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1. Carrier Dynamics and Charge Separation Analysis in Polymer Fullerene Blends (Banerji)

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The nature of excited species in pBTTT:PCBM polymer fullerene blends depending on their phase morphology has been investigated with transient absorption spectroscopy on ultrashort times [1]. With an insight on the carrier separation mechanism and the carrier population of the investigated material system we now present first THz-measurements on these samples revealing their photoconductivity a few picoseconds after optical excitation. The pump fluences are on the order of $10^{13}/\text{cm}^2$ in contrast to previous studies [2],[3] where due to the high excitation density deactivation pathways such as bimolecular recombination overlay the carrier dynamics leading to steep decrease in the carrier mobility product on the first picoseconds upon excitation. We can show long lived conducting species in a 1:4 pBTTT:PCBM blend under weak excitation of the polymer in agreement with previous studies on charge separation and device performance in such blends. Additionally, we show the complex photoconductivity within our accessible THz frequencies shortly after excitation.

We also present the planned THz Emission Spectroscopy project and its theoretical framework to access the charge separation mechanism starting from a measured THz waveform which is generated in such a material system in Auston Switch configuration with constant applied bias. There we present first steps in modelling the measurement data starting from the photocurrent j and the subsequent generation of an oscillating electric field $E_{\text{THz}} = d/dt j$ as well as the electro optic detection mechanism in a non-linear crystal. We aim to connect both techniques to fully characterize the charge generation mechanics and charge transport properties on ultrashort timescales.

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[3] Cunningham, P. D. & Hayden, L. M. Carrier Dynamics Resulting from Above and Below Gap Excitation of P3HT and P3HT/PCBM Investigated by Optical-Pump Terahertz-Probe Spectroscopy †. J. Phys. Chem. C 112, 7928–7935 (2008).

2. SwissFEL Instrument ESB – Femtosecond Pump-Probe Diffraction and Scattering (Beaud/Patterson/Abela)

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The availability of hard X-ray FEL sources with femtosecond X-ray pulses has opened a new field of pump probe techniques such as X-ray diffraction, resonant X-ray diffraction, diffuse scattering or resonant inelastic scattering, which are ideal tools to investigate the dynamics of cooperative interactions in crystalline materials that exhibit long-range electronic and magnetic order or short range correlations. An important class of these materials, which can show complex phase diagrams, are correlated electron systems having a strong interaction between lattice, charge, orbital and spin degrees of freedom. This class of materials is known to show for example high temperature superconductivity, colossal magnetoresistance, metal-to-insulator transition, electron fractionalization and novel quantum-critical states. New materials combining several functional properties, multiferroics, are good candidates for future device applications. To study and characterize the dynamics in these and other crystalline materials, the ESB instrument at the SwissFEL ARAMIS hard X-ray free electron laser is designed to combine time-resolved laser spectroscopy methods with X-ray diffraction and scattering techniques. The instrument will feature pink and monochromatic X-ray mode with shot-to-shot diagnostics of the X-ray intensity and arrival time as well as a microfocus capability to obtain X-ray spot sizes between 2 and 500 μm . A commercial high power laser system will provide a variety of optical pump pulses ranging from 800 nm with less than 30 fs, over 1100 nm to 15000 nm with 40 fs to 100 fs pulse duration up to single cycle THz pulses. Laser and X-ray can be delivered in vacuum or air to one of two endstations: a six circle diffractometer featuring a detector arm with a Jungfrau 1M area detector and a polarization analyser and to a general purpose station in combination with a Jungfrau 16M area detector mounted on a robot arm offering high flexibility.

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[2] R. Follath et al., SRI Conference Proceedings, (2015)

[3] G. Ingold et al., SRI Conference Proceedings, (2015)

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3. Tools and Methodologies for UV and deep-UV Coherent Spectroscopy (Cannizzo)

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In the last two years we have devoted ourselves to improve existing and conceive novel schemes for ultrafast UV and deep-UV (DUV) spectroscopy. The goal is expediting a whole progress of ultrafast coherent spectroscopy in the DUV-UV and to make such techniques more accessible and easier to implement and operate. These tools include a portable and easy to operate broadband (FWHM of 80 nm at 300 nm) UV source and a low-noise single-shot multi-camera detection. Continuing these efforts towards the implementation of a DUV multidimensional spectrometer with shaped pulses, we have: 1) established single-shot interferometry to carry out phase sensitive measurements with conventional, not phase stabilized set-ups, 2) examined a novel type of FROG based on coherent anti-Stokes Raman scattering and 3) explored the possibility to transfer the optical phase of broadband Vis pulses into the phase of a UV pulse generated by means of angularly dispersed achromatic doubling. The first represents a substantial simplification to build-up UV-Vis multidimensional coherent set-ups; the second could provide a background free characterisation of broadband UV pulses; the last paves the way to exploiting Vis pulse-shaping technology to generate shaped broadband deep-UV pulses.

4. Efficient long-range ultrafast energy transfer in a novel family of multichromophoric antenna complexes (Cannizzo/Häner/Feurer)

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In this contribution, we investigate mechanisms responsible of a very efficient long-range energy transfer (EnT) in a family of DNA-like multi-chromophoric (MC) light-harvesting systems (LHS).

In these assemblies phenanthrenes are π -stacked in a defined configuration in a DNA-helix like structure and experience a robust and strong mutual coupling. This gives origin to an EnT over nanometers with unitary quantum yield and a very high absorption cross-section. An energy acceptor (a pyrene) can be incorporated in a defined place of the MC-LHS to make the EnT site-specific and unidirectional, while neutral bridges (e.g. DNA nucleotides) can be inserted as a molecular spacer between two phenanthrenes to measure the spatial extension of the inter-chromophore coupling. This capability of placing the acceptor and neutral bridges in different sites with respect to the donors and of varying the length of the MC assembly helps us to clarify the relations among structure, spatial arrangement, EnT mechanism and coupling distances.

This study was carried out by synergically adopting DUV-to-Vis transient absorption spectroscopy and TDDFT calculations. We observed the presence of short-lived higher energy delocalized states which are formed instantly upon excitation in such systems and last from a few 10s to 100s of fs. This transient delocalized state mediates EnT with high efficiency and later collapses into a long-lived localized state. This result violates the common opinion that efficient energy and charge transfers need long-lived states, making such MC systems ideal models to investigate the effect of femtosecond shaped pulses and ps THz fields on transfer phenomena over long distances (>nm). They also suggest new strategies to design efficient light harvesters

5. Ultrafast study of a novel family of carbon nanomaterials (Cannizzo/Feurer)

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Carbon nanodots (CDs) are a novel family of optically-active carbon-based nanomaterials discovered only a few years ago. They are 1-10 nm nanoparticles composed by carbon, oxygen and hydrogen and endowed with a rather appealing combination of properties, such as tunable and strong fluorescence in the visible, excellent solubility in aqueous environments, photo- and chemical stability, sensitivity to perturbations like the presence of metal cations, and the capability of behaving as efficient photo-activated acceptors or donors of electrons and protons. Because of this unique combination of properties, CDs have the potential to complement or even replace semiconductor nanoparticles in several applications and domains, in particular where bio-toxicity is an issue. CDs are particularly interesting because of their enhanced fluorescence, and their fundamental properties are the subject of a strong debate in the literature. Understanding the optical properties of CDs at the fundamental level is crucial to move towards applications such as optoelectronics, bio-imaging, physicochemical sensors and markers.

We carried out an extensive study on CDs characterized by different core structures: a pure graphitic and N-rich β -carbon nitride one. Thanks to a versatile DUV-to-Vis femtosecond time-resolved transient absorption (TA) spectrometer with time resolution of 40 fs (standard deviation), we could extensively vary pump wavelength and polarization, to gain a deeper understanding of the photophysical properties of CDs and of the dynamics of the higher excited states. Our results provide unanticipated insight on the photocycle of carbon nanodots in aqueous solution, tracking down the steps of the intra- and inter-dot photo-excited relaxations and their characteristic timescales. In particular, we observed for carbon nitride CDs rotational diffusion of the transition dipole moments on timescales (10s ps) much faster than the rotational diffusion of the entire nanoparticles (10s ns). This finding reveals for the first time a diffusional energy transfer occurring through surface electronic states of the nanodots, making them appealing for chemical sensing or as light harvester antennas. In graphitic dots, we observe very likely a photo-induced formation of conductive electrons, absent in the N-rich CDs in the investigated spectral region.

Modelling and further experimental evidences, including UV two-dimensional spectroscopy, are underway to rationalize such an unexpected behaviour.

6. Revealing the Origin of the Cycloid Spin-Order Melting in Multiferroic TbMnO₃ (Carbone/Johnson)

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One fascinating topic in the field of nonequilibrium dynamics concerns the manipulation and control of magnetic order using ultrashort laser pulses. Preliminary experiments established a characteristic timescale for the magnetic disordering of a strongly correlated system with exotic spin pattern [1, 2]. In this context, an unexpected phenomenon has been recently observed in TbMnO₃ [3], which is a prototypical example of multiferroic chiral magnet. In this system, the melting of the long-range magnetic order was observed to proceed on timescales of 20 ps after the excitation with 1.55 eV photons [3]. Such slow dynamics naturally imply a delayed transfer of energy from the photoexcited carriers to the cycloid spin system. Here, we elucidate the energy pathway and the involvement of other degrees of freedom in this spin-order melting process by performing ultrafast optical spectroscopy with a combination of broad detection window and high temporal resolution. We clarify that the exchange of energy from the electronic to the spin degrees of freedom is mediated by high-energy coherent optical phonons that couple to the photogenerated charge density. The emergence of these coherent collective modes also allow gaining insights into the nature of the photoexcited charge density and into one of the long-standing questions in manganite physics, namely the origin of the fundamental charge gap in these materials.

[1] M. Först et al., Phys. Rev. B 84, 241104 (2011)

[2] S.L. Johnson et al., Phys. Rev. Lett. 108, 3, 037203 (2012)

[3] J. A. Johnson et al., Phys. Rev. B 92, 184429 (2015)

7. Investigation of electron-phonon coupling in carbon-based materials with optically-driven lattice via ultrafast THz and electron techniques (Carbone)

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Electron-phonon coupling influences most of the collective properties of solids, determining the stability of orders like superconductivity, charge and spin density waves. The ability to control electron-phonon coupling in non-equilibrium configurations may provide new ways to change materials' properties and steer their functionalities.

Here, we set out to understand if optical modulation of the lattice can change electron-phonon interaction. Carbon-based materials, exhibiting IR active phonons at high energies (150-200 meV) where intense optical pulses can be obtained with moderate effort, provide an interesting playground where our scientific problem can be investigated with a variety of experimental strategies.

We explore the response of bilayer graphene in response to the resonant excitation of the in-plane bond stretching E_{1u} phonon with pulses at 6.3 μm via terahertz time-domain spectroscopy and time- and angle-resolved photoemission (ARPES) [1].

Drude scattering times in the optical conductivity significantly increase as well as momentum-integrated relaxation rates of hot quasi-particles. These two independent observations can be explained by a transient three-fold enhancement of the electron-phonon interaction λ , which can quantitatively reproduce the cooling of the electronic temperature and the acceleration of the quasi-particle relaxation observed in the ARPES experiments when the optical excitation is resonant with the phonon. The increase of λ leads to an enhancement of the carriers' effective mass and to a transient modification of their thermal capacity.

Our data may provide useful perspective for explaining the enhancement of superconductivity observed in K-doped fullerenes [2]. However, the microscopic origin of the enhancement of the electron-phonon coupling is not clear yet. A non-linear phononic coupling mechanism [3] could be responsible of a transient crystal structure different from the one at equilibrium [4], inducing changes in the electronic structure and therefore in λ [5]. In addition, it has been theoretically shown that phonon nonlinearities can reduce the electronic bandwidth and thus increase the density of states at the Fermi level [6].

To further elucidate this problem, we will perform new studies adopting ultrafast electron techniques on various carbon allotropes.

Ultrafast electron diffraction will allow us to directly visualize with femtosecond resolution the structural dynamics associated with the resonant excitation of similar phonon modes in graphite or carbon nanotubes [7]. Important insights into the anharmonic phonon coupling mechanisms stemming from the phonon excitation can also be obtained [8]. Possible modulation of the electronic structure and charge distribution upon phonon pumping can be instead investigated by fs-resolved energy loss spectroscopy (EELS) in a transmission electron microscope [9]. Ultrafast electron microscopy can also be used to corroborate the optically-induced superconducting state in materials like K-doped fullerenes by probing their behavior in response to external magnetic fields with the cryo-Lorentz technique [10].

The combination of intense THz optical excitation with ultrafast electron methods represents a very powerful strategy to provide direct insights into the nature of many-body interactions and the possibility of their control in optically-driven materials.

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[2] M. Mitrano et al, Nature 530, 461 (2016).

[3] M. Först et al, Nature Physics 7, 854 (2011).

[4] R. Mankowsky et al, Nature 516, 71 (2014).

[5] I. Gierz et al, Phys. Rev. Lett. Phys. Rev. Lett. 114, 125503 (2015).

[6] M. Knap et al, arXiv:1511.07874v2 (2016).

[7] F. Carbone et al, Phys. Rev. Lett. 100, 035501 (2008).

[8] M. Harb et al, Phys. Rev. B 93, 104104 (2016).

[9] F. Carbone et al, Science 325, 181 (2009).

[10] A. Tonomura, Journal of Electron Microscopy 51 (Supplement), S3 - S11 (2002).

8. Probe magnetism in a dynamical transmission electron microscope: a study on skyrmions in FeGe (Carbone)

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Lorentz-Fresnel mode in Transmission Electron Microscopy is a powerful tool to study the real-space configuration of magnetic structures in thin magnetic specimens. A high coherent electron source is required to visualize magnetic contrast.

We adapted an Ultrafast-TEM to work with ns-pulses, achieving enough brightness and coherence to get proper Lorentz images of magnetic structures, such as magnetic domain walls, magnetic helices and, notably, magnetic skyrmions.

Magnetic skyrmions are nano-scale spin structures, observed in several materials with chiral space-group, in a rather small region in the magnetic field-temperature phase diagram. They are considered promising candidates as information carriers in logic or storage devices due to their nanometric size (<100 nm) and robustness. Since they are topologically protected particles, with topological charge being the winding number, their spin texture is unable to be unwrapped by smooth continuous deformation of the fields.

It is therefore of interest to study their formation, annihilation and dynamics as a result of the interaction with light.

Preliminary pump-probe data to address the fully reversible dynamics under ns-laser excitation are shown. In addition, we observed that light excitation can cause a plethora of irreversible effects on the magnetic structures. As an example, we show that it is possible to write magnetic skyrmions in a ferromagnetic background using a single laser pulse (10 ns, 532 nm), if the fluence is above a given threshold.

9. A broadband femtosecond time-resolved circular dichroism spectrometer in the near-UV (Chergui)

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We present the first time-resolved circular dichroism spectrometer with broadband deep UV femtosecond probe pulses (260 – 360 nm) and shot-to-shot polarization state switching via a photoelastic modulator. Our setup has the additional benefits of a high pulse repetition rate (20 kHz) with low intensity noise (< 1% rms) and a shot-to-shot data acquisition system. The scheme offers a unique opportunity to combine time-dependent electronic information from traditional transient absorption spectroscopy with structural information encoded in the chirality of molecular systems. Here we evaluate the capabilities of the setup by applying it to enantiomerically pure samples of Δ, Λ -[Ru(bipy)₃]²⁺.

10. Ultrafast exciton dynamics in CH₃NH₃PbBr₃ single crystals (Chergui)

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Organo-metal halide perovskite-based solar cells have witnessed an incredibly fast emergence in the last years. This success is primarily due to the rapid increase in conversion efficiency, now approaching 21% [1], and to the low manufacturing costs that make hybrid perovskite materials an attractive alternative to silicon. Moreover, the high photoluminescence quantum efficiency and the narrow and tunable emission band that characterizes these semiconducting materials, make them the perfect candidate for high-performance optoelectronic devices [2]. In order to optimise these unique features, detailed understanding of the photophysics of organo-metal halide perovskites is needed.

In this regard, ultrafast spectroscopy is a powerful approach to reveal the dynamics of charge carriers and gain a deeper insight into the phenomena governing the unique behaviour of these materials. Here, we perform femtosecond broadband transient-reflectivity measurements on solution-grown single crystals of CH₃NH₃PbBr₃. We tune the pump photon energy to 3.1 eV, in order to excite uncorrelated electron-hole pairs well above the bandgap energy (2.4 eV) at difference pump fluences. The high temporal resolution of our experimental set-up (<50 fs) [3] allows to follow the evolution of the sample reflectivity in the first hundreds of fs, revealing how the resonant exciton at the absorption onset is affected by the many-body dynamics of the photoinduced carriers. We complement these results with equilibrium ellipsometry measurements in a broad spectral range and at different temperatures. Our approach gives access to the evolution of the sample complex optical conductivity without the need of a Kramers-Kronig analysis.

11. Exciton Bleaching as a Probe of Ultrafast Interfacial Electron Injection (Chergui)

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Recently, we have demonstrated the existence and room temperature stability of strongly bound excitons in anatase TiO₂ single crystals and nanoparticles [1], clarifying the details of the nonequilibrium dynamics resulting upon photoexcitation [2]. A natural step forward involves the ability to exploit the newly discovered excitons as a promising route for novel technological applications. An interesting possibility regards the detection of the interfacial electron transfer between molecular adsorbates into anatase TiO₂, which has been subject of huge interest for several years for the fields of solar energy conversion and photocatalysis. An unambiguous, universal and possibly laboratory-based probe of charge injection is needed that can be implemented under the operating conditions of devices. In this regard, a promising route is offered by the detection of the specific spectral signature of the exciton, as opposed to the rather featureless absorption of conduction band electrons. Here, we show via ultrafast broadband UV spectroscopy that a pronounced bleaching of the exciton feature occurs in anatase TiO₂ nanoparticles following the injection from an external dye (N719). These results offer a new methodology that can be applied to the case of solid-state sensitizers, such as hybrid organic-inorganic perovskites or gold nanoparticles. We argue that this framework can also be extended to other transition metal oxides possessing high-energy collective excitations at room temperature, e.g ZnO.

[1] E. Baldini et al., <http://arxiv.org/abs/1601.01244>, submitted.

[2] E. Baldini et al., in preparation.

12. Tracking photo-induced ultrafast charge transfer in solvated ferricyanide (Chergui)

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The ultrafast ligand-to-metal charge transfer (LMCT) transition of solvated ferricyanide is studied by combining photoelectron spectroscopy (PES) of liquids and transient IR absorption (TA-IR), following photo excitation of the LMCT band centered at ~420 nm. Through PES' high sensitivity to the oxidation state of the iron center, impulsive photo-reduction of the latter is observed in a sample of aqueous ferricyanide solution, followed by ultrafast reoxidation with a ~ 600 fs time constant. Samples of ferricyanide solvated in H₂O and ethylene glycol are studied by TA-IR, probing in the ~2040 – 2130 cm⁻¹ mid-IR region containing the triple-degenerate T_{1u} CN stretch band of the complex. A strongly-broadened, red-shifted excited state decays with the same time constant found by PES. We also observe significant excitation of the $\nu = 1$ vibrational level in the electronic ground state, which decays on a 10 ps time scale.

In a complementary transient absorption UV experiment (TA-UV), a different LMCT band of ferricyanide solutions in H₂O and ethylene glycol was pumped at ~ 300 nm while probing the absorption in the 275-375 nm UV region. A ~ 500 fs time constant was found for the decay of the excited state, with the longest time constant given by a global fit in the order of 10 ps. As can be concluded from these experiments, after impulsive population of the Fe²⁺ excited state of ferricyanide through an LMCT transition, redistribution of vibrational energy involving coupling to solvent modes occurs. Before returning to the ground state, the molecule remains hot for about 10 ps, which matches previously reported vibrational energy relaxation times.

13. THz-induced electroabsorption spectroscopy setup - year in review (Feurer/Banerji/Moser)

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We report on highlights from the electroabsorption spectroscopy setup induced with single cycle THz pulses from the past year, achieved partly by improved noise suppression. These include results from polymer-fullerene blends in the form of PBTTT-, or BTTT-2-PCBM thin films as well as with the neat polymer PBTTT. The applied THz field seems to mimic the effect of blending the polymer with fullerene in that a shift of the polymer ground state absorption is observed consistent with the shift due to blending. Electroabsorption effects were also observed in perovskite thin films (MAPbBr₃, CsPbBr₃ and MAPbI₃) where a sharp absorption feature around 520 nm in all samples is red- shifted by the THz field and results in a signal with exceptional signal-to-noise ratio. Additionally we present an outlook for the coming year, which includes the implementation of a LiNbO₃ THz-generation source in a pulse-tilted and non-collinear geometry that promises to significantly improve the achievable THz field strength.

14. THz spectroscopy of vanadium dioxide (Feurer)

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Vanadium dioxide (VO₂) exhibits a reversible first order phase transition from a monoclinic insulator to a metallic tetragonal (rutile) structure when the temperature overcomes the critical value of 68°C. VO₂ thin films of different thickness are deposited via pulsed laser deposition on bare sapphire substrates and in the slits of gold nanoslit-array samples. Whereas the former sample is measured in a low-field THz spectrometer the latter is put in a high-field THz setup where the THz field, due to field enhancement in the slit region, induces the phase transition in VO₂.

15. Design concept for a THz driven streak camera with femtosecond time resolution (Feurer)

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The resolution of streak camera systems strongly depends on the slew rate of the deflecting element, being proportional to the amplitude and the frequency of the deflector. An attractive approach to reach femto and even sub-femtosecond resolution are THz driven electron streak cameras, which have been only recently proposed. Here, the ultrafast streaking field is generated by exciting a suitable resonant THz antenna, e.g. a split ring resonator with an intense THz pulse. With today's THz sources streak field amplitudes in excess of 1 GV/m are within reach.

We present the concept for a proof of principle system. The THz pulse will be generated by rectifying the pulse from an existing 800 nm laser system in a suitable crystal as LiNbO₃. For the source of the electron beam to be streaked, we plan to use an RF photo gun yielding a relativistic 6.5 MeV beam. We describe the setup of the system and present simulations of the beam dynamics.

16. Investigating protein-ligand interactions using two-dimensional infrared spectroscopy with photoswitchable peptide ligands (Hamm)

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Azidohomoalanine (AHA) is an infrared probe that is shown to be sensitive to its environment and it was previously incorporated into proteins and peptides. Its properties have been exploited to investigate protein folding as well as protein-ligand interactions.

Here, AHA is incorporated in two different positions on the opposite sides of the binding groove of PDZ2 domain from human phosphatase 1E where it serves as a reporter for ligand binding. We show that ligand binding to the AHA labelled PDZ2 domain causes 5 cm⁻¹ red shift of the AHA located in the binding groove of the protein, confirming that not only AHA labelled peptides, but also AHA labelled proteins, can be utilized for investigation of ligand binding.

Moreover, it has been shown that introducing the photoswitch into a helical peptide, by linking it to two cysteine side chain residues causes the disruption of the helical structure, leading to unfolding of the helix upon cis to trans photo-isomerization of the photoswitch.

By introducing the photoswitch to the peptide, both via cysteine linking and incorporating it into the backbone of the peptide, conformational change can be induced by photo-isomerization. This conformational change should lead to a change in the affinity of AHA labelled PDZ2 for the given ligand, allowing us to induce the ligand unbinding from the protein in a controlled manner.

17. Different Types of Terahertz Spectroscopy on Water (Hamm)

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The kinetics of the hydrated electron in its generation were studied by transient terahertz spectroscopy [1]. There, the photoionization of the water was achieved by the use of 800 nm, 400 nm and 267 nm pulses. To paint a more complete picture, this series was extended to a 200 nm wavelength, where photoionization of water by two-photon absorption, has been explored more extensively. Using the same experimental set-up we can furthermore study low frequency modes of liquid water.

Two-dimensional Raman-THz spectroscopy is a multidimensional spectroscopy used to investigate hydrogen bond networks and their relaxation dynamics. Neat water [2] and aqueous salt solution [3] have been measured so far, leading to a discussion about the effects on inhomogeneous broadening of such collective intermolecular modes. As a next step to give more insights about the origin of these effects we want to perform the same experiment varying the temperature of the water sample, ultimately going to supercooled water. Technical difficulties ask for the need of a static sample in a temperature-controlled environment.

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18. Effects of Intermolecular Charge Transfer on the 2D-Raman-THz Response of Water (Hamm)

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The experimental 2D-Raman-THz response of bulk water [1] bears information about intermolecular motions in water. Due to the complexity of the signal the support of MD simulations is needed for the interpretation of the signal. Vice versa the comparison of the experimental response to simulation can give a measure of the quality of the force field. Amongst different force fields, the polarizable TL4P water model qualitatively reproduces features of the bulk response of water [2]. However, TL4P underestimates the 200cm⁻¹ hydrogen bond vibration band in the 1D THz spectrum of water. This is due to the missing transition dipole moment which would arise from intermolecular charge transfer.

We examine the effect of the addition of intermolecular charge transfer to TL4P on the 2D-Raman-THz response, as well as the effects on the thermodynamic properties of the force field.

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19. Iterative reconstruction of molecular wave functions from angle-resolved photoelectron spectroscopy data using Fourier transform based phase retrieval algorithms (Hengsberger/Osterwalder)

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Further advancement in efficiency of molecular optoelectronic devices requires detailed knowledge of the charge transfer mechanisms at metal-organic interfaces and thus requires rigorous time-resolved spatial visualization of these processes. It was shown that unambiguous information about the wave functions of well-ordered organic large planar molecules on single crystalline metal substrates is encoded in angle-resolved photoelectron spectroscopy (ARPES) data [1-3]. Within the plane wave approximation for the photoelectron final state, the recorded ARPES intensity distribution is related to the squared modulus of the Fourier transform of the initial state wave function [1]. The latter can be computed by inverse Fourier transform of the ARPES data, provided the phase distribution in the detector plane is known. The phase distribution may be retrieved from the parity of the wave function [1], dichroism measurements [3] or iteratively, by employing knowledge about the shape of the wave function [2]. We suggest that the phase problem in ARPES based reconstruction of molecular wave functions can be solved in a more robust manner by exploiting the analogy to the phase problem in coherent diffraction imaging (CDI) [4]. Namely, if the far field optical or photoelectron intensity distribution is measured at the oversampling condition, both the amplitude and the phase of the object can be reconstructed purely from the experimentally available modulus of its Fourier transform using state-of-the-art phase retrieval algorithms, currently available in CDI [5-7]. We performed an optical analogue experiment [8] on micrometer-sized structures and reconstructed their amplitude and phase distributions from the far-field diffraction patterns. By employing the same algorithm to a set of ARPES data, we reconstructed both amplitude and phase of the lowest unoccupied molecular orbital (LUMO) of a sub-monolayer of pentacene molecules [8].

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20. Valence Level Photoelectron Diffraction of CO adsorbed on Pt(111) (Hengsberger/Osterwalder)

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Due to the pressing need for better catalysts a strong research effort is put into time-resolved investigations of the geometrical structure of adsorbates. The overall structural dynamics of surface catalytic systems is found to be on a (sub-)picosecond timescale with typical bond lengths in the 100 pm range. Attempts to resolve these dynamics by optical means require wavelengths and pulse durations on a similar length- and timescale. X-ray photoelectron diffraction (XPD) is a technique that provides possibilities to elucidate the molecular adsorption geometry. Combining a suitable trigger for an adsorbates vibrational mode of interest and XPD (excited by a short XUV pulse) into a pump-probe scheme may therefore yield time-resolved information about the geometrical orientation of adsorbates. The projects final goal is to study the time-evolution of an ensemble of adsorbed CO molecules excited into a coherent vibrational motion by a few cycle THz pulse. In the present study we investigate the system in a static fashion. The forward scattering anisotropy due to photoelectron diffraction emerging from valence level emission of adsorbed CO molecules on Pt(111) is investigated. It comprises a direct indication of the molecular C-O bond direction and hence the molecular orientation. Both, COs 5σ and 4σ frontier orbitals, show distinct photoelectron diffraction patterns at 140 eV final-state kinetic energy with the former having a detectable anisotropy along the forward scattering direction. Photoelectron diffraction patterns emerging from valence level emission are compared to those of more localized emitters, namely the C1s core level, at similar final state energies. Furthermore, different photon energies have been examined in order to obtain a favourable ratio of photoelectron intensities of adsorbates and substrate in view of our planned pump-probe experiment.

21. Modulation of the ferroelectric polarization in polar $\text{Sn}_2\text{P}_2\text{S}_6$ through THz-excitation of IR-active phonons (Johnson/Beaud/Staub)

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Terahertz radiation in the low frequency region ($f < 5$ THz) can be a very efficient method to drive modification of the ferroic order in solid-state samples [1-3].

By a combined used of broadband THz excitation (0.5 – 2.2 THz) and time resolved X-ray probing, we demonstrate the feasibility of direct and efficient excitation of the ferroelectric polarization in a polar semiconductor ($\text{Sn}_2\text{P}_2\text{S}_6$). Thanks to experimental setup optimization, we are able to produce E-field amplitudes up to 0.5 MV/cm in the sample plane, which can excite strong lattice vibrations modulating the ferroelectric polarization.

With this field, we achieved lattice excitations strong enough to induce structure factor modulations as high as 25% in poled areas of the sample (i.e. showing a net ferroelectric polarization), while only up to 6-8% in unpoled ones.

The high-amplitude THz field is not yet sufficient to achieve a deterministic reversal of the ferroelectric polarization. Nonetheless the measured dynamics show signs of nonlinearities, indicating sample excitation levels well beyond the harmonic approximation of the energy potential describing the ferroelectric phase.

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22. Coherent structural dynamics of an ultrafast CDW-to-metal transition (Johnson/Beaud)

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We use time-resolved x-ray diffraction to directly monitor the coherent structural dynamics during a photoinduced charge-density-wave (CDW)-to metal transition in the prototypical CDW compound $K_{0.3}MoO_3$. Above a critical fluence, we observe the destruction of the periodic lattice distortion and, strikingly, its subsequent transient recovery on a sub-picosecond timescale. The rich structural dynamics can be explained with a simple model of the time-dependent interatomic potential during the nonthermal phase transition and indicate the presence of a strongly time-dependent damping factor shortly after photoexcitation. Utilizing double-pump excitation, we can manipulate the transient damping and induce a second recovery.

23. Structural dynamics in a prototypical shape memory alloy (Johnson/Beaud)

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Magnetic memory shape alloys with magnetically induced strain up to 10% have already several technological applications [1]. The Heusler alloy Ni_2MnGa is the model system for these compounds. The phase transition between the high temperature phase, austenitic phase, and the low temperature, martensitic phase occurs simultaneously with the appearance of a superlattice modulation preceding the phase transition [2]. In order to understand this, a charge density wave (CDW) scenario was suggested [3-4]. Time-resolved techniques have been able to identify the amplitude mode of the CDW in the low temperature phase [5-6]. The pre-martensitic phase has, however, not yet been fully explored. Here, we report a structural dynamic study combined with a magnetic study in the pre-martensitic phase using time-resolved X-ray diffraction and time-resolved magnetic optical Kerr effect. The fluence dependence shows a complex behavior showing a modification of the underlining CDW potential linked to magnetism.

24. Two-dimensional THz-spectroscopy on the low-bandgap semiconductors InSb and InAs (Johnson)

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We performed THz-pump/broadband THz-probe measurements on the low-bandgap semiconductors InSb and InAs in a 2D-spectroscopy scheme in order to study their nonlinear response in the range of its fundamental plasmon and phonon excitations. Already at moderate field strengths below 100 kV/cm, we observe strong nonlinear contributions to the THz reflection. On timescales above 4 ps, the response is defined by the non-equilibrium electronic distribution giving rise to impact ionization, intervalley scattering and subsequent thermalization. On shorter timescales we observe coherent features appearing at mixing frequencies of the 1 and 2 plasmon and phonon frequencies. In contrast to single-trace pump-probe measurements, the 2D-method allows to disentangle various coherent and incoherent contributions to the response and may give a more complete picture of electron-phonon coupling in high electric fields.

25. Ultrafast demagnetization and structural dynamics in TbMnO₃ (Johnson/Beaud/Staub)

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TbMnO₃ is a well-studied low temperature multiferroic. Below 41K the magnetic system orders antiferromagnetically into a spin density wave. As temperature decreases further the magnetic order changes to cycloidal, below 27K, and a ferroelectric polarization arises.

We present our results on photoinduced demagnetization dynamics in TbMnO₃, focusing on the timescales and pathways of the transition between the multiferroic and the high temperature phase. The magnetic and orbital orders are tracked via the (0 q 0) and (0 2q 0) reflections using resonant X-ray diffraction at the Mn L2 edge. In particular, we observe that the demagnetization of the multiferroic state occurs on the same timescale for different pump wavelengths, which excludes a strong influence of the detail of the photoexcitation pathway (Mn3d – Mn3d vs. O2p – Mn3d transitions, i.e. just above vs. well above bandgap) and points to a mostly thermal effect. From similar decay timescales for (0 q 0) and (0 2q 0) peaks at temperatures below 27K we conclude that spin and orbital orders are strongly coupled. Finally, a comparison of the dynamics for p- and s-polarized X-rays reveals that the transient state following photoexcitation of the multiferroic phase is a spin density wave phase, as in the thermal adiabatic transition.

In addition, we will present our results on structural dynamics of low temperature TbMnO₃. These preliminary data point to a picosecond heating timescale that is significantly faster than the 20-30ps demagnetization dynamics. The latter are instead consistent with the slower structural deformation timescale.

26. Observing a phonon-driven structural phase transition in Sn₂P₂Se₆ (Johnson)

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Understanding the nature of phase transitions is key for unravelling the main interactions in solids and set a foundation for applications.

Sn₂P₂Se₆ is a ferroelectric semiconductor material that exhibits a phase with an incommensurate structural modulation over a narrow temperature range between the paraelectric and ferroelectric phases [1]. This incommensurate phase is characterised by two frozen phonons that produce a static structural modulation. In this structural dynamics study we examine the timescale of the disappearance of this phase upon photoexcitation using time resolved x-ray diffraction and compare it to other purely structural phase transitions. The time-scale observed indicates that the electronic system does not directly couple to the two phonon modes, but rather indirectly via other phonons. This is in contrast to systems like SrTiO₃, where the structural response is much faster.

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27. Exploring the power of the attoCOLTRIMS (Keller)

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Here, we show a progress report of current projects on the attoCOLTRIMS setup: a unique combination of a reaction microscope detector and a two-color (XUV-IR) pump-probe setup with attosecond time resolution.

Thanks to the possibility to tune the XUV pulse length and structure, passing from an attosecond pulse train (APT) to a single attosecond pulse (SAP), we were able to perform a thorough comparison study of the most established techniques in the attosecond field, i.e. RABBITT and streaking [1].

In addition, by exploiting the photoelectron-ion coincidence detection and the full 3D momenta reconstruction, we can acquire angular resolved photoelectron- and ion-distributions to shed light on molecular photoionization time delays.

Although this topic has been studied theoretically in the attosecond community [2,3,4], it has been only recently that they can be tackled experimentally [5,6,7]. We show that our system is a unique tool to investigate for example the photoemission time delays in the dissociative photoionization of CO where we disentangle the contribution from different states, or the influence of shape resonances on the photoemission time delays in N₂O and C₂H₂.

Lastly, we give a short overview of future plans to keep this machine at the forefront of the field.

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28. Attosecond dynamical Franz-Keldysh effect (Keller)

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We have investigated a manifestation of the attosecond dynamical Franz-Keldysh effect in dielectric nanofilms. A dielectric material exposed to few-cycle intense laser pulses undergoes a transient modification of its band structure. With the intensity and central frequency of our laser, the laser-matter interaction is found to have a mixed classical and quantum mechanical character. This regime of light-matter interaction has not been explored very deeply so far. Furthermore, the role of intra-versus interband transitions for attosecond electron dynamics in dielectrics has been a highly debated topic.

We have applied attosecond transient absorption spectroscopy together with time-dependent density functional theory calculations to resolve and characterize ultrafast electron dynamics in a diamond nanofilm under the influence of a near-infrared (NIR) few-cycle laser pulse. We have found that the NIR-induced intraband current is the main origin of the observed transient optical signal in the extreme ultraviolet spectral range of the attosecond probe. Orbital decomposition and reduction, followed by a highly simplified two-band parabolic model allowed us to pinpoint the physical origin of the dynamics. With this, the process could be identified as the dynamical Franz-Keldysh effect, which was observed in the few-femtosecond/petahertz domain for the first time.

29. Non-Dipole Effects on Coulomb Focused Photoelectrons from Strong-Field Ionization with Elliptical Polarization (Keller)

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In the past few years, strong-field ionization in mid-infrared (mid-IR) laser fields has gained importance as the basis for the generation of coherent soft x-rays [1] and for the discovery of a variety of strong-field features, such as holographic electron interferences [2], low-energy structures [3,4] and non-dipole effects [5]. These processes are typically described through the recollision of the electron wave packet with the residual ion. Here, we study strong-field ionization and rescattering beyond the long-wavelength limit of the dipole approximation with elliptically polarized mid-IR pulses. We have measured the full three-dimensional photoelectron momentum distributions (3D PMDs) with velocity map imaging and tomographic reconstruction. Through these ellipticity-resolved measurements combined with classical trajectory Monte Carlo (CTMC) simulations, we identify a sharp ridge of low-energy photoelectrons in the polarization plane PMD which appears at small ellipticities. We have traced the source of the sharp ridge to Coulomb focusing due to slow recollisions (i.e. recollisions where the electron's momentum approaches zero). Building on this new understanding of the PMD, we extend our studies on the role played by the magnetic field component of the laser-field when operating beyond the long-wavelength limit of the dipole approximation. In this regime, we find that the PMD exhibits an ellipticity-dependent asymmetry along the beam propagation direction: the peak of the projection of the PMD onto the beam propagation axis shifts from negative to positive values while increasing the ellipticity. We pinpoint the sharp ridge as the origin of the ellipticity-dependent PMD asymmetry.

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30. Attoline: Gouy Phase Shift for Annularly Truncated Beams and Ultrafast Fragmentation Dynamics of Acetylene C₂H₂ (Wörner/Keller)

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Here, we present two projects performed at our attosecond pump-probe beamline. The first one discusses a detailed study of the Gouy phase shift of an annularly truncated infrared (IR) beam. The annular beam shape results from the reflection on a mirror with a center-hole. By recording RABBITT traces simultaneously in two spatially separated foci, we could reconstruct the IR phase across the focus. The annular beam experiences a phase shift of more than 2π , which exceeds by far the Gouy phase shift of an ideal Gaussian beam. In addition, the imposed phase variation is still significant even a few centimeters away from the focus. Hence, phase sensitive measurement techniques, such as RABBITT and streaking, have to take the Gouy phase into account carefully. Furthermore, we demonstrated that the Gouy phase contribution to photoemission delays extracted from RABBITT/streaking can account to up to 50 as/mm close to the focus. This result is of importance for phase sensitive measurements with spatially separated targets. Our findings allow for a more precise system calibration to resolve attosecond electron dynamics and avoid systematic errors.

The second project presented investigates the ultrafast molecular dynamics in acetylene following photoexcitation above the ionization threshold. Acetylene is the simplest molecule containing a C-C triple bond and is thus well suited to observe its characteristics. The molecules under investigation are ionized using a XUV probe pulse and the subsequent induced relaxation dynamics are measured by recording the relative ion yields for different delays of the probing IR beam with a time-of-flight mass spectrometer. The recorded dynamics allows to infer possible relaxation mechanisms. Furthermore, the dynamics observed are compared to similar measurements conducted on ethylene and iodoacetylene. Ethylene contains a C-C double bond instead of the triple bond present in acetylene. Iodoacetylene on the other hand is highly polar. This allows to investigate the role of different possible internal degrees of freedom in determining the fast relaxation of the first excited states of the molecular cation.

31. An Introduction to the MMPT Force Field Method for Simulating Reactivity, Infrared Spectra and Grothuss Mechanism of Reactive Systems with Excess Protons (Meuwly)

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The method of Molecular Mechanics with Proton Transfer (MMPT) resembles a QM/MM scheme which treats the proton transfer (PT) process in its full dimensionality while addressing three important aspects of the problem: speed, accuracy, and versatility. In recent development, MMPT force field provides new advances in coupling and delocalizing multiple reactive sites of PT reaction. For investigating molecular systems quantum mechanically, MMPT has been also interfaced with other modules which perform path-integral and ring polymer molecular dynamics simulations. In the recent applications, MD simulations has been performed by MMPT to compute physical quantities of interests, including kinetic isotope effects and infrared spectra etc., of which the results are compared and supported by experiments and quantum mechanical approaches.

32. Spectroscopy, Dynamics and Binding of Benzonitrile in Lysozyme : Implications for Protein-ligand Binding Studies (Meuwly)

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Being in the vibrational spectral window of proteins and peptides, nitrile groups have been extensively studied experimentally and theoretically as infrared spectroscopic probe for proteins. Benzene in the engineered cavity of L99A mutant of T4 phase lysozyme was found to stabilize the enzyme [1]. Combining benzene and the nitrile group, herein, we focus on studying benzonitrile as a spectroscopic probe in T4 phase lysozyme via developing a 'computational approach' based on classical molecular dynamics simulation. The C-N bond is treated as a Morse oscillator and fluctuating point charge model is used to take polarizability into account. The force field parameters are determined from the fitting of ab initio data. Upon solvation in water, the nitrile peak is red shifted by 6 cm⁻¹. One dimensional absorption spectra are calculated from the fitted frequency fluctuation correlation function (FFCF). Using the results of benzonitrile in water as reference, the vibrational Stark shift, time scales of spectral diffusion of (benzo)nitrile in native and mutant lysozyme are calculated and compared to investigate the effect of protein-ligand interactions on the vibrational spectra of benzonitrile. The vibrational Stark shift of (benzo)nitrile in L99A is relatively stronger than the same in native or L99G mutant of lysozyme. While the FFCF of (benzo)nitrile in water has three distinct timescales, the same in lysozyme shows two timescales and a static component. The largest binding free energy, calculated using MM-GBSA method, is obtained for benzonitrile in L99A. To our knowledge, these results represent the first direct theoretical calculations of combined vibrational Stark shift and spectral diffusion dynamics of nitrile probe in the protein interior after the measurement of vibrational Stark shift of nitrile probe in hALR2 enzyme [2].

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33. Control of Hydration Through Intermolecular Degrees of Freedom: Molecular Dynamics of [Cu(II)(Imidazole)₄] (Meuwly)

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Understanding of Cu-imidazole coordination environment in aqueous solution is important to follow the biological functions of Cu-containing proteins. Such coordination domains occur in many biological systems and plays important role in oxidation and electron transport process. Here, solvent structure and dynamics of aqueous [Cu(II)(Imidazole)₄] was characterized using VALBOND force field and QM/MM molecular dynamics. Asymmetric axial water coordination around the metal atom was observed and agrees fairly with the MXAN experiment. The exchange of axial water molecules with neighbouring shell follow concerted mechanism and occurs on the ps time scale. Fluctuations in the Cu-N-N-N dihedral plane controls the exchange dynamics of water molecules in the first solvation shell.

34. Reactive simulations for O₂ formation in Interstellar Clouds (ISC) using Kernel Based methods (Meuwly)

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The observation and quantification of complex homo-nuclear species of O remains one of the most hard task in Astrochemical Models in ISC. Their presence is important achievement in the development of life in extra-terrestrial environments but, due the lack of dipole moment in O₂, this key molecule remains invisible.

The surface-gas reaction mechanism is supposed to be the main route for the formation of O₂. The surface has multiple roles: storage, increase the reaction frequency and relaxation of the new-formed species. Amorphous Solid Water (ASW) is the most abundant grain species in ISC.

Calculations are done using CHARMM 41 program, with CHARMM 36 Force Field for water molecules and Oxygen atoms, O₂ ground state is modelled using the Reproducing Kernel Hilbert Space (RKHS) interpolation scheme [1], using as grid build from high level Ab-Initio Potential Energy Curve (PEC) [2].

The water surface is characterized using Monte Carlo simulations at 50 K: at this temperature average diffusion between two holes is in the order of 50 ps. Reactive simulations in surface and bulk phase show that the 81% of the events is reactive within the first 100 ps, half of them during the first 10 ps. The relaxation is instead a slow process: fitting from 4 ns long simulations shows that it takes place between 100 ns and 250 ns after the formation.

O₂ formation is observed on surface and bulk phase in ASW. The reaction is diffusion-limited, due the lower probability of finding two atoms in the same cavity. The slow relaxation acts as heat source for the ice grain and can be considered as main source energy in these environments. Also, the implementation of RKHS scheme is able to reproduce the correct behaviour of the PEC and the time its evolution, allowing to reproduce high quality data with a fraction of the cost respect to a QM/MM scheme.

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35. Reactive Molecular Dynamics simulations of Claisen rearrangement reactions (Meuwly)

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Claisen rearrangement reaction is a [3,3]-sigmatropic rearrangement with synthetic and mechanistic importance in organic chemistry and biochemistry, via the transformation of chorismate to prephenate by chorismate mutase (CM) [1]. In aqueous solution and in CM the reaction is catalysed by the stabilisation of the cyclic transition state (TS).

The Claisen rearrangement of different model systems based on a well parametrised reactive force field (FF) of allyl-vinyl-ether (AVE) is studied by Multisurface Adiabatic Reactive Molecular Dynamics (MS-ARMD [2]) simulations. The focus is on the mechanistic details, primarily the effect of the catalysis, and to show the versatility of MS-ARMD. In comparison to preceding works by other groups, using QM/MM methods, MS-ARMD comes with approximately the cost of conventional FF. It allows extensive studies of the dynamics and energetics of a reaction, as well as calculating converged reaction rates. The quality of the simulation is dependent on the quality of the parametrisation of FF. The reactive FF utilised here is parametrised to MP2/6-311++G(2d,2p) reference points.

The calculated TS energy of AVE in gas phase compares well to experiment values [3] (29.8 kcal/mol compared to 30.6 kcal/mol), with the deviation being within chemical accuracy. Comparing the potential of mean force from umbrella sampling in gas and condensed phase with MS-ARMD to QM/MM results [4] establishes the quality of the FF.

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36. Ultrafast photobiology and photochemistry at SwissFEL's Experimental Station A (Milne/Knopp/Abela)

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The Swiss hard X-ray free electron laser SwissFEL started construction at the Paul Scherrer Institute in late 2012, with a planned startup date of 2017 for the ARAMIS hard x-ray undulator section and first user operation in 2018. This poster will present an overview of Experimental Station A (ESA), which will be the first experimental station to come online in mid-2017 and will consist of two instruments: ESA Prime and ESA Flex. ESA Prime is designed to investigate ultrafast photochemical and photobiological processes using a range of X-ray techniques, including serial femtosecond crystallography (SFX), wide-angle scattering (WAXS) and spectroscopy (XAS/XES/RXES) over the full ARAMIS range of 2-12.4 keV. ESA Flex is a flexible instrument designed to accommodate user experiments with an X-ray spectrometer for IXS/XES/RXES/HEROS measurements. The poster will also present examples of our recent research where these techniques have been used to investigate a variety of photophysics, including applying X-ray spectroscopy to probe DNA damage mechanisms, nonlinear X-ray optics, and ultrafast dynamics of functional materials.

37. Ultra-Broadband Time-Resolved Terahertz Spectroscopy (Moser)

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Broadband THz generation and detection employing laser-induced gas plasmas has been under development for the last decade,[1] with primary results dating back to the early 2000s.[2] Significant improvements, such as the introduction of the air biased coherent detection (ABCD) technique [3] and the use of different gas media,[1] have allowed to greatly increase the signal-to-noise ratio. Thus, the technology has reached a state, where optical-pump-THz-probe time-resolved spectroscopy can be successfully carried out, offering enhanced time resolution and spectral bandwidth with respect to the classical optical rectification methods in non-linear crystals.

Here, we present our newly built ultra-broadband time-resolved THz spectrometer with linear time-domain spectroscopy, optical pump-THz-probe and optical pump-NIR push-THz probe capabilities. The setup is based on a CPA Ti:Sapphire laser (800 nm, 1 kHz repetition rate, 45 fs pulse duration), equipped with two NOPAs and makes use of the above-mentioned technology with, in particular, dual-color excitation in air for generation and biased coherent detection in a butane plasma. In addition to its enhanced temporal resolution (< 200 fs), this setup will allow to probe photogenerated species, such as polarons, phonons, and plasmon-phonon couplings, with spectral signatures way above the limit of conventional optical rectification and extend the photoconductivity spectral analysis up to a probe frequency of 20 THz.

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38. Excited state dynamics in diketopyrrolopyrrole-based push-pull organic dye-sensitized solar cells (Moser)

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DN-F10 is a blue-colored push-pull dye, where the conjugated bridge between an electron donor moiety and the acceptor part is constituted by a diketopyrrolopyrrole (DPP) chromophore. This molecule is an attractive redox sensitizer for solid-state dye-sensitized solar cells (ss-DSSCs) based on mesoporous TiO₂ anodes, as it encompasses high-performance and aesthetic properties.¹ Despite its successful use in practical devices, much has still to be understood regarding the detailed mechanisms and dynamics, by which charge separate upon photoexcitation, within the molecule.

We present a detailed investigation of electronic excited state dynamics focused on the intermolecular interaction by comparing the dynamics of donor-absent R1 dye. The dyes in solution and adsorbed on a redox-inactive metal-oxide surface, such as Al₂O₃, were scrutinized by femtosecond pump-probe laser spectroscopy.

Since intermolecular interaction can affect to charge transport process that controls the photon-to-electron conversion efficiency in DSSCs,² these observations are expected to help determine the crucial factors that still limit the photovoltaic performances of organic dye-based solar cell systems and foster new, improved designs.³

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39. Charge and Energy Transfer Cascade in Methylammonium Lead Bromide Perovskite Nanoparticles Aggregates (Moser)

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In just about four years, hybrid organic-inorganic lead halide perovskites have moved quickly from a scientific curiosity known only by a handful of specialists to the up-front of the most desirable and most studied semiconductor materials for photovoltaics. The architectures of solid-state efficient perovskite photovoltaic devices have evolved from methyl ammonium lead triiodide nanoparticles deposited within mesoscopic metal oxide scaffolds towards the use of homogeneous thin films in planar multilayer configurations. The observation by photoluminescence nano-imaging and transient absorption microscopy of the surface of multigrain thin films in perovskite solar cells have suggested that their efficiency is influenced by the nanoscopic structure of the active semiconducting layer. Energy transfer between crystal grains and photon recycling effects were shown recently to contribute to a large extent to the photocarriers long path lengths. Controlled nanoparticle aggregates, thus, constitute ideal model systems for the characterization of interfacial non-radiative energy- and charge transfer processes at grain boundaries, which appear to be key to the exceptional photovoltaic performances of perovskite devices.

Prepared organo-lead trihalides colloids are constituted of dispersed aggregates of quasi-2D platelets of a range of thicknesses, decorated with more 3D-like spherical nanoparticles. These types of nanostructures possess different optical properties that allow for probing them individually. Here we achieved a complete photophysical study of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite nanoparticles suspended in chlorobenzene and highlight some important interaction properties. Excitons in this material are characterized by a significantly larger binding energy compared to its triiodide counterpart and, hence, have a richer exciton dynamics. Using time-resolved transient absorption and photoluminescence spectroscopies, we highlighted the photophysical interactions between the various types of nanostructures and evidenced in particular an energy and charge transfer cascade from the smaller quantum wells to the 3D particles. Upon photoexcitation, localized excitons within one nanostructure can either recombine on a ps timescale, yielding a short-lived emission, or form charge-transfer states (CTSs) across adjacent domains, resulting in longer-lived photoluminescence up to the ms timescale. Furthermore, CTSs exhibit a clear signature in the form of a strong photoinduced electroabsorption (Stark effect) evidenced in femtosecond transient absorption measurements. This observation lead us to propose a mechanism for the formation and splitting of charge transfer excitons at domain boundaries.¹

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40. Impact of monovalent doping on the stabilization of α -FAPbI₃ perovskite phase (Röthlisberger)

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In this work, we investigate the influence of monovalent cation substitution on the properties of FAPbI₃-based perovskites. The relative stability of the perovskite α phase and of non-perovskite α' phase is studied as a function of dopant nature, concentration and temperature. The efficiency of monovalent cation dopants and their combinations for the stabilization of the perovskite phase is analyzed. It is shown that varying the dopant concentration allows to change the relative stability at different temperatures. On this basis, an optimal dopant content is suggested. The corresponding optical spectrum onset shifts by 0.1-0.2 eV upwards with respect to pure FAPbI₃.

41. Multiple Time Step Algorithms for Efficient Multiscale Molecular Dynamics Simulations in Ground and Excited States (Röthlisberger)

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Ab initio Molecular Dynamics (AIMD) is a highly versatile tool to determine static and dynamic properties of biomolecular and condensed phase systems in ground as well as electronically excited states. Unfortunately, the feasibility of AIMD simulations of extended systems is often limited by the high computational cost.

Time-reversible Multiple Time Step (MTS) techniques [1] exploit the time scale separation of fast and slow degrees of freedom to increase the computational efficiency of MD simulations. In MTS approaches the “fast” contributions to the nuclear forces are evaluated at every time step, while the “slow” components have to be computed only once every n steps to reproduce the correct dynamics. Recently, MTS schemes, originally devised for classical MD, have started to be applied also to AIMD, via the introduction of a suitable splitting of the ab initio forces into “fast” and “slow” components.

We present here our implementation, and first applications, of two time-reversible MTS algorithms [2,3] in the widely-used, Density Functional Theory (DFT) based ab initio MD code CPMD. In both cases, the separation in “fast” and “slow” components is achieved introducing reference forces (FREF, to be used at every step) and higher level forces (FHIGH, to be used every n steps to calculate the difference FREF-FHIGH, used as slow the force component).

In the first implementation [2], both the reference forces and the higher level contributions are calculated ab initio, using quantum mechanical electronic structure methods of different accuracy, e.g. two DFT calculations with different rung exchange-correlation functionals or, thanks to an interface with external quantum chemistry codes (as GAUSSIAN09, TURBOMOLE), DFT and correlated wavefunction based methods such as MP2.

The second implementation [3] uses DFT forces only in the correction steps, while the intermediate propagations are fully classical, based on force fields. This MM-QM/MM approach enables exact time propagation at the ab initio level with classical time steps, hence it is particularly suitable to also reproduce large-scale conformational changes in extended biomolecular systems by accessing classical time scales with ab-initio accuracy.

Further improved performances can be achieved with some extensions that are currently under development: the use of stochastic thermostats that limits the resonances due to the fast forces and allows to further increase the outer time step; an on-the-fly adaptation of the large time-step that will ensure that the optimal balance between accuracy and efficiency is always maintained also in regions of phase space where the differences between reference and high-level forces become larger; the combination with machine learning approaches and schemes for fast evaluation of hybrid functionals, also developed in our group. Future developments also include the extension of MTS to excited state dynamics.

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42. Laser induced magnetization dynamics in multiferroic CoCr_2O_4 (Staub/Johnson)

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CoCr_2O_4 is a special type-II multiferroic with strong magneto-electric coupling, as reversing the orientation of the magnetization induces switching of the electrical polarization. Here, we report results about dynamics after femtosecond laser pulse excitation above the band gap probed via time-resolved X-Ray magnetic circular dichroism method, which allow us to detect the dynamics of Co and Cr sublattices in a separate way. We will discuss influence of the multiferroic ordering on the demagnetization process of both sublattices. We will compare this results to experiment above the multiferroic transition $T=26$ K, where studied material exhibits only ferrimagnetic ordering.

43. Femtosecond structural dynamics of the single-layer manganite $\text{Pr}_{0.5}\text{Ca}_{1.5}\text{MnO}_4$ (Staub/Johnson/Beaud)

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Mixed-valence manganites have attracted considerable interest as they exhibit metal-insulator transitions and colossal magnetoresistance. Lattice distortions are crucial in these phase transitions and are closely linked to charge and orbital order (CO/OO), especially via the Jahn-Teller effect. Thus, resolving the structural dynamics in manganites following the photoinduced melting of the CO/OO phase is an important step towards their understanding. Here we study the 2D-compound $\text{Pr}_{0.5}\text{Ca}_{1.5}\text{MnO}_4$ to investigate how its reduced dimensionality influences the ultrafast structural response to femtosecond photoexcitation as compared to its 3D counterpart. Furthermore, we clarify the coupling of an additional structural symmetry break to the CO/OO phase by comparing the respective melting dynamics.

44. Time-resolved X-ray absorption spectroscopy indicates a new photodissociation mechanism of dissolved CBr₄ (van Bokhoven)

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Commercial catalytic reactions can be improved by optimizing the slowest reaction step in the catalytic cycle. Nucleophilic substitution, in which one bond is broken and another bond is created, often represents the rate determining reaction step, as for instance in the Monsanto process in which acetic acid is synthesized from carbon monoxide and methanol. Understanding the initial carbon-halogen bond breakage of halogenated methanes in such reactions is therefore of utmost importance.

Photodissociation of dissolved CBr₄ - a prototype bond breaking reaction - has been extensively investigated in numerous time-resolved studies. While the proposed mechanism considers the recombination of Br and CBr₃ radicals created upon the C-Br bond cleavage and the subsequent decay of C₂Br₆ to Br₂ and C₂Br₄, it does not address the bromination of solvent molecules observed in the gas phase. To elucidate the photodissociation mechanism of CBr₄ in methanol and to assess the contribution of photobromination of the solvent we have performed time-resolved X-ray absorption spectroscopy (XAS) measurements on the 30 ns – 10 μs time scale. Unlike previously employed techniques, XAS is an element selective technique, sensitive to the electronic and geometrical structure of the absorbing atom and is therefore suited for the identification of transient species.

From a fitting analysis of transient spectra a quantitative description of photodissociation dynamics was obtained. We have identified a new decay channel corresponding to photobromination of methanol yielding HBr. The resulting species was found to be the Br-dominant component in the reaction mechanism as confirmed by both XAS and liquid chromatography-mass spectrometry (LCMS). Within the time-window of our experiment we find that the formation of HBr is driven by the reaction between CBr₃ radicals and methanol. The initial high and low levels in the concentration of HBr and Br radicals, respectively, indicate a fast reaction between Br radicals and methanol to yield HBr. We find that the final decay species in the mechanism are HBr and C₂Br₆. Our findings are well supported by DFT calculations of X-ray absorption spectra and a LCMS analysis of a CBr₄ ex-situ sample. In our future studies we aim to investigate the initial stage in the photodissociation dynamics of dissolved CBr₄ and extract the reaction rate constant for bromination of methanol.

45. Analysis of pump-probe experiments: The pump penetration depth matters (van Bokhoven)

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Understanding the propagation of the probe wave within the excited medium is the key to the analysis of any pump-probe experiment. We present an analytic treatment of the case where the pump pulse undergoes linear absorption, resulting in an excitation profile that varies exponentially in space: $n_{\text{pump}}(z) = n_0 + n_{\text{exc}} \exp(-z/z_0)$.

Contrary to common usage, it is not appropriate to approximate such an exponential profile by a rectangular one. The dependence of the underlying Maxwell's equations on spatial derivatives introduces the ratio between probe wavelength and pump penetration depth z_0 as a new relevant parameter for the probe propagation. In consequence, this leads to dispersive effects that do not appear in rectangular approximations. Since this dispersion also affects the reflection and transmission coefficients at the sample surface, the pump penetration depth has to be considered also for probe pulses in reflection mode.

We demonstrate the importance of these findings for the example of optical pump-terahertz probe spectroscopy. It is shown how data extraction procedures based on approximations may often lead not only to incorrect material parameters, but also to a questionable qualitative interpretation of the data.

46. Ultrafast indirect excitation of low frequency modes of CO on Pt (van Bokhoven/Sigg/Feurer)

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For a detailed microscopic understanding of chemical surface reactions e.g. in catalysis the study of the dynamics of elementary processes like charge/energy transfer and bond breaking/making of molecules is of central importance. The ultimate tool for these femto-chemistry investigations is time resolved X-ray spectroscopy using a free electron Laser [1, 2]. To initialize the surface chemical reaction, two approaches can be applied. One is the direct excitation of molecular resonances with an ultrashort THz pulse as proposed in [3]. The other one is the indirect coupling of the excitation pulse to the molecular resonances via the substrate [4-7]. Whilst the first approach is expected to be coherent and thus quasi instantaneous within the excitation pulse duration, the timescales of the second approach need careful consideration.

Our model system to study both processes is carbon monoxide adsorbed on platinum. We investigate the time evolution of the IR active carbon monoxide stretch mode upon direct or indirect excitation of the THz active hindered translation mode. For a surface sensitive IR detection, we measure the attenuated total internal reflection of a CaF₂ prism [8]. The prism is covered with 0.5 nm platinum forming nano-particles of 5±1 nm in diameter. After reduction of the platinum, we observe IR absorption of carbon monoxide adsorbed on platinum in the atop-position. Upon excitation of the system with an ultrashort NIR laser pulse, we measure an ultrafast transient ground state bleaching together with a redshifted absorption.

To analyze the data, we fit the transient transmission spectra with differential curves derived from the linear FTIR transmission measurement. A pump induced wavelength shift to lower energies of the carbon monoxide stretch absorption is sufficient to describe the data. The time evolution of the wavelength shift shows an ultrafast 700 fs redshift followed by a decay on a timescale of 10 ps. The redshift originates from an anharmonic coupling of the hindered translation mode to the carbon monoxide stretch mode [6]. The excitation radiation is absorbed by the platinum nano-particles creating hot electrons that decay via phonons in the metal. Subsequently, this heat is transferred to the adsorbed carbon monoxide. That means we indirectly excite the hindered translation mode of carbon monoxide on platinum on the ultrafast timescale. The decay of the signal with a time scale of 10 ps implies the damping of this mode.

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47. Time-resolved X-ray absorption spectroscopy to study photocatalytic systems for hydrogen production (van Bokhoven)

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Time-resolved XAS has been applied to investigated molecular Cu-based photosensitizers, Co-based catalysts and supramolecular assembly of photosensitizer with catalyst. Photosensitizers and catalysts based on earth abundant chemical elements are economically most relevant. In particular Cu complexes can serve as the replacement of Ru-based photosensitizers. The excited state lifetime of the parent compound $[\text{Cu}(\text{dmp})_2]^+$ is quite short (1.7 ns in acetonitrile). On the basis of our previous time-resolved XAS data we understood that the reason of such short lifetime is the formation of exciplex with 5-coordinated Cu center. Recently we have measured time-resolved XAS spectra for similar complex but with bulky ligand groups that block access of solvent to the metal center. We found that exciplex is not formed in this case and the excited state lifetime was extended by three order of magnitude (1.0 μs) Supramolecular photocatalytic systems with the assembling of the $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizer and cobaloxime catalyst have the potential for ultrafast (sub-picosecond) electron transfer from the photosensitizer to the catalyst through oxidative quenching of the photosensitizer. We found that this process is not dominant for the studied system and the charge transfer follows the reductive quenching.

48. Accelerating Quantum Instanton Calculations of Kinetic Isotope Effects (Vanicek)

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Path integral implementation of the quantum instanton approximation currently belongs among the most accurate methods for computing quantum rate constants[1] and kinetic isotope effects,[2] but its use has been limited due to the rather high computational cost. Here we demonstrate that the efficiency of quantum instanton calculations of the kinetic isotope effects can be increased by orders of magnitude by combining two approaches: The convergence to the quantum limit is accelerated by employing high-order path integral factorizations of the Boltzmann operator,[3] while the statistical convergence is improved by implementing virial estimators for relevant quantities.[4,5] We also introduce a more convenient procedure for optimizing dividing surfaces that are used during the calculations. We demonstrate increased efficiency of the improved approach using H^+H_2 model exchange as an example, we apply the proposed method to obtain several kinetic isotope effects on $\text{CH}_4+\text{H}=\text{CH}_3+\text{H}_2$ forward and backward reactions.[6]

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49. Quantum Control for Tryptophan-containing Hormones and Neurotransmitters Identification (Wolf)

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In the recent past, we have demonstrated the potential of using phase-shaped deep UV pulses for manipulating the fluorescence response of amino acids for their label-free selective discrimination. We are now focusing on tryptophan derivatives which are essential for human metabolism, namely the neurotransmitter serotonin and the hormone melatonin. In fact, these two molecules are needed to regulate organs, to synchronize the circadian rhythms, and they influence the central nervous system being at the origin of feelings like well-being and happiness.

We show that our coherent control approach can be successfully applied for identifying molecules of this family, in spite of their quasi-identical fluorescence absorption and emission spectra and very similar time resolved fluorescence depletion dominated by the tryptophan response. Our process of discrimination could pave the way to further experiments for imaging the biosynthetic pathway from tryptophan to melatonin, or monitoring the evolution of serotonin and melatonin concentration in cells.

50. Optimized Ultrafast Laser Cell Poration (Wolf)

part 1: *Courvoisier, S., Saklayen, N., Huber, M., Chen, J., Diebold, E. D., Bonacina, L., Wolf, J.P., Mazur, E. ; part 2:* *Courvoisier, S., Götte, N., Zielinski, B., Winkler, T., Sarpe, C., Senftleben, A., Bonacina, L. Wolf, J. P., Baumert, T.*

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Improvement of methods to modify and control the genetic expression of cells in terms of efficiency, cell survival, and throughput benefits widely to biology and medicine. Within the field of ultrafast laser induced transfection, we investigated two approaches: One is based on a plasmonic substrate that induces the local poration of cell membrane for high-throughput application, while the second investigates the effect of temporal envelope modification of femtosecond laser pulse for a direct and optimized laser-cell interaction.

In the former study, after optimizing computationally the geometrical parameters of a tipless pyramid plasmonic substrate for 800 nm excitation, we fabricated this device. We demonstrate that such a substrate can induce efficient and low toxicity transient poration of cells over a large surface and potentially high-throughput by a purely optically induced ultrafast process.

The second study demonstrates that spectral phase shaping of fs-laser pulses can be used to optimize laser-cell membrane interactions in water. The energy and peak intensity thresholds required for cell poration with single pulse in the nJ range can be substantially reduced (25% reduction in energy and 88% reduction in peak intensity) by using temporal Airy pulses, controlled by positive third order dispersion, as compared to bandwidth limited pulses. Temporal Airy pulses are also effective for controlling the morphology of the induced pores, with prospective applications from cellular to tissue opto-surgery and transfection.

51. Real-Time Monitoring of Bacterial and Organic Pollution in a Water Stream by Fluorescence Depletion Spectroscopy (Wolf)

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We demonstrate an approach for a real-time, consumable-free optical system operating on a liquid jet which can be easily derived from the water distribution infrastructure. We apply a pump-probe scheme based on the acquisition and nanosecond manipulation of UV-excited fluorescence to increase the selective identification of bacterial against organic pollutants in water.

52. Filamentation broadening and glass-compression of 1.8 μm for High Harmonic Generation (Wolf/Wörner)

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We present a filamentation broadening approach to shorten a 1.8 μm pulse in order to generate high harmonics. We report an increase of high harmonic efficiency and cut-off. This supports a substantial reduction of the mid-IR pulse duration. Sufficient stability and minimum energy losses can lead us to time resolved spectroscopy at the carbon K-edge with attosecond resolution.

53. Real-time monitoring of atmospheric aerosols by fluorescence and pump-probe techniques using a portable instrument (Wolf)

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The optical identification of bioaerosols in the atmosphere and its discrimination against combustion related particles is a major issue for real-time, field compatible instruments. We show that by embedding advanced pump-probe depletion spectroscopy schemes in a portable instrument, it is possible to discriminate amino acid containing airborne particles (bacteria, humic particles, etc..) from PAH containing combustion particles (Diesel droplets, soot, vehicle exhausts) with high selectivity. Our real-time, multi-modal device provides, in addition to the pump-probe depletion information, fluorescence spectra (over 32 channels), fluorescence lifetime and Mie scattering patterns of each individually owing particle in the probed air.

54. Full-dimensional wave-packet calculations of conical intersection dynamics of NO₂ for the interpretation of time dependent XUV photoelectron spectroscopy (Wörner)

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The coupled electronic and nuclear dynamics of NO₂ after photoexcitation around 400 nm to the A band are an important model system to understand conical intersection dynamics. After excitation from the 2A1 ground state to the 2B2 excited state the asymmetric stretch vibration is excited, which allows the coupling of the two states, leading to a subsequent electronic relaxation.

The system has been investigated extensively in theory [1] as well as in experiments [2,3] in the last years. We investigate the nuclear wave packet dynamics on a high level of theory to provide a more detailed interpretation of these results: We use full valence MRCI potential surfaces and propagate the wave function on them with a split step operator approach, treating the interaction with the pump pulse and the non-adiabatic coupling between the states explicitly. Subsequently, photoelectron spectra are calculated using the reflection principle. We compare our results with XUV time-resolved photoelectron spectra measured in our laboratory.

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55. Dynamical symmetries of atoms and molecules probed by bicircular high-harmonic spectroscopy (Wörner)

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

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56. Absorption and emission characteristics of organic – inorganic lead halide perovskites (Röthlisberger)

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Absorption and emission characteristics of organic – inorganic lead halide perovskites play an important role for their potential use in photonics applications. Here we investigate, the origin of the peculiar band gap shift as a function of temperature and the dual emission of these materials.¹ Low temperature time-integrated photoluminescence studies of MAPbI₃, and MAPbBr₃ highlighted the presence of a well-defined second emission peak whereas FAPbBr₃ exhibited a single emission peak. From MD simulations that have been performed for MAPbI₃, the additional photoluminescence peak can be assigned to the presence of molecularly disordered orthorhombic domains. This supports the hypothesis that the two photoluminescence peaks are associated to MA-ordered and MA-disordered domains with different emission characteristics due to the presence/absence of a Stark effect induced by the dipolar field of the organic cations. It is worth emphasizing that the disordered domains are not tetragonal inclusions but rather orthorhombic domains with a molecular disorder. On the other hand, FAPbBr₃ exhibits only a single emission peak at low temperature because the difference between ordered and disordered domains is much smaller (10 to 20 meV in FAPbBr₃ versus 80 to 90 meV in MA-perovskites) in agreement with the lower dipole moment of FA. The DFT band gaps of various systems as a function of the pseudocubic lattice parameter are computed, to investigate the origin of the effect of temperature on the photoluminescence peak, suggesting that the unusual blueshift is due to the lattice expansion of MAPbI₃ resulting in a stabilization of the antibonding top of the valence band.