperature solution chemistry. The perovskite's structural response to photogenerated carriers is believed to be responsible of these transport properties, due to the formation of polarons. Here we follow the element-specific evolution of core states via time-resolved photoelectron spectroscopy on single-crystalline CsPbBr<sub>3</sub>; a prototypical inorganic LHP. In the same experiment, the evolution of carriers in the valence states is tracked via momentum-resolved photoemission, providing a comprehensive picture of the coupled carrier-lattice evolution.

## 20. Nanographene Favors Interactions with the Electron Acceptor Rather than the Electron Donor in a Planar Fused Push-Pull Conjugate (Feurer)

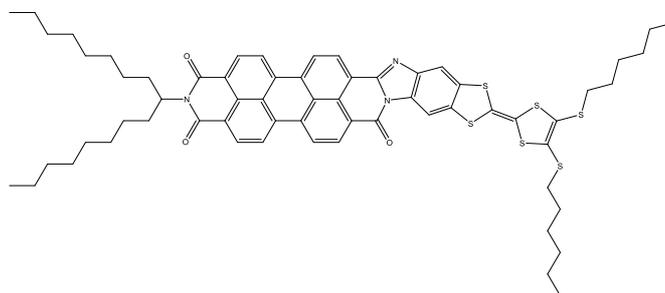
Ping Zhou\*<sup>1</sup>, Michel Volland<sup>2</sup>, Leonie Wibmer<sup>1</sup>, Robert Häner<sup>1</sup>, Silvio Decurtins<sup>1</sup>, Thomas Feuerer<sup>3</sup>, Shi-Xia Liu<sup>1</sup>, and Dirk M. Guldi<sup>2</sup>

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Graphene films have attracted a lot attention due to their potential application in nanoelectronic devices [1]. Noncovalent functionalization of graphene does not disrupt the extended  $\pi$ -conjugation. Incorporation of intercalators in the form of redox- and/or photoactive building blocks enables the usage of electron donor-acceptor (D–A) interactions. Accordingly, the noncovalent functionalization of nanographene (NG) or graphene sheets with either aromatic electron donors or acceptors, as demonstrated in the case of carbon nanotubes, is widely exploited in contemporary research.[2] Herein, we report the exfoliation of graphite via intercalation and immobilization of planar  $\pi$ -conjugates tetrathiafulvalene–perylene-3,4,9,10-tetracarboxylic diimide (TTF–PDI). The resultant nanohybrids have been characterized by complementary spectroscopic and microscopic techniques.[3].



Scheme 1. Chemical structure of fused D–A TTF-PDI

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## 21. Time-resolved THz Stark spectroscopy (Feurer)

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Energy shifts of molecular electronic transitions due to an external electric field, or Stark effects, are dominated by two molecular features; there exists a difference dipole moment over the transition and/or a difference in polarizability. Provided an isotropic distribution of molecules is maintained, these effects manifest spectrally as a broadening of the absorption peak in the case of the former or a shift in the case of the latter. By employing an intense THz single cycle pulse as external electric field source in a conventional femtosecond pump-probe setup, we can overcome many of the limitations of the conventional AC-electric field set-up. By using a femtosecond supercontinuum as probe, we can study the evolution of Stark effects on ultrafast timescales. Future experiments are envisaged where, by first optically exciting the molecule, field effects can be studied during the photocycle.

## 22. Dynamic quantum-criticality of heavy-fermions: Evolution of quasiparticles, Fermi-surface and crystal-electric-field states (Fiebig)

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Strongly-correlated electronic systems display fascinating states of matter that are intriguing both from practical as well as fundamental point of view: magnetic order, superconductivity, multiferroicity and more. As such, after having explored the ground-state properties of these materials, their dynamic response to ultrafast electromagnetic excitation is now gaining a lot of attention from researchers around the globe. The photo-induced non-equilibrium state along with the dynamical processes guiding its relaxation back into the ground state need to be explored. This is particularly important because they are a hallmark of interactions stabilizing the strongly correlated state.

In this contribution, we explore the dynamics of heavy-fermion systems near quantum critical points (QCPs) after excitation with ultrafast THz pulses. A quantum phase transition (QPT) refers to a second-order phase transition between the ground states of a many-body system occurring around  $T = 0$  K that is determined by quantum instead of thermal fluctuations of the order parameter. Because of this, novel quantum states of matter appear, with consequences for their physical properties up to high temperatures. The emergence of these states can tell us a lot about the nature of QCPs. Recently, we have demonstrated that time-resolved THz spectroscopy can give us a very direct access to the QCP physics [1] because its energy matches that of elementary excitations characterizing the ordered state. We excite quantum critical heavy-fermion systems directly by THz pulses of  $\sim 1$  ps. We then measure the quasiparticle weight in the heavy-fermion compounds for temperatures from 2K to 300 K. By monitoring the dynamical response to this excitation while tuning our heavy-fermion systems around the QCP, we observe time-resolved collapse and resurgence of the quasiparticles. Additionally, this method distinguishes contributions from the heavy Kondo band and from the crystal electric-field (CEF) split satellite bands by different THz response delay times [1]. We find that an exponentially enhanced, high-energy Kondo scale controls the formation of heavy bands, once the CEF states become thermally occupied [2]. Our experiments, corroborated by temperature-dependent, high-resolution dynamical mean-field calculations reconcile the apparent observation of large Fermi volume at temperatures much higher than the Kondo lattice temperature. Further, we would like to investigate the subtleties of QCP physics by strain tuning in epitaxial thin films of heavy-fermion compounds. Strain, we anticipate, can provide an extended platform for continuous tuning of QCP as it would directly act on the balance between 4f-electron exchange and screening.

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### **23. Tracking the order parameter motion during a coherent antiferromagnetic spin precession (Fiebig)**

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Recently, antiferromagnets attract increasing attention for spintronics applications. The high frequency of antiferromagnetic (AFM) resonances suggests the possibility to coherently control AFM order on picosecond time scales. AFM spin dynamics, however, are often obscured by the relative inaccessibility of the AFM order parameter. Here, we directly reveal the dynamics of the AFM order using time-resolved optical second-harmonic generation (SHG). Exploiting the inverse Faraday effect, we optically excite a specific magnon mode in hexagonal YMnO<sub>3</sub> and track the ensuing order-parameter dynamics. The coherent Z-mode precession results in a symmetry reduction of the AFM order. SHG as a symmetry sensitive technique allows us to separate electron from spin dynamics, which enables a time-resolved quantitative tracking of the AFM order parameter. Specifically, we can estimate the optically induced spin canting angle to be approximately 0.5°. In combination with the simultaneously measured Faraday rotation, we obtain access to both the compensated and uncompensated components of the order parameter, which allows us to track its motion during the AFM spin precession. Probing dynamic symmetry reductions constitutes a general approach, which allows tracking AFM spin dynamics also in anharmonic situations, such as spin reorientations.

### **24. Transient infrared response of PDZ2 domain protein upon light induced ligand perturbation (Hamm)**

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In order to study the early stage perturbation of the system, we have designed a photo-controllable peptide ligand which binds in a different manner to the PDZ2 domain protein, depending on the state of the photo-switch. Photo-induced isomerization of the ligand leads to ca. 4 fold difference in affinity towards PDZ2 domain protein. This change in the ligand structure gives rise to an ultrafast change in the global amide I and amide II response of the system. In order to isolate the protein response from the one of the peptide, we have isotope labeled the PDZ2 domain which red-shifted the amide I and amide II bands by ca. 40 wavenumbers. Transient infrared spectra show an interesting behavior of the system; the data analysis reveal rearrangements of the protein structure happening on three distinctive timescales.

### **25. The Impact of Nuclear Quantum Effects on the Structural Inhomogeneity of Liquid Water (Hamm)**

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The 2D-Raman-THz response of liquid water is studied in dependence of temperature and isotope substitution (H<sub>2</sub>O, D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O). In either case, a very short-lived (i.e., between 75-95 fs) echo is observed that reports on the inhomogeneity of the low-frequency intermolecular modes, and hence on the heterogeneity of the hydrogen bond networks of water. The echo lifetime of D<sub>2</sub>O is 6.5 ± 1% slower than that of H<sub>2</sub>O, and both can be mapped upon each other by introducing an effective temperature shift of  $\Delta T = 4.5 \pm 1$  K. In contrast, the temperature dependent echo lifetimes of H<sub>2</sub><sup>18</sup>O and H<sub>2</sub>O are the same within error. D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O have identical masses, yet H<sub>2</sub><sup>18</sup>O is much closer to H<sub>2</sub>O in terms of nuclear quantum effects. It is therefore concluded that the echo is a measure of the structural inhomogeneity of liquid water induced by nuclear quantum effects.

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Shalit A., Ahmed S., Savolainen J. and Hamm P., Nat. Chem. 9, 273–278 (2017)

## 26. Signatures of intra-/intermolecular vibrational coupling in halogenated liquids revealed by multidimensional Raman-THz spectroscopy (Hamm)

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The spectral properties of liquids in the terahertz (THz) region play an important role in chemistry, as they reflect motions of large molecules and molecular complexes which, in turn, govern chemical reactivity and processes like solvation. These specific properties of liquids can be addressed either via resonant THz spectroscopy or Raman spectroscopy. However, due to the ultrafast dynamics and the large anharmonicity of intermolecular modes, low frequency one-dimensional spectra (both Raman and THz) are mostly blurred and indistinct. Multidimensional spectroscopy can enhance spectral resolution by spreading spectra in more than one frequency dimension, thus increasing significantly the amount of information that is possible to extract [1].

Here, we demonstrate the unique capabilities of 2D Raman-THz spectroscopy, a novel 2-dimensional spectroscopic technique developed in our group [2], of measuring coupling between low-frequency vibrational modes, information that are not present in a 1D linear spectrum. To that end, we recorded the 2D Raman-THz responses in the spectral range between 1 and ~ 8 THz of liquid bromoform and dibromomethane. The spectra reveal cross peaks which we attribute to the coupling between the relatively sharp intramolecular modes and the much broader intermolecular degrees of freedom of these solvents.

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## 27. Investigating S-protein/S-peptide structural changes in time-resolved manner (Hamm)

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Understanding detailed mechanisms of biomolecular recognition has important implications in many different fields and can enable novel strategies for rational drug design. Transient spectroscopy techniques represent a promising tool to enrich the static pictures of interacting partners with essential dynamic aspects. Ability to control protein-peptide interactions is the main requirement for the application of ultrafast transient IR spectroscopy. RNase S complex is a promising model system for understanding both protein-peptide interactions and folding/unfolding transitions. This non-covalent complex is composed of S-protein and S-peptide fragments obtained by the proteolytic cleavage of a single peptide bond within RNase A. Precise mechanism of S-peptide coupled binding and folding is still not elucidated. Additionally, a recent MD simulation study suggested that relatively large conformational changes occur in the S-protein upon binding to S-peptide.

Here, we present the design of photoswitchable non-covalent RNase S complex. Five different RNase S variants are composed of wild-type S-protein and photoswitchable S-peptide variants. Upon ultrafast light induced photoswitching of peptides, change in the binding affinity is produced. Such design, coupled with transient IR spectroscopy, will enable further insight into the mechanism of specific recognition by capturing conformational transition steps in real-time.

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## 28. Surface versus Solution Dynamics in the Reductive Quenching of Re(I) Carbonyls on ZrO<sub>2</sub> (Hamm)

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Rhenium(I) carbonyls have been studied as both photosensitizers and CO<sub>2</sub> reduction catalysts in the past [1]. A recent study has shown the non-innocence of a TiO<sub>2</sub> semiconductor film in the complex electron (back-)transfer dynamics of these systems [2], making the study of the specific quenching mechanisms an interesting topic. We present time resolved optical-pump-IR probe spectroscopy of a photosensitized surface and focus on the electron transfer quenching of the triplet excited state of a surface-attached metal carbonyl complex. The excited state of [ReI(bpyBP)(CO)<sub>3</sub>Cl], with bpyBP = [2,2'-bipyridine]-4,4'-diylbis(phosphonic acid) is quenched by sacrificial and reversible electron donor molecules in aqueous and polar organic solvents within its lifetime (40 ns). The decay kinetics on a redox inert mesoporous ZrO<sub>2</sub> surface and the dependence of the photochemical reaction on the quencher concentration are discussed in comparison with the same processes in solution.

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## 29. Dynamic studies of diffusional processes at buried interfaces using transient IR spectroscopy (Hamm)

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Atomic layer deposition (ALD) is a useful technique with the advantage of a notable control of the thickness of the deposited films on the sub-nanometer scale. In many photochemical systems the application of ALD has been shown to protect the anchoring groups of adsorbed photosensitizer molecules from attack by the solute environment. This method usually increases the stability of the system and efficiently prevents molecule desorption. [1,2] In photocatalysis the challenge is, that the active site of the molecule retains its activity and availability for chemical transformations while the anchoring groups are enclosed by ALD deposited material. [3] Time resolved IR measurements can help to elucidate the effects on photochemical reaction dynamics that arise from embedding the molecules in an ALD deposited protection environment.

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## 30. Ultrafast broadband transient CD and 2D-UV spectroscopy of peptide backbone conformational dynamics (Hamm)

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An important motivation for the development of broadband multidimensional spectroscopies is to access electronic couplings in biomolecules. Current broadband 2D-UV setups allow probing in the range from 250-370 nm, where aromatic amino acid and nucleobases absorb. The recent development of a broadband transient CD setup provides an additional tool to observe biomolecule structure and dynamics in the same probe region. Direct access to peptide backbone transitions is not possible in this wavelength regime as peptide bond absorption occurs only below 250 nm. By substituting the carbonyl

oxygen with sulfur, the strong  $\pi$  absorption of the peptide bond is shifted from 190 nm to around 270 nm, directly into the accessible probe window. Thio-substitutions can thus be used as a direct, site-specific label of the peptide backbone in order to study its conformation. Here, we present the feasibility of probing backbone conformational changes by transient CD and 2D-UV spectroscopy using a simple proline derived dipeptide as a model. In the future, we expect thio-substitutions to become a powerful UV-label to study ultrafast dynamics of peptide secondary structure motifs.

### 31. Distance dependence of vibrational energy transfer on surfaces: calibrating an Ångström molecular ruler using 2D ATR-IR spectroscopy (Hamm)

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Intermolecular vibrational energy transfer has been recently reported in concentrated aqueous solutions,[1] crystals [2] and on surfaces.[3] While it is theoretically expected that this phenomenon has a similar distance dependence to the one shown by FRET and NOESY (given by the transition dipole-dipole coupling picture), no systematic experimental verification of this model has been reported yet.

Our system consists of the  $^{12}\text{CO}$  and  $^{13}\text{CO}$  isotopologues of  $[\text{Re}(\text{dcbpy})(\text{CO})_3\text{Br}]$  (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid), coadsorbed on a mesoporous  $\text{TiO}_2$  layer with 4-cyanobenzoic acid or a third isotopologue of the complex ( $^{13}\text{C}^{18}\text{O}$ ) as a diluent. Ongoing experiments aim to rigorously assess the distance dependence by systematically changing the ratio of the diluent molecule while keeping the ratio of the  $^{12}\text{CO}$  and  $^{13}\text{CO}$  isotopologues constant and evaluating the effect in the cross-peak dynamics. We observe, at a preliminary level, a moderate effect of controlled dilution on a  $\text{TiO}_2$  surface in the energy transfer dynamics, and they are discussed in the context of the transition dipole-dipole model.

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### 32. Feynman Diagram Description of 2D-Raman-THz Spectroscopy Applied to Water (Hamm)

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2D-Raman-THz spectroscopy of liquid water, which has been presented recently (Proc. Natl. Acad. Sci. USA 110, 20402 (2013)), directly probes the intermolecular degrees of freedom of the hydrogen-bond network. However, being a relatively new technique, its information content is not fully explored as to date. While the spectroscopic signal can be simulated based on molecular dynamics simulation in connection with a water force field, it is difficult to relate spectroscopic signatures to the underlying microscopic features of the force field. Here, a completely different approach is taken that starts from an as simple as possible model, i.e., a single vibrational mode with electrical and mechanical anharmonicity augmented with homogeneous and inhomogeneous broadening. An intuitive Feynman diagram picture is developed for all possible pulse sequences of hybrid 2D-Raman-THz spectroscopy. It is shown that the model can explain the experimental data essentially quantitatively with a very small set of parameters, and it is tentatively concluded that the experimental signal originates from the hydrogen-bond stretching vibration around  $170\text{ cm}^{-1}$ . Furthermore, the echo observed in the experimental data can be quantified by fitting the model. A dominant fraction of its linewidth is attributed to quasi-inhomogeneous broadening in the slow modulation limit with a correlation time of 370 fs, reflecting the lifetime of the hydrogen-bond networks giving rise the absorption band.

D. Sidler and P. Hamm, J. Chem. Phys. 2019, accepted

### 33. Energy Transfer Processes in DNA-Organized, Multi-segmental Chromophore Stacks (Häner)

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Previous studies in the field of DNA-organized multi-chromophoric systems containing phenanthrene and pyrene derivatives showed highly efficient excitation energy transfer from phenanthrene to pyrene.[1-3] Furthermore, the energy transfer still takes place when the phenanthrene antenna is separated from the pyrene acceptor (segmented system) by up to three DNA base pairs.[4] These results lead us to the construction of multi-segmented systems in which a number of light-harvesters and acceptors are distinctly aligned at well-defined positions - rather than distributed randomly - still profiting from a self-assembling synthesis route and, at the same time, maintaining DNA base pairing specificity (Fig.1). Herein, the light-harvesting properties of such systems are described. Single strands and duplexes were characterized by UV-vis and fluorescence spectroscopy and in addition, for first studies on a multi-segmented polymer, atomic force microscopy (AFM) was used.

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### 34. Towards pulse shaping in a strong-field, tabletop narrowband Terahertz source (Johnson)

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In many solid state systems the frequencies of magnetic and vibrational excitations lie within the terahertz (THz) frequency range. It is then natural to suppose that for some of these excitations, THz frequency electromagnetic radiation can be used to coherently drive changes in material properties. Typical high intensity terahertz sources focus on broadband, nearly single cycle pulses. These sources, while useful for applications where interesting processes are triggered by a high transient field, are less appropriate for driving underdamped material resonances. For these applications, a narrowband source (bandwidth < 10 %) can more efficiently drive material dynamics. As these dynamics become large enough for nonlinearities to become non-perturbative, it is also useful to be able to shape the temporal profile of the driving pulse, as has been shown theoretically by Itin and Katsnelson [1].

Here, we describe the specifications of the setup and the design of the THz source based on a modification of the method demonstrated by Liu et al [2]. The setup uses chirped IR pulses for a difference-frequency generation (DFG) process resulting in narrowband pulses with frequencies between 5 and 20 THz. Both the temporal overlap between the two incoming IR pulses and their individual chirp properties and center frequencies can be tuned in the setup. Simulations using SISYFOS [3] show different pulse shapes and their resulting THz fields.

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### **35. Dynamics of a phonon-mediated laser-driven structural phase transition in Sn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> (Johnson)**

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We investigate the structural dynamics of the incommensurately modulated phase of Sn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> by means of time-resolved x-ray diffraction following excitation by an optical pump. Tracking the incommensurate distortion in the time domain enables us to identify the transport effects leading to a complete disappearance of the incommensurate phase over the course of 100 ns. These observations suggest that a thin surface layer of the high temperature phase forms quickly after photo-excitation and then propagates into the material with a constant velocity of 3.7 m/s.

### **36. Probing attosecond collective electron dynamics in metals (Keller)**

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We investigated the ultrafast electronic response of the transition metal Ti following the interaction with an intense optical laser pulse [1]. While thermalization effects occur on the femtosecond timescale, the collective electron motion associated with screening dynamics naturally lies on the attosecond timescale in metals.

In our experiment, we used attosecond transient absorption spectroscopy (ATAS) to track this ultrafast response. We combined a near-infrared (NIR) pump pulse with an attosecond extreme-ultraviolet probe pulse, tuned around a collective resonance at the Ti M<sub>2,3</sub> edge. Simultaneously to the ATAS measurement, we recorded a streaking trace to extract directly the response time of the absorption modification to the NIR pulse. Our results show a quasi-instantaneous linear change of the absorption following the fluence of the driving pulse.

Using time-dependent density functional theory calculations, we could reproduce the measured signal. To further understand the physical mechanism responsible for the observed behavior, we applied a decomposition of the first-principles simulation into three contributions: (1) electronic structure normalization, (2) state-filling and (3) local-screening modification. Our result shows that local-screening effects play a significant role. In particular, we found that the absorption of the NIR pulse results in the localization of the electronic density on the d-orbitals. This process happens faster than the optical cycle (measured response time is less than 1.2 fs).

Our findings demonstrate the possibility of modifying the electronic properties of transition metals on a timescale faster than electron thermalization, by means of manipulating the relative occupation of localized and de-localized orbitals with light.

[1] M.Volkov, S.A.Sato, F.Schlaepfer, L. Kasmi, N.Hartmann, M.Lucchini, L.Gallmann, A.Rubio and U.Keller arXiv:1811.00801 (2018)

### 37. Investigation of angular resolved photoionization time delays (Keller)

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Here, we show a summary of recent projects performed with the attoCOLTRIMS setup. This instrument is a unique combination of a reaction microscope detector and a two-color (XUV-IR) pump-probe setup with attosecond time resolution (1, 2).

By exploiting the coincidence detection and the possibility to resolve the angular distribution of both photo-electron and -ions we could carry out three investigations that help to deepen our understanding of atomic and molecular photoionization time delays.

All investigations have been carried out exploiting the interferometric XUV pump/IR probe RABBITT technique.

First, we demonstrate how the angular dependence of the atomic time delays is affected by correlation effects associated to the mechanism of autoionization, thus giving access to angle-resolved multi-electron dynamics on the attosecond time scale (3). The measurements have been performed in argon in a spectral energy range where the  $3s13p6np$  series of autoionizing resonances can be efficiently populated.

Next, we present two studies on the diatomic molecules  $H_2$  and  $CO$  that demonstrate how the phase of the escaping electron wavepacket is a sensitive probe not only of the electron dynamics, but also of the nuclear dynamics. The electronic-nuclear coupling is particularly important in molecules containing light nuclei (4) as is the electron localization at the moment of ionization (5).

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### 38. Efficient 206 nm deep-UV generation with 2 W average power from 100-kHz picosecond pulses (Keller)

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We present a 100-kHz all-solid-state deep-ultraviolet source delivering few-picosecond pulses at 206 nm with 2 W of average power based on non-collinear sum frequency generation. This scheme features high conversion efficiency by pulse front tilt matching and beam flattening.

The 206 nm radiation is derived in three steps by fifth harmonic generation from a 1030-nm, 1.6-ps  $Yb^{3+}$ :YAG laser. The steps are second harmonic generation (SHG), fourth harmonic generation (FHG) and sum frequency generation (SFG). Almost loss-less beam flattening of the pump pulse is achieved by means of a cascaded  $\chi(2)$ -effect in lithium triborate (LBO). The flattened profile is then imaged throughout the setup to preserve the flat top beam character.

We send 55 W of the flattened pump into an LBO crystal where it is collinearly frequency-doubled to 32.8 W of 515 nm radiation. The spatiotemporal properties ( $M^2 = 1.4$ ) and the temporal shape of the pump (ripples due to  $\sim 1.5$  ps<sup>3</sup> of third order dispersion) limit the achievable internal conversion efficiency to 60%.

The fourth harmonic stage is pumped with up to 15.5 W of 515 nm light from the SHG stage. In order to reduce two-photon absorption and prevent potential crystal degradation both the FHG and SFG stage are designed for low intensities ( $<100$  MW/cm<sup>2</sup> of  $4\omega$ ). Both stages use uncoated beta barium borate (BBO) crystals and a large aperture beam size of (11.4 $\times$ 2.6) mm<sup>2</sup> ( $1/e^2$  intensity diameter). We achieve an internal conversion efficiency of the FHG stage of 40.6% and a maximum fourth harmonic power output of 5.1 W.

The  $4\omega$  radiation from the FHG stage is non-collinearly mixed with 11.5 W of the remaining flattened fundamental in the SFG stage and yields a high internal  $4\omega$  to  $5\omega$  conversion efficiency of 48.4%. This corresponds to stable 2.0 W of output power at 206 nm. The high efficiency of the non-collinear SFG design requires a significant free-space pulse front tilt on the  $1\omega$  and  $4\omega$  pulses which reduces the group velocity mismatch and allows for temporal overlap over the complete beam profile.

To our best knowledge, these FHG and SFG efficiencies as well as the 2-W average output power of few-picosecond pulses at 206 nm beat the current world record [1] by more than a factor of two. So far, the obtained results show no fundamental limitations in the power scalability of the design.

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### 39. Unfolding the physics of shape resonances in the photoionization delays in N<sub>2</sub>O molecules (Keller)

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The phenomenon of molecular shape resonances has been a heavily discussed topic in the field of molecular spectroscopy, however it remained not without controversy [1].

The shape resonance results from the intricate balance between the combined Coulomb ( $1/r$ ) and centrifugal ( $1/r^2$ ) potentials, which results in the formation of a barrier in the molecular potential. This barrier traps the photoelectron, spatially and temporally, in a quasi-bound state after photoionization characterized by a high angular momentum  $l$  [2]. The electron wave packet eventually tunnels through the barrier into the continuum, leading to a local enhancement of the cross-section and a significant change in the photoelectron angular distribution [3]. It has been recently shown that shape resonances can induce photoionization delays up to  $\sim 160$  as in N<sub>2</sub>O [4].

In this work we study the dynamical behavior of the ejected electron wave packet created by single photoionization when affected by the shape resonance in a cold target of N<sub>2</sub>O molecules using an attosecond pulse train (ATP) in the extreme ultraviolet (XUV) domain (photon energies 20 – 40 eV). We detect both the fragment-ion and the photoelectron in coincidence in a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) detector [5], such that we can access the angular resolved photoionization dynamics for fixed-in-space molecules. Specifically, we focus on the NO<sup>+</sup> fragmentation channel which appears to be the dominant contribution across the whole energy range [6]. In particular we inspect the dependence of the photoionization time delays as a function of the photoelectron emission angle and the N<sub>2</sub>O molecular orientation.

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#### 40. Technical developments towards 100 kHz keV attosecond beamline (Keller)

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Technical developments towards 100 kHz keV attosecond beamline are presented. We demonstrate a novel pulse shaping scheme using which high-power MID-IR pulses were compressed to sub-two cycle duration. Furthermore, we show HHG noise correlation study and discuss the design aspects of 100 kHz MID-IR driven attosecond beamline.

#### 41. Coherent Three-color four-wave-mixing in the extreme ultraviolet (Knopp)

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Nonlinear x-ray experiments with Free Electron Lasers (FELs) are expected to combine the advantages of nonlinear and x-ray spectroscopies. XUV FEL based coherent four-wave mixing (FWM) signals have been measured in forward and back scattering configuration

#### 42. The Effects of S-Nitrosylation on the Conformational Dynamics of Myoglobin (Meuwly)

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S-Nitrosylation is a type of post-translational modification occurs in a variety of proteins by the covalent attachment of nitrogen monoxide (NO) group to the thiol side chain of cysteine or to transition metal center of broad spectrum of proteins. Further, it is known that S-nitrosylation directly impact the regulation of numerous signal transduction pathways in cellular systems. [1] However, effects of the modification to conformational dynamics in protein structure yet to be fully understood. Herein, the main objective of the study is understanding the effects of S-Nitrosylation of Cys-10 to conformational behavior of myoglobin. Therefore, two different complexes based on wild-type myoglobin (PDB entry 2NRM) [2] and S-Nitrosylated Myoglobin been prepared; both systems have been solvated in water with a buffer region of 15 Å to edges of cubic box which has dimensions of 74Å x 74Å x 74Å. Important bonds (S-N, N=O) and torsion angle (C-S-N=O) have been parametrized by the means of density functional theory at B3LYP/6-31G\*\* level. Molecular dynamic simulations carried out with CHARMM [3] software package via utilization of CHARMM36 force field. [4] RMSD values between X-Ray structures and simulations were around 1.3Å which indicates good conformational agreement. Also, radial distribution functions and corresponding coordination numbers of the simulated S-NO have been calculated to understand water dynamics around NO group as well. As a future work, distributed charge model [5] going to be apply to simulations to better understand the effects of multipoles to S-NO probe.

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### 43. Diffusional dynamics of oxygen in and on amorphous solid water in interstellar space (Meuwly)

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Most of the knowledge that we have of interstellar media (ISM) comes from telescopic observations and direct observation using space probes. For more direct molecular level information computational exploration of the energetics and dynamics is a potentially rich source of information. The oxygen molecule is considered to be a key player in the reaction networks for the formation and accretion of complex organic molecules. However, direct experimental data is scarce.

First, the diffusional dynamics of atomic oxygen in and on amorphous solid water is characterized from MD simulations (a). Contrary to the interpretation of previous experiments (b) it is not necessary to postulate tunneling dynamics to be responsible for the observed diffusional dynamics of atomic oxygen on ice. Rather, surface roughness leads to a quadratic temperature dependence of the diffusivity (c), with an average time of 240 ps between two diffusive events. Explicit wave packet simulations demonstrate that no tunneling takes place under these conditions.

Based on this insight the formation of molecular oxygen (O<sub>2</sub>) on cold ASW surfaces is investigated. Using the Multi Surface Adiabatic Reactive Molecular Dynamics (MS-ARMD (d)) dynamics bond-breaking and bond-formation is studied. If the two oxygen atoms are sufficiently close to one another, O<sub>2</sub> formation is readily observed. In an ensemble of 1000 simulations, 79.3% of them lead to the bound state within 100 ps, with half of them reacting during the first 20 ps of the simulation. However, the O<sub>2</sub> vibrational relaxation times are slow, on the microsecond time scale. The reason of this is the insignificant coupling between the vibrational mode of the oxygen and the surrounding water, especially if a rigid water model is used.

These studies show how O and O<sub>2</sub> dynamics in and on cold amorphous solid water under conditions relevant to the interstellar medium are dominated by ultrafast processes.

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### 44. Studying reactions in a time-resolved manner with the Minimum Dynamic Path (Meuwly)

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Understanding reactivity lies at the heart of chemistry. Once the potential energy surface (PES) for a system is known, its reactions can be studied by computational means. While the minimum energy path (MEP) between two minima of the PES gives some insight into the topological changes required for a reaction to occur, it is an unrealistic depiction of the reactive process. To obtain a more realistic view, molecular dynamics (MD) simulations are required, which involves generating thousands of trajectories to sample a few reactive events. Here, the concept of a minimum dynamic path (MDP) is introduced, which, contrary to the MEP, provides insight into the reaction dynamics in a time-resolved manner. Insights obtained from studying the MDP, such as the active modes involved in the reaction, could be exploited to drive a reaction. The MDP is applied to the well-known 2-dimensional Müller-Brown PES and a realistic 12-dimensional reactive PES for sulfurochloridic acid.

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## 45. Reactive collision dynamics investigation of Methane-MgO (Meuwly)

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Methane is the principle component of natural gas and acts as a greenhouse gas. The conversion of Methane into more valuable chemicals is not possible by ordinary redox or acid-base chemistry [1]. Fast Hydrogen-atom Transfer (HAT) [1,2] was found to be important for Oxidative Coupling of Methane (OCM) [1]. OCM can therefore supply industry with value-added products, starting from cheaper and more abundant feedstock. The smallest possible species to be used in OCM is MgO to describe the following reaction:



Multi-Surface Adiabatic Reactive Molecular Dynamics (MS-ARMD [3]) simulations of the reaction were performed on a fully-dimensional potential energy surface (PES). The PES, which describes HAT, was fitted to MP2 calculations. Reactive molecular dynamics simulations were performed using stratified sampling for  $b$ . Calculations were performed for  $b = 0$  to  $b_{\text{max}}$  ( $\Delta b = 0.5 \text{ \AA}$ ). The thermal rate coefficient from trajectory calculations is determined from Reference [4] and Ref. [5].

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## 46. Vibrational Spectroscopy of $\text{N}_3^-$ in the Gas- and Condensed-Phase (Meuwly)

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Azido-derivatized amino acids are potentially useful, positionally resolved spectroscopic probes for studying the structural dynamics of proteins and macromolecules in solution. To this end a computational model for the vibrational modes of  $\text{N}_3^-$  based on accurate electronic structure calculations and a reproducing kernel Hilbert space representation [1] of the potential energy surface for the internal degrees of freedom is developed. Fully dimensional quantum bound state calculations [2] find the antisymmetric stretch vibration at  $1974 \text{ cm}^{-1}$  compared with  $1986$  from experiment. [3] This mode shifts by  $74 \text{ cm}^{-1}$  (expt:  $61 \text{ cm}^{-1}$ ) to the blue for  $\text{N}_3^-$  in water. [4] The decay time of the frequency fluctuation correlation function is  $0.8 \text{ ps}$ , in reasonable agreement with experiment ( $0.8$  to  $1.2 \text{ ps}$ ) [5,6] and the full width at half maximum of the asymmetric stretch in solution is  $20.6 \text{ cm}^{-1}$  compared with  $25.2 \text{ cm}^{-1}$  from experiment. [4] A computationally more efficient analysis based on instantaneous normal modes is shown to provide comparable, albeit somewhat less quantitative results compared to a quantum mechanical treatment of the vibrations.

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## 47. Computational study of N+O<sub>2</sub> and O+NO reactions on new analytical surfaces (Meuwly)

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In atmospheric chemistry the study of high temperature (10000-20000 K) non-equilibrium reactions is of great importance. In particular the study of reactions involving NO + O or O<sub>2</sub> + N, which are present in thin shock layer regions like the ones created by hypersonic vehicles.

In this work we study the forward and reverse reaction using QCT (quasi-classical trajectory) reaction dynamics calculations. For this purpose, we have constructed a full dimensional potential energy surfaces (PES) for the 2A', 4A' and 2A'' electronic states of NO<sub>2</sub>. Over 30000 ab initio points are calculated at the MRCI+Q/aug-cc-pVTZ level. Following a reproducing kernel Hilbert space approach [1] a full dimensional surface is constructed. State to state cross section, rate coefficients and equilibrium constant have been computed over a wide range of temperature (600 - 20000 K). Our results of cross section and total rate coefficients are compared with available theoretical [2,3,4,5] and experimental results [6,7] reported in literature. Our reported value of equilibrium constant, can serve as wide temperature benchmark for this reaction.

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## 48. Scattering study of C+NO collisions on 2A', 2A'' and 4A'' potential energy surfaces at 15-20000 K (Meuwly)

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Studies involving the collisions between C, N and O containing species are potentially important in the area of low temperature reactions in the interstellar medium and high temperature combustion chemistry. In this work, full dimensional potential energy surfaces for the 2A', 2A'' and 4A'' electronic states of CNO system have been constructed following a reproducing kernel Hilbert space approach [1]. For this purpose, more than 50000 ab initio energies are calculated at the MRCI+Q/aug-cc-pVTZ level of theory. The dynamical simulations for the C + NO → O + CN, N(2D/4S) + CO reactive collisions are carried out on the newly generated surfaces using quantum and quasiclassical trajectory (QCT) calculation method. Trajectory surface hopping method is used within the Landau-Zener formalism to investigate the effect of nonadiabatic transitions on the title reaction [2]. Reaction probabilities, cross sections, rate coefficients and branching ratios are calculated for the title reaction and compared with available theoretical [3,4] and experimental results reported in literature [5–7]. Rate coefficients and branching fractions calculated in this work are in a good agreement with the experimental [5–7] results. Reaction probabilities obtained from QCT simulations agree well with the quantum mechanical results [8]. Vibrational relaxation time for the C+NO collisions are also calculated for a wide range of temperatures. At low temperatures more than 50% of the trajectories from collision complexes with lifetimes > 100 fs while at high temperatures the lifetimes decrease to < 60 fs.

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## 49. Experimental Station Alvra @ SwissFEL: The Pilot Experiments (Milne)

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This poster will present an overview of SwissFEL's experimental station Alvra and the pilot experiments that have been performed there during the last year.

- 1) SwissFEL: The Swiss X-ray Free Electron Laser Appl. Sci. 7, 720 (2017); doi:10.3390/app7070720
- 2) Opportunities for Chemistry at the SwissFEL X-ray Free Electron Laser CHIMIA 71, 299-307 (2017); doi:10.2533/chimia.2017.299

## 50. Ultra-Broadband Time Resolved THz Spectroscopy Applied to the Study of Hot Carrier Dynamics in Lead Halide Perovskites (Moser)

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Time resolved terahertz spectroscopy (TRTS) is a very useful ultrafast laser spectroscopy technique for the study of charge carriers in semi-conductors [1]. Its sensitivity to both carrier mobility and concentration can help elucidate the mechanisms of their temporal evolution. However, traditional techniques of THz generation and detection, such as optical rectification and electro-optic sampling, are generally limited in bandwidth and temporal resolution to <3THz and 0.5-1 ps, making the study of the early dynamics an arduous task susceptible to analysis errors due to the convolution with the instrument response function (IRF). The development of gas photonics helped to solve this problem with the generation and detection of ultra-broadband and short THz pulses, thanks to the air-biased coherent detection technique [2-3] and the use of dual color laser induced plasmas for generation.[4]

We present the application of ultra-broadband TRTS to the study of early charge carrier dynamics in lead halide perovskites. These materials have become one of the dominant topics in solar energy research, thanks to their outstanding performance and facile processability. Through changes in mobility we can follow the evolution of hot carriers and relate it to carrier cooling and polaron formation times found in the literature [5]. In addition, a saturation behavior, highly dependent on cation and anion composition, can be studied through fluence dependent measurements.

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## 51. Transient-absorption study of pentacene derivatives with stable radicals (Moser)

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Pentacene and its derivatives show remarkable properties for optoelectronic applications due to their unique  $\pi$ -electron systems. [1,2] Upon UV and visible light excitation, these molecules are excited to a singlet excited state, which may then drive to a triplet state through a spin flip of the electron. This process, known as intersystem crossing (ISC), has been widely studied for pentacene in the solid state. [3]

Here, we synthesize stable pentacene derivatives with free radicals to enhance the ISC process. [4] Using transient-absorption (TA) spectroscopy, we show that a fast S1 to T1 transfer, in the tens of picoseconds time scale, occurs only for pent-trityl molecules. This unique behavior can be coupled with TREPR measurement to study the effect of electron spin polarization transfer (ESPT). [5]

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## 52. Rationalizing the Charge Transfer Mechanism of Pentamethine Cyanine Dyes (Moser)

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Cyanine dyes have been exploited for several years as a material for use in organic solar cells [1] as a result of their tunable absorption wavelength and high extinction coefficients, the latter of which allows for the active layer of the device to be very thin (20 nm). [2]

Typically, the dye is used alongside a fullerene-based acceptor in a bilayer heterojunction configuration. However, recent studies have shown that high bulk photoconductivity can be seen in pristine pentamethine cyanine (Cy5) films without the presence of a D/A interface. [3]

Here, femtosecond transient absorption spectroscopy has been employed to investigate the photophysics of Cy5 in solution and to begin to rationalise the charge transfer mechanism and reduced Langevin recombination that has been reported in the pristine Cy5 film. [3]

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### 53. Non-linear effects in CsPbBr<sub>3</sub> perovskite in a strong quantum confinement regime (Moser)

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Hybrid organic-inorganic and all-inorganic lead halide perovskites have emerged as promising materials for different technological applications, such as photovoltaic devices, LEDs, and Lasers. These semiconductors have been studied in the bulk and in the form of nanoparticles with different quantum confinement geometries (1D to 3D). However, most papers in the literature regarding 3D quantum confined perovskite or quantum dots (QDs) were studied in a weak confinement regime, with particle sizes equal or larger than the exciton Bohr radius. Here, we explored the non-linear properties of perovskites in a strong quantum confinement regime. We synthesized colloidal dispersions of CsPbBr<sub>3</sub> perovskite QDs with nanoparticle radius of the order of 2-4 nm. The QDs were characterized by transmission electron microscopy, while their optical properties were studied by steady-state and time-resolved photoluminescence spectroscopy and ultrafast transient absorption spectroscopy. The photoluminescence maximum and first excitonic absorption peak were observed at wavelengths  $\lambda = 450$  and  $440$  nm, respectively. Based on Poisson statistics for exciton population in QDs, we calculated the absorption cross-section of the material at 3.2 eV to be  $6.7 \times 10^{-15} \text{ cm}^{-2}$ . The formation of biexcitons was evidenced by the non-linear optical response of QDs submitted to increasing photoexcitation energy fluences. The biexciton binding energy was derived as being 99 meV. This value is significantly larger than the typical binding energy reported in the literature and is clearly attributed to the strong quantum confinement regime.

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### 54. THz Endoscopy for Cancer Diagnosis (Moser)

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We are developing a compact prototype for THz endoscopy, in order to perform THz in-vivo imaging of inner organs in the body. We aim in particular at cancer tumor detection in hollow organs and in live tissues. Our R&D efforts at this stage is directed to the design of a miniaturized THz endoscopic imaging system, using a thin and flexible home-made waveguide.

## 55. Reconstruction of effective THz fields for probing structural dynamics on metal catalyst surfaces (Osterwalder)

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

## 56. Development of a nonadiabatic quantum transition-state theory for electron transfer reactions (Richardson)

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Despite the tremendous success of the Marcus theory of electron transfer rates, it is not always accurate due to the absence of nuclear quantum effects and anharmonicity. In recent year, interest in understanding nuclear quantum effects in nonadiabatic reactions have been blooming. Different from the idea of extending heuristic methods (i.e. ring-polymer molecular dynamics) to treat these reactions, we propose a new quantum transition-state theory that accounts for quantum delocalization, zero-point energy, and tunneling in electron-transfer reactions. The method utilizes a natural constraint based on energy conservation, and we have proven that it tends to the correct classical limit and is exact for linear crossings. It can be computed by path-integral molecular dynamics, thus applicable to molecular systems as well as to treat reactions in solution. We showed that it has good performance on a difficult model system with multiple transition states, avoiding the problems of the Wolynes method.

## 57. On the identity of the identity in linearized nonadiabatic dynamics: Would you know one if you saw 1? (Richardson)

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Simulating nonadiabatic dynamics across multiple electronic states remains a significant challenge in theoretical chemistry. As examples of nonadiabatic systems include electron transfer and tunnelling as well as a host of ultrafast processes, gaining theoretical insight into their dynamics and thereby deepen the understanding gained from experiments is highly desirable.

While wavefunction based methods have been quite successful for small molecular systems, larger problems, especially in the condensed phase, are only accessible with semiclassical approaches, relying on Newtonian trajectories. Methods such as the linearized semiclassical initial value representation (LSC-LVR) are however known to fail in predicting electronic populations in the long-time limit.

We present a simple modification to these methods, consisting of two parts. First the problem is recast in terms of two correlation functions, one of which contains the identity operator. Secondly, instead of

computing the value of the latter using the traditional definition in terms of the trajectory, we simply invoke the exact behaviour of this quantum operator and set its classical equivalent to one.

This simple approach is tested for a number of asymmetric spin-boson systems. The result is a drastic improvement in accuracy for electronic state populations with no modification of the algorithm.

M.A.C. Saller, A. Kelly and J. Richardson, *J. Chem. Phys.*, submitted Nov. 2018, arXiv: 1811.08830

## **58. Development of novel simulation techniques for excited state dynamics (Richardson)**

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Modern high energy lasers enable the study of ultrafast phenomena in molecules. In order to explain the observed dynamics, the rapid development of experimental techniques needs to be accompanied by improved theoretical simulations. When simulating molecular dynamics in a computer, one usually separates the electron and nuclear motion in the famous Born–Oppenheimer approximation. Such a separation is however not possible if the molecular process involves more than one electronic state, which is the case for interaction with a high-energy light field. Failure of the BO approximation occurs also for a wide range of other nonadiabatic processes, such as proton-coupled electron transfer and ultrafast internal conversion through conical intersections.

We are developing a general method to go beyond the BO approximation and include nonadiabatic phenomena in MD simulations. The idea is to map the potential energy surfaces of the involved electronic states to a single effective potential energy surface in an extended phase space [1,2]. We investigate different variations of this mapping by changing the size of the extended phase space. The method can include nuclear quantum effects by using the by now well-established methodology of simulating the nuclei as classical ring-polymers [3]. This approach allows for scaling to large particle numbers, which is important in order to reach condensed-phase system sizes. We will show how the method can be used as a general tool to calculate approximate absorption spectra and time correlation functions of ultrafast processes. Benchmark calculations will be demonstrated for vibrations for a model of the pyrazine molecule.

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## **59. Experimental and Theoretical Investigation of the Assembly of a Cationic Polythiophene with Single Stranded DNA (Röthlisberger)**

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In view of the potential use of conjugated polyelectrolytes in biosensing applications, the assembly of a cationic polythiophene (CPT) with single stranded (ss) polyadenine (polyA) and polycytosine (polyC) DNA fragments was investigated by means of steady state and transient absorption spectroscopy, circular dichroism, Raman spectroscopy and classical molecular dynamics (MD) simulations. A complementary investigation of polyA and polyC alone revealed that the former maintains a rigid and elongated structure, stabilized by stacking interactions between the adenines, while the latter displays a high degree of flexibility and adopts different structures stabilized by a varying number of hydrogen bonds. The CPT/polyA assembly is characterized by limited interactions between the polymer and the DNA. Moreover, the addition of CPT has a small effect on the conformational dynamics of polyA, with the adenine base stacking still remaining prominent. The conformation of CPT fluctuates significantly. On the contrary, intermolecular interactions between CPT and polyC in CPT/polyC are more abundant, leading to a stable conformation. Especially responsible for this feature is the presence of stacking interactions between cytosines and thiophene rings. The polyC structure is characterized by the

constant presence of numerous hydrogen bonds between cytosine bases. Given the intermolecular interactions between CPT and polyC, the structure of the polymer is also more stable compared to CPT/polyA. These differences between CPT/polyA and CPT/polyC, as well as for the DNA part of each duplex compared to polyA and polyC alone respectively, demonstrate that CPT is indeed a promising candidate to be considered for the detection of different DNA sequences in the context of biosensing applications.

## 60. Development and Implementation of New Methods to Study Ultrafast Phenomena in First-Principles Molecular Dynamics (Röthlisberger)

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We present our latest endeavor in developing and implementing new computational methods/tools to study ultrafast phenomena with better accuracy and efficiency. It is well known that the high computational cost in evaluating the exact exchange potential (within a DFT/plane wave framework) often limits the exploration of *ab initio* molecular dynamics trajectories. A new scaling scheme has been implemented to make the evaluation of the exact exchange potentials considerably faster [1]. In DFT, the double hybrid functionals provide an improvement over standard hybrids due to a more accurate description of the correlation contribution, however, at the cost of calculating the second-order perturbation theory term with Kohn-Sham orbitals. In plane wave basis, the unoccupied orbitals form a very large set in contrast to the typical atom-centred bases. We working on an approach to employ genetic algorithms to reduce the number of unoccupied orbitals used by selecting only major contributors. Molecular ultrafast phenomena often necessitate the simulation of non-adiabatic molecular dynamics involving one or more excited electronic state. We are currently implementing the *ab initio* multiple spawning (AIMS) scheme within the DFT/TDDFT framework, as a part of the plane-wave based code CPMD. Stemming from the family of Gaussian wave packet based methods, this method can take into account the nuclear quantum effects by construction while an efficient implementation of the so-called spawning scheme keeps the computational expense rather low in comparison to other trajectory surface hopping schemes.

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## 61. Deep Eutectic Solvents and their applications: An insight through spectroscopy and simulation (Röthlisberger)

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Deep eutectic solvents (DES) are emerging as popular green solvents in many industrial uses. They are easily synthesised, have high viscosity and conductivity together with negligible vapour pressure. To see how the solvent affects the charge transfer dynamics in a regular molecular rotor charge transfer molecule, ultrafast excited state dynamics of 4-(N, N' dimethylamino) benzonitrile [DMABN] has been investigated in the DES (0.75 Acetamide + 0.25 KSCN). Subsequently measured reaction times of the photoexcited intramolecular charge transfer molecule (DMABN) in the DES have been compared with reaction times obtained from conventional solvents like n-hexane and acetonitrile. A strong dynamic solvent control over reaction time is noticed in DES. From steady state fluorescence, a dual emission from the locally excited (LE) and intramolecular charge transfer (CT) states of the molecule has been observed in DES, similar to polar solvents. The distribution of dual emission (LE/ CT) as well as the reaction time change considerably in the studied temperature range. The observed change at higher temperature is an effect of faster rotation of the N(Me<sub>2</sub>)-CH bond of DMABN [1, 2].

To have a deeper understanding, we have performed all atom molecular dynamics simulations of DMABN in the above-mentioned DES in close collaboration with Prof. T. Feurer's group (University of Bern). The structural and transport properties of the solvent have been computed (from a 250 ns simulation NPT ensemble and 100 ns simulation in NVE ensemble, respectively) and compared to the experimental findings. To understand the molecular basis of the different time scales found in the experiments, we are currently pursuing excited state QM/MM simulations. Excited state forces of the charge transfer molecule (DMABN) are calculated at the QM level (DFT/TDDFT with CAM-B3LYP functional), while the rest is represented by a classical force field.

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## 62. Photo-induced excited state non-adiabatic dynamics : combined theoretical/experimental studies (Röthlisberger)

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It has been a long-standing challenge to understand the molecular mechanisms of photo-induced ultrafast processes in nature. Due to the presence of a larger number of states in the excited manifold, the systems often encounter regions of strong non-adiabatic coupling, while employing the excess energy to induce other physical or chemical transformations. Therefore, excited-state non-adiabatic molecular dynamics simulation is being performed more often than ever to improve the current state of understanding of photo-induced processes. Together with Prof. U. Keller's group (ETHZ), we have investigated photo-ionisation hydrogen abstraction dynamics of acetylene in gas phase. The ultrafast dynamics, following a XUV pump pulse (causing the ionization), have been simulated by *ab-initio* trajectory surface hopping (TSH) simulations at SA(5)-CASSCF/6-31G\*\* level. Observation of C-H bond dissociations in the TSH simulations explains the presence of the peak corresponding to the C<sub>2</sub>H<sup>+</sup> ion in the steady state mass spectrum. An IR-probe induced resonant excitation and dumping mechanism has been proposed by analysing the trajectory data, which explains the effect of the pump-probe delay on the modulation of the reaction yield.

In another MUST collaboration, we investigate complex photochemistry of biological systems in condensed phase. Together with Prof. J.-P. Wolf's group we have been investigating the effect of temporal phase and duration of light pulses on the photo-induced isomerization of retinal protonated Schiff base in rhodopsin, which is considered to be one of the most efficient ultrafast photochemical processes in nature [1]. To this end, we have been performing full quantum dynamical simulations on a modified version of the so-called Hahn-Stock model [2] for rhodopsin chromophore, with explicit light matter interaction. The effect of different positive and negatively chirped pulses of different duration on the overall wave packet dynamics is being investigated to rationalise the experimental findings.

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### **63. High power broadband THz source based on an ultrafast Yb-based thin-disk laser oscillator (Südmeyer)**

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We demonstrate 0.33 mW of broadband THz radiation with spectrum spanning up to 5 THz via optical rectification in GaP, driven by a thin-disk laser oscillator generating 95-fs pulses at 48 MHz and 20 W of average power. After optimization of crystal length and pulse duration for the highest THz bandwidth, we also show a gapless spectrum spanning up to 7 THz, which is to our knowledge the broadest among Yb-laser driven THz systems.

### **64. Broadband IBS coatings for new frontiers of sub-100-fs thin-disk laser oscillators (Südmeyer)**

*Norbert Modsching,\* Jakub Drs, Julian Fischer, Clément Paradis, François Labaye, Maxim Gaponenko, Olga Razskazovskaya, Christian Kränkel, Valentin J. Wittwer, Thomas Südmeyer*

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Ion-Beam-Sputtering (IBS) allows producing dielectric layers with high accuracy, precision and damage threshold at low scattering and absorption of light. This satisfies the needs for state-of-the-art optical coatings applied in the field of ultrafast lasers as mode-locked thin-disk laser oscillators (TDLs). We identified in our Kerr-lens mode-locked (KLM) TDLs the dispersive mirrors as the limiting components to achieve sub-50-fs pulses. We developed and fabricated optimized broadband dispersive mirrors using a Navigator 1100 IBS machine enabling operation of an Yb:LuO TDL with pulse durations as short as 35 fs (34-nm FWHM) [1] and Yb:CALGO TDL with pulse durations down to 30 fs (46-nm FWHM) [2].

Further, we investigated scaling of the average power in the sub-100-fs pulse duration regime of a KLM Yb:LuO TDL. Implementing a double pass on the disk and optimizing the operation parameters enabled us to increase the output power by a factor of two and the optical-to-optical efficiency by a factor of three compared to our previous result [1]. We obtain 95-fs pulses at an average output power of 21.1 W, which is the highest average power demonstrated by any sub-100-fs oscillator.

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### **65. Molecular quantum dynamics based on exact factorization of the wavefunction (Vanicek)**

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Quantum dynamics simulations are now established as an essential tool for understanding experiments that probe matter at the microscopic level and on fundamental time-scales. Most of the methods of modern quantum chemistry are based on a particular ansatz for the molecular wavefunction, known as the Born–Oppenheimer expansion. A major limitation of this standard way of treating non-adiabatic electron-nuclear dynamics is an unfavorable scaling with the number of included electronic states. To tackle situations beyond the reach of traditional methods, a new theoretical approach based on exact factorization of the molecular wavefunction was suggested [1,2,3]. We propose a method, based on the polar representation of the time-dependent electronic wavefunction, which allows direct numerical solution of the equations of motion emerging from the wavefunction factorization formalism. Then, using a relaxed formulation of the exact factorization approach, also referred to as the time-dependent Born–Oppenheimer approximation [1], we present a full-dimensional quantum calculation of concerted

electron-nuclear dynamics initiated by outer-valence ionization of propiolic acid molecule. Obtained results are analyzed and compared with the standard nonadiabatic quantum calculations using the Born–Oppenheimer expansion. We discuss how the new technique can help in understanding quantum phenomena taking place during the first few femtoseconds of molecular rearrangement.

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## 66. Efficient geometric integrators for nonadiabatic quantum dynamics in the adiabatic basis I (Vanicek)

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The popularity of the split-operator algorithm to propagate nuclei on coupled electronic surfaces is due to its ease of implementation and preservation of geometric properties of the exact solution [1]. In addition, as we have recently shown [2], the split-operator algorithm can be composed to arbitrary orders of accuracy in the time step. However, because the method does not work for non-separable Hamiltonians, it requires a diabatic model, which is not always easily obtainable from ab initio electronic surfaces.

To this end, we present a complementary approach to the split-operator algorithm that is applicable to non-separable Hamiltonians. The methods are based on composing the explicit and implicit Euler methods to arbitrary orders of accuracy using the identical composition schemes [3,4] as for the split-operator algorithms. Furthermore, if the implicit steps are solved with a high accuracy [5], the methods preserve all the geometric properties preserved by the split-operator algorithm and, in addition, are also energy conserving.

The order of convergence and the preservation of geometric properties are demonstrated by applying the methods to a test system – a one-dimensional two-surface NaI model in the adiabatic basis.

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[2] J. Roulet, S. Choi, and J. Vanicek, Efficient geometric integrators for nonadiabatic quantum dynamics in the diabatic basis (NCCR MUST annual meeting, 2019).

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## 67. Efficient geometric integrators for nonadiabatic quantum dynamics in the diabatic basis II (Vanicek)

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The first- and second-order split-operator algorithms are widely used integrators for solving the time-dependent Schrödinger equation. These two integrators preserve some important geometric properties of the exact evolution operator: both are unitary and symplectic while only the second-order split-operator algorithm is time-reversible [1]. Higher-order split-operator based integrators are not commonly used because they are thought to be inefficient due to the large number of Fourier transforms they require. The aim of this study is to show that higher-order integrators based on the split-operator algorithm can be much more efficient (by orders of magnitude) if higher accuracy is desired.

For this, the first- and second-order split-operator algorithms were implemented. In addition, we also implemented several higher-order integrators by composing the second-order split-operator algorithm

with different composition schemes [2-5]. To test the different integrators, we performed a convergence analysis by computing the photodissociation of NaI on a two-state one-dimensional model [6].

From the results, we observe that the higher-order integrators converge faster, in the time step, and are also more efficient than the first- and second-order integrators. We also confirm that, as long they are obtained using symmetric composition methods, the higher-order integrators preserve all the geometric properties of the second-order split-operator algorithm.

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## 68. On-the-fly ab initio semiclassical evaluation of time-resolved electronic spectra (Vaníček)

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We present a methodology [1] for computing vibrationally and time-resolved pump-probe spectra, which takes into account all vibrational degrees of freedom and is based on the combination of the thawed Gaussian approximation with on-the-fly ab initio evaluation of the electronic structure [2, 3]. The method is applied to the phenyl radical and compared with two more approximate approaches based on the global harmonic approximation – the global harmonic method expands both the ground- and excited-state potential energy surfaces to the second order about the corresponding minima, while the combined global harmonic/on-the-fly method retains the on-the-fly scheme for the excited-state wavepacket propagation. We also compare the spectra by considering their means and widths [4], and show analytically how these measures are related to the properties of the semiclassical wavepacket. We find that the combined approach is better than the global harmonic one in describing the vibrational structure, while the global harmonic approximation estimates better the overall means and widths of the spectra due to a partial cancellation of errors. Although the full-dimensional on-the-fly ab initio result seems to reflect the dynamics of only one mode, we show, by performing exact quantum calculations, that this simple structure cannot be recovered using a one-dimensional model. Yet, the agreement between the quantum and semiclassical spectra in this simple, but anharmonic model lends additional support for the full-dimensional ab initio thawed Gaussian calculation of the phenyl radical spectra. We conclude that the thawed Gaussian approximation provides a viable alternative to the expensive or unfeasible exact quantum calculations in cases, where low-dimensional models are not sufficiently accurate to represent the full system.

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## **69. Monitoring structural dynamics during the generation of free charge carriers (Vauthey)**

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Photoinduced electron transfer between perylene and dimethylaniline has been measured with femtosecond transient absorption. Using diffusional encounter theory the obtained kinetics could be reproduced over six orders of magnitude in time, three orders of magnitude in viscosity and one order of magnitude in concentration in several solvents with a single consistent set of parameters. The kinetics were extracted based on physical knowledge instead of algebraic models. As opposed to chemometric approaches like target analysis or singular value decomposition, this allows to disentangle the spectroscopic data into species associated contributions which are spectrally high resolved, photometrically quantitative and may change their shape with time. Together with the information obtained from the diffusional modeling, small but significant spectral dynamics on the nanosecond timescale are attributed to the diffusional separation of the ion pair into the bulk.

## **70. High harmonic generation in strongly correlated systems: Mott insulators and spin systems (Werner)**

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Strong light-matter couplings lead to intriguing non-perturbative phenomena such as high-harmonic generation (HHG). HHG has been originally studied in gas systems and is used as attosecond laser sources. Recently, HHG was observed in semiconductors, which triggered intensive research of HHG in solid states.

In this poster, we mainly discuss possibility and mechanism of HHG in Mott insulators [1][2], which is another paradigmatic insulating phase in solid states. For the Mott insulator, We study the Hubbard Model, driven by AC fields using the dynamical mean-field theory (DMFT) implemented with the Floquet Green's functions. We show that the energy cut-off in the HHG spectrum scales linearly against the field strength but that the qualitative behavior of the HHG spectrum is different between weak- and strong-field regimes. Our analysis reveals that the dominant contribution to HHG comes from the recombination of doublons and holons, and the qualitative difference in the two regimes originates from different doublon/holon dynamics under the driving. We also discuss the similarity and the difference among the HHG spectra in Mott insulators, semiconductors and disordered systems. Finally, we briefly discuss novel possibility of HHG from spin systems reflecting dynamics of magnetic excitations [3].

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## **71. Optical detection of downy mildew in vineyard: real time and spatially resolved airborne spore monitoring (Wolf)**

*Vittorio Pini\**, *Vasyl Kilin*, *Michel Moret*, *Jérôme Kasparian*, *Jean-Pierre Wolf*

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Wine-production is an important economic activity in several Swiss agricultural areas. Unfortunately, fungal pathogens affect the wine quality and production yields in a significant manner. Current control strategies rely essentially on the extensive and pre-programmed use of fungicides. This practice is expensive, causes a progressive damage to the environment and is potentially dangerous for operators

and the final consumer. In order to optimize and reduce treatments, early detection of fungal pathogens, preferably spatially resolved and in real time, is highly desirable. We established a novel approach for the direct assessment of airborne fungal spores by combining real-time optical particle sizing and the monitoring of the local vineyard parameters, such as air and soil humidity, temperature and sunlight exposure. We set-up several automated measuring stations in various vineyards located in the commune of Dardagny (GE). From May to September 2018, an airborne impactor was set up to trap airborne particles and provide control parameters for our measuring method. We present the correlation between the data collected by station and hyperspectral multiphoton microscopy analysis on our control filters. Our results open new perspectives for a big data approach to and fluorescence-based devices for the direct detection of fungal airborne spores.

## **72. Water window high-order harmonic source based on filamentation pulse compression for transient-X-ray absorption spectroscopy (Wolf)**

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We present a 0.2 TW sub-two-cycle near-IR carrier-envelope-phase stable source based on two-stage pulse compression by filamentation for driving high-order harmonic generation extending beyond the oxygen K absorption edge. The 1 kHz repetition rate, high temporal resolution enabled by the short driving pulse duration and bright high-order harmonics generated in helium make this an attractive source for molecular-dynamics studies [1].

In close collaboration with the group of H. J Wörner, we observed the reaction dynamics of photoexcited molecules in the gas phase by transient-X-ray absorption spectroscopy using a previous version of the HHG source [2]. By probing element-specific core-to-valence transitions at the carbon K-edge or the sulfur L-edges, we characterized their reaction paths and observe the effect of symmetry breaking through the splitting of absorption bands and Rydberg-valence mixing induced by the geometry changes. We are now expanding on this success by investigating the charge/energy transfer dynamics at multiple core shell absorption edges over the full soft X-ray water window (284-545 eV) from solids and liquids using a few micrometer thick water jet (from H.J. Wörner's lab).

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## **73. Vision is sensitive to pulse duration of femtosecond laser (Wolf)**

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The vision process, which entails a long cascade of events going from initial photon absorption to nerve-impulse generation, is triggered by the rhodopsin-bound 11-cis-retinal to all-trans retinal isomerization. The ultrafast investigation of this primary vision step started with the pioneering paper by the Shank's group where the arrival in the isomerization state in less than 100 fs was time-resolved using a transient absorption scheme. Moving on this pathway, we recently investigated whether it is possible to manipulate the photo-isomerization of photoreceptor molecules in a living mouse. We first present here a pulse duration study, where a green femtosecond pulse is chirped from 50 fs to a few hundred femtoseconds, and we demonstrated that increasing the pulse duration decreases the vision process. To understand that process, we also show pump-probe experiment in living mice. These observations are interpreted as a competition between direct and reverse isomerization dynamics about the conical intersection.

## 74. Detection of Trace Amounts of Volatile Organic Compounds via Laser-Induced Condensation (Wolf)

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We present laser-induced condensation as a method for detecting of ultra-low concentrations of volatile organic compounds (VOC) featuring a detection threshold well below 1 ppb. The method was tested in lab scale experiments and compared with quantitative photo-ionization detection (PID) measurements. Furthermore this method has been shown to be sensitive to the laser excitation wavelength between 1.6 – 2.0  $\mu\text{m}$  range.

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## 75. Attosecond Transient-Absorption Spectroscopy of Strong-Field Excited Molecules (Wörner)

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In this poster we demonstrate the application of the technique of XUV transient absorption spectroscopy to the study of the ionisation induced dissociation of small gaseous molecules through strong field ionisation. XUV core-valence absorption spectroscopy is a powerful technique which allows the energy structure of unoccupied energy levels to be directly measured while indirectly probing their spatial distribution. The ability to generate femtosecond XUV pulses through high harmonic generation also allows for the technique to be implemented into a transient absorption experiment, allowing the probing of the temporal evolution of these unoccupied levels on an electronic time scale. The strong field ionisation in our experiment is achieved using an intense, CEP stable, sub-5-femtosecond visible pump pulse, which is also used for the high harmonic generation. The experimental setup, consisting of an interferometrically stabilised, spatially separated, colinearly recombined, pump-probe beamline and a high resolution XUV spectrometer, has an ultimate energy resolution under 50 meV at 50 eV with  $\sim 50$  as pump-probe delay stability. Our results show that, despite the huge variety of possible excitations that can occur when one considers a broadband, intense IR/visible pump pulse, in the case of CF<sub>3</sub>I, Rydberg/cationic excited state dynamics remain coherent and observable up to a picosecond after excitation, demonstrating the feasibility of broadband strong field pump experiments on simple molecular system as an alternative to the more traditional UV pump. Simultaneous ion TOF measurements are being implemented to allow for more accurate assignment of fragments in dissociation experiments, contributing to the ultimate goal of the experimental setup, which is the observation of all intermediate states on a few femtosecond time scale of various systems as they pass through conical intersections of different geometries.

## 76. Two-Color HHG from liquids (Wörner)

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Chemical bonding is essentially governed by the electronic structure of its entities. Therefore, information about the electronic properties of a system provide direct access to its bonding characteristics. Moreover, changes in the electronic configurations manifest itself in chemical reactions. To record electronic motion in real time is an experimental challenge due to its occurrence in the attosecond time regime. So far, only high harmonic generation (HHG) can provide the necessary time resolution. Therefore, HHG spectroscopy has evolved as a standard tool to investigate electronic dynamics in matter with unprecedented time resolution. However, these studies were limited to gas and solid targets and excluded for chemical processes relevant phase, the liquid phase. Only very recently, HHG from liquid target has been shown.

Here, we report our recent two-color experiment of HHG from liquid samples. The experimental setup consists of a Mach-Zehnder interferometer to create a collinear two-color beam. The fundamental beam from a Ti-Sapphire laser system is 800 nm. Its polarization can be controlled via a  $\lambda/4$  plate. The 400 nm pulse is created utilizing a beta-barium borate (BB) optic in one of the arms followed by a  $\lambda/2$  plate. The two collinear beams are then focused on the flat jet liquid sample. The flat jet is created utilizing two colliding round jets with a size of each  $\sim 35$  micron resulting in a thickness less than 1  $\mu\text{m}$ . The homogenous flat surface is necessary to create phase matching conditions for HHG. A varied line spacing spectrometer for the extreme ultraviolet- regime records the emitted light under vacuum condition. The variation of the temporal delay between the fundamental and second order pulses allows the record of two-color interferograms for bio-chemical relevant solvents.

## 77. Time-resolved Soft X-Ray Transient Absorption in the Liquid Phase (Wörner)

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X-ray absorption spectroscopy (XAS) has evolved into a powerful tool to investigate the electronic properties of matter. So far, such experiments have been limited to facility-scale light sources, such as synchrotrons or free electron lasers. Here, we report the development of a table-top transient absorption setup, based on high-harmonic generation to generate broadband continua covering the water window (284-538 eV). A flat jet with a thickness of approximately 1  $\mu\text{m}$  is used as the target, enabling transient-absorption measurements to be performed in transmission mode on liquids and solvated species. This setup has been demonstrated to yield promising results on static absorption spectra at the carbon and oxygen K-edges. Preliminary time-resolved studies have been performed on a range of alcohols showing a distinct femtosecond response to strong-field ionization. These results demonstrate the feasibility of soft X-ray transient absorption on liquid samples with femtosecond and possibly attosecond temporal resolution.

Combined with the site specificity of X-ray spectroscopy this development opens new perspectives in the investigation of electronic dynamics in liquids and solutions.