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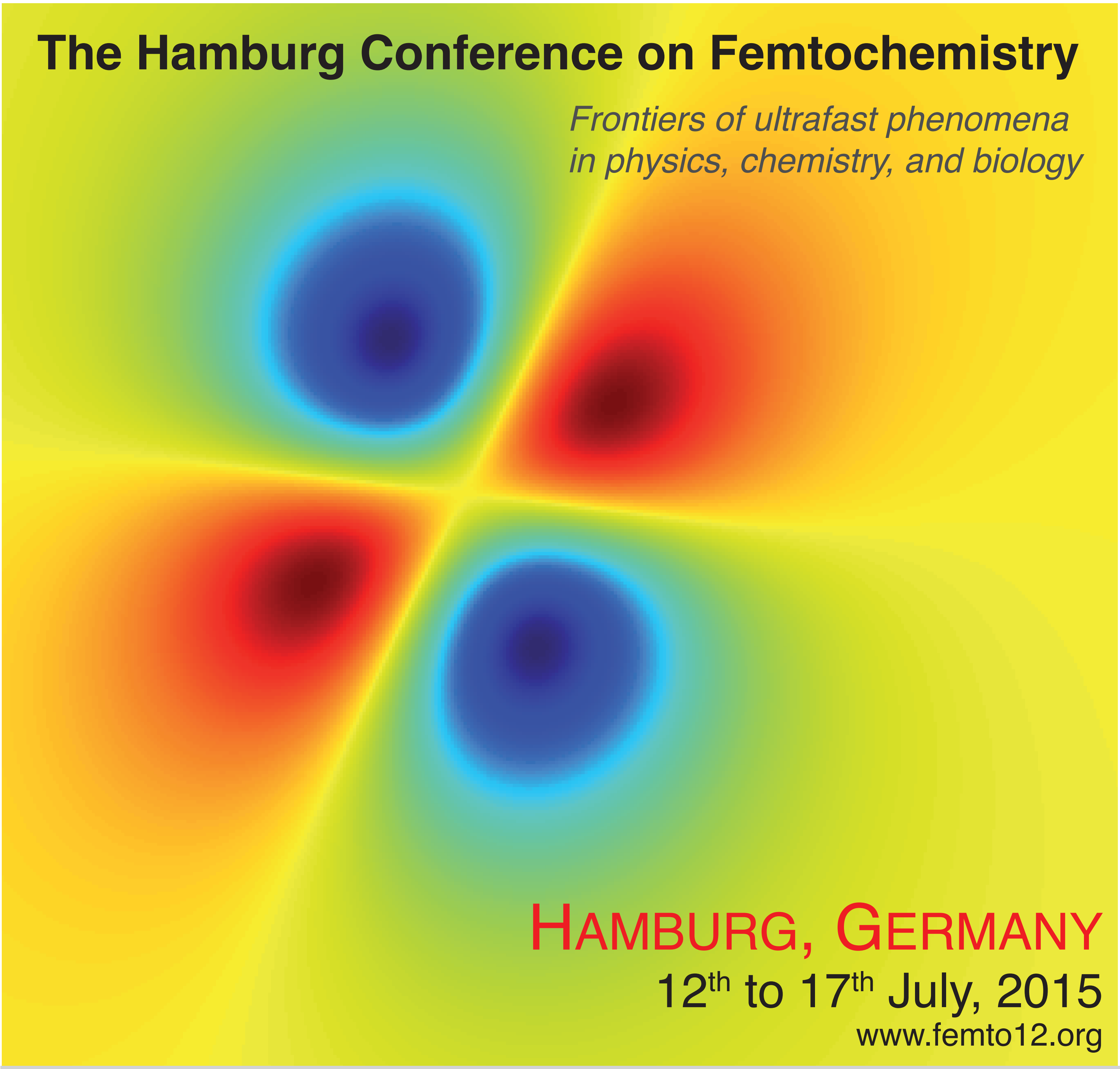

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Frontiers of ultrafast phenomena
in physics, chemistry, and biology

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Mapping Atomic Motions with Ultrabright Electrons: The Chemists' Gedanken Experiment Enters the Lab Frame

R. J. Dwayne Miller[1,2,3]

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Electron sources have achieved sufficient brightness to literally light up atomic motions during transition state processes to directly view the unifying conceptual basis of chemistry. Two new electron gun concepts have emerged from detailed calculations of the propagation dynamics of nonrelativistic electron pulses with sufficient number density for single shot structure determination (Siwick et al. JAP 2002). The atomic perspective, that these sources have opened up, has given a direct observation of the far from equilibrium motions that lead to structural transitions (Siwick et al. Science 2003). Recent studies of formally a photoinduced charge transfer process in charge ordered organic systems has directly observed the most strongly coupled modes that stabilize the charge separated state (Gao et al Nature 2013). It was discovered that this nominally 280 dimensional problem distilled down to projections along a few principle reaction coordinates. Similar reduction in dimensionality has also been observed for ring closing reactions in organic systems (Jean-Ruel et al JPC B 2013).). Even more dramatic reduction in complexity has been observed for the material, $Me_4P[Pt(dmit)_2]_2$, which exhibits a photo-induced metal to metal centre charge transfer process for unit cells on par with proteins. This study represents the first all atom resolved structural dynamics with sub-Å and 100 fs timescale resolution. We are tuned to see correlations. At this resolution, without any detailed analysis, the large-amplitude modes can be identified by eye from the molecular movie. The structural transition clearly involves a dimer expansion and a librational mode that stabilizes the charge transfer. This phenomenon appears to be general and arises from the very strong anharmonicity of the many body potential in the barrier crossing region. The far from equilibrium motions that sample the barrier crossing region are strongly coupled, which in turn leads to more localized motions. In this respect, one of the marvels of chemistry, and biology by extension, is that despite the enormous number of possible nuclear configurations for any given construct, chemical processes reduce to a relatively small number of reaction mechanisms. We now are beginning to see the underlying physics for these generalized reaction mechanisms. The "magic of chemistry" is this enormous reduction in dimensionality in the barrier crossing region that ultimately makes chemical concepts transferrable. With the new ability to see the far from equilibrium nuclear motions driving chemistry, it will ultimately be possible to characterize reaction mechanisms in terms of reaction modes, or reaction power spectra, to give a dynamical structure basis for understanding chemistry.

Ultrafast electron diffractive imaging with sub-Angstrom resolution

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Ultrafast electron diffraction (UED) is a powerful tool to image structures with atomic resolution on femtosecond time scales. UED has been applied to investigate transient states in isolated molecules, but progress has been hampered by the limited temporal resolution and the random orientation of molecules in the gas phase. While gas UED experiments have reached picosecond resolution [1], diffraction from molecules in the gas phase presents unique challenges that have so far prevented the resolution from reaching the range of 100 fs that is needed to follow atomic motions. An additional challenge is the random orientation of the molecules, which greatly diminishes the information contained in the diffraction patterns and prevents the reconstruction of the structure directly from the data. We have recently shown sub-ps resolution and that by diffracting from impulsively aligned molecules it is possible to retrieve a molecular image directly from the data [2,3]. We have so far succeeded in recording static 3D molecular images and in recording the structure of a transient excited state [4]. We are currently pursuing two approaches to improve on the temporal resolution. The first is to use an RF cavity to compress sub-relativistic electron pulses, in combination with a tilted front pulse laser excitation to match the speed of electrons and laser through the sample. The second is the use femtosecond electron pulses with MeV energy where the velocity mismatch is not significant. We anticipate that these efforts will transition gas UED well into the femtosecond regime.

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Ultracold electron beams for ultrafast diffraction of macromolecules

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At Eindhoven University of Technology we produce highly charged, highly coherent electron bunches by femtosecond photoionization of a laser-cooled and trapped atomic gas. Ultimately this should enable single-shot electron diffraction of macromolecules. The special properties of this source have been studied and explained in terms of a detailed model of the photoionization process. Using a simple graphite sample we recently generated the first diffraction patterns, which provided direct evidence that the ultracold electron source has the required coherence. We are currently preparing crystalline samples of the 2D membrane protein hydrophobin. In addition we are implementing resonant microwave cavities for further acceleration and phase space manipulation of the cold electron bunches.

Imaging molecular dynamics with laser-driven Coulomb explosion technique

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The motions of electrons and nuclei are strongly coupled for dissociative ionization of molecules driven by intense laser pulses. The correlation dynamics of electrons and nuclei determine the reaction pathways as well as the quantum states of reaction products. However, experimental study of the correlation dynamics of electrons and nuclei is one of the most challenging topics for polyatomic molecules in intense laser fields. In this talk, I will report our recent progresses in the field of imaging the laser-driven ultrafast dynamics of molecules with Coulomb explosion technique. (1) We clarified the three-body fragmentation dynamics of CO_2 in intense laser fields [1,2]. Both sequential fragmentation and non-sequential fragmentation were observed. (2) We identified the electronic state of fragmental ions of Ar_3 in intense laser fields. Both the direct Coulomb explosion and the indirect Coulomb explosion with Rydberg excitation were observed. (3) We simulated the explosion dynamics of polyatomic molecules in intense laser fields and reproduced the experimental observations. The simulation clearly demonstrates how the electrons and nuclei are coupled in the process of dissociative ionization of molecules in intense laser fields.

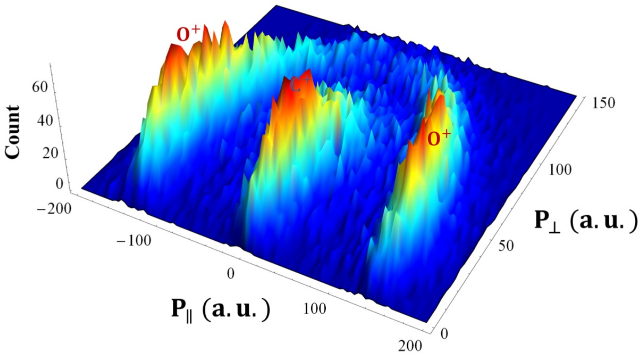

Figure 1: Experimental measured two-dimensional momentum distributions of correlated atomic ions generated in the three-body fragmentation of CO_2^{3+}.

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Molecular features in complex environment: cooperative team players during excited state bond cleavage

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Photoinduced bond cleavage is often employed for the generation of highly reactive carbocations in solution and to study their reactivity. Benzhydryl derivates are prominent precursors in polar and moderately polar solvents like acetonitrile or dichloromethane. Depending on the leaving group, the photoinduced bond cleavage occurs on a femtosecond to picosecond time scale and typically leads to two distinguishable products, the desired benzhydryl cations and as competing by-product the benzhydryl radicals. Conical intersections are the chief suspects for such ultrafast branching processes. We show for two typical examples, the neutral benzhydrylchloride and the charged diphenylmethyltriphenyl-phosphonium ions that the role of the conical intersections depends on the interplay of molecular features with the environment. It turns out to differ significantly for both precursors. Our analysis is based on quantum chemical, quantum dynamical and on-the-fly calculations. The experimental optical signal we use for comparison is recorded by the Riedle group (LMU, Physik) with high temporal resolution. In case of benzhydrylchloride we can directly connect the observed signals to two early conical intersections close to the Franck Condon region. In case of the diphenylmethyltriphenylphosphonium ion dynamic solvent effects are needed to activate a conical intersection at larger distances along the reaction coordinate. We developed two methods with increasing complexity to describe the dynamic impact of the solvent environment within a quantum dynamical description. The first method includes the solvent effects in a continuum-like fashion [1], the second treats the solvent environment explicitly [2]. Both methods show that the solvent cage hinders the free dissociation and thus opens the pathway to the conical intersection that allows the formation of the experimentally observed diphenylmethyl cations.

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Signatures of light-induced conical intersections on the dynamical properties of molecular systems

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Nonadiabatic effects are ubiquitous in physics, chemistry and biology. They are strongly amplified by conical intersections (CIs) which are degeneracies between electronic states of triatomic or larger molecules. A few years ago it has been revealed that CIs in molecular systems can be formed by laser light even in diatomics [1]. The energetic and internuclear positions of these light-induced conical intersections (LICIs) are depend on the laser frequencies while the strength of their nonadiabatic couplings can be modified by the field intensities. Strong impact of these LICIs on different dynamical properties of the diatomics has been discussed in several papers [1,2,3]. Recently our attention is focused on the description of the photodissociation dynamics of the D_2^+ molecule [4,5,6]. Kinetic energy release (KER) and angular distribution of the photodissociation probabilities are calculated with and without LICIs for different values of laser parameters. By analyzing this dynamical process carefully, we found a robust effect in the angular distribution of the photofragments which serves as a direct signature of the LICI providing undoubted evidence for its existence [7].

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Rotational dynamics of molecules in He nanodroplets induced and probed by laser pulses

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Laser-induced alignment, the method to confine the principal axes of molecules along axes fixed in the laboratory frame, is now used in a range of applications in physics and chemistry. With a few exceptions all studies have focused on isolated molecules in the gas phase. Extension of alignment to molecules in He droplets is of interest for at least two reasons. First, alignment of molecules inside He droplets should enable studies or exploitation of the orientational dependence of molecular interactions as well as for extraction of molecular frame information in the presence of a dissipative environment. Second, the ability to control the degree of alignment implies being able to control the rotational angular momentum and coherence of the molecules inside the droplet. Some or all of the angular momentum and coherence may be transferred to the surrounding He atoms and as such open possibilities for laser-controlled excitation of collective angular momentum states, possibly quantized vortices [1].

The talk will present our experimental findings of laser-induced alignment of molecules in He droplets conducted both with femtosecond [2-3] and nanosecond pulses [4].

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Tower of Light Lecture: Light and Enlightenment

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Human civilization would not exist without Light—Light defines Life as we know it. In this **"Tower of Light"** lecture, we shall overview some historical developments and recent breakthroughs, from exploration of the nature of light, to 4D imaging, and to the vast applications in the physical and medical sciences. We shall end the Lecture with some thoughts on the needed enlightenment for future generations to co-exist on our planet.

Chemical Implications of Spin

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Spin has important theoretical implications and many practical applications across different scientific disciplines. Spin is an intrinsic property of electrons but also of the nuclei. Two topics related with nuclear and electron spin, respectively, will be introduced in this presentation. In the first case, a theoretical suggestion to separate nuclear spin isomers in a polyatomic molecule using ultrashort laser pulses and concepts from pump-probe spectroscopy will be presented [1,2]. To this aim, model wave packet simulations in reduced dimensionality in a push-pull molecular system have been employed. In the second case, electronic spin transitions are modelled to investigate the role of intersystem crossing in the deactivation of DNA/RNA nucleobases and related species. The direct consequences of spin for DNA photostability and photodamage will be discussed. The latter simulations are done employing full dimensional ab initio molecular dynamics, where electronic transitions both mediated by non-adiabatic and spin-orbit couplings are allowed [3].

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Coherent control of ultrafast electron dynamics

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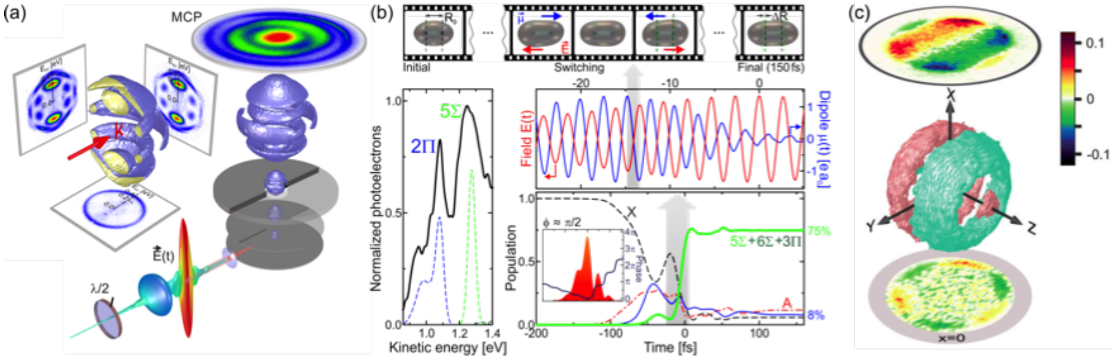
The ability to generate shaped ultrashort laser pulses of controllable envelope and instantaneous frequency with zeptosecond precision [1] has made it possible to manipulate the electron dynamics of quantum systems with unprecedented accuracy. In order to demonstrate three-dimensional control with polarization-shaped laser pulses we have developed a tomographic reconstruction method to measure the three-dimensional photoelectron angular distributions (PAD) in a Velocity Map Imaging (VMI) set-up. As an example, we have demonstrated the creation and manipulation of designer free-electron wave packets [2, 3]. In addition, we have shown how precision pulse shaping is used to manipulate the concerted electron and nuclear dynamics and selectively populate different bound electronic states in a molecule [4, 5]. Finally, we present a femtosecond laser-based approach to chiral recognition of randomly oriented chiral molecules in the gas phase. To this end, PAD resulting from REMPI of small chiral organic molecules are studied. The observed asymmetry in the PAD using left- and right-handed circularly polarized femtosecond laser pulses, i.e. the Photoelectron Circular Dichroism (PECD), is in the ± 10 percent regime [6, 7].



(a) Creation of designer electron wave packets, (b) control of coupled electron / nuclear dynamics and (c) tomographic reconstruction of the PECD of Camphor.

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Direct observation of ultrafast quantum many-body dynamics in a strongly-correlated ultracold Rydberg gas

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Many-body correlations govern a variety of important quantum phenomena such as the emergence of magnetism and superconductivity in condensed matter. Understanding quantum many-body systems is thus one of the holy grails of modern sciences. Here we demonstrate a new pathway to it; a strongly-correlated ultracold Rydberg gas is created with a broadband picosecond laser pulse, and its ultrafast many-body electron dynamics is directly observed by time-domain Ramsey interferometry with attosecond precision. Our new approach will offer a versatile platform to observe and manipulate nonequilibrium dynamics of strongly-correlated quantum many-body systems on the ultrafast timescale.

Coherent Control of Photofragment Distributions Using Laser Phase Modulation in the Weak-Field Limit

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Recently, the possibility of quantum interference control of photochemical reactions in the weak-field limit has been discussed [1-4]. To that end, we demonstrate quantum interference control of the final state distributions of photodissociation fragments by means of pure phase modulation of the pump laser pulse in the weak-field regime [4-6]. One example is based on realistic wave packet calculations of the transient vibrational populations of the $Br_2(B,v_f)$ fragment produced upon predissociation of the $Ne\text{-}Br_2(B)$ complex, which is excited to a superposition of overlapping resonance states using pulses with different phase modulation. Transient phase effects on the fragment populations are found to persist for long times (more than 50 ps) after the pulse is over. Another example is the non-adiabatic process: $I + Br^* \leftarrow IBr \rightarrow I + Br$, where the relative yield of excited Br* can be changed by pure phase modulation. This control can be extended beyond transient effects to "infinite time" by weak-field excitation via the bound A state of IBr.

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Dynamics of electrons at work in solar energy conversion

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Solar energy is the most abundant renewable energy source available. Conversion of light into electricity and chemical energy are the two major paths for solar energy conversion. Nanostructured organic materials are being explored for applications in photovoltaic solar energy conversion, as well as photocatalysis for solar fuel generation. Light harvesting, energy transport, charge photogeneration and recombination, charge transport are the elementary processes accounting for the conversion of light energy into useful charge carriers. We show how a combination of time resolved spectroscopy covering the time scales from femtoseconds to milliseconds and spectral range from the X-rays to the far infrared (THz frequencies) is a powerful tool to study the light induced processes and provide mechanistic information valuable for design of novel or optimized materials.

Electronic Dynamics in Photocatalytic and Energy Transporting Systems

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Femtosecond pump-probe experiments on photocatalytic and organic model systems reveal detailed insights into the behavior of their electronic excitations. This is helpful in designing materials, composite structures and interfaces for photonic applications like water splitting devices or organic solar cells. In the case of light harvesting, long living mobile excitons are crucial. To characterize their migration properties the dynamics caused by the bimolecular exciton-exciton annihilation process is analyzed. For J-aggregates, which represent chain like molecular nanostructures, a reasonable high and strictly one dimensional mobility was found [1]. In the case of disordered systems the impact of inhomogenous broadening has to be considered [2]. We developed a formulation of the Förster theory which takes this explicitly into account and tested it for a guest-host system with well-defined spectral properties. The predicted diffusion constants agree well with those derived from the observed exciton dynamics. Most photocatalytic systems rely on efficient charge separation processes. Iridium photosensitizers have proven to be good absorbers for light driven water splitting. Their molecular properties can be well studied in homogeneous systems. Time resolved photoluminescence shows that the electron transfer from a donor substrate to the sensitizer, which is the first step in the photocatalytic reaction path, is surprisingly improbable [3]. However, the long triplet lifetime of the Ir-complex in combination with a high substrate concentration leads nevertheless to an efficient system. The situation is different in a heterogenous system when the sensitizer is at the surface of a semiconductor like TiO_2. Then we observe very fast electron injection into the conduction band. A different route is taken with new semiconductor materials like carbon nitride. Here the semiconductor itself absorbs the light and the charge carriers have to get to the surface where the catalytic active sites are. By analyzing the time dependent absorption and fluorescence of carbon nitride we find indications for an anisotropic mobility of the carriers.

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Ultrafast electron spectroscopy at liquid interfaces

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For decades, ESCA or PES (termed XPS, for X-ray photoelectron spectroscopy, in the case of soft X-ray photons) was restricted to conventional laboratory X-ray sources or beamlines in synchrotron facilities. This approach enabled frequency domain measurements, but with poor time resolution. Indirect access to time-resolved processes in the condensed phase was only achieved if line-widths could be analyzed or if processes could be related to a fast clock, that is, reference processes that are fast enough and are also well understood in the condensed phase. Just recently, the emergence of high harmonic light sources, providing short-wavelength radiation in ultrashort light pulses, added the dimension of time to the classical ESCA or XPS technique and opened the door to (soft) X-ray photoelectron spectroscopy with ultrahigh time resolution. The combination of high harmonic light sources (providing radiation with laser like beam qualities) and liquid microjet technology recently enabled the first liquid interface PES experiments in the IR/UV-pump and extreme ultraviolet-probe (EUVprobe) configuration. In the talk different features of the technology and a number of recent applications involving solvation phenomena near water and protic solvent interfaces will be highlighted.

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Water structure at hydrophobic surfaces probed with surface sum-frequency generation

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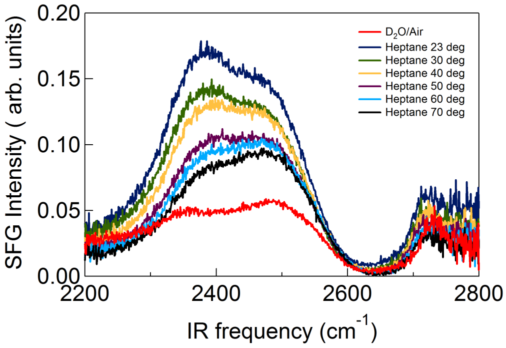
We study the structure of water molecules at different oil surfaces (hexane, heptane, and polydimethylsiloxane), and at an anti-freeze protein surface with surface sum-frequency generation (SFG) spectroscopy. In the experiment we combine broadband femtosecond IR pulses (bandwidth of ~200 cm^{-1}) with relatively narrow-band light at 800 nm (bandwidth of 15 cm^{-1}). The IR pulses have a sufficiently large bandwidth to measure the complete SFG spectrum of the OH(OD) stretch vibrations of H_2O(D_2O). We observe that the SFG intensity is 4-10 times higher at a water-oil interface than at a water/air interface, which indicates that water molecules are more strongly oriented at the interface with oil than at the interface with air.[1] We also observe that the SFG spectrum is red shifted compared to that of the water/air interface, which points at a strengthening of the hydrogen bonds. These observations indicate that the methyl and methylene groups of oil that protrude into the water phase act as a template for the water network to fold around, thus enhancing the water structure and the hydrogen-bond interaction. With increasing temperature the SFG intensity decreases and the SFG spectrum shows a significant blue-shift, indicating that the ordering of the water decreases (see Figure). Structuring of water also forms an essential element of the working mechanism of anti-freeze proteins. We use SFG to study the properties of water at the ice-binding surface of antifreeze protein III at temperatures well above the freezing point. The SFG spectrum shows a relatively narrow peak centered at 3250 cm^{-1}, highly similar to the infrared and Raman spectrum of ice. We thus find evidence for the presence of highly structured ice-like water layers at the surface of the protein at temperatures well above the freezing point [2]. Decreasing the temperature to the biological working temperature of the protein (-2 to 0 °C) increases the amount of ice-like water, while a single point mutation in the ice-binding site is observed to completely disrupt the ice-like character of the water layer, in accordance with the elimination of the antifreeze activity. These observations indicate that not the protein itself, but rather the ordered ice-like protein hydration shell is responsible for the recognition and binding to ice.



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Ring-opening dynamics of 1,3-cyclohexadiene studied by time-resolved molecular orbital spectroscopy

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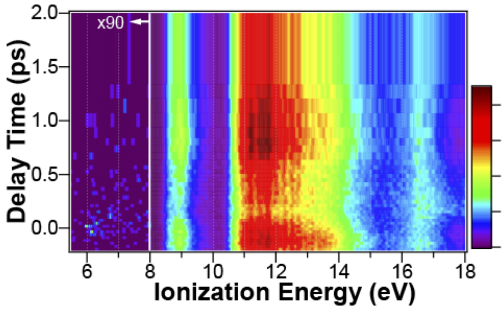
Chemical bonds in a molecule are characterized by the electron spatial distributions, which are well understood by a molecular orbital (MO) theory. The ionization energy of each MO, measured by photoelectron spectroscopy, is correlated with its orbital energy under Koopmans' theorem. Therefore, by observing time-resolved photoelectron spectroscopy (TRPES) with high harmonic pulses [1], we can gain insight into transient molecular geometries and determine the location where chemical reactions take place, which is called time-resolved MO spectroscopy [2]. In this work, we investigated the ring-opening dynamics of 1,3-cyclohexadiene. Figure 1 shows the photoelectron spectrum and the corresponding MOs of 1,3-cyclohexadiene. Figure 2 shows the photoelectron spectrogram probed by 29.5-eV high harmonic pulses [1]. The photoelectron intensity from $\sigma_{\text{C-C}}$ observed around 13 eV was decreased within the excitation pulse duration and was constant upto 600 fs, while those from $\sigma_{\text{C=C}}$ and $\pi_{\text{C=C}}$ around 11.5 eV were increased gradually. After 600 fs, the photoelectron intensities of these MOs, $\sigma_{\text{C-C}}$, $\sigma_{\text{C=C}}$ and $\pi_{\text{C=C}}$, were increased. The C-C single bond breaks by the ring-opening reaction upon photoexcitation, while the C=C double bonds remain. Therefore, these MO-dependent dynamics suggests that the ring-opening reaction proceeds during 600 fs. Time-resolved MO spectroscopy can probe the conformal changes sensitively.



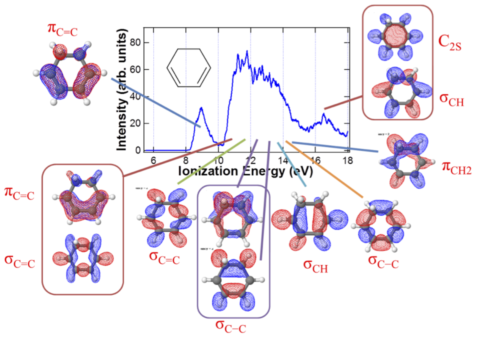


Figure 1 Figure 2: Photoelectron spectrogram

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Tabletop imaging of structural evolutions in chemical reactions

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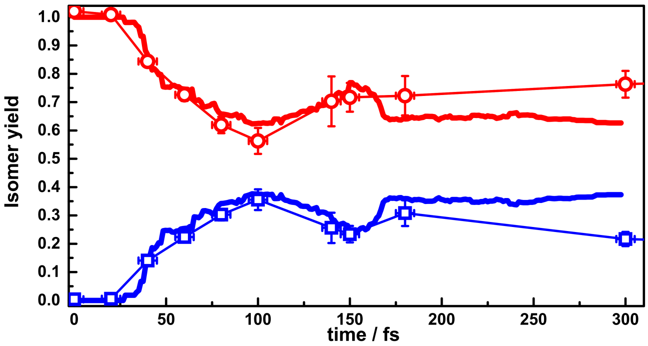
Since laser driven tunnel ionization preferentially ionizes the highest occupied molecular orbital (HOMO) compared to lower lying orbitals, the dynamics within the cation typically involves mostly the electronic ground state. We present a tabletop approach to efficiently launch dynamics from ionization of the HOMO-1 orbital of small organic molecules, which so far required limited VUV sources like FELs or high harmonics. 266 nm ultrashort laser pulses are capable of initiating rich dynamics through strong field multiphoton ionization – an interesting regime located between weak field multi photon - and tunnel ionization. We have imaged proton migration - as one of the fundamental processes in chemistry and biology - with femtosecond resolution in the first excited state of the acetylene cation and have shot a molecular movie of the to and fro isomerization process. Additionally, a new dissociation channel (C=C bond breaking) has been observed. Our results present the most complete picture of population transfer on the excited state of the acetylene cation. Our table-top approach is generally applicable and can be used for other small organic molecules. The experimental results are in excellent agreement with the timescales and relaxation pathways predicted by new and quantitative ab initio trajectory simulations.



Acetylene (red) and vinylidene (blue) yield in the cation. Exp. (symbols), theory (line)

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Probing transition states in photodissociation reactions by femtosecond XUV transient absorption

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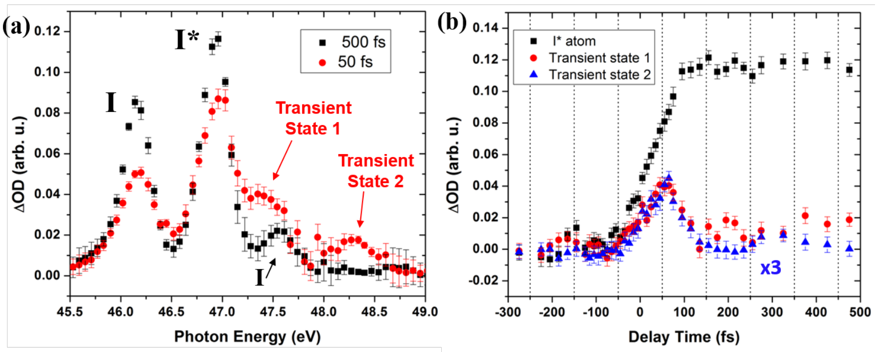
Femtosecond extreme ultraviolet (XUV) pulses produced by high harmonic generation are used to probe photodissociation reactions of methyl iodide and allyl iodide by the real-time evolution of core-to-valence transitions near the iodine N edge. The gaseous alkyl iodide molecules are photoexcited by an ultraviolet (266 nm) pump pulse, accessing repulsive valence-excited states, which dissociate along the C-I bond to form I($^2P_{3/2}$) or I*($^2P_{1/2}$) and the corresponding alkyl radical. On a sub-100 fs timescale, during the process of C-I bond breaking, new core-to-valence electronic states appear in the iodine N pre-edge absorption spectra, indicative of transition states, which decay concomitantly with the rise of the characteristic atomic iodine resonances. The transient features observed during dissociation are assigned to repulsive valence-excited transition states that connect with core-electron transitions and represent the evolution of the valence electronic structure during the bond-breaking reactions. The dissociation times are measured by monitoring the rise of sharp atomic iodine resonances.[1] In the case of allyl iodide, the transition state resonances peak after ~50 fs and decay to complete C-I dissociation in the major I* product channel in ~70 fs.



(a) Differential absorption spectra of allyl iodide near the atomic iodine pre-edge resonances, at 50 and 500 fs following 266 nm excitation. (b) Time-resolved differential absorption lineouts of allyl iodide.

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Lattice dynamics in few-layer Molybdenum disulfide investigated by Ultrafast Electron Diffraction

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Molybdenum disulfide (MoS_2) is a prototype example for transition metal dichalcogenides (TMDs), which form a group of van der Waals bound two-dimensional layered materials [1]. Due to their unique electronic and optical properties such as circular dichroism, a strong spin-orbit coupling and a shift from indirect to direct band gap semiconductor with decreasing film thickness from bulk to monolayer, TMDs are interesting for both fundamental research and industrial applications such as electronic devices [2, 3]. We study dynamical processes following optical excitation in few-layer MoS_2 by means of time-resolved Ultrafast Electron Diffraction (UED), which has become a promising technique to directly provide insights into dynamics in crystalline solids at the microscopic level with a sub-picosecond temporal resolution [4, 5]. Our highly compact UED-setup is fully characterized by experiments and many-body simulations [6].

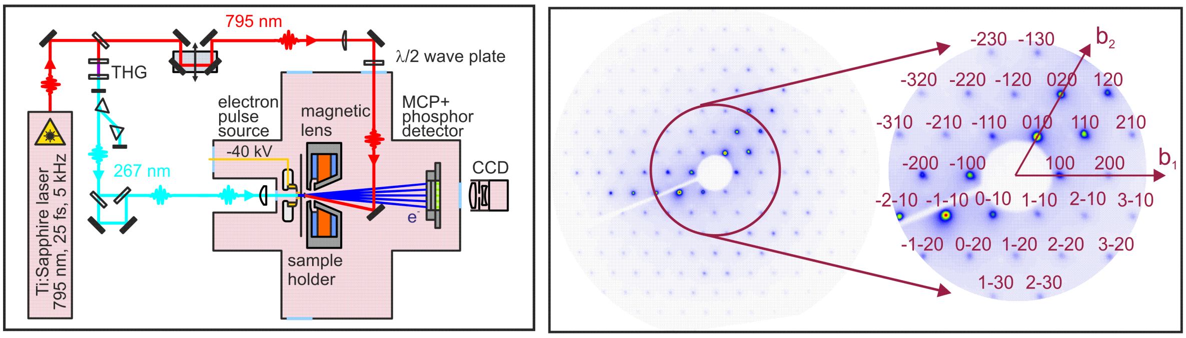

Fig. 1. Left: Ultrafast Electron Diffraction-setup. Right: Measured Electron Diffraction Pattern of Molybdenum disulfide.

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Vibrationally coherent transfer in an electronically decoupled DTE-BODIPY dyad investigated by pump-probe experiments and theoretical modelling

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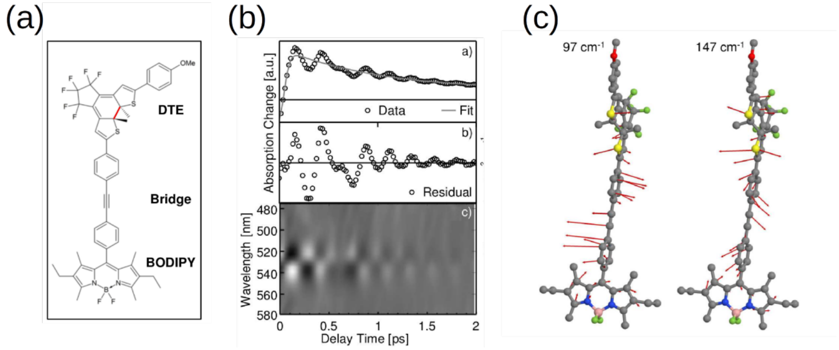
A combined experimental and theoretical investigation has been performed of the photo-induced ring-opening reaction of an electronically decoupled DTE-BODIPY dyad [1]. The femtosecond time-resolved UV/Vis pump-probe experiment exhibits a low-frequency oscillatory signal [2], which can be interpreted in terms of two time scales: (1) an ultrafast planarization of the DTE moiety [3] and (2) a slower coherent vibrational energy transfer to the BODIPY moiety induced by the geometrical DTE changes [4]. This assignment is based on Fourier transformed experimental data and a theoretical investigation at the TDDFT level of theory, along with a normal mode analysis that indicates several prominent vibrations in line with the above interpretation. Quantum dynamical simulations are performed to model the coherent, ultrafast transfer process in the presence of intramolecular vibrational redistribution and an external solvent environment.



(a) Molecular structure of the investigated DTE-BODIPY dyad (b) 1D cut and 2D representation of the fs UV/Vis pump-probe experiment indicating a coherent signal, (c) calculated vibrational frequencies corresponding to the experimental observations.

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A new photophysical insight into high turn over numbers for H_2 generation in Ru(II)-polypyridine-Pt(II) photocatalytic complexes

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Photocatalytic water splitting is a promising approach to produce solar based renewable hydrogen. Understanding the photodynamics that follow upon optical excitation is of prime importance for the design of efficient photocatalysts. We synthesized two closely related Ru(II)-polypyridine-Pt(II) photocatalysts (Figure 1) which show a remarkable difference in turn over numbers (TON). RuPt (left) shows a TON of 99 within 18 hours. Interestingly, functionalizing the peripheral ligands with ester groups (right) increases the TON to 720. We have studied the photophysics by ultrafast transient absorption and photoluminescence in combination with DFT calculations. An important aspect to address involves the nature of the metal.[1] For RuPt we observe a similar ps inter-ligand electron transfer process from the peripheral ligands to the bridging ligand (acting as an electron reservoir) as we reported recently[2][3] for the equivalent RuPd complex. Functionalizing RuPt with ester groups leads to remarkable changes in the photorelaxation pathways and the electron storage position, strongly increasing the H_2 TON value. This insight provides a new design concept for efficient molecular photocatalysts.

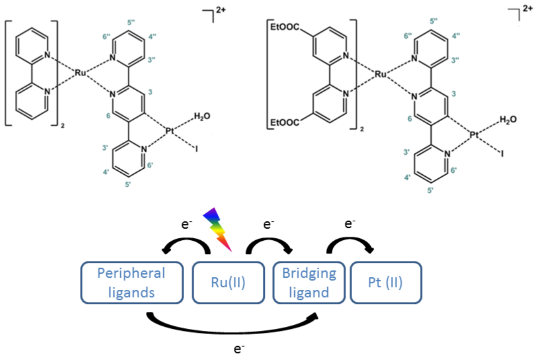

Figure 1: Structure of $[Ru(bpy)_2(2,5tpy)PtI(H_2O)]^{2+}$ (left, RuPt) and $[Ru(dceb)_2(2,5tpy)PtI(H_2O)]^{2+}$ (right, EtRuPt).The panel below shows a generally accepted picture of intramolecular electron transfer processes induced by photoexcitation, with the bridging ligand acting as electron reservoir.

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Nonlinear photo-oxidation and femtosecond FWM imaging of graphene

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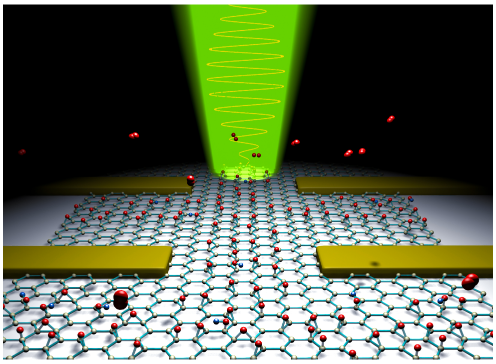
We have developed a method for tuning the electrical and optical properties of graphene by using femtosecond laser pulses [1]. Ultrathin, durable, flexible, transparent graphene is promising material for applications in electronics, photonics and optoelectronics. Focusing a femtosecond laser beam to graphene in ambient air induces non-linear photo-oxidation that locally changes the properties of graphene. By choosing the proper laser pulse parameters oxidation can be achieved without ablation or cutting of graphene. Femtosecond four wave mixing (FWM) microscopy is an efficient tool for imaging the oxidized patterns. FWM signal is very strong even from single layer graphene and the oxidized patterns can be distinguished from pristine graphene with excellent contrast. Local modification of graphene properties by direct laser writing provides a new all-optical method to develop all-graphene electronic and optoelectronic devices. Similar photo-oxidation effect has been observed also for suspended carbon nanotubes [2].



Femtosecond laser pulses induce local oxidation of graphene [1].

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Chirality-Sensitive Ultrafast Spectroscopy

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Ultrafast structural dynamics can be investigated by a variety of methods. For example, we have shown the applicability of coherent multidimensional spectroscopy for photochemical reactions on the example of *cis-trans* isomerization [1]. A different approach – the topic of this presentation – is to employ chirality as a signature of (time-dependent) structure. In general, chirality arises from symmetry considerations: A chiral object cannot be superimposed with its mirror image. Progress will be shown toward chirally selective time-resolved spectroscopy of molecules in the condensed phase. For this purpose, a variety of fundamental and practical issues have to be addressed. Solutions to some of the problems will be discussed. As a means to introduce and probe chirality via light in the most flexible fashion, we have developed vector-field shaping with independent ultrafast control over amplitude, phase, and polarization of an ultrashort pulse as a function of time [2]. In a second project, we have developed shot-to-shot detection of full spectra at 100 kHz repetition rate with a synchronized 50 kHz chopper [3]. This is helpful since chiral signals are small and it is thus desirable to increase the signal-to-noise ratio for a given measurement time. In time-resolved spectroscopy of population dynamics one also has to take care that anisotropic contributions to the signal are avoided. With linearly polarized pump and probe pulses in transient absorption spectroscopy, the "magic angle" configuration is commonly employed. However, for pulses with other polarizations or more than two laser beams the situation is more complicated. We have derived conditions for anisotropy-free measurements with arbitrary polarizations and geometry [4]. Another necessary ingredient for chiral spectroscopy is a detection method that provides chiral sensitivity. We have constructed a highly sensitive polarimeter and combined it with accumulative spectroscopy to measure the optical rotation change upon a chirality-modifying photochemical reaction [5]. With this setup we further achieved all-optical discrimination between racemic and achiral molecular solutions [6]. A second option for chiral detection is to measure photoinduced changes in circular dichroism (CD). Femtosecond time-resolved CD spectroscopy is challenging and prone to artefacts, thus in the literature single-wavelength detection is mostly employed. We have developed broadband time-resolved CD spectroscopy [to be published]. It is based on a "light-pulse enantiomer" setup that can create a copy, as well as its precise polarization-mirrored image, of any (polarization-shaped) input laser pulse. Thus, we can switch between opposite chiralities of the (probing) laser field on a shot-to-shot basis and measure broadband time-resolved CD spectra. As an example, we investigated the ultrafast dynamics of hemoglobin upon oxygen release.

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Ultrafast Dynamics of Carbon Dioxide Reduction Photocatalysts Studied with Equilibrium and Transient Two-Dimensional Infrared Spectroscopy

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The photocatalytic reactions that leverage light energy to power chemical transformations operate on a vast range of time scales, from femtosecond light absorption to much slower substrate binding, release and catalyst regeneration. Considerable progress has been made in the last decade to use ultrafast multidimensional spectroscopy to study ground electronic state equilibrium dynamics in systems ranging from small molecules and peptides to liquids and proteins. Advances have come slower in using transient versions of these methods to study excited electronic states on the same footing as their well-understood ground states. It is particularly important to be able to study the vibrationally equilibrated excited states of photocatalysts, since those are states relevant to catalysis reaction dynamics. We have used both equilibrium and non-equilibrium, transient two-dimensional infrared (2D-IR) spectroscopy to investigate the ground S_0 and long-lived (~60 ns) excited triplet metal-to-ligand-charge-transfer state (^{3}MLCT) of several ReCl(CO)$_3$bpy CO_2 reduction catalysts in a series of solvents.[1-3] Transient 2D-IR spectroscopy enables direct comparison of solvation dynamics on distinct electronic states. This talk will summarize our previous findings regarding the differences in spectral dynamics for the S_0 and ^{3}MCLT, where we find a pronounced slowdown in solvation dynamics as reported by spectral diffusion that we have attributed to the ~8 Debye change in the molecular dipole moment.[1-2] Additionally, we will discuss both chemical substitutions on the bipyridyl ligand,[3] as well as the role of preferential solvation in controlling the electron transfer from the sacrificial donor triethanolamine (TEOA). Our data suggest preferential solvation by the polar TEOA co-solvent, which has important implications for the question of whether or not the primary charge transfer process is diffusion controlled.

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Electronic Dynamics in Aqueous Solutions Studied by Ultrafast UV Photoemission and XAS Spectroscopy

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In this presentation, we report laser-based ultrafast photoemission spectroscopy and XFEL-based ultrafast X-ray absorption spectroscopy of aqueous solutions. UV and VUV photoemission spectroscopy of liquid microjets enables observation of valence electron dynamics in aqueous solution within the depth less than several nanometers from the surface. Appropriate solute concentration minimizes electrokinetic charging of liquids and enables reliable measurements of electron binding energies. Time-and angle-resolved photoemission spectroscopy of liquid microjets is performed using a linear time-of-flight spectrometer and polarization rotation of the probe pulse (50 – 100 kHz). Anisotropic photoemission from photoexcited solute and isotropic photoemission from hydrated electron were observed. SACLA is a hard X-ray free electron laser constructed in Japan. Time-resolved XAS was performed for $[Fe(III)(C_2O_4)_3]^{3-}$ in water near the Fe K-edge. The Fe K-edge exhibited red-shift upon 268-nm excitation with two time-constants of 140 fs and 3 ps, and the EXAFS feature has diminished. The analysis aided by DFT calculations indicate photoreduction of Fe(III) via LMCT transition, followed by the release of CO_2^- which induces a secondary reducing reaction of unexcited $[Fe(III)(C_2O_4)_3]^{3-}$.

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Orbital-specific mapping of chemical dynamics with ultrafast x-rays

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Charge and spin density changes at the metal sites of transition-metal complexes and in metalloproteins determine reactivity and selectivity. To understand their function and to optimize complexes for photocatalytic applications the changes of charge and spin densities need to be mapped and ultimately controlled. I will present our approach of using atom- and orbital-specific x-ray free-electron laser spectroscopy [1] and quantum chemical theory [2] to map the frontier-orbital interactions of a transition-metal complex in solution on the femtosecond time scale [3]. Spin crossover and ligation are found to define the excited-state dynamics. The solution pathways will be contrasted to the gas-phase dynamics of the same molecule measured with photoelectron spectroscopy at the x-ray free-electron laser FLASH and with a lab-based source of femtosecond VUV pulses based on high-order harmonic generation. It is demonstrated how correlating orbital symmetry and orbital interactions with spin multiplicity allows for determining the reactivity of short-lived reaction intermediates. I will discuss how this complements approaches that probe structural dynamics and how it can be extended [4] to map the local chemical interactions and their dynamical evolution in metalloproteins.

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Measurement and Control of Attosecond Charge Migration

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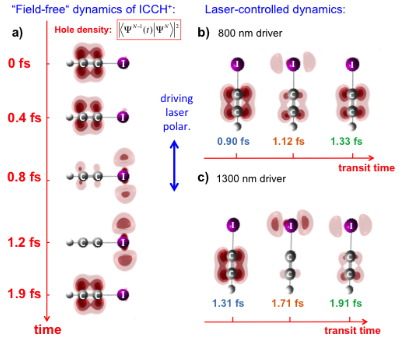
We advance high-harmonic spectroscopy to resolve molecular charge migration [1] in time and space and simultaneously demonstrate extensive control over the process. A multi-dimensional approach enables us to reconstruct both quantum amplitudes and phases of spatially oriented molecules [2,3] with a resolution of 70-130 attoseconds and to separately reconstruct field-free (a) and laser-driven charge migration (b,c) using driving lasers centered at 800 nm (b) or 1300 nm (c). Our techniques make charge migration in molecules measurable on the attosecond time scale and open new avenues for laser control of electronic primary processes [4].



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Deciphering attosecond molecular dynamics with pump-probe schemes

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The development of attosecond laser pulses allows one to probe the inner working of atoms, molecules and surfaces on the timescale of the electronic response. In molecules, attosecond pump-probe spectroscopy enables investigations of the prompt charge redistribution and localization that accompany photo-excitation processes, where a molecule is lifted from the ground Born-Oppenheimer potential energy surface to one or more excited surfaces, and where subsequent photochemistry evolves on femto- and attosecond timescales. In this talk I will present a few theoretical examples of realistic molecular attosecond pump-probe experiments in which simple molecules are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. The evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions is calculated with attosecond time-resolution and is visualized by varying the delay between the pump and probe pulses. The results of these calculations [1-7] allow us to explain several experimental observations as well as to guide future experimental efforts to uncover ultrafast electron and nuclear dynamics in molecules.

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Investigation of XUV-induced ultrafast electron dynamics in complex molecules

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Electron transfer within a single molecule is the fundamental step of many biological processes and chemical reactions. Theoretical studies have pointed out that very efficient charge dynamics along the molecular backbone can be driven by purely electronic effects, which can evolve on a temporal scale ranging from few femtoseconds down to tens of attoseconds [1]. Here, we report the application of XUV (17-35 eV) attosecond pulses to prompt ionization of the amino acid phenylalanine and the subsequent detection of ultrafast dynamics on a sub–4.5-femtosecond temporal scale (Fig. 1), which is shorter than the vibrational response of the molecule [2]. This ultrafast dynamics can only be associated with a purely electronic process, thus constituting the first experimental measurement of charge migration in a biomolecule.

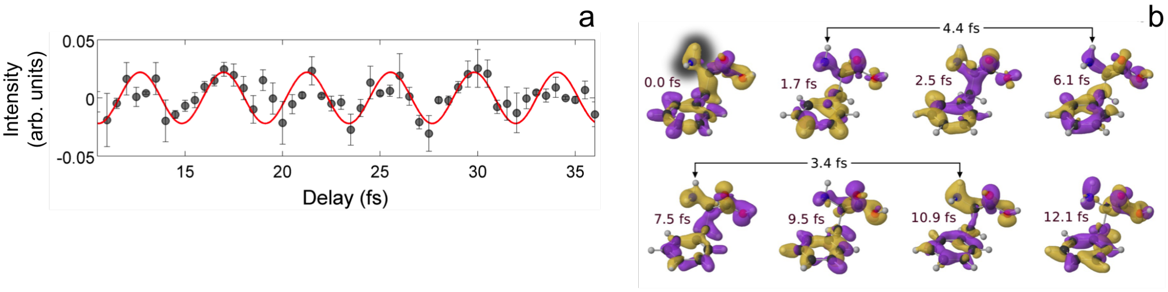

Figure: (a) Oscillatory pattern observed in the measured dication yield (m/q=60) as a function of the XUV pump- IR probe delay. (b) Calculated variation of the hole-density as a function of time.

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Electron transfer between the fragments of a dissociating molecule

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Charge transfer and charge migration reaction drive numerous important processes in physics, chemistry and biology. Ultrashort X-ray pulses represent a very efficient tool for studies of charge transfer dynamics, combining element- and, thus, site-selectivity with femtosecond time resolution. Here, we used 70 fs X-ray free-electron laser pulses at 1.5 keV to image intramolecular electron transfer in iodomethane molecules during dissociation induced by a synchronized infrared (IR) laser pulse. Inner-shell X-ray ionization creates positive charge, which is initially localized on the iodine atom. We map the electron transfer between the methyl and iodine fragments as a function of their interatomic separation set by the IR-X-ray delay. As illustrated in Figure 1, the delay-dependent kinetic energy spectra of highly-charged iodine ions contain a band of extremely low-energy fragments, which can appear only if the remaining part of the molecule remains neutral and there is no Coulomb explosion. Therefore, the delay-dependent yield of this channel reflects the inversed probability of the electron transfer from the methyl group to the iodine atom. We observe signatures of this electron transfer up to 20 Å internuclear separation, show that its effective spatial range can be estimated from a classical over-the-barrier model [1], and discuss possible reasons for the observed oscillatory behaviour of the electron transfer rate.

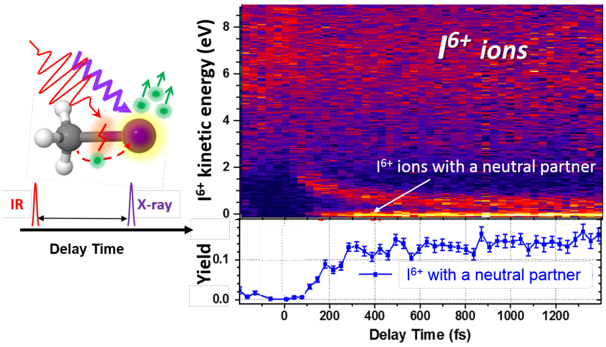

Figure 1. Delay-dependent kinetic energy spectrum of the measured I^{6+} ions (top) and the yield of the lowest-energy channel (bottom)

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Hydration of Phospholipids and the DNA Backbone Studied by Femtosecond 2D-Infrared Spectroscopy

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Ionic phosphate groups are key functional groups of numerous macromolecules and play a central role in the hydration of biomolecular structures. While x-ray diffraction, nuclear magnetic resonance, and linear vibrational spectroscopy have identified time-averaged hydration patterns, in particular around phosphates [1], ultrafast structural dynamics and fluctuations originating from phosphate-water interactions have remained mainly unexplored. Here, new insight into phosphate hydration from femtosecond two-dimensional infrared (2D-IR) spectroscopy will be presented for a series of model systems of increasing structural complexity. Results for phosphate ions solvated in H_2O [2] serve as a benchmark for the behavior of the much more complex phospholipid [3,4] and DNA structures. Phosphate stretch and DNA backbone vibrations are highly sensitive local probes of hydration dynamics. Femtosecond 2D-IR spectroscopy in the frequency range from 900 to 1300 cm^{-1} maps anharmonic couplings and population transfer between the different modes and establishes the basic femtosecond time scales of structure fluctuations in the hydrated systems. In DNA, the basic coupling pattern within the manifold of backbone vibrations is deciphered and their delocalized character established. The fastest fluctuations of bulk water around solvated phosphate ions occur on a 50-fs time scale, resulting in ultrafast spectral diffusion of the phosphate's vibrational bands. In contrast, hydrated phospholipids and DNA display a slower 300-fs time scale of limited fluctuations, leaving the inherent structural disorder and the hydrogen bonds between the biomolecule and the first water layer intact for longer than 10 ps. In phospholipids and DNA, orientation of water molecules in the strong interfacial electric fields and steric hindrance reduces the flexibility of the water shell. Fluctuations on the 300-fs time scale are connected with low-frequency motions of the biomolecules and hindered water motions. Processes of energy exchange with the water shell will be discussed as well [3,5].

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Water dynamics at the interface of DNA

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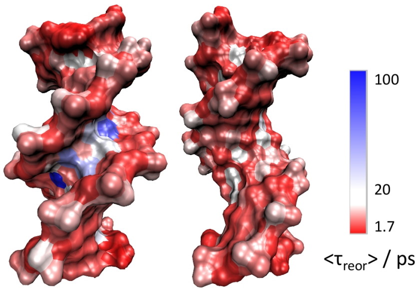
The hydration layer encasing DNA is of major importance for its biomolecular function and plays a role in a great variety of processes including DNA-ligand binding, drug intercalation and in the protection of the delicate DNA structure against heat denaturation. The dynamics of water in the vicinity of DNA has thus been actively studied with a broad range of techniques, most prominently by time-dependent Stokes' shift measurements[1], ultrafast infrared spectroscopy[2], NMR[3] and numerical simulations[4]. Here we combine molecular dynamics simulations and an analytic jump model [5] to map the water reorientation and hydrogen-bond dynamics at the DNA interface. We show that the water reorientation dynamics is governed by hydrogen-bond exchanges towards a new water acceptor and we confirm that water dynamics is particularly retarded in the minor groove. For these strongly confined water molecules, a pronounced dynamical heterogeneity is found and we establish that water dynamics changes sensitively with the DNA groove width fluctuations.



Map of the water reorientation time at the interface of a DNA dodecamer.

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Picosecond Photobiology: Watching a Signaling Protein Function in Real Time via Time-Resolved X-ray Diffraction and Solution Scattering

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To understand how signaling proteins function, it is crucial to know the time-ordered sequence of events that lead to the signaling state. We recently developed on the BioCARS beamline at the Advanced Photon Source the infrastructure required to characterize structural changes in proteins with 150-ps time resolution, and have used this capability to track the reversible photocycle of photoactive yellow protein following trans-to-cis photoisomerization of its p-coumaric acid (pCA) chromophore. Briefly, a picosecond laser pulse photoexcites pCA and triggers a structural change in the protein, which is probed with a suitably delayed picosecond X-ray pulse. When the protein is studied in a crystalline state, this "pump-probe" approach recovers time-resolved diffraction "snapshots" whose corresponding electron density maps can be stitched together into a real-time movie of the structural changes that ensue [1]. However, the actual signaling state is not accessible in the crystalline state due to crystal packing constraints. This state is accessible in time-resolved small- and wide-angle X-ray scattering studies, which probe changes in the size, shape, and structure of the protein [2]. The mechanistically detailed, near-atomic resolution description of the complete PYP photocycle developed from these studies provides a framework for understanding signal transduction in proteins, and for assessing and validating theoretical/computational approaches in protein biophysics [3]. This research was supported in part by the Intramural Research Program of the NIH, NIDDK.

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The energy transfer events taking place with a purple bacterial LH2 complex

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The LH2 complex from Rhodopsuedomonas acidophila provides an excellent light harvesting complex within which to investigate the ultrafast energy transfer events that take place within the first few ps of photosynthesis. This is because there is both high resolution structural information and because the different pigment groups present within it are all spectrally well resolved. This lecture will present an up to date picture of all these energy transfer reactions. I will both focus on what is known and on what are to remain open questions.

Ultrafast Surface Chemistry and Catalysis with an X-ray Laser

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The development of X-ray photon sources delivering femtosecond X-ray pulses, combined with the possibility of triggering chemical reactions by means of femtosecond lasers, pawed the way to the realization of the surface femtochemistry dream, i.e., the possibility to follow on a femtosecond timescale the evolution of the electronic structure during a chemical reaction at a surface. In this talk I will present two examples of ultrafast studies on catalytically relevant reactions at surfaces: CO desorption [1] and CO oxidation on Ru(0001) [2]. By employing as a probe X-rays pulses from the Linac Coherent Lighe Source (LCLS) X-ray free electron laser (FEL) and as a pump a femtosecond infrared laser synchronized with the probe, we have studied by means of time resolved X-ray emission (trXES) and time resolved X-ray absorption (trXAS) experiments the ultrafast evolution of bond distortions, weakening and breaking during the reactions. Thanks to the combination of trXAS, trXES and novel theoretical calculations, we successfully detected both transient intermediates but also the transition state region in the surface chemical reaction. Along with XES and XAS, time resolved photoemission spectroscopy (trPES) is an X-ray spectroscopy perfectly suited to reveal dynamical changes in the electronic structure. I will briefly discuss its applicability in surface femtochemistry experiments and the advantages of trXES and trXAS.

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Ultrafast photoexcitation and relaxation pathways in TiO_2 photocatalysis

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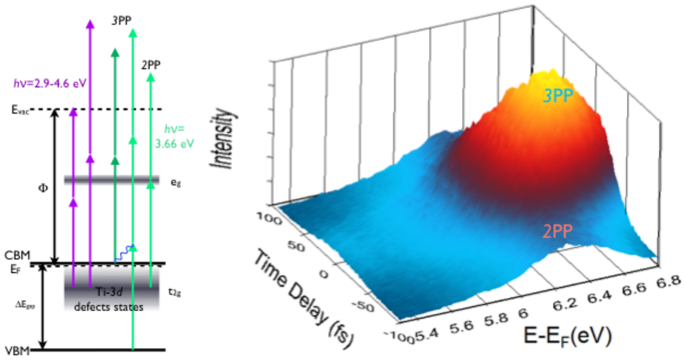
We investigate the ultrafast optical excitation and electron relaxation pathways for the clean as well as molecule and metal nanoparticle covered rutile TiO_2(110) surface. Using high power, broadly tunable (2.9-4.6 eV), 20 fs NOPA excitation source, we perform multiphoton photoemission (*m*PP) spectroscopy of TiO_2 surface. The energy, momentum, and pump-probe delay time resolved mPP spectra provide information on the initial and intermediate states in the multi-photon excitation process (Figure 1) [1]. The excitation is initiated from the valence band or the Ti-3d defect states on reduced TiO_2 surfaces. The intermediate states are either higher-lying Ti-3d bands of e_g symmetry [1], or the adsorbate induced unoccupied resonances [2-5]. The excitation of adsorbate resonances can initiate femtochemistry, such as proton-coupled electron transfer, provided that their decay by reverse charge transfer to the conduction band of TiO_2 is sufficiently slow.



mPP excitation and relaxation scheme, and experiment for the bare TiO_2 surface.

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Nonlinear THz Spectroscopy of Molecules and Materials

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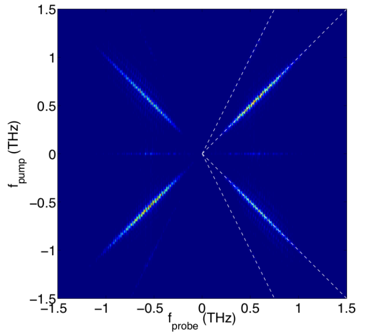
In recent years, nonlinear terahertz spectroscopic measurements have been demonstrated on a wide variety of molecular and material systems. Strong THz fields and metamaterial field enhancement have enabled some highly nonlinear THz-induced responses including phase transitions and chemical reactions as well as visible light emission. After a brief review of THz-induced collective material responses [1,2], molecular effects under current study will be discussed. Finally 2D THz spectra of molecules will be presented.



THz 2D spectrum. All the features are real and are spectrally resolved from the other features. A small prize is offered to a student who correctly identifies the sample. It doesn't count if I already told you or someone else who told you.

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Ultrafast Carrier Dynamics in Graphene and Graphene Nanostructures

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Graphene is an attractive candidate for many optoelectronic applications because of its vanishing bandgap and high carrier mobility. An essential process for such applications is the dissipation of the energy of photo-excited charge carriers in graphene. Two competing energy relaxation mechanisms for optically excited carriers exist: They can (i) thermalize with intrinsic carriers near the Fermi level, heating them to higher energy states through the process of 'hot carrier multiplication'; or (ii) the excess energy of the optically excited carrier can be lost via emission of phonons. With optical excitation-THz probe spectroscopy, an optical method for probing photoconductivities on ultrafast timescales, we reveal highly efficient energy transfer from an optically excited carrier to multiple heated charge carriers (relaxation path (i)) [1]. Carrier heating is also highly efficient when intrinsic carriers are accelerated by a strong electric field [2]. We further show how the branching ratio between (i) and (ii) can be tuned externally [3]. While presenting an advantage for some applications, the vanishing bandgap of graphene can also be a disadvantage in applications such as photovoltaics. A chemical synthesis approach was recently shown for making well defined, narrow graphene nanoribbons (GNRs) with widths as small as ~1 nm [4]. In these structures, carrier confinement in the lateral dimension induces a bandgap corresponding to visible wavelengths. Carbon nanotubes (CNTs) are similar one-dimensional graphene nanostructures with potential bandgap. The complex photoconductivity of semiconducting GNRs and CNTs reveals that, while the mechanism of photoconductivity is very similar in the two nanostructures, the charge mobility is quite different [5].

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Femtosecond X-ray Spectroscopy in Catalysis?

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Time-resolved x-ray spectroscopy experiments are well-developed to probe the time-evolution of laser-excited states. It is possible to perform such experiments with synchrotrons [1], x-ray FEL's [2] and laboratory sources [3]. As yet, most (excitonic) electronic state calculations for such experiments are based on fixed configurations for the initial, intermediate and final states. A second topic I will discuss is the potential application of time-resolved experiments to track chemical reactions in a catalytic system at work. Using a dispersive monochromator one can in principle measure an x-ray (emission) spectrum momentarily, allowing fs time-resolved spectroscopy. It remains to be seen how one can couple this to chemical reactions on timescales from fs to ns, μs, ms and seconds. A complication for fast experiments is the realization of a trigger that is not optical or electromagnetic. A last topic is the dynamics of core excitation and decay processes by using the energy domain instead of the time-domain. For example using x-ray Raman scattering, one can probe the exact lifetime of excited states.

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Charge transport, trapping and decay in metal oxides

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Titanium dioxide (TiO_2) and zinc oxide (ZnO) are among the most popular materials in solar energy conversion processes, either into electrical or chemical energy. These are entirely based on the generation of charge carriers (electrons and holes) by absorption of light, their transport and eventually, their localization due to the electron-phonon coupling and/or defects. In order to investigate these processes, element and geometry sensitive tools are required at high temporal resolution and at the working conditions of solar devices (i.e. room temperature). To this aim, we implemented picosecond (ps) and femtosecond (fs) X-ray absorption spectroscopy at the K-edges of Ti and Zn, on colloidal solutions of nanoparticles (NP) of typically ~20 nm diameter. In the anatase form of TiO_2, the NPs are known to have an ordered core with a defect-rich surface shell containing a high degree of Ti under-coordination and since the spectral changes pointed to the reduced centres being in an amorphous-like environment, it was also concluded that these traps are mostly localized at pentacoordinated trapping site located in the shell region.[1] Using the slicing scheme at the SLS (Villigen), we find that electron trapping occurs within 200 fs, implying that the electron does not migrate prior to trapping.[2] ZnO NPs were studied by ps and sub-ps XAS, X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS) at both synchrtrons and X-ray Free electron lasers. Time-resolved XAS results measured both 100 ps (Advanced Photon Source) and 2 ps (SACLA X-FEL) after photo excitation show clear signatures of structural changes due to the trapped electronic excitation in the nanoparticle. Our simulations of the XAS signals indicate that the primary contribution to our measurement is from a hole trapped at a native oxygen vacancy in the lattice, leading to an inward structural distortion of the neighbouring Zn atoms (VO++). This analysis is confirmed by the XES signal, which shows a slight charge density change on the Zn atoms, leading to a shift in the XES signal. Our transient XAS measurements from SACLA reveal that this charge trapping occurs on a sub-ps timescale, as in TiO_2.

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Ultrafast Solvated Electron Dynamics in Liquids and Supercritical Fluids

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The solvated electron is the "mother of all spin centers". Formally, it constitutes an unpaired negative elementary charge embedded in a condensed-phase matrix where it is self-stabilized by polarizing its surroundings. In the language of solid-state physics, the electron moves together with its polarization cloud as a quasi-particle, the so-called "polaron". In the context of solvated electrons in liquids, a heavily debated issue is the motif of electron binding. Is the electron trapped in a localized cavity within the liquid or do we have to regard it as a solvated radical anion cluster in which the spin density is diffusely smeared across a larger number of solvent molecules? How does the binding mode affect the physico-chemical properties of the system and is the reactivity of a "cavity electron" different to that of a "radical cluster electron"? To address some of these issues, we have recently studied extensively the ultrafast spectroscopy of solvated electrons in H-bonded solvents like water, alcohols, and ammonia [1-4]. The electrons were generated chemically (e.g. in metal-ammonia solutions) or photolytically via multi-photon ionization of the neat solvent. The solvent was studied over a wide range of thermodynamic conditions ranging from the tightly packed cryogenic liquid all the way over to the supercritical fluid with gas-like densities. In this talk, we will describe some of the progress we have made in understanding the chemical reactivity of solvated electrons with a particular emphasis on the dynamics of geminate recombination following an ultrafast ionization with energies above and below the band gap of the solvent. Such studies will be discussed in terms of Onsager's seminal theory for the initial recombination of ions in condensed media and in terms of detailed Monte-Carlo simulations to account for the molecular-level mechanisms that bring about an annihilation of the excess charge and spin densities.

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Cluster ionization in intense extreme-ultraviolet and near-infrared pulses

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Laser-cluster interaction is of fundamental interest for the understanding of many-body physics and electron-electron correlation effects. When an intense near-infrared (NIR) or extreme-ultraviolet (XUV) laser pulse interacts with a cluster, a large number of electrons and high charge ions are generated. If the ionization step depends of the wavelength, for sufficiently intense laser field, the build-up of the potential as electrons are stripped away from the cluster leads to the formation of quasi-free electrons and a nanoplasma. At the early stage of the cluster expansion, the nanoplasma cools down by evaporative electron emission. Charge recombination processes also take place leading to the formation of excited atoms. We investigate here the role of charge recombination processes in the ionization and dissociation dynamics of rare gas and molecular clusters induced by intense XUV and NIR laser pulses. Using time-resolved photoion and photoelectron spectroscopy, we observe that a large number of excited atoms are formed within the first few picosecond of the cluster expansion [1,2]. Surprisingly, we found that the relaxation of these excited atoms open novel ionization channels driven by electron correlation effects or by autoionization [3]. Experimental signatures of electron-correlation driven energy transfer following charge recombination in both rare gas and molecular clusters will be presented and discussed.

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Imaging macromolecules using X-ray free-electron lasers

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The short wavelength of X-rays allows us to resolve atoms, but in practise the achievable resolution is limited by the destruction of the sample by the radiation that forms the image. For over 100 years, the workaround to this problem of radiation damage has been to average signals from repeating copies of the object arranged in a large crystal. As first suggested by Solem and Chapline in the 1980's, and Hajdu in 2000, the achievable resolution of images of single biological objects could be improved by using intense X-ray pulses that vaporise the sample, but which are short enough in duration to freeze the blurring of the sample. With the advent of X-ray FELs we have been able to confirm this principle, and are now applying it to overcoming a major bottleneck for protein crystallography, which is the need for large well-diffracting crystals. The intense pulses also open up opportunities to help solve the crystallographic phase problem. The work suggests the feasibility of obtaining structures from much smaller samples, all the way down to the single molecule.

Photodynamics of Structural Isomers of Pyrenylethynyl-modified 2-Adenosines - Effect of Altered Electronic Interaction

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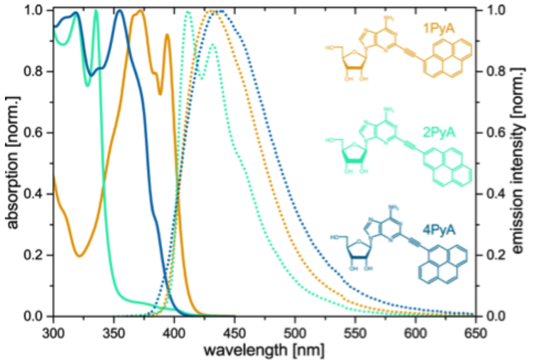
We present the photodynamics of newly developed structural isomers of pyrene-based fluorescent nucleotide analogues, which are suited for the investigation of conformational dynamics of RNA. Usually, nucleotides are linked to the 1-position of pyrene, as the high ground-state electron density there facilitates synthesis. Recently, linkage at different pyrene positions was established, causing changed electronic interaction between pyrene and the aromatic system linked to it with an ethynyl bridge [1]. Here, we present the photophysical behaviour of 2-(1-pyrenylethynyl) adenosine (1PyA) [2, 3], and of its structural isomers 2-(2-pyrenylethynyl) adenosine (2PyA) and 2-(4-pyrenylethynyl) adenosine (4PyA, see Figure 1). Although the absorption spectra are clearly distinct, emission occurs in a similar spectral range. Time-resolved ultrafast transient-absorption spectroscopy and time-correlated single-photon counting unveil very different and complicated excited-state lifetimes in all of the investigated compounds. The kinetics is characterized by pronounced spectral evolution on all time scales up to 1 ns. Therefore, we use lifetime-density analysis as alternative, model-free approach for analysing the transient absorption data [3, 4].



Lewis-structures of 1PyA (orange), 2PyA (sky blue), and 4PyA (blue) are depicted along with their absorption (solid) and emission (dashed) spectra in MeOH. 1PyA and 4PyA absorption is considerably redshifted compared to 2PyA, which is also the only derivative showing pyrenes structured emission.

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Dynamics simulations of the photophysics of the deprotonated nucleotide of guanine

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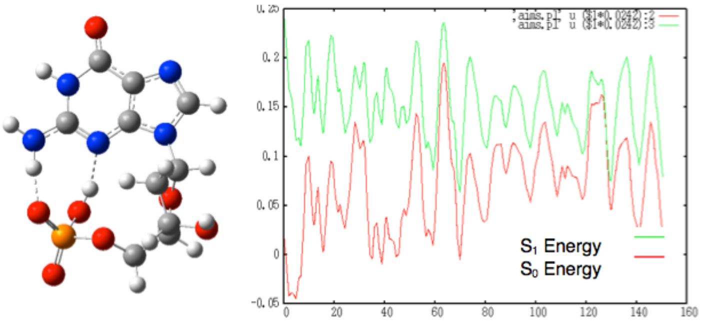
The time-resolved photoelectron spectra of the deprotonated nucleotides have been measured recently [1]. Among these, dGMP$^-$, the deprotonated nucleotide of guanine, is of special interest due to the presence of an intramolecular hydrogen bond between the phosphate group and the guanine amino group. This bond must be relevant for the photophysics because *ab initio* calculations show that the decay to the ground state involves an out-of-plane bending of the amino group [2]. Moreover, the time-resolved spectra decay on different time scales (50 and 600 fs) depending on the detected electron kinetic energy (eKE). Here dynamics simulations using CASSCF and the Ab Initio Multiple Spawning method [3] will be presented focusing on the evolution of the excited-state population of dGMP$^-$ during 1 ps after excitation, and on the evolution of the ionization potentials that give rise to the experimental spectra. Particular attention will be paid to the relationship between the dynamics and the detected eKE.



Structure of the DGMP anion with the relevant H bonds and Energy profile for a representative trajectory

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Broadband Pump-Probe and 2D UV Studies of Nucleobases: Breaking of Paradigms

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Photostability of DNA and related RNA is dictated by excitonic interaction between nucleotides and deactivation pathways of excitation energy, which affects the migration of excitons among them. Previous time-resolved studies performed with narrow excitation spectra indicated that in single nucleotides and nucleobases photoexcitation decays monoexponentially within a few ps [1,2], whereas in DNA it takes much longer time (several time scales have been reported; from tens to hundreds ps [2]). In order to reveal the underlying mechanisms of such significant differences in photodeactivation of nucleotides and DNA, we first performed experimental investigations of the excitation dynamics in nucleobases using our recently developed [3] broadband two-dimensional (2D) electronic and transient absorption (TA) spectroscopies with a time resolution of ~ 8 fs in the UV, covering a spectral range of 250-300 nm. We found that the dissipation of excitation in nucleobases in aqueous solutions occurs in two steps – fast relaxation within 500 – 700 fs from the excited S_1 ($\pi\pi^*$) state to the so-called "dark" state (which we believe to be $n\pi^*$ state) due to a conical intersection of their potential surfaces, and then – relaxation from the "dark" state to S_0 ground state within 1.5 – 1.7 ps which is also due to the intersection of their potential surfaces. In the TA these processes appear as a "butterfly"-shaped spectra from which we were able to establish a relevant spectroscopic model. Our findings allow explaining why the excitation in DNA lives much longer than in single nucleotides. These processes can be visualized in the 2D spectra and assigned through a high level theoretical treatment that gave quantitative agreement to the experiments and provided a solid foundation for comparing theory and experiment.

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Influence on ultrafast dynamics of artificially modified double-stranded DNA.

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Recently, a double-stranded DNA has been reported based on the hydroxyquinoline (Hq) ligand that was found to be similarly stable as natural A-T pairs.[1] In the context of modified DNA systems with introduced artificial functions, such as electron transfer, this system seems to be a promising candidate for investigations of ultrafast processes.[2] Therefore, the Hq-Hq pair was combined with a DNA-based donor-acceptor system consisting of 6-N,N-dimethylaminopyrene conjugated to 2′-deoxyuridine as photoinducible electron donor, and methyl viologen attached to the 2′-position of uridine as electron acceptor. In order to examine the influence of hydroxyquinoline on ultrafast dynamics in DNA, time-resolved pump-probe absorption measurements were performed under magic angle conditions in a quartz glass cuvette with a homemade micro-stirring device to avoid photo-degradation (path length of 1 mm and sample volume of 200 μl). For various donor-acceptor DNA and reference systems the pump wavelength was set to 350 nm and the range of probe wavelengths varied between 480 and 700 nm. A further reference system, methyl viologen (Mv^{2+}) in aqueous buffer solution, was investigated after 300 nm excitation. It turned out that at least two processes are necessary to adequately describe the dynamics after photoexcitation, i.e. direct electron transfer between donor and acceptor and charge separation implying the (artificial) base pairs by formation of an Hq radical anion as intermediate. In comparison to natural DNA systems,[3] we found a positive influence of the artificial Hq-Hq pairs on the photoinduced electron transfer rate for both processes.

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Retrieving Quantitative Structural Information in a DNA Hairpin fluorescently labeled with 2-Amino-Purine

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A combination of time-resolved fluorescence (TRF) spectroscopy and molecular dynamics (MD) simulations is used to unravel the local structural heterogeneity of the "Primer Binding Site" (PBS) DNA hairpin of HIV-1, labeled with 2-amino-purine (2AP), a fluorescent analog of adenine. Femtosecond down-conversion fluorescence spectroscopy [1] is used and complemented by streak camera experiments to resolve the fluorescence population and anisotropy decay of the labeled hairpins over 5 orders of magnitude in times scales (see figure). The population of conformers undergoing static quenching is determined and compared to the population of conformers in which 2AP is expected (MD simulations) to be in aromatic stacking interaction with a nearby nucleotide. A good agreement is obtained for the three studied positions of the 2AP labeling inside the DNA hairpin. In addition, cluster analysis of the MD simulations enables quantitative sampling of the hairpin local structural heterogeneity by disclosing the relative populations in a variety of representative conformers.

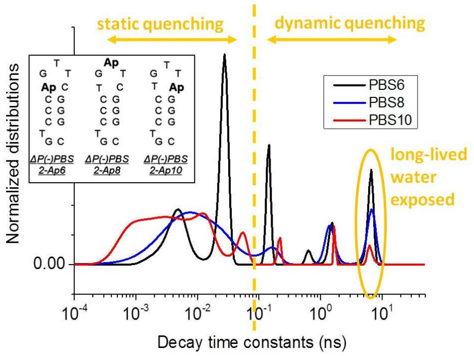

Figure: Site-specific distribution of fluorescence decay times of 2AP-labeled PBS.

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Non-equilibrium dynamics of carboxyhemoglobin in a highly-excited vibrational state

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In this work, we report on recent progress in the relaxation dynamics of the carbon monoxide stretch in carboxyhemoglobin following coherent excitation using a chirped mid-IR pulse. Coherent vibrational ladder climbing [1, 2] has been achieved here up to level n=9, a record high value in this system, as evidenced by spectrally resolved pump-probe experiments (Fig. 1(a)). The observed peaks on Fig. 1(a) are proportional to differences in population between two consecutive energy levels, hence the several negative peaks observed at early times due to population inversions resulting from the coherent nature of the excitation. For delays greater than 8 ps, the signal for the highest levels vanishes, allowing to retrieve by summation the actual populations as a function of time (Fig. 1(b)). These vibrational dynamics will be compared with recent transient two-dimensional infrared spectra at different waiting times as well as with a numerical resolution of the relaxation using a simple master equation [3].

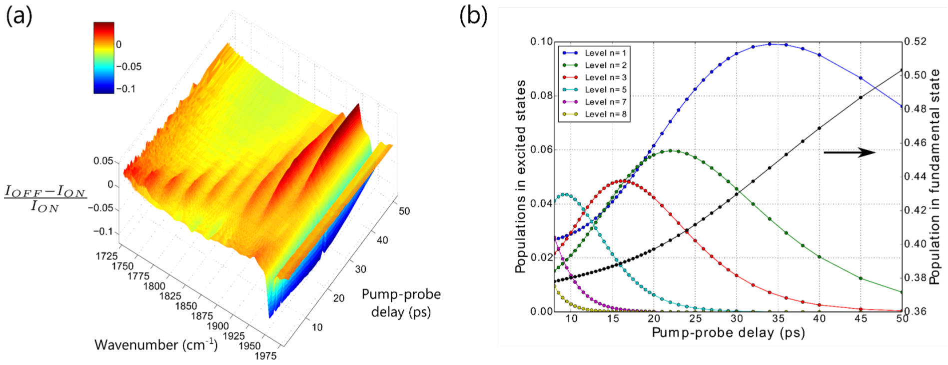

Fig 1: (a) Series of differential transmission spectra as a function of pump-probe delay after excitation by the mid-IR chirped pulse (b) Evolution of the vibrational populations in the excited states (colored curves, left axis) and in the fundamental state (black curve, right axis) derived from (a).

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The Ring-Opening of Provitamin D_3 in Liposomes

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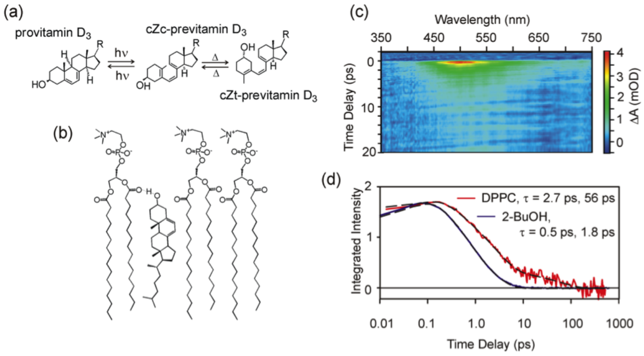
7-dehydrocholesterol (provitamin D_3, Pro) is the precursor to the photochemical formation of vitamin D_3 in mammals. The photochemistry of Pro has been studied extensively in alkane and alcohol solution [1,2]. In contrast, the reaction *in vivo*, occurs in the lipid bilayer of epidermis plasma membranes [3]. It is hypothesized that the membrane constrains the conformational freedom of previtamin D_3 preventing formation of the cZt conformer and thus enhancing formation of vitamin D_3 from the cZc conformation [3,4]. We have performed broadband ultrafast transient absorption measurements on Pro in DPPC liposomes as a model for the plasma membrane [4]. The excited state lifetime is lengthened, but there is no evidence for constrained ground state relaxation.



(a) Photochemical reaction of provitamin D_3 (Pro), (b) cartoon of Pro in a DPPC layer, (c) Excited state absorption of Pro in a DPPC Liposome at 30% loading, (d) comparison of the decay of the excited state absorption in 2-butanol and the DPPC liposome .

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Renal Osmolyte Induced Perturbation to Hydrogen Bonding Structure of Water

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The mammalian kidney is known to accumulate various osmolytes to counteract the deleterious effects of urea and salt concentrations. The mode of operation of osmolytes has long been a controversial issue. One school of thought is direct interactions of osmolytes with protein backbone [1]. While the other believes indirect action where osmolytes modify solvent water's properties which in turn dictate the protein's stability in high osmolyte solutions [2]. Since the observables like solvation behavior obtained from thermodynamic measurement of protein-free binary solution of osmolytes correlates very well with their action on protein, we have focused on all the renal osmolyte solutions over wide concentration ranges [3]. Femtosecond IR pump-probe studies on two different IR probes, OD and azide stretch modes in all five renal osmolyte solutions, have been performed. Our findings confirm that the renal osmolytes (sorbitol, trimethylglycine, taurine and myo-inositol) do modulate the hydrogen bonding network and dynamics while the denaturant (urea) does not. This has been possible by employing two different vibrational probes, i.e., OD and azide stretch modes, that not only complement each other but also directly or indirectly participate in water H-bonding networks in high osmolyte solutions. The microscopic picture obtained from both experiments and MD simulations provides clear evidence that denaturant would perturb protein structure via direct interactions with protein itself, while the protecting osmolytes do indirectly through modulating water H-bonding structure even though the magnitude and spatial extent vary depending on the osmolytes. Note that, apart from being of physicochemical and biochemical importance, these osmolytes are of biotechnological importance since they are energy-boosting ingredients or pharmaceutical excipients. We thus anticipate that studying the properties of such highly concentrated osmolyte solutions can shed light on properties of water inside living organism.

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Adiabatic Control of Vibrational Dynamics by a Tailored Femtosecond Optical Frequency Comb: Uniformity of Spectral and Temporal Modulation

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A harmonic modulation of the phase of the field of an optical frequency comb (OFC) is investigated when formed in the temporal or spectral domains. The system of electronic-vibrational states is described by seven-level Λ system having five transitional states, representing vibrational structure of the excited electronic state, one initial and one final vibrational state of the ground electronic state, Fig. (left). The harmonic modulation of the phase of the field is described by the sinusoidal function, which is introduced either in the spectral or in the temporal phase. Analytical and numerical studies of the quantum yields demonstrated uniformity of both approaches. Fig. (right) shows Rabi oscillations between the initial and the final states accomplished by a series of pulses having spectral sinusoidal modulation. Importantly, the excited state manifold is insignificantly perturbed resembling the quasi-dark state formation by the applied field. The physical problem of our interest is a controlled population transfer in ultracold molecules KRb from the Feshbach state to the fundamentally ground spin singlet state aiming at formation of ultracold molecules [1-4].

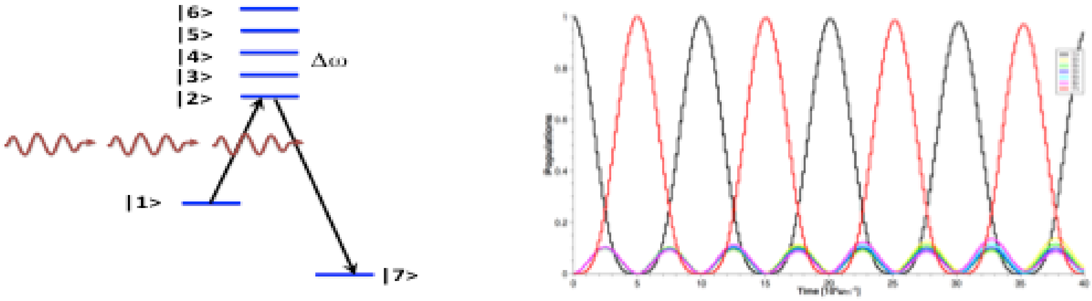

Figure: A schematic seven-level system interacting with the phase-locked pulse train, (left); Population dynamics in seven-level system induced by OFC (right).

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Concerted electronic and nuclear fluxes during adiabatic intramolecular processes

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Theory and numerical techniques for the title processes are presented and applied to three systems of increasing complexity: concerted electronic and nuclear fluxes in vibrating and dissociating H_2^+ ($^2\Sigma_g^+$, JM = 00) (as an exploding quantum bubble); rhombus-to- rhombus tunneling isomerization of B_4; and Cope rearrangement of semibullvalene by coherent tunneling. Times associated with these processes range from femtoseconds (H_2^+), over picoseconds (B_4) to kiloseconds (semibullvalene).

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The ultrafast dynamics and the geometrical change upon $S_1 \leftarrow S_0$ excitation in cyclopentanone molecule

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Spectroscopic interest in cyclic ketones [1,2,3] lies both in the relationship between the flexible structure and a selection rule on optical transitions and the triplet states, playing an important role in the photochemical properties of cyclic ketones. We have investigated the intramolecular energy transfer from vibrationally hot S_1 electronic state in cyclopentone molecule with time-resolved mass spectrometry and time-resolved photoelectron imaging [4] technique. The time domain experiments with femtosecond resolution have provided rich insights into the photophysics of cyclopentanone molecule. The molecules are populated onto the vibrationally hot $S_1(n,\pi^*)$ state by absorption of one 266-nm photon. The initial populated molecules in S_1 state undergo ultrafast internal conversion to ground state in 80 fs and intersystem crossing to triplet $T_1(n,\pi^*)$ occurring in 3.14 ps. The geometry change upon $S_1 \leftarrow S_0$ excitation and $D_0 \leftarrow S_1$ ionization has been investigated with *ab intio* calculations. It is shown that the dihedral angle between the C=O bond and the plane given by the carbonyl and the α-carbons is 180° either in S_0 or D_0 state and is reduced to 143.6 ° by out-out-plane deformation of the oxygen in S_1 state. The ionization was bridged by Rydberg intermediate states. The symmetry methylene group wagging and the symmetric skeletal ring breathing of the cation were observed in the photoelectron kinetic energy spectrum.

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Formulation of non-adiabatic molecular dynamics triggered by core ionization

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High-intensity ultrafast laser pulses in vacuum-ultraviolet (VUV) to X-ray regime generated by Free-Electron Laser offer unique opportunity to probe molecular dynamics [1], enabling real-time tracking of non-adiabatic dynamics over a wide range of potential energy surfaces (PES). Molecular decay dynamics in these experiments is distinct from what is covered by conventional molecular dynamics (MD) in that it include electronic decay processes (Auger and fluorescence) that cause transitions far beyond the typical energy scale in standard MD. We hence develop a new molecular calculation toolkit XMOLECULE [2] and a new non-adiabatic MD scheme. XMOLECULE realizes Hartree-Fock-Slater (HFS) calculation of an arbitrary molecular electronic configuration based on core-hole adapted numerical atomic orbitals provided by XATOM toolkit [3]. Based on this fast on-the-fly calculation, we propose a new non-adiabatic calculation scheme which extends the surface hopping scheme [4] by combining high-energy electronic transitions as "large hop" and lower-energy non-adiabatic transitions as "small hop" .

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Ultrafast isomerization of a BF_2-coordinated molecular switch

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Molecular photoswitches are systems that can be interconverted between two different structural conformations by light. Due to the high isomerization yields, azobenzene and its derivatives are popular photoswitches which find applications in molecular machines, biological conformational switches and sensors. Recently, azo-BF_2 compounds have been synthetized [1,2] showing strong electronic transitions in the visible range for both the *cis* and *trans* isomer forms. We investigated the isomerization dynamics of one such compound by ultrafast transient absorption spectroscopy. Besides characterizing the timescales of the reaction, we find pronounced coherent oscillations associated with vibrational wavepacket evolution. The possibility to use the wavepacket dynamics to extract information on the nuclear coordinates involved in the isomerization reaction will be discussed.

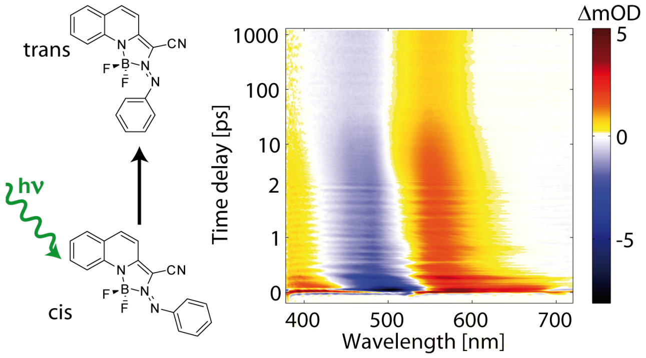

Figure: Spectrally and time-resolved transient absorption map of the photoinduced cis-to-trans isomerization process in the azo-BF_2 molecular switch shown on the left

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Ultrafast radiatonless dynamics of acetone, methyl ethyl ketone and cyclohexanone in the S_1 ($n\pi$*) and Rydberg states by femtosecond photoelectron imaging

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We have studied the photodynamics of acetone, methyl ethyl ketone and cyclohexanone using femtosecond time-resolved time-of-flight mass spectrometry and photoelectron imaging in a cold molecular beam. Excitation wavelengths were chosen in the range $320 \geq \lambda \geq 250$ nm. After S1←S0 ($n\pi$*) photoexcitation, ketones are known to show cleavage of an α- CC bond in a Norrish type-I reaction. Two possible reaction channels are discussed in the recent literature: A direct dissociation on the S1 potential energy hypersurface through a conical intersection or a dissociation on the T1 hyper- surface after intersystem crossing and passage of a transition state at the maximum of a potential energy barrier.[1] In case of methyl ethyl ketone a third channel involving a hot ground state is discussed.[2] The photoelectron spectra of acetone show a sharp band due to the S1 state. The observed progression of the C=O stretch vibration reflects the initially active vibrational mode. A fast motion of the prepared wave packet out of the Franck- Condon region presumably causes the band to decay within 100 fs. At and above excitation energies equal to the aforementioned barrier height, an additional photoelectron band of unknown origin is observed. Resonant intermediate steps in the multi-photon ionization scheme manifest themselves as a third photo- electron band that is assigned to the 3p Rydberg states. In the methyl ethyl ketone spectra, the resonant 3p and 3d Rydberg states are the dominant features and decay within 200 fs. At excitation energies sufficient to excite the 3d Rydberg state, a coupling of the 3d and 3p states can be observed. In cyclohexanone, a coupling of the 3p and 3d states and, contrary to methyl ethyl ketone, also coupling with the 3s Rydberg state can be observed. The signals of the 3d and 3p Rydberg states decay within 100 fs, whereas the 3s state is determined to be long lived on the experimental time scale.

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Femtosecond Stimulated Raman Spectroscopy with and without Actinic Excitation: Application to Azobenzene and beta-Carotene

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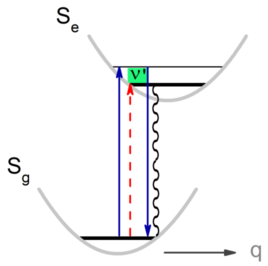
We show that femtosecond stimulated Raman (FSR) spectroscopy can record excited-state spectra even *without* a preceding actinic pump pulse, when the ps-Raman pump is resonant with the corresponding optical transition. This is illustrated with the Raman spectra of Azobenzene and beta-Carotene. Excited state (S_1, and S_2) Raman spectra are also measured conventionally, upon actinic excitation, both on the Stokes- and anti-Stokes side. The sign of the Raman signals depends on whether stimulated emission (SE) or excited state absorption (ESA) is more strongly involved in the Raman process. For Azobenzene positive lines from S_1 are detected while all recorded S_2-bands for beta-carotene are negative. The results are discussed in connection with quantum chemical calculations [1,2,3].



Vibrational modes in the excited state (S_e) can be probed from the electronic ground state (S_g), i.e. without a preceding actinic excitation.

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Time-Resolved Photofragmentation Studies in the Gas-Phase: Rotational and Vibrational Coherence of Substituted Fluorescein Ions in Different Charge States

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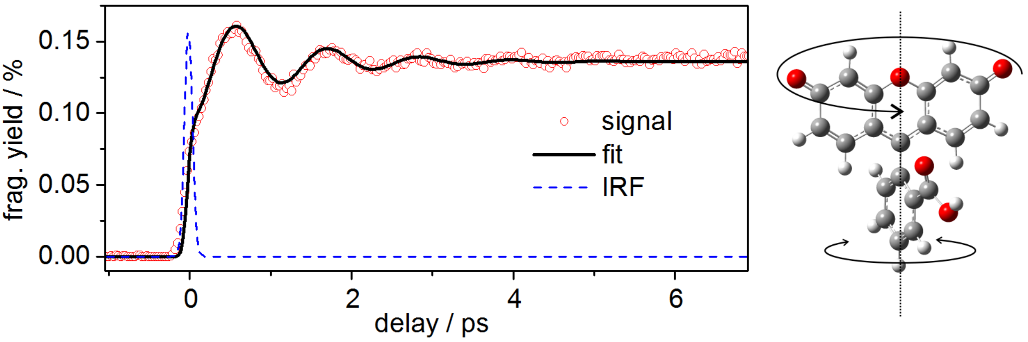
Fluorescein (**1**) and its halogenated derivatives 2′,7′-dichlorofluorescein (**2**) or 2′,7′-difluorofluorescein (**3**) are applied in biology and biochemistry as fluorescence markers, due to their exceptionally high quantum yields and ease of conjugation to biomolecules [1]. The prescence of three protic groups yields up to four pH-dependent charged states (cation, dianion, and monoanion in two tautomeric forms), which differ in their photophysical properties [2]. Time-resolved photodetachment anisotropy (TR-PA) on the fluorescein monoanion (**1**$^-$) has shown a strong dependence of the photoelectron intensity on the relative polarization between the pump and probe pulses, which is further sinusoidally modulated, revealing rotational dephasing and vibrational wavepacket dynamics [3]. We here present transient photofragmentation studies performed on isolated fluorescein ions and their derivatives in a Paul-type ion trap. We analyze the charge state and substitution dependent behavior of both rotational dephasing and vibrational coherence detected by the neutral loss of CO_2 (main fragmentation channel) after pump-probe photoexcitation. Results on the dynamics are supplemented by IR multiple-photon dissociation (IRMPD) experiments in the OH-stretching region, as a tool for structural analysis of ions in the gas-phase.



*Transient photofragmentation signal of the fluorescein monoanion (***1**$^-$*).*

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Time-resolved photoelectron spectroscopy of isolated multiply charged anions: Excited state electron tunneling detachment

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Multiply charged anions in gaseous phase exhibit several unique properties which can be investigated using time-resolved photoelectron spectroscopy. Electron loss, an important relaxation pathway in the photophysics of such systems, is crucially affected by the repulsive Coulomb potential of the remaining negative charges. Our spectroscopic results show the presence of electronically excited states which are metastably bound within this potential and decay via electron tunneling emission through the repulsive Coulomb barrier[1],[2]. Following excitation in the UV/VIS a series of triply and quadruply charged chromophore anions ($[\text{M-BDSZ}]^{3-}$ and $[\text{BDSZ}]^{4-}$: BDSZ = bisdisulizole, M = H, Li, Na, K, Cs) undergo very efficient electron tunneling loss via low lying singlet states. By exchanging the counter ion in our mass selected anions we were able to stepwise tune the dynamics of the excited state tunneling process on a picosecond timescale. We also investigated binuclear platinum H_2PtPOP^{2-} (PtPOP = $[Pt_2(P_2O_5H_2)_4]^{4-}$) complexes, a system which was extensively studied in condensed phase [3] and is known for very efficient intersystem crossing. In our gas phase experiments we found fast ISC competing with delayed electron detachment presumably originating from excited state tunneling out of the initially populated singlet as well as a lower lying triplet state. Timescales and energetics of these processes change significantly when metal cations (K,Ag) are added to the PtPOP complex. Excited state electron tunneling can provide important insight into the energy dissipation pathways in multiply charged anions as a function of the controllable exact molecular composition.

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Small Molecular Systems in High-Intensity X-ray Pulses

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Free-Electron Lasers, such as the FLASH or LCLS, enable completely new experiments in the XUV to hard X-ray spectral range by providing extremely short light pulses with very high peak intensities. These unique properties allow studying (time-resolved) multi-photon absorption in atomic and molecular systems in the gas phase. Using high-Z constituents (e.g. selenium or iodine) as markers to create localized centers of absorption in small to medium-sized molecular systems, we have studied X-ray multi-photon ionization and charge transfer processes using many-ion coincidence spectroscopy. Studies in the soft and hard X-ray regime revealed charge redistribution within the molecular environment, and nuclear motion outrunning sub 10fs FEL pulses [1,2], while recent results on multi-photon ionization using the CXI nano-focus station revealed extremely ionized molecular systems with only a few electrons remaining. Deploying femtosecond optical lasers to control the initial geometry of the molecule, we measured charge transfer from the X-ray absorbing high-Z constituent towards the environment as a function of internuclear separation [3]. This technique can be applied to study charge transfer in a variety of (larger) systems.

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Calculation of resonance Raman intensities including Franck-Condon and Herzberg-Teller effects

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Vibrational resonance Raman (RR) spectroscopy is a useful tool to provide information on structures and properties of molecular excited states [1]. Therefore, an accurate simulation of absorption and RR spectra, by quantum chemistry methods, can help in the interpretation of experimental data as well as in the design of new compounds for specific applications e.g. in dye-sensitized solar cells or as photocatalysts [2-4]. In this contribution, the effects of Franck-Condon (FC) and Herzberg-Teller (HT) vibronic couplings are investigated on the prototype molecule of Rhodamine 6G [5,6]. First, the sum-over-state expressions for the RR polarizability are derived assuming displaced harmonic potential energy surfaces between the ground state and the excited states. Then, time dependent density functional theory is employed to calculate the derivatives of the excitation energies and of the transition dipole moments with respect to the normal modes of vibration. These quantities are required for the calculation of the RR intensities. Finally, the effects of the FC and HT contributions on the RR spectrum and on the RR excitations profiles of Rhodamine 6G are discussed.

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Time-resolved spectroscopic study of fragment fluorescence in methane/air mixtures using picosecond photodissociation

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The possibility to measure concentrations of atmospheric trace species is of vital importance for understanding atmospheric chemistry and the evolution of global warming. Methane (CH4) is the most abundant hydrocarbon on earth and it is an important greenhouse gas. Hence, it is important to both measure and understand the methane atmospheric and combustion chemistry. Previously, the photodissociation of methane has been studied using weak nanosecond pulses in the UV regime, but also using extremely intense femtosecond laser pulses. It has been found that the dissociation processes are completely different in these two cases; photolysis with a weak light source implies single-photon excitation to low-lying repulsive electronic states, which results in breakage of typically only one or two molecular bonds. Photolysis using ultra-intense light sources, such as femtosecond laser pulses, on the other hand, results in multi-photon excitation to high-lying dissociative states, which causes breakage of multiple bonds and creation of a multitude of photofragments. Photodissociation of methane using picosecond laser pulses, i.e., photolysis with a light source of intermediate intensity, has, to the best of our knowledge, not been investigated previously. In the present work, 80-picosecond laser pulses of 266-nm wavelength with an intensity of $1.9 \cdot 10^{11}$ W/cm^2 were used for fragmentation of methane/air gas mixtures at ambient pressure and temperature. Emission spectra are, for the first time, studied with ultrahigh temporal resolution using a streak camera. Fluorescence spectra from CH(A-X, B-X, C-X), CN(B-X,$\Delta \mathrm{v} = 0, \pm 1$), NH(A-X), OH(A-X) and N_2^+(B-X) were recorded and analyzed, see Figure 1. By fitting simulated spectra to high-resolution experimental spectra, rotational and vibrational temperatures are estimated, showing that CH(C), CN(B), NH(A), and OH(A) are formed in highly excited vibrational and rotational states. The fluorescence signal dependencies on laser-intensity and CH_4/air equivalence ratio were investigated as well as fluorescence lifetimes. These studies suggest that CH(A,B,C) might be formed through neutral dissociation via a super-excited state of CH_4, reached by 3-photon excitation, and that 2-photon ionization/dissociation, rather than collisional quenching, dominates the deactivation of these fragments. All fragments observed are formed within 200 ps after the arrival of the laser pulse. The CN(B-X) $\Delta v = 0$ fluorescence was studied temporally resolved under high spectral resolution and it was found that the vibrational levels are not populated simultaneously, but with a rate that decreases with increasing vibrational quantum number. This observation indicates that the rate of the chemical reaction that forms the CN(B) fragments is decreasing with increasing vibrational state of the product.

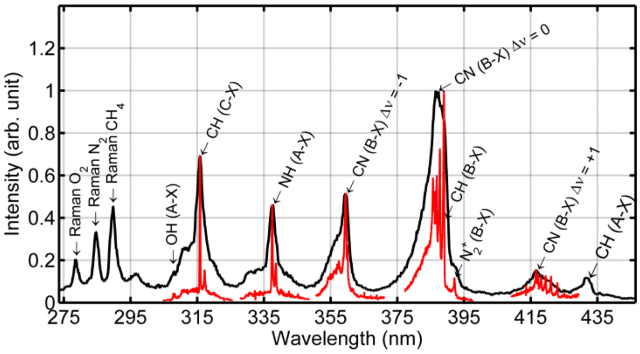

Figure 1: Low-resolution emission spectrum (black) induced by intense 80-picosecond laser pulses. The red spectra were recorded with a high-resolution grating in the spectrograph.

Assessing the Driving Force for the Ultrafast ISC in 2-NF

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The observation of ultrafast intersystem crossing (ISC) of a range of nitrated polycyclic aromatic hydrocarbons (NPAHs) has raised the question of what drives the formally spin-forbidden process to proceed on an ultrafast timescale. We suspect that the ultrafast timescale restricts the dynamics to be non-ergodic and only involve a few vibrational degrees of freedom, as previously demonstrated in ultrafast spin-allowed IC [1]. Previous investigations have pointed to the importance of a twisting motion of the nitro moiety, either as the direct mechanism driving the ISC [2] or controlling the branching into photo degradation versus triplet formation [3]. In addition to the intriguing mechanism underlying the ISC, the photochemistry of NPAHs has historically attracted interest as the group of NPAHs generally are considered atmospheric pollutants with carcinogenic and mutagenic properties. In this investigation we have performed UV pump, IR probe femto-second transient absorption spectroscopy on 2-Nitrofluorene (2-NF) in deuterated acetonitrile. 2-NF has previously been observed to exhibit ISC on a femto-second timescale [4]. We have assessed the possible twisting of the nitro group out of the aromatic plane by the rotational anisotropy measurements and compared experimental values to calculated rotational anisotropies at specific vibrational frequencies. The transient absorption spectra at magic angle have also been measured (Figure 1 left) and the interpretation is guided by DFT calculations at the (TD)-PBE0/IEFPCM/6-311+G(d,p) level of theory. This includes ground and excited state optimizations as well as relaxed potential energy scans (PES') along the key coordinates. We observe a mono-exponential behaviour in the rotational anisotropy experiments on a time scale that corresponds to tumbling of the entire molecule in solution. This observation is backed by a very flat nitro group rotation PES and the initial dynamics do not appear to be directed by this coordinate. Rather, the C-N stretch, symmetric N-O stretch and O-N-O scissoring appear to be key in the initial dynamics leading to ISC and IC back to the ground state (Figure 1 right), consistent with recent computational investigations on nitrobenzene in the gasphase [5], where a similar mechanism may be at play.

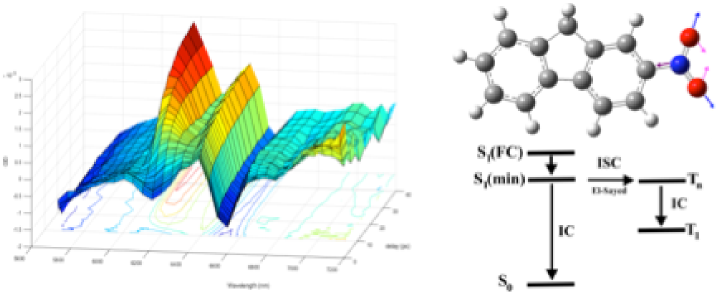

Figure 1 (left): Experimental spectrum at magic angle showing bleaches (blue) as well as induced absorptions (red) and (right) an illustration of the key coordinates above a schematic representation of the observed dynamics.

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Controlled molecules to investigate ultrafast chemical dynamics directly in the molecular frame

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A molecule's chemical behavior is governed by its electronic and nuclear properties. Imaging the temporal evolution of the valence electrons and the positions of the atoms during a chemical reaction provides direct insight into fundamental chemical processes. State-selected, strongly aligned and oriented molecular ensembles serve as ideal samples to study ultrafast chemical dynamics in the molecular frame [1]. Such dynamics can be extracted via the investigation of molecular-frame photoelectron angular distributions [2]. We have developed techniques to manipulate the motion of molecules in cold supersonic beams using strong inhomogeneous electric and laser fields [3]. The state-selected molecules are aligned or oriented with a DC field in conjunction with strong laser pulses (duration tunable between 50 fs and 500 ps). This allows for non-adiabatic as well as adiabatic alignment. Here, we will present our work on the alignment and orientation of carbonyl sulphide (OCS). We have created coherent superposition of pendular states in the strong field of the alignment laser that resulted in pendular motion [4]. Furthermore strong laser-field- free orientation of absolute-ground-state OCS was achieved [5]. In addition, we present our progress controlling the rotational degrees of freedom of molecules with CW laser fields. This requires CW laser powers on the order of a TW in a focal waist of 25 μm. We demonstrate that such high powers can be achieved at moderate pump power levels inside a laser cavity.

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Controlling the motion of large molecules and particles

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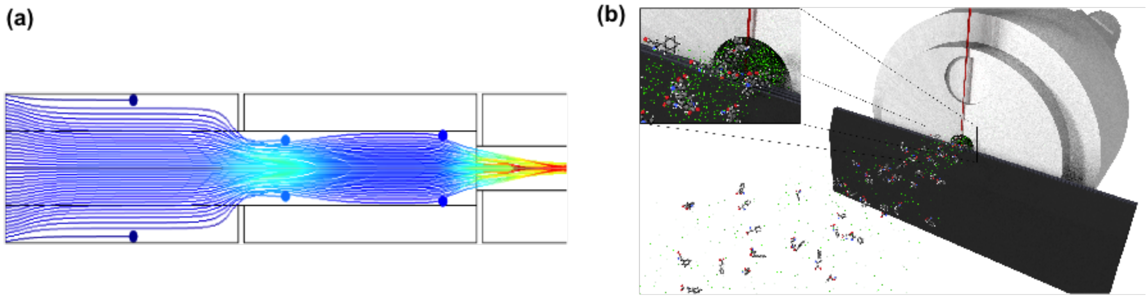
Recent years saw the development of several techniques to control small neutral molecules. We can now routinely select individual structural isomers, create beams of size-selected clusters, and disperse molecules according to their rotational quantum states, generating colder molecular ensembles and in certain cases even single-quantum-state samples. Here, we report on our efforts to extend these techniques to much larger molecules, nanoparticles and biological systems. We are developing new beam sources for these large systems based on soft vaporization techniques (aerodynamic lenses, laser desorption, acoustic desorption, etc.) to provide high molecular fluxes over long measurement times (> 12 h), as required in typical FEL based imaging experiments. These will, furthermore, be coupled to efficient cooling schemes (supersonic expansions, buffer-gas cells) to provide internally cold molecules for further manipulation using static or dynamic electric fields. These will include the separation of structural isomers using Stark separation, alignment and orientation using laser-based strong-field techniques, as well as spatial control of particles using shaped laser beams. This will allow improved guiding of nanoparticles, for instance, into the focus of an FEL beam, thus increasing hit-rates significantly. This would be a major step towards single-particle diffractive imaging with atomic resolution.



(a) Trajectory simulation of nanoparticle focusing in an aerodynamic lens system. (b) Production of volatile molecules using laser desorption

Resolving the dynamics of valence-shell electrons and nuclei through laser-induced diffraction and holography

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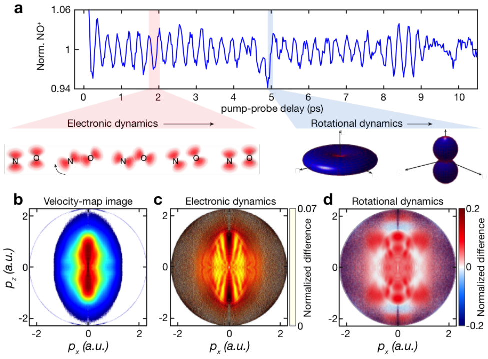
We have studied a coupled electronic-nuclear wave packet in nitric oxide using time-resolved strong-field photoelectron holography and rescattering. We show that the electronic dynamics mainly appears in the holographic structures whereas nuclear motion strongly modulates the angular distribution of the rescattered photoelectrons. We use impulsive stimulated Raman scattering (ISRS) to prepare a coupled electronic and rotational wave packet in the neutral NO molecule. The wave packet is probed by strong-field ionization and the photoions and photoelectrons are detected by a velocity-map-imaging spectrometer. An overview of the experimental results is given in the Figure.



Resolving electronic and nuclear dynamics through holography and rescattering. (a) Time-dependent normalized NO+ signal and illustration of the prepared electronic and rotational dynamics, (b) photoelectron momentum distribution of excited NO molecules recorded at a delay of 1.56 ps, (c) normalized difference of momentum distributions at maxima and minima of the NO+ signal dominated by electronic dynamics (1.55 and 1.72 ps, respectively), (d) normalized difference of momentum distributions at maxima and minima of the NO+ signal dominated by rotational dynamics (4.92 and 1.50 ps, respectively).

Developing ultrafast low-energy electron diffraction

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Time-resolved high energy electron diffraction experiments provide access to ultrafast structural dynamics in bulk media [1]. Applying this technique to quasi-two-dimensional systems such as ultrathin films and surfaces remains challenging, due to limitations from low scattering cross-sections of energetic electrons.

Here, we present the development of ultrafast low-energy electron diffraction (ULEED) employing few-picosecond low-energy electron pulses in a laser-pump/electron-probe scheme. Well-collimated electron pulses are extracted from a laser-driven tungsten needle emitter, allowing for the measurement of high-quality diffraction patterns.

In a first application, we study the structural dynamics of an ordered polymer adsorbate on free-standing graphene by ULEED in transmission [2]. We give a detailed account of the characteristic time scales of the superstructure dynamics, including the energy transfer from the graphene to the adsorbate layer, the loss crystalline order in the polymer, and the formation of amorphous components at extended spatial frequencies.

Realizing ULEED in a backscattering geometry, we demonstrate first results obtained with a new miniaturized laser-driven electron source. At low electron energies around 100 eV, we observe the nearly commensurate charge density wave (CDW) at the 1T-TaS_2 surface, as well as the optically-driven transition to the incommensurate phase [3]. The study demonstrates the capability of ULEED to access complex electronic and structural dynamics at surfaces.

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Spatial and Temporal Resolution Studies on a Highly Compact Ultrafast Electron Diffractometer

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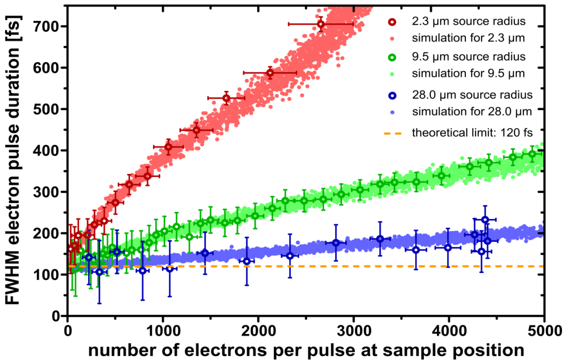
Time-resolved diffraction with femtosecond electron pulses has become a promising technique to directly provide insights into photo induced primary dynamics at the atomic level in molecules and solids. Ultrashort pulse duration as well as extensive spatial coherence are desired, however, space charge effects complicate the bunching of multiple electrons in a single pulse. We experimentally investigate the interplay between spatial and temporal aspects of resolution limits in ultrafast electron diffraction (UED) on our highly compact transmission electron diffractometer [1]. To that end, the initial source size and charge density of electron bunches are systematically manipulated and the resulting bunch properties at the sample position are fully characterized in terms of lateral coherence, temporal width and diffracted intensity. We obtain electron pulse durations down to 120 fs (see figure) and transversal coherence lengths up to 20 nm. The performance of our compact UED setup at selected electron pulse conditions is finally demonstrated in a time-resolved study of lattice heating in multilayer graphene after optical excitation.



Measured (circles) and simulated (transparent point clouds) electron pulse durations as a function of the number of electrons per pulse for each of the three studied source sizes (1/e^2-radii: 2.3 μm red, 9.5 μm green and 28.0 μm blue).

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Vibrationally resolved geminate recombination of solid state triiodide using ultrafast electron diffraction

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Triiodide is a model system suited for studying dissociation and recombination processes in chemistry. We use ultrafast electron diffraction to probe the structural changes in the partially reversible geminate recombination of triiodide initiated by 400 nm optical pump pulses in thin crystalline samples of tetra-*n*-butylammonium triiodide (TBAT). We observed a large-amplitude librational mode (~ 18 $\mathrm{cm^{-1}}$) that resembles the behavior of rotationally hot photoproducts in the reorientational relaxation following triiodide dissociation in EtOH [1]. By exploring dynamics on different time scales using electron bunches with different charges, we are able to further resolve the high frequency vibrations (> 100 $\mathrm{cm^{-1}}$) that modulate the librational amplitude. These oscillations come from recombination dynamics that trail the fast dissociation occurring within 100 fs. The frequencies that we can extract from these time-resolved measurements match well with those recorded in static Raman and IR spectroscopic studies [2]. The diffraction method also allows us to distinguish the dynamics from two crystallographically distinct types of triiodide chains (straight and bent) due to their differing mode frequencies, therefore complementing the spectrally-resolved optical pump-probe study such as ref 3.

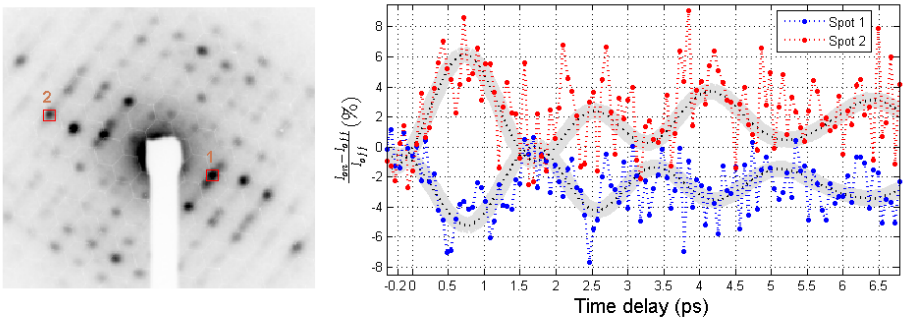

Figure 1: (a) Static electron diffraction pattern of the triiodide sample with the locations of the analyzed spot areas labelled. (b) Time-resolved relative changes of the integrated spot areas of (a). The data were collected with 60 fs time steps and probe electron pulses of 0.67 fC. Wavelet decomposition coefficients (plotted in black and grey) underlying the time-series data represent the low frequency librational mode.

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Time-resolved photoelectron spectroscopy of alkyl vinyl ethers

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Ethylene is the smallest organic molecule containing a π bond. Upon photoexcitation, it experiences a torsion of C=C bond, and either pyramidalization of the CH_2 plane or H migration from one carbon atom to another before returning back to the ground state [1]. When excited to 3πs- Rydberg state at 200 nm, the molecule returns to the ground state within 80 fs [2]. In this contribution, we address the question of how addition of methoxy group modifies these dynamics. Earlier studies of methyl vinyl ether revealed that photo excitation to the lowest lying $\pi\pi^*$ -state (200-175 nm) led to vinoxy (CH_2=CHO) formation with high quantum yield [3]; however, it remained unclear whether its generation occurred on the ground state or the excited state potential energy surface. Here, we investigated a series of different alky vinyl ethers to decipher the possible dissociation channels upon photoexcitation to the 3πs- Rydberg state at 200 nm using time-resolved photoelectron spectroscopy and *ab initio* calculations. Our experimental results indicated two very fast relaxation channels on the order of 20 and 70 fs, respectively, independent of the length of the alkyl chain. In agreement, ab initio calculations revealed two different reaction channels both having ~50% quantum yield. One channel proceeds through the $\pi\pi^*$ -state back to the ground via torsion of the C=C double bond, in accordance to the ethylene dynamics. The other channel leads to direct dissociation of the C=O bond on the $\pi\sigma^*$ -state, forming the vinoxy and alkyl radicals. The latter reaction proceeds over a small energy barrier and takes place within 20 fs if enough vibrational energy is stored in the C-O dissociation mode. Otherwise, the molecule is forced to take the slower relaxation pathway via the $\pi\pi^*$-state.

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Ab Initio Recovery of Transient Structures with Femtosecond Electron Diffraction and Charge Flipping

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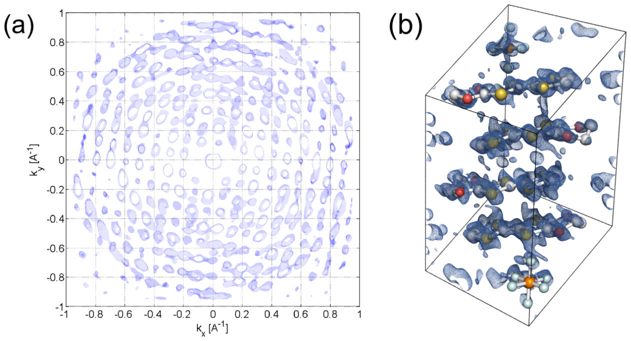
Determining short-lived molecular structures from time-resolved diffraction data remains a challenging problem in crystallography. Current methods start with a linear model based on known steady-state structures and involve careful refinement against diffraction from a single Bragg plane [1]. Here, we present preliminary work that eliminates the need for such a starting guess structure: femtosecond electron diffraction (FED) data of single crystal $(\text{EDO-TTF})_2\text{PF}_6$ is collected with ~300 fs time resolution over a select range of crystal tilt. Atomic positions of the initial and final states are resolved *ab initio* using the Charge Flipping (CF) numerical method [2]. Experiments are on-going to do the same for the transient intermediate state that occurs at t = 3–10 ps [3].



3D isosurface plot of a) measured electron diffraction intensities in reciprocal space and b) electrostatic potential of (EDO -TTF)$_2$PF$_6$ initial state resolved by FED and CF.

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Optical fiber-based free electron source

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Ultrafast electron diffraction (UED) is a highly successful technique for structural dynamics investigations of phase transitions, electron-phonon coupling and chemical reactions on sub-picosecond timescales [1,2,3]. Back-illuminated thin metal film photocathodes are currently the most commonly employed electron sources here due to their robustness, ultrafast temporal response, and compatibility with both high electric fields and large photo-excitation damage thresholds. Extending the technique to tracking ultrafast structural changes within systems with large unit cell sizes of up to tens of nanometers requires reduction of the source emittance while maximizing brightness. These requirements can be met by reducing the electron source size and shaping the emission profile to a uniform, rather than Gaussian distribution. The conventional approach of focusing the UV laser onto a large area planar photocathode subject to the spatial constraints of high voltage electrodes make these requirements difficult to achieve. Following our recent work [4], we present here for the first time ultrafast photoemission results from an optical fiber-based electron source. This new concept is meant to ease alignment difficulties between the emitter metal and the optical trigger as well as the control of the laser spot size and profile. The optical fiber features a standard fiber connector at the air-side end and the vacuum end is polished and coated with a 30nm gold (Au) layer deposited on top of 3nm of chromium (Cr). The size of the emitting area, given by the core size of the fiber, is 50 micrometers in this proof of principle experiment, and the triggering is done with 265nm laser wavelength. We discuss details of the emission quality of our fiber devices and strategies for improving the emittance through use of single mode and tapered fiber structures.

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Towards Femtosecond Electron Diffraction of Proteins

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To study protein dynamics in real-time with atomic resolution is one of the dream experiments in biophysics. Up to now experimental tools with full atomic and ultrafast time resolution combined are lacking, yet are becoming available. Femtosecond electron diffraction (FED) is a promising tabletop technique with complementary features to XFEL measurements [1]. It combines the high spatial resolution of diffraction methods with the high temporal resolution of femtosecond optical spectroscopy. The current electron brightness and time resolution enabled first studies of structural dynamics with atomic resolution on a timescale of few hundred femtoseconds [2] and even gave insight into the structural dynamics during a chemical reaction [3]. One major challenge remaining for the application of FED to study protein dynamics is sufficient sample preparation. Samples to be used for a diffraction study with electrons as probe need to be single-crystalline, reversible and match a size of about 100-150 nm thickness combined with a lateral size on the order of 100 μm x 100 μm. Further, they need to withstand vacuum conditions. The presented work will outline and discuss current approaches for sample development on the model system Bacteriorhodopsin and give an overview on the femtosecond electron diffraction method including the limitations for samples. First diffraction tests on the model system Bacteriorhodopsin are reported in comparison to the latest results from the study of a spin-crossover material [4] to demonstrate the intrinsic capabilities of FED.

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Diffractive imaging of controlled molecules with x-rays and electrons

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The aim of this work is to investigate the structure and intrinsic dynamics of molecules in the gas-phase by diffraction using either x-rays or electrons. The gas-phase molecules are prepared in cold, supersonic beams and can be size, isomer, and quantum-state selected by means of electric deflection [1]. These samples can be strongly aligned by intense laser pulses. Controlling the molecules' state, structure, and spatial orientation increases the amount of information that can be gained from diffraction patterns. For instance, the recorded data will be available directly in the molecular frame, which allows for 3D reconstruction of the molecular structure by holographic or tomographic approaches. [1,2,3] We report on a recent x-ray diffraction experiment in which 130 pm radiation (photon energy 9.5 keV) was diffracted off an ensemble of aligned gas-phase 2,5-diiodothiophene molecules in order to study the molecular structure with atomic resolution. The two iodine atoms of the molecule contribute to the scattering signal the most [4], which leads to a diffraction pattern dominated by two-point interference. We provide an overview on how our experimental approach could be utilized to study dissociation dynamics of molecules by holographic reconstruction to recover atomic locations [3]. For electron diffraction experiments a DC electron gun was developed, which can produce millions of electrons per 100 ps pulse and uses an electro-static lens for focusing to ~100 μm (rms). Benchmark electron diffraction data from solid-state and simple gas-phase samples as well as measurements exploiting an implemented velocity-map-imaging spectrometer allow for characterization of the electron beam. We present the setup combining the electron gun with an existing controlled-molecules apparatus [5].

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Two-Color Strong-Field Photoelectron Spectroscopy and the Phase of the Phase

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Coherent superposition of fundamental 800 nm (ω) laser field with its second-harmonic (2ω) generates laser pulses with asymmetrical electric field distribution. Controlling a time-lag between $\omega/2\omega$ fields with sub-fs precision makes the electron trajectory tagging possible. Here, we propose two-color 'phase-of-the-phase spectroscopy' which applied to rare gas atoms and CO_2 provides relative-phase-tagged photoelectron spectra. We show that a relative phase contrast (RPC) and 'phase-of-the-phase' (PoP) obtained from Fourier transformed photoelectron spectra provides more information than conventional photoelectron spectroscopy. Simple model based on electron trajectories, wavepacket spreading and multiple rescattering shows universality of the rescattering process. Detailed inspection of PoP and RPC spectra reveals target sensitive features they can be used to extract structural or even dynamical information with high accuracy.

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Accumulative Polarimetry and Circular Dichroism Spectroscopy of Chiral Femtochemistry

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Steady-state circular dichroism (CD) or optical activity (OA) are common techniques to analyze chiral samples. However, the utilized long optical path lengths, high concentrations, and long integration times are not suitable for ultrafast spectroscopy. Hence, only few chirality-sensitive spectroscopic approaches in the liquid phase are known in the literature [1]. In this presentation we introduce our recently developed spectrometers for CD and OA detection. In the case of OA probing, a sensitive polarimeter was developed via the combination of common-path optical heterodyne interferometry and accumulative femtosecond spectroscopy [2]. With this setup it is possible to detect the optical rotation change accompanying a chirality-modifying photochemical reaction with femtosecond time resolution [2]. Furthermore, one can achieve all-optical discrimination between racemic and achiral molecular solutions [3]. The second chirality-sensitive detection method we have developed is based on the detection of photoinduced changes of CD signals. Due to the small changes in CD which must be detected, this type of spectroscopy is prone to artifacts. Hence, typically only single-wavelength detection is employed [1]. Here, we present broadband time-resolved CD spectroscopy which is based on a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse. Hence, by passing a broadband probe pulse through this setup we can switch between opposite handedness on a shot-to-shot basis to detect pump-induced CD changes. To demonstrate the capabilities of this approach we investigated the early photochemistry of hemoglobin. By virtue of the flexibility of the setup not only ultrafast pump—probe CD experiments are possible but also ellipsometry or anisotropy spectroscopy can be performed.

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Coherent Control of Photofragment Distributions Using Laser Phase Modulation in the Weak-Field Limit

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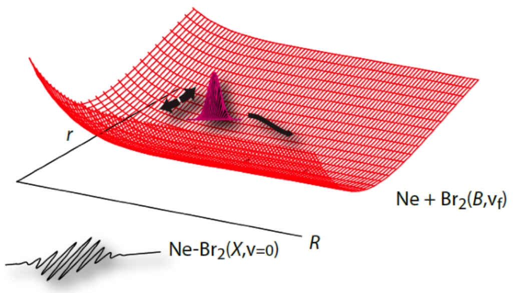
Recently, the possibility of quantum interference control of photochemical reactions in the weak-field limit has been discussed [1-3]. To that end, we demonstrate quantum interference control of the final state distributions of photodissociation fragments by means of pure phase modulation of the pump laser pulse in the weak-field regime [4]. We consider realistic wave packet calculations of the transient vibrational populations of the $Br_2(B,v_f)$ fragment produced upon predissociation of the Ne-$Br_2(B)$ complex, which is excited to a superposition of overlapping resonance states using pulses with different phase modulation. Transient phase effects on the fragment populations are found to persist for long times (more than 50 ps) after the pulse is over.



Schematic picture showing the vibrational predissociation of the van der Waals complex.

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Enantiomeric Excess determination of Chiral Molecules from Multiphoton Ionization with Femtosecond Laser Pulses

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Photoelectron Circular Dichroism (PECD) shows asymmetries in the electron emission from chiral enantiomers relative to the light propagation direction and was so far investigated using synchrotron radiation [1]. The magnitude of PECD is several orders larger than typically chirooptical asymmetries. We have demonstrated that PECD on randomly oriented chiral enantiomers is accessible via a 2+1 REMPI (Resonance Enhanced Multi-Photon Ionization) using femtosecond laser pulses. We detected highly structured asymmetries in the +/- 10% regime [2]. In this contribution we present our recent findings on the bicyclic Ketones Camphor, Norcamphor and Fenchone [3]. From the results on variation of the laser intensity, we conclude an underlying dissociative ionization. A quantification of different enantiomeric mixtures reveals the sensitivity of the PECD to the enantiomeric excess. The enantiomeric excess in mixtures of R- and S-Fenchone can be distinguished in the 1% regime.

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Two-photon double ionization of noble gases: First application of the intense HHG beamline at Lund Laser Center

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Nonlinear ionization using high-energy photons is very interesting as a tool for probing electron correlation and dynamics of highly excited systems. It allows, within a XUV-pump XUV-probe approach, to observe ultrafast dynamics intrinsic to the target system. So far such experiments have been limited to free electron lasers [1]. But in the last years intense high harmonic generation (HHG) sources reaching sufficient pulse energies have been developed at Forth [2], RIKEN [3] and recently at the Lund Laser Centre [4]. These are uniquely suited to extend the studies of multiple ionization/excitation dynamics using XUV light on the few to sub-femtosecond timescale. We present first results on two-photon double ionization of neon using the full harmonic spectrum from generation in argon (20 eV to 45 eV). To achieve the high flux needed, we generate in a loose focusing regime that allows to use up to 80 mJ energy from a 10 Hz Titanium:Sapphire laser. We measure the generated XUV energy and the XUV focal spot size, which gives us an estimation of the intensity in the gas jet target. We detect Ne^{2+} and show that the yield is quadratically dependent on the intensity of the XUV pulses [5]. The observation of two-photon double ionization indicates that the beamline provides a sufficiently high XUV flux to proceed to pump-probe experiments. We are currently implementing a split mirror composed of two silica plates mounted on nm-precision piezo actuators. The split mirror setup has been tested using an IR laser, is currently being installed in the beamline in order to perform XUV-pump XUV-probe experiments.

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Control of the ultrafast dissociation dynamics of dicationic nitrogen molecules by femtosecond IR pulses

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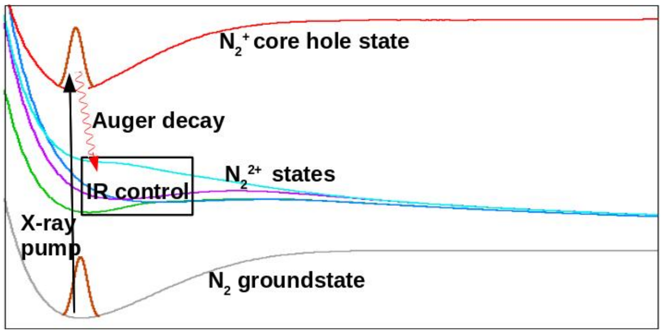
We theoretically investigate how short infrared pulses can control the dynamics of singlet dicationic nitrogen molecules that have undergone Auger decay. These molecules can either quickly fragment or remain trapped in metastable states. By varying the time delay between the x-ray pump and the infrared probe pulses, we find that molecular fragmentation can either be suppressed or enhanced. Few femtosecond IR pulses after the Auger decay can stabilize the dicationic molecules against fragmentation.



Schematic IR control after Auger decay.

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Laser control of exciton localization in perturbed molecular aggregates

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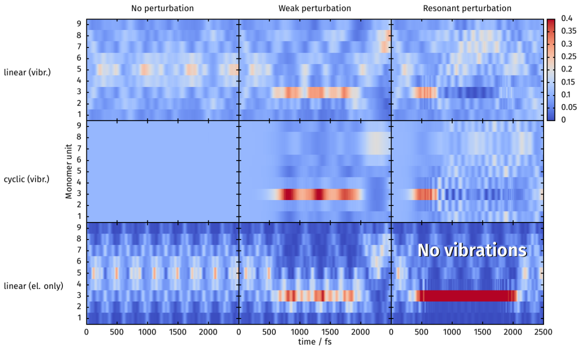
A site specific perturbation of a photo-excited molecular aggregate can lead to a localization of the excitonic energy on the site where the perturbation acts.[1] We investigate such localization dynamics in linear and cyclic aggregates. Vibronic eigenstates or wave packets in the excited state manifold can be prepared by using different excitation pulses. This selective excitation has a significant influence on the localization of excitons. We acknowledge financial support by the DFG within the GRK1221 and FOR1809



Localization effects in perturbed nonamer.

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Two-dimensional spectroscopy of coupled electron-nuclear motion

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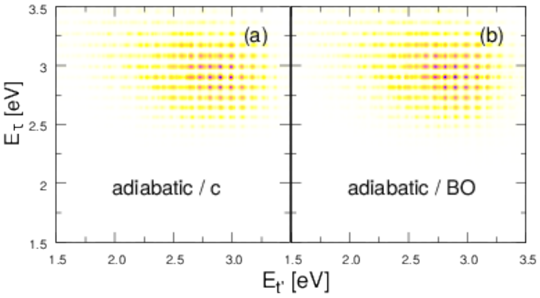
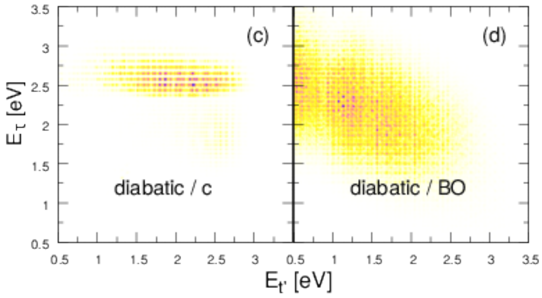
We theoretically investigate the photon-echo spectroscopy for a model [1] which involves the coupled (c) quantum dynamics of an electron and a nucleus. This model serves to illustrate the limiting cases of an adiabatic and a diabatic motion [2]. In the first case, an interpretation of the two-dimensional (2D) spectra using the Born-Oppenheimer (BO) approximation is feasable. It is then possible to identify pure vibrational coherences in fixed electronic states. For the case of strong non-adiabatic coupling, i.e., a diabatic motion, the 2D-spectra reveal a complicated structure which is related to the breakdown of the BO-approximation. The spectra are then dominated by vibronic coherences. Financial support by the DFG within the FOR 1809 is acknowledged. This project was supported by the COST-action CM1204.





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Extended quantum jump description of vibronic two-dimensional spectroscopy

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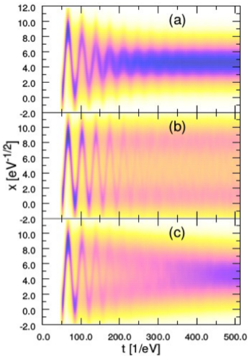
We calculate two-dimensional (2D) vibronic spectra for a model system involving two electronic molecular states. The influence of a bath is simulated using a quantum-jump approach. We use a method which includes an explicit treatment of dephasing [1]. In this way it is possible to characterize the influence of dissipation and dephasing on the 2D-spectra, using a wavefunction based method. The latter scales with the number of stochastic runs and the number of system eigenstates included in the expansion of the wave packets to be propagated with the stochastic method and provides an efficient method for the calculation of the 2D-spectra. Financial support by the DFG within the FOR 1809 is acknowledged.



Averaged probability distribution of the excited state wave packet. (a) relaxation; (b) dephasing; (c) relaxation and dephasing.

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Laser-induced magnetization dynamics probed by Lorentz microscopy

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Lorentz microscopy is a widely applied technique for the nanoscale mapping of magnetization structures [1]. Its adaptation to time-resolved in-situ imaging offers fascinating prospects for studying ultrafast magnetization dynamics [2,3]. In this contribution, we present the recent development of ultrafast transmission electron microscopy (UTEM) in Göttingen, together with first applications of laser-induced magnetization dynamics. First, we employ Lorentz microscopy with in-situ femtosecond optical excitation of iron thin films. We demonstrate that single femtosecond pulses induce a dense network of magnetic vortices and antivortices (cf. Fig. 1). Second, we combine Lorentz microscopy with UTEM in a laser-pump/electron probe scheme [4]. Figure 1 shows a first Lorentz image of permalloy nanoislands recorded with femtosecond electron pulses.

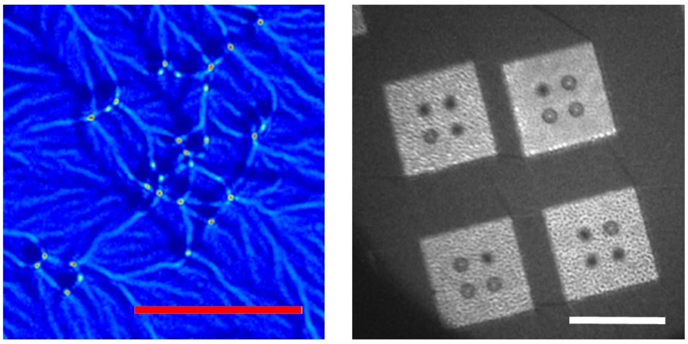

Fig. 1: (left) Lorentz image of a laser induced magnetic vortex antivortex network. (right) Lorentz image of a nano-patterned permalloy thin film acquired with sub-picosecond electron pulses. Vortices within the nanostructure are visible with high contrast. Scale bars: 3 μm.

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Observation of molecular to metallic transition between $Au_{102}(pMBA)_{44}$ and $Au_{144}(SC_2H_4Ph)_{60}$ nanoclusters by using ultrafast mid-IR transient absorption spectroscopy

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Ultrafast electronic relaxation and vibrational cooling dynamics of highly monodisperse samples of $Au_{102}(p\mathrm{MBA})_{44}$ (*p*MBA = *para*mercaptobenzoic acid) and $Au_{144}(SC_2H_4Ph)_{60}$ nanoclusters were studied by using femtosecond transient mid-IR spectroscopy.[1,2] In this study visible or NIR pump pulses were used to electronically excite the sample and a mid-IR pulse was used to probe the system dynamics by monitoring transient absorption of vibrational modes of the ligands. This kind of relaxation dynamics studies can be used to determine the molecular or metallic behavior of gold nanoclusters since the relaxation dynamics is highly sensitive to the existence of an electronic energy gap in the cluster. Drastically different electronic energy relaxation dynamics is observed for Au_{102} and Au_{144} clusters. By combining the transient absorption results with DFT calculations relaxation dynamics similar to molecular systems can be assigned to Au_{102} while Au_{144} shows behavior typical to metallic clusters [1,2]. These results clearly indicate that molecular to metallic behavior transition occurs between these two cluster sizes, and that the transition region can be further narrowed by studying other cluster sizes.

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2D Spectroscopy of CdSe Quantum Dots

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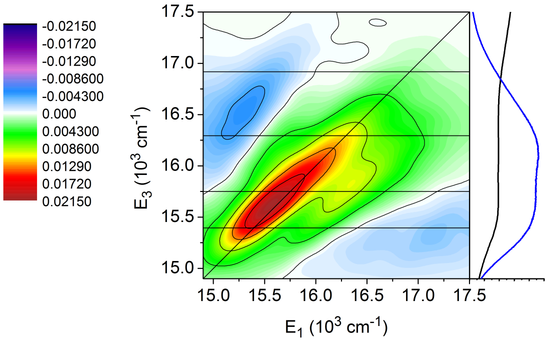
Quantum dots are semiconductor nanocrystals whose size leads to quantum confinement of charge carriers, manifesting as optoelectronic properties such as a size-tunable band gap, quantized energy levels and multiple exciton generation under the right conditions [1]. If quantum dots are to be used as efficient light harvesters in solar cells, these properties have to be understood. We perform 2D electronic spectroscopy of colloidal CdSe quantum dots by at room temperature and at 77 K. The results reveal a rich electronic structure with a number of cross peaks showing the connections between the levels. Absorption bleach is the major contribution for the lowest excitonic transition (see figure). However, the diagonal and cross peaks are also carrying signatures of biexcitonic shift for various combinations of excitonic states, which would be inaccessible in a transient absorption experiment. This enables us to carry out a detailed analysis of the excitonic shifts and their time evolution. By the analysis we gain important information about coupling between various excitonic states, which is essential knowledge to track the energy flow in the excitonic states after light absorption.



Main plot: Rephasing 2D spectrum of 7 nm CdSe QDs at room temperature at 100 fs population time. Horizontal lines mark excitonic levels. Right: Laser (blue) and absorption (black) spectra.

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Femtosecond Time-Resolved Spectroscopy of Iron(II) Complexes with Long-lived Metal-to-Ligand Triplet State

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Ru-based organometalic complexes are explored for a large range of energy conversion applications, such as in dye-sensitized solar cell (DSSCs)[1], where use is made of the redox properties of the long-lived triplet metal-ligand charge transfer state ^{3}MLCT. Research efforts aiming at replacing Ru by abundant metals such as Fe remained unfruitful, since the ^{3}MLCT deactivates within 100fs.[2] A possible way to stabilize the ^{3}MLCT temporally is by increasing the ligand field strength in order to avoid spin-cross modulation. Wärnmark and coworkers reported a long-lived, up to 13 ps, MLCT by using δ-donating mesoionic ligands.[3] In the same direction Gros et al. have synthesized and provided novel Iron complexes with modified carbene ligands, Fe(CarbenCOOH)$_2$. Transient Absorption Spectroscopy reveals that the ^{3}MLCT lifetime of Fe(Carben)$_2$ is almost doubled upon addition of a carboxylate group for grafting on TiO$_2$[4].

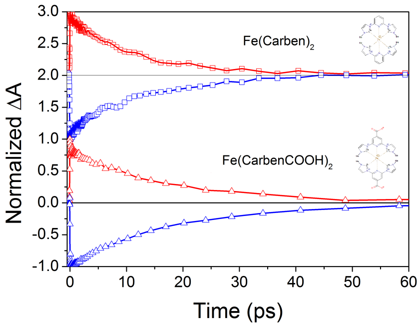

Figure 1. Kinetic traces of excited state absorption (ΔA>0, red) and ground state bleach (ΔA<0, blue) GSB of Iron complexes. Traces are shifted vertically for clarity. 3MLCT lifetimes are 9 ps (Fe(Carben)$_2$), and 16.5 ps (Fe(CarbenCOOH)$_2$).

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Estimation of photo-excited carrier mobilities in wide gap semiconductors by transmission coherent phonon detection.

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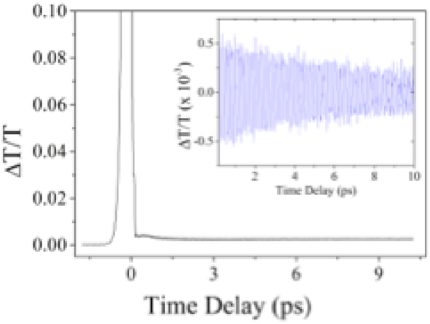
We have developed a new estimation method to measure the mobility of photo-excited carriers in semiconductors through conventional transmission pump-probe coherent phonon measurements. We used a noncollinear optical parametric amplifier as a light source. Figure 1 shows a typical pump-probe result for ZnS. By subtracting the smoothed signal from the raw data, we obtained the coherent LO phonon signal (Fig.1 inset).As was found in other semiconductors [1,2], we observed increasing decay rate of the coherent phonon as the pump pulse intensity increased. Furthermore, by a nonlinear least squares fitting using a damped oscillating function, we found increases in the frequency and a linear relationship between the frequency and the decay rate (Fig. 2). Using a classical coupled oscillator model, we could explain our results by a mixing of damped two-photon generated plasma, and from the linear dependence we can deduce the damping rates for both lattice and electron systems leading to an estimation of the photo-excited carrier mobility (68cm^2/V). The detailed result including discussions for other semiconductors will be shown in the presentation.



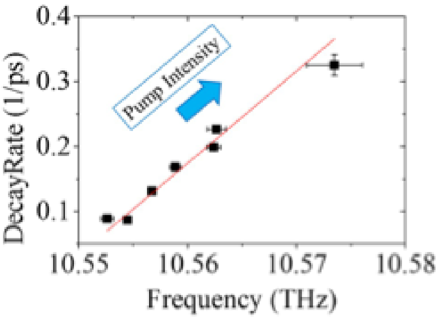


Fig.1(Left) Coherent phonon signal in ZnS measured at 77K. The center wavelength of the pump and probe pulses were 570nm. Fig. 2 (Right) Decay rates versus frequencies of the coherent phonon signal in ZnS measured for various pump intensities.

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Exploiting Transient Absorption Spectroscopy for Mechanistic Insight into Asymmetric Photoredox Organocatalysis

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Recently, photoredox catalysis merged with organophotoredox catalysis has been utilized extensively to accomplish asymmetric alkylation of aldehydes [1,2]. Nevertheless, a mechanistic explanation with spectroscopical evidence for this reaction is still lacking. Here we report a detailed investigation of photoredox organocatalysis on a timescale ranging from tens of femtoseconds to hundreds of microseconds using our transient absorption spectrometer [3]. The reaction we study is an enantioselective intermolecular α-alkylation of aldehydes with the photoredox catalyst *N,N'*-bis(3-ethylheptane)-1,4,5,8-naphthaldiimide (NDI) and an imidazolidinone organocatalyst. We record and analyze the temporal-spectral maps for all possible mixtures of the reagents and catalysts, which allows us to observe the interaction between photoredox catalysis and organocatalysis. Through our investigations, oxidation by the triplet state of NDI is demonstrated as the key intermediate for the catalysis. The intersystem crossing of NDI is surprisingly fast and efficient. It does depend on the substitution pattern, a fact that can explain the differing efficiency in the catalysis. NDI functions as an energy carrier to initiate and drive the organocatalysis. In contrast, electron transfer involving the singlet state of NDI seems to be a loss pathway of the energy. Furthermore, a slight permanent ground state bleaching has been observed, suggesting that a part of the NDI radical anions fail to be converted back to the initial neutral ground state of the NDI.

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Thermal and nonthermal melting of silicon under femtosecond x-ray irradiation

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Silicon under irradiation with intense femtosecond laser pulses can undergo a phase transition via two different channels: thermal and nonthermal. First one occurs if electron-phonon coupling heats the lattice enough to trigger melting, while the second one results from the modification of the interatomic potential energy surface by excitation of electrons from the valence to the conduction band. We developed a model to include both channels on the same footing.

Tight-binding molecular dynamics (TBMD) is used to model atomic dynamics on the potential dependent on the state of electronic system. Simultaneously, electronic state is traced with the Boltzmann equation for low-energy electrons (the valence and the bottom of the conduction band), and Monte Carlo model for photoabsorbtion, high-energy electrons, and deep shell holes. Our results show that electron-phonon coupling triggers phase transition into a low-density liquid phase for deposited doses > 0.65 eV/atom. For deposited doses of over 0.9 eV/atom, silicon undergoes a phase transition into high-density liquid phase triggered via interplay of thermal heating and nonthermal change of the atomic potential.

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Explicit Correlated Exciton-Vibrational Dynamics of the FMO Complex

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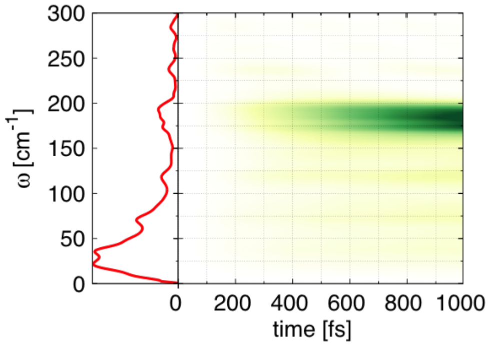
The coupled exciton-vibrational dynamics of a three-site model of the Fenna–Matthews–Olson complex is investigated using the numerically exact multilayer multiconfiguration time-dependent Hartree approach [1]. Thereby the specific coupling of the vibrational modes to local electronic transitions is adapted from a discretized experimental spectral density [2]. The solution of the resulting time-dependent Schrödinger equation including three electronic and 450 vibrational degrees of freedom is analyzed in terms of excitonic populations and coherences. Emphasis is put onto the role of specific ranges of vibrational frequencies. It is observed that modes between 160 and 300 cm^{-1} are responsible for the sub-picosecond population and coherence decay. Further, it is found that a mean-field approach with respect to the vibrational degrees of freedom is not applicable.



Local vibronic excitation of a BChl a monomer during exciton dynamics in the FMO complex. The left panel shows the spectral density (taken from [2]).

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Unraveling Photochemical Reaction Pathways of Diphenylcarbene in Solvent Mixtures

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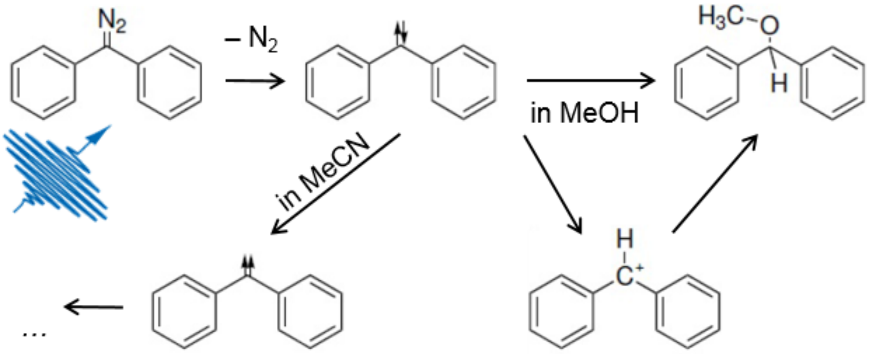
The primary reaction pathways of singlet diphenylcarbene (DPC) in the presence of a solvent can be summarized as an interplay of an intersystem crossing to the triplet state (e.g., in neat acetonitrile) and the formation of an ether product (in alcohols) which can either be formed by reaction with an alcohol in a concerted or stepwise manner or via a short-lived cation resulting from an ultrafast intermolecular proton-transfer reaction [1]. Recent studies on DPC embedded in argon matrices at low temperatures revealed dramatic changes in the reactivity when the carbene environment was modified by small amounts of methanol dopant molecules [2]. Connecting these findings with experiments in the liquid phase at room temperature, we employ femtosecond transient-absorption spectrocopy in the visible and ultraviolet regime to unravel the reactivity of DPC in solvent mixtures. Our studies corroborate that the dynamics are far from a linear combination of those observed in neat solvents, with the efficiency of different reaction channels varying significantly in dependence on the solvent mixing ratio.



Photoinitiated reaction pathways of DPDM after UV excitation.

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Time-Resolved Phase-Sensitive Second Harmonic Generation Spectroscopy of the Hydrated Electron at the Water/Air Interface

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When high energy radiation passes through aqueous media, one of the primary products is the hydrated electron.[1] Although discovered over 50 years ago, many aspects of it are still a topic of discussion. Moreover, recent studies observed a significant role of such electrons in single- and double-strand breaks in DNA, as well as in decomposition of ozone.[2, 3] The above introduces a need to study the hydrated electron especially at the interfaces – be it water/macro-molecule or water/air – where these processes occur. In order to satisfy this need, we perform experiments based on second harmonic generation, which is surface specific for symmetry reasons,[4] and have developed a lock-in method that is phase-sensitive and based on the interference with a reference beam.[5] The measured signal, in contrast to conventional second harmonic experiment, is proportional to sample concentration, and the real and imaginary parts of the 2$^{\text{nd}}$ order non-linear susceptibility can be determined independently. The hydrated electron is generated at the water/air interface using the charge-transfer-to-solvent excitation of iodide and probed at 1320 nm, the second harmonic of which is resonant with the p $\leftarrow$ s transition of the bulk hydrated electron. Focusing on the initial solvation dynamics (<5 ps), a fast decay of the second harmonic signal is observed that we assign to a contraction of the pre-hydrated electron. This decay is accompanied by a phase shift of the signal.

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Tracking Solvent Controlled Photoinduced Electron Transfer Using Broadband Fluorescence Up-Conversion

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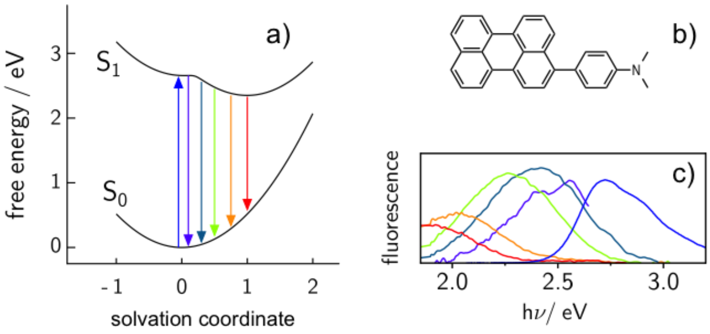
Solvation dynamics is crucial for understanding charge transfer reactions in liquids.[1] Here we revisit the kinetics of a donor-acceptor molecule [2] in several solvents of varying static and dynamic dielectric properties, harnessing the power of femtosecond broadband fluorescence up-conversion [3] and a theoretical model based on the Generalized Smoluchowski Equation approach.[4] By doing so we combine unprecedented photometric resolution, which sheds light on otherwise inaccessible data, with a proper and well-grounded physical description of the phenomenon.



a) Free energy surface for the LE/CT of b). c) Broadband fluorescence spectra at consecutive times allowing to track the reaction progress.

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Inclusion of Some Push-Pull N-Methylpyridinium Salts within Surfactant Solutions: Is Their Excited State Intramolecular Charge Transfer Mediated by Twisting?

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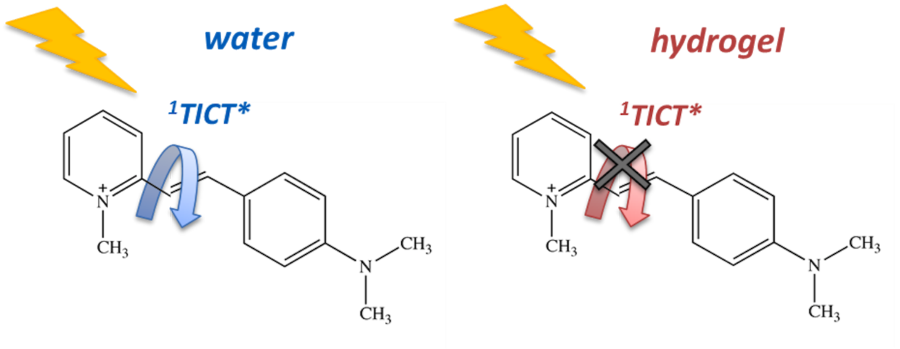
Push-pull N-methylpyridinium salts are known to be extremely sensitive to their immediate environment, being their absorption spectrum subjected to a net negative solvatochromism.[1] These compounds are also characterized by an excited state deactivation strictly dependent on the physical properties of the chemical surrounding, with the formation of intramolecular charge-transfer (ICT) states accordingly stabilized.[1,2] In order to get a deep insight into the environment-dependent photophysics of these pyridinium derivatives, some N-methylpyridinium salts were dissolved within surfactant micelles and hydrogels.[3,4] The excited state dynamics of the molecules in surfactant solutions was investigated by means of femtosecond transient absorption spectroscopy, revealing the distribution of the dyes between the hydrophobic surfactant domains and the water pools making up the microscopic structure of the non-homogeneous solutions. In particular, the comparison between the spectral shapes of those transients experiencing an aqueous surrounding and those embedded in the hydrophobic domains of the hydrogels allowed the fully relaxed excited state to be assigned to a twisted intramolecular charge transfer (TICT) state. The latter cannot be formed in the rigid hydrogel domains where the excited state charge separation is thus prevented and the stationary fluorescence comes from a scarcely polar locally excited (LE) state.[4]



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Femtosecond Soft X-ray RIXS of $Fe(CO)_5$: Orbital-specific Mapping of Excited State Dynamics in Solution

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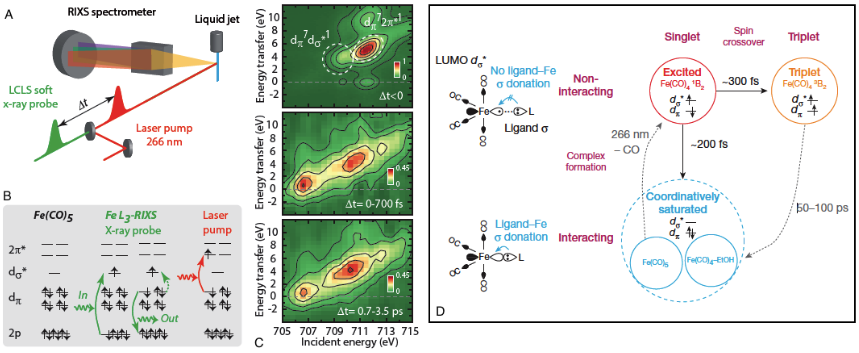
Utilizing ultrashort soft X-ray pulses from the LCLS we carried out a pump-probe resonant inelastic X-ray scattering (RIXS) experiment on $Fe(CO)_5$ photodissociation in ethanol [1]. This allowed us to follow the evolution of the valence orbital structure of iron carbonyl molecules with 300 fs (FWHM) time resolution within the first 3.5 ps. Supported by ab initio electronic structure calculations we identified relevant reaction steps – sub-picosecond excited state relaxation involving change in spin state and interaction with the solvent.



(A) Scheme of the experiment [1,2]. (B) Valence orbitals of $Fe(CO)_5$ which are probed via Fe 2p3d RIXS. (C) Ground state and transient RIXS maps. (D) Schematic reaction pathway of photodissociation product $Fe(CO)_4$ in ethanol solution.

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Femtosecond X-ray Experiments on Functional Transition Metal Systems

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Photocatalytic processes as well as biological function often involve i) intramolecular dynamics as changes in structure, electronic- and/or spin state and ii) intermolecular processes as ligand exchange reactions or coordination of solvent molecules. We use a combination of time-resolved (TR) X-ray spectroscopic and scattering techniques to measure all the aforementioned properties. Hereby, X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are mainly sensitive to the local environment around the absorbing metal center, and X-ray diffuse scattering (XDS) can be used to understand the interplay of the solute with its solvent environment. Benchmark experiments have already proven the scheme combining TR-XAS and TR-XES [1] with XDS [2]. Recently we have undertaken the next step towards answering important questions in modern chemistry, which are relevant in photocatalysis and/or biology. We have applied our suite of techniques to functional Fe- and Ir-based catalytic centers important in (bio-) chemical transformation [3] as well as photocatalytic Hydrogen generation [4], i.e. to unravel the interplay between dynamic structural and electronic processes which determine their efficiency within the catalytic process. Extending these advanced X-ray techniques at intense XFEL sources with femtosecond time resolution is important to understand the initial steps of (photo) chemical reactivity. We will show our strategy towards the implementation of these techniques at the Femtosecond X-ray Experiments (FXE) scientific instrument of European XFEL, the world's most intense X-ray source to become operational in 2016.

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Direct Dynamics Simulations of Metal Complexes in Solution for Interpretation of XFEL Results

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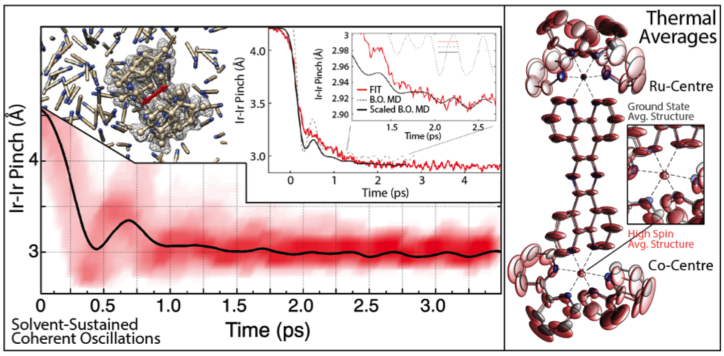
We have implemented a multi-scale QM/MM MD method which electrostatically embeds a sub-region modelled using DFT with a Grid-based Projector-Augmented Wave (GPAW) description[1] into a larger system described using classical, point-charge-based force fields. The method provides precise on-the-fly simulations of dynamics on the Born-Oppenheimer surface, while the effectiveness of GPAW makes it possible to sample hundreds of ps of the phase spaces of intricate chemical reaction dynamics in complex solvated molecules such as the bi-metallic complexes shown in figure 1. The statistical quantities allow us a direct utilization of the results in model-fitting of time-resolved X-ray scattering data, obtained at X-ray Free-Electron Lasers (XFELs).



Left: Excited state Ir-Ir oscillation of a $Ir_2(dimen)_4{}^{2+}$ *complex in solution, reproducing the experimentally fitted pinch within 7%. The solvent sustains the coherence lifetime[2], and the solute-solvent interactions are used in the ongoing work of interpreting XFEL data. Right: 50% ellipsoids of two spin configurations of a bimetallic complex, showing Co-N elongation, in accordance with experiment[3], with a possible differentiation of the bonds.*

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THz-field-induced optical birefringence in polar liquids

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The characteristic frequencies of rotational, translational and librational dynamics of liquids are often located in the terahertz (THz) range. Because of the inherent complexity of the intermolecular dynamics, linear THz spectroscopy does not resolve all features of the collective modes, for instance their mutual coupling and linewidth broadening mechanisms. In this respect, nonlinear spectroscopies have the potential to provide more insight into the intermolecular dynamics of liquids [1,2]. Here, we use intense THz pulses (field strength >2.5 MV/cm at ~1 THz) to drive nonlinear effects in polar liquids. Analogous to the anisotropic optical Kerr effect (OKE), we probe the induced transient optical birefringence in polar liquids following THz pumping [3]. In all cases, we observe an instantaneous electronic response proportional to the square of the THz electric field. In case of aprotic polar solvents (such as dimethyl sulfoxide, benzonitrile and tetrahydrofuran), the slower nuclear relaxation part of the transient signal resembles that of the OKE whereas in hydrogen-bonded solvents (such as methanol, ethylene glycol and t-butanol), the nuclear relaxation is not observed in contrast to OKE. Interestingly in case of water with small anisotropic polarizability, we resolve a signal whose relaxation tail has comparable magnitude but opposite sign with respect to the instantaneous electronic response. The latter relaxation has the same dynamics as its OKE counterpart. We discuss our results in terms of different mechanisms of the molecular alignment through resonant (THz) versus off-resonant (optical) excitation of collective molecular modes.

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Tracking Chemical Reactions with Ultrafast X-ray Techniques

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Time resolved X-ray Absorption Spectroscopy (TR-XAS) [1], X-ray Emission Spectroscopy (TR-XES) [2] and X-ray Diffuse scattering (TR-XDS) [3] techniques deliver information about structural, electronic and solvent changes in real-time. Synchrotron based studies are limited with 100ps time resolution, while new intense and ultrashort hard X-ray pulses from X-ray Free Electron Laser sources (LCLS, SACLA and soon European XFEL) opens up the fs time domain. We show sub-ps results from SACLA on laser-induced ligand detachment reactions of aqueous Iron(II) hexacyanide ($[Fe^{II}(CN)_6]^{4-}$) molecules monitored via combined TR-XAS, TR-XES and TR-XDS techniques. While the final reaction product ($[Fe^{II}(CN)_5H_2O]^{3-}$) has been known for a long time [4], the intermediate steps observed here hint towards the fairly long-lived existence of an intermediate penta-coordinated complex, $[Fe^{II}(CN)_5]^{3-}$, which has not been reported in prior work. The discovered reaction pathway sequence is based on the comparison of simulated XANES data with the measured XANES spectrum. Femtosecond-resolved XAS results exhibit hitherto unreported dynamics with 2 ps lifetimes. Femtosecond-resolved XES studies also reveal similar 2 ps decay in the K-beta emission signal. The preliminary analysis of the TR-XDS shows a similar (though here ca. 3 ps long) behavior in the low-Q region. The status of this analysis will be presented, which may unravel the interplay between intra- and intermolecular dynamical processes and solvent effects during this light-driven chemical reaction. With these new X-ray tools at hand at powerful XFEL sources we have designed the Femtosecond X-ray Experiments (FXE) scientific instrument at European XFEL, which will provide a suite of simultaneous femtosecond X-ray tools for structural dynamics research.

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Ambient Thione Formation Elucidated with Time-Resolved Sulfur-1s Spectroscopy

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Sulfur analogues to alcohols (R-SH) are abundant in nature and their chemistry is similar to alcohols. However, clear differences render understanding of sulfur chemistry important. Recent results on the model system 4-methylbenzenethiol from transient absorption spectroscopy indicate Sulfur radical generation upon UV excitation and formation of another species which eludes identification by optical spectroscopy and it was theorized that the hydrogen atom attaches to the aromatic ring [1,2]. We used transient Sulfur-1s spectroscopy as a new element- specific probe of transient electronic and molecular structure to elucidate the nature of the reaction products. Two induced absorption peaks below the ground-state bleach clearly indicate formation of two new sulfur-species. Using TDDFT calculations we identified the thio-radical and a thione isomer with the photoejected hydrogen atom attached to the aromatic ring [3]. As far as we know—and contrary to aromatic alcohols—this is the first time that keto-enol tautomerie has been directly observed for solvated aromatic thiols under ambient conditions.

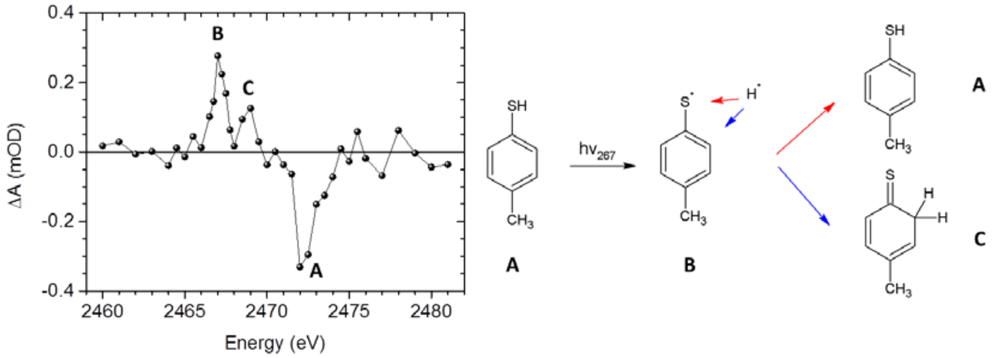

Fig. 1 Differential sulfur-1s spectra 100 ps after 267-nm excitation and reaction products.

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Ultrafast, Infrared Spectroelectrochemistry in Attenuated Total Reflectance Geometry

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To shed light on the impact that charged metal-liquid interfaces [1] exert on ultrafast molecular dynamics, we make use of the surface sensitivity of recently established 2D Attenuated Total Reflectance Infrared Spectroscopy (2D ATR-IR).[2,3] To this end, we introduce a multilayered electrode composed of a nanometer thick stack of indium tin oxide and noble metals in a homemade electrochemical ATR cell. In order to demonstrate the applicability of the method, Carbon monoxide (CO) was adsorbed onto a platinum-coated ITO electrodes and the effect of purposely tuned electric fields on the vibrational dynamics was assessed by Stark shift spectroscopy (Fig.1). The contribution will focus on three points of investigation: (i) Disentangling of the ultrafast infrared response from sample and conductive layer (ii) occurrence of lineshape distortions in dependence of sample preparation details and (iii) extending investigations regarding the electrochemical 2D ATR IR signals of self-assembled monolayers with different local vibrational probes.[4,5]

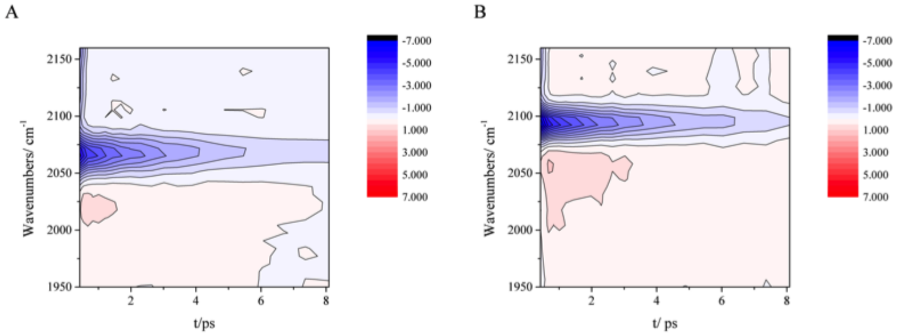

Figure Background subtracted IR pump/ IR probe spectra of Pt-CO(ads.) in contact with NaClO$_4$ 0.1 M (aq.) at the applied potentials of -1.0 V (Ag/AgCl) (A) and +1.0 V (Ag/AgCl) (B).

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Ultrafast carrier dynamics of the organolead trihalide perovskite $CH_3NH_3PbI_3$ on mesoporous TiO_2

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We investigated ultrafast carrier dynamics in the organolead trihalide perovskite $CH_3NH_3PbI_3$ using femtosecond broadband transient absorption experiments. The perovskite was prepared on mesoporous TiO_2 either by 1-step deposition from solution or by 2-step methods employing deposition of lead iodide followed by an on-surface reaction with methylammonium iodide. Upon photoexcitation at 400 or 500 nm, the carrier dynamics were monitored by a broadband supercontinuum in the range 320-920 nm. Initial ultrafast carrier relaxation with time constants of < 0.08, 0.2 and 2.6 ps was assigned to carrier - carrier and carrier - optical phonon scattering, and a pronounced sub-band-gap absorption was found at early times. Transient carrier temperatures were extracted from a Boltzmann fit to the high-energy wing of the photobleach band, enabling a separation into contributions from acoustic phonon decay (50 ps and > 1000 ps) and Auger recombination (9, 75 and 450 ps). Carrier relaxation was accompanied by formation of an absorption band around 550 nm, with a characteristic structure consistent with a transient Stark effect, *i.e.* a red-shift of the perovskite spectrum due to formation of a directed electric field in the material, and possibly also an additional contribution of the elevated lattice temperature. A substantial Stokes shift between the relaxed photobleach and photoluminescence bands was also observed. Furthermore, contributions from transient absorption features of unreacted lead iodide can be neglected.[1]

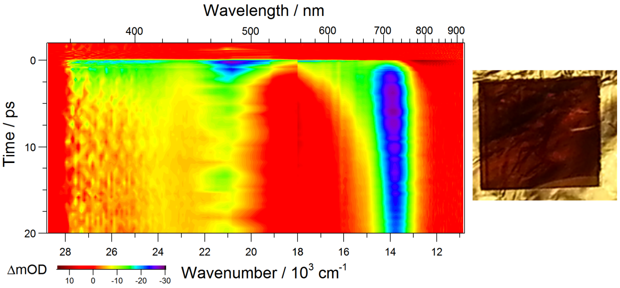

Figure 1. (Left) Contour plot of transient absorption spectra for $CH_3NH_3PbI_3$ on mesoporous TiO_2 after photoexcitation at 500 nm. (Right) Optical image of the perovskite.

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Ultrafast Frenkel Exciton Dynamics in Helical π-Stacks of Self-Assembled Perylene Bisimides

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Although the exciton dynamics of molecular aggregates have been investigated, the exciton delocalization and localization in H-aggregates have remained unexplored due to small oscillator strength of Frenkel state and their weak fluorescing nature. However, a recent study has proposed the fluorescence measurement as an alternative method to determine exciton delocalization size [1]. Therefore, we have focused on obtaining emission from Frenkel exciton state of the archetypal H-aggregates (a couple of PBI systems, PBI dimer and multimer (Figure 1)) [2]. We present, for the first time, time-resolved fluorescence study of H-aggregates obtained by a broadband fluorescence upconversion technique. By recording the vibronic peak ratio in the transient fluorescence spectra, the initial exciton delocalization size and localization dynamics are directly unraveled. In the dimer case, exciton localization and the concomitant excimer formation processes occur on several hundreds of femtoseconds. On the other hand, in the case of PBI multimer, the photoexcitation energy is delocalized over at least three molecular units and moves coherently along the chain in tens of femtoseconds. This comparative study suggests the possibility of long-range coherent energy transfer in artificial photon accessing materials.

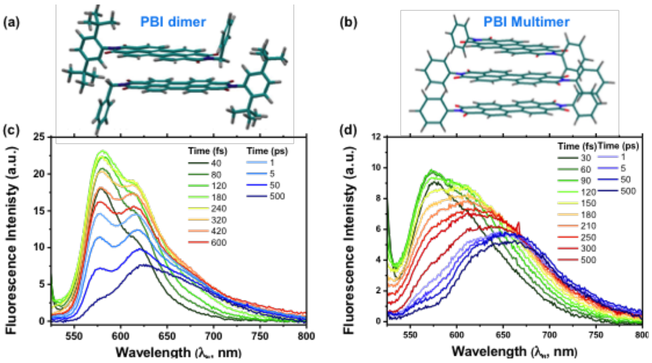

Figure 1. The molecular stacking models of PBI dimer (a) and PBI multimer (b), and the transient fluorescence spectra of PBI dimer (c) and multimer (d).

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Real-Time Monitoring of Chromophore Isomerization and Deprotonation during the Photoactivation of the Fluorescent Protein Dronpa

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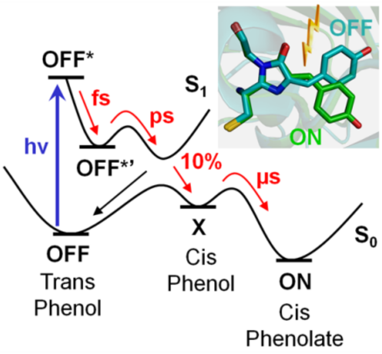
Dronpa [1] is a photochromic green fluorescent protein (GFP) homologue used as a probe in super-resolution microscopy. It is known that the photochromic reaction involves cis/trans isomerization of the chromophore and protonation/ deprotonation of its phenol group [2], but the sequence in time of the two steps and their characteristic time scales are still the subject of much debate [3,4]. We will report a comprehensive UV-visible transient absorption study of the photoactivation mechanism of Dronpa, covering all relevant time scales from ~100 fs to milliseconds [5]. We were able to measure both the spectrum and the anisotropy of the main ground-state photoactivation intermediate, which allows us to assign it unambiguously to a cis-phenol form. We conclude that trans→cis isomerization of the chromophore occurs on the picosecond time scale, concomitantly to the excited-state decay. In addition, we found the deprotonation step to follow in ~10 μs and lead directly from the cis-phenol intermediate to the final ON state.



Model for the photoactivation mechanism of Dronpa.

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The excited state intramolecular charge transfer dynamics in aminoanthraquinone

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Anthraquinone and its derivatives are considered as the important molecules due to their structural similarity to both quinone antitumor drug and anthraquinoid vat dyes [1-3]. A special interests of 1-aminoanthraquinone are the amino derivatives as catalytic DNA photonucleases [4-6]. The amino group is a strong electron donor and induces an intramolecular charge transfer (ICT) property after an excitation [7]. The electronically excited states of 1-NH_2AQ have been investigated focusing on the mechanism of twisted ICT (TICT) and following radiationless dynamics. Ultrafast broadband absorption measurements were performed based on the Ti-sapphire femtosecond laser system. The NOPA of 480nm and the white light continuum pulses were used as the pump and probe lasers, respectively. The two laser beams were focused in the sample solution which flowed in a quartz cell with optical length of 1 mm. The angle between polarizations of both beams were set to a magic angle to avoid rotational diffusion effects. To describe properly the dynamics observed in the visible range, global fit analysis of all of the kinetics at different wavelength regions is performed with singular value decomposition. Transient absorption spectra show two characteristic bands: excited state absorption and stimulated emission. The mechanism of TICT is proposed by dipole moments and the conformational relaxation with the twisted angle of the amino group. A small energy barrier is predicted to be 0.2595 eV on the potential surface of the S_1 state using quantum chemical calculations. TICT would be extended to 5 ps by the barrier. The internal conversion and intersystem crossing via twisting of the amino group observed in experiments are possible to be responsible for the ultrafast deactivation of the S_1 state.

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Ultrasensitive ultrafast vibrational spectroscopy employing the near field of gold nanoantennas

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Plasmonic antennas are metallic nanostructures that have the ability to confine electromagnetic fields to volumes many times smaller than the diffraction limit. The strong field enhancement accompanying this process provides an avenue for performing localized nonlinear spectroscopy on molecules in the nanoenvironment of the antennas. Here we have used this idea and developed a novel experimental technique for performing ultrasensitive two-dimensional infrared (2DIR) spectroscopy on nanoscopic volumes of material. Using our nanoantenna-based technique we were able to locally amplify the transient absorption signals of test molecules by a factor of $6{\cdot}10^4$ compared to standard infrared pump-probe spectroscopy. In our experiments we use gold nanoantennas that are fabricated using electron-beam lithography and display a strong resonance in the infrared. We demonstrate our technique by performing pump-probe and 2DIR spectroscopy on the carbonyl vibration of a 5 nm layer of polymethylmetacrylate (PMMA) that is deposited on top of the nanoantennas. We discuss the nonlinear amplification mechanism as well as strategies for further increasing the sensitivity of the technique. The unprecedented signal enhancements achieved pave the way for performing nonlinear infrared experiments on nanoscale systems consisting of molecular monolayers, such as responsive coatings, supported lipid bilayers and DNA or protein microarrays.

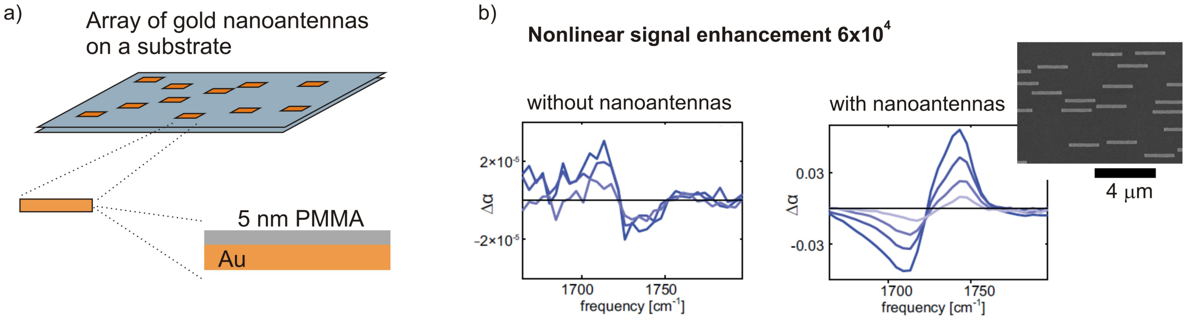

Figure . a) Experimental scheme. Using electron-beam lithography we have patterned a CaF_2 substrate with gold nanoantennas. An ultrathin layer (5 nm) of PMMA is deposited on top of the nanoantennas. b) Infrared pump-probe spectra of the carbonyl vibration of PMMA in the presence and absence of the nanoantennas. The inset shows an SEM image of the nanoantennas.

Peptide Conformation Photocontrol With a Retinal-Like Molecular Switch

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Biomolecular photocontrol requires photoswitches witch undergo efficient isomerization in response to an optical excitation and substantial conformational change to drive functional changes in a biomolecule [1]. With this aim, we present an experimental and computational study to analyze how the photochemistry of a molecular switch changes when it is covalently linked to a peptide as compared to unbound in solution. We focus here on a recently reported, retinal-like molecular switch linked to alpha-helical peptide [2]. We perform pump-probe spectroscopy as a function of temperature, and use molecular dynamics and hybrid quantum mechanics/molecular mechanics (QM/MM) methods to rationalize the effect of the peptide on the photoreaction. We observe that the peptide-linked switch in water exhibits a biexponential decay of the excited-state compared with the monoexponential one found for the free switch in methanol (MeOH). This is explained in terms of heterogeneity of the ground-state structure as found by molecular dynamics, which in turn leads to different excited-state energy barriers along the photoisomerization pathway, as calculated by ab initio multiconfigurational QM/MM methods for representative peptide structures.

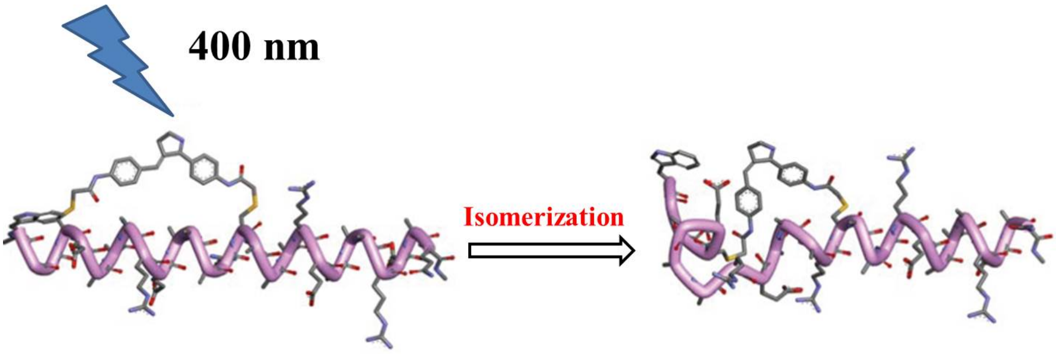

Figure: Illustration of the cross-linked peptide. The E form of the switch stabilizes the alpha helix, while the Z form disrupts it. Adapted from [2].

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Sparse distribution of fluorescence lifetimes reveals Hofmeister effect on coenzyme FAD

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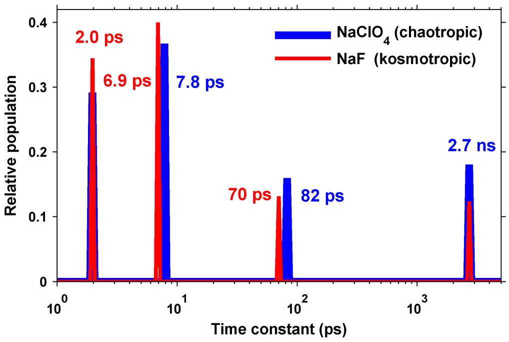
The ion specific regulation of the solubility and aggregation of proteins and other colloids is known as Hofmeister effect [1]. Aggregation is promoted by the so called kosmotropic anions, while open structures are favored in the presence of chaotropic ones. The exact physico-chemical background of this phenomenon – observed almost exclusively on macromolecules – is still unexplained. A crucial problem is that the required quantum chemical/molecule mechanical calculations are hardly feasible on such large systems. Here we show the experimental evidence of the Hofmeister effect on coenzyme FAD, a molecule of fundamental biological importance but minimal size. In aqueous solution the flavin and adenine groups of FAD form both open and stacked conformations, characterized by long- and short-lived fluorescence, respectively [2]. Detecting time-resolved fluorescence from FAD in the 100 fs – 10 ns time window and analyzing it by a novel method based on the principles of compressed sensing [3], we obtained a highly sparse distribution of fluorescence lifetimes in a wide range. The lifetime distribution can be directly mapped to the population distribution of the different conformation states of the molecule. The data clearly indicate the regulatory effect of the chaotropic and kosmotropic anions on this distribution, exactly as required by the Hofmeister effect.



Regulatory effect of anions on the sparse distribution of fluorescence lifetimes.

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Kinetics of excitation energy transfer in NADH

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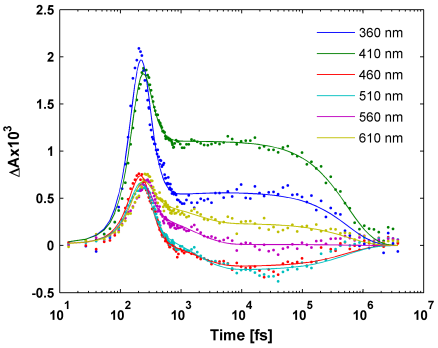
The transfer of the excitation energy from the adenine (A) to the dihydronicotin-amide (NA) group of the coenzyme NADH was observed long time ago [1,2], but the kinetics and mechanism of this process are still unexplored. The energy transfer is very efficient in aqueous solution where a stacked conformation is preferred, and less effective in the presence of ethanol, facilitating an open conformation [2]. Here we present a kinetic study of the transfer process, monitored by femtosecond transient absorption (TA) at different ethanol concentrations. A global analysis of the TA following the excitation of A resulted in three exponential components with time constants of 180 fs, 1.7 ps and 650 ps. The weight of the two slower components reduced markedly at high ethanol concentrations. The decay associated difference spectra indicate the presence of parallel processes in which the majority of the NADH molecules in stacked conformation undergo a two-step energy transfer. In the first step the energy remains on A, but stabilized in an additional, long-lived excited state. In the second step (1.7 ps) it is transferred to NA, which finally relaxes to its ground state (650 ps). The data clearly show that an increasing ethanol concentration does not increase the NA-to-A distance but shifts the conformational equilibrium toward the open form.



Transient absorption of NADH in water, excited at its adenine group (266 nm).

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Multiple Emissions in Push-Pull Cationic Dyes

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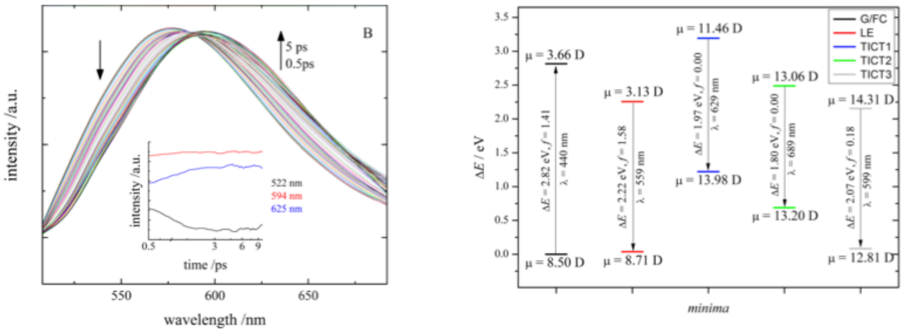
The long-standing controversy about the presence of multiple emissive minima in the lowest excited state of push-pull methylpyridinium derivatives was definitively proved by both experimental (femtosecond up-conversion measurements) and theoretical (Density Functional Theory calculations) approaches [1,2]. From the fluorescence up-conversion data the Time Resolved Area Normalized Spectra (TRANES) were calculated, showing isoemissive points and therefore allowing us to discriminate the sub-picosecond emitting states from the occurrence of ultrafast solvation dynamics and to disentangle the overlapping fluorescence of the different components (even when they are very close in energy). Vibronic TD-DFT computations provide deeper insights about the structural and electronic characteristics of the distinct emissive minima of the excited state potential energy surface. The Locally Excited (LE) minimum exhibits a flat geometry and an electric dipole moment smaller than the ground state; the Twisted Intramolecular Charge Transfer (TICT) minimum shows a rotation of the methylpyridinium moiety with respect to the rest of the structure, and a significantly larger electric dipole moment.



Left: fluorescence up-conversion (TRANES); right: energy levels of ground and excited state minima.

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Ultrafast electron transfer between Water-soluble Corrole and DNA

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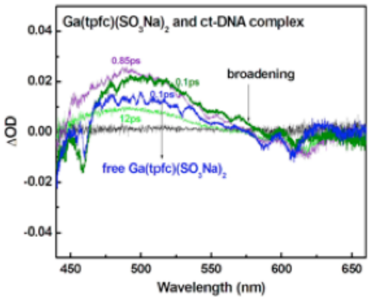
Ultrafast electron transfer (ET) and recombination processes in the complex of water-soluble anionic Ga(III) corrole (Ga(tpfc)(SO_3Na)$_2$) and calf thymus DNA (ct-DNA) have been investigated using femtosecond transient absorption spectroscopy. A broader positive absorption (450 ~ 583 nm) of the complex is observed compared to that (450 ~ 570 nm) of free Ga(tpfc)(SO_3Na)$_2$ at 0.10 ps time delay after photoexcitation of Ga(tpfc)(SO_3Na)$_2$ into its Soret band. The control experiments performed on the model DNAs ([poly(dG-dC)]$_2$ rich in guanine bases and [poly(dA-dT)]$_2$ poor in guanine bases) suggest the spectral broadening is due to the formation of the intermediate guanine radical cation in DNA. The forward ET occurs within the pulse duration (τ_f < 156 fs) and the lifetime (τ_b) of the following backward ET is determined as about 426 fs. Based on the results of both steady-state absorption and electrochemical measurements, negative driving forces are estimated for both forward and backward ET processes. Molecular orbital calculations show that the HOMO energy level of Ga(tpfc)(SO_3Na)$_2$ is lower than that of guanine base. All the results support the experimental observation of ET processes between photoexcited Ga(tpfc)(SO_3Na)$_2$ and guanine base of DNA. In spite of outside binding mode, the interaction of Ga(tpfc)(SO_3Na)$_2$ in the higher singlet excited state with ct-DNA may also result in ET on femtosecond time scales.



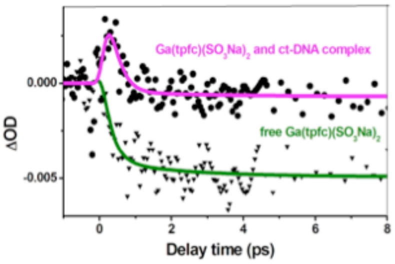


Fig. 1. Femtosecond transient absorption spectra of Ga(tpfc)(SO_3Na)$_2$ and ct - DNA complex at three different delay times. Fig.2. The evolution of the transient absorption of free Ga(tpfc)(SO_3Na)$_2$ and Ga(tpfc)(SO_3Na)$_2$ and ct-DNA complex at 580nm.

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Control of Ultrafast Photodissociation by Laser-Induced-Potentials

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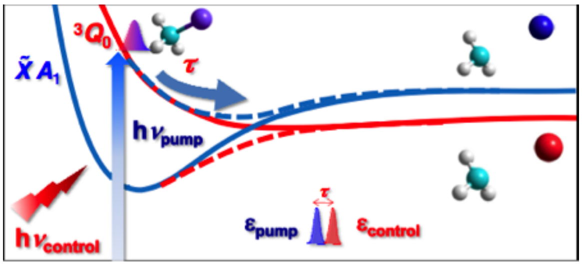
Experiments aimed at understanding ultrafast molecular processes are now routine, and the notion that external laser fields can constitute an additional reagent is also well established. The possibility of externally controlling a reaction with radiation increases immensely when its intensity is sufficiently high to distort the potential energy surfaces at which chemists conceptualize reactions take place [1]. Here we explore the transition from the weak- to the strong-field regimes of laser control for the dissociation of a polyatomic molecule, methyl iodide [2]. The control over the yield of the photodissociation reaction proceeds through the creation of a light-induced conical intersection. The control of the velocity of the product fragments requires external fields with both high intensities and short durations. This is because the mechanism by which control is exerted involves modulating the potentials around the light-induced conical intersection, that is, creating light-induced potentials.



Shaping potentials by strong laser pulses is a powerful means for controlling product yields. Control over the velocity of the products is achieved through light-induced conical intersections and modulating the potentials around them by light-induced potentials

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Excited-State Vibrational Wave Packet Motion in Perylene Bisimide Investigated by Femtosecond Broadband Pump-Probe Spectroscopy

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The impact of coherent dynamics on exciton relaxation pathways or chemical reactions of molecular structures and biological systems has been drawing constant attraction [1]. In this regard, coherent vibrational wave packet dynamics of an N,N'-bis(2,6-dimethylphenyl) perylene bisimide (**DMP-PBI**) were investigated by using femtosecond broadband pump-probe spectroscopy with a wide spectral coverage and high spatiotemporal resolution. Clear modulations were observed in the transient absorption intensities of the stimulated emission bands of **DMP-PBI** with the oscillation frequencies of 140 and 275 cm^{-1}. Fourier transform analysis of each oscillatory mode revealed characteristic phase inversion behaviors near the maxima of the steady-state fluorescence, indicating that the observed vibrational coherence originates from an excited-state wave packet motion. Quantum calculations of the Raman spectra and the respective vibrational modes at the low-frequency region suggest that core elongation motions accompanied by deformation of the dimethylphenyl substituents are responsible for the observation of such coherent wave packet dynamics.

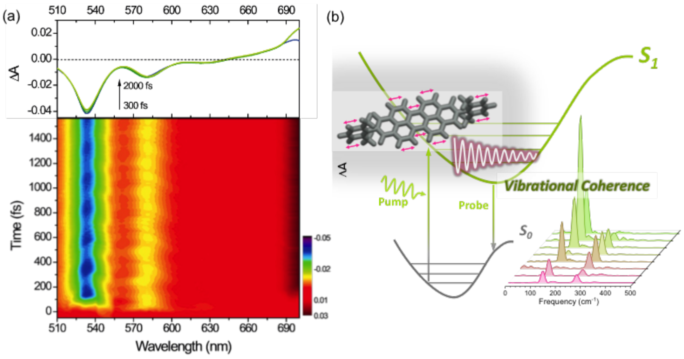

Figure 1. (a) Broadband pump-probe spectra and 2D contour map of ***DMP-PBI****. (b) Schematic illustration of the coherent wave packet dynamics described in this work.*

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Photoelectron Circular Dichroism observed in the ATI Signal from Chiral Molecules with Femtosecond Laser Pulses

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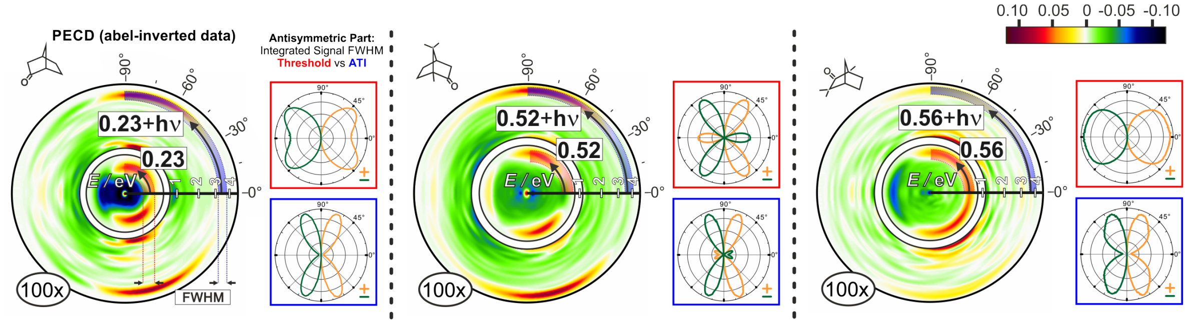
Photoelectron circular dichroism (PECD) is investigated experimentally as a function of the number of absorbed circularly polarized photons[1-3]. Three structurally different chiral molecules yet showing similar absorption spectra are studied. They are isotropically distributed in the gas phase and ionized with femtosecond laser pulses. We measure and analyze the photoelectron angular distribution of threshold electrons ionized with three photons and compare them to those of above-threshold electrons ionized with four photons. Increasing the number of circularly polarized photons leads to an increase in the contribution of higher order Legendre polynomials to the PECD signal. One-dimensional PECD quantifications do not necessarily reflect the increase of total angular momentum absorbed by the chiral molecule. The presented data set can serve as a guideline for theoretical modelling of the interaction of circularly polarized light with chiral molecules in the multiphoton regime.



Abel inverted PECD images from the bicyclic ketones norcamphor, camphor and fenchone and the integrated signal comparing threshold ionization (red) and ATI (blue).

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Bimolecular Photoinduced Electron Transfer Beyond the Diffusion Limit: The Rehm-Weller Experiment Revisited with Femtosecond Time-Resolution

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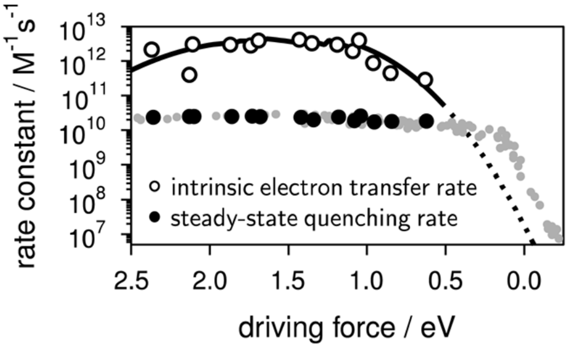
To access to the intrinsic, diffusion free, rate constant of bimolecular photoinduced electron transfer reactions, fluorescence quenching experiments have been performed with 14 donor/acceptor pairs, covering a driving-force range going from 0.6 to 2.4 eV, using steady-state and femtosecond time-resolved emission, and applying a diffusion-reaction model that accounts for the static and transient stages of the quenching for the analysis [1]. The intrinsic electron transfer rate constants are up to two orders of magnitude larger than the diffusion rate constant in acetonitrile. Above ca. 1.5 eV, a slight decrease of the rate constant is observed, pointing to a much weaker Marcus inverted region than those reported for other types of electron transfer reactions, such as charge recombination. Despite this, the driving force dependence can be rationalized in terms of Marcus theory.



Driving-force dependence of the intrinsic bimolecular charge separation rate constant (open circles) and of the steady-state quenching rate constant (black circles) and comparison with literature data.

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Direct femtosecond time-resolved observation of vibronic coupling between $\pi\pi^*$ and $\pi\sigma^*$ states in pentafluorobenzene

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In the series from monofluoro- to hexafluorobenzene, the so-called perfluoro effect lowers the energy of the optically dark $\pi\sigma^*$ electronic state localized on the C–F bond until it becomes almost isoenergetic with the optically bright $\pi\pi^*$ state. The crossing is assumed to occur in the case of pentafluorobenzene. We have studied the ultrafast non-radiative dynamics of these two states in jet-cooled pentafluorobenzene using femtosecond time-resolved time-of-flight mass spectrometry and photoelectron imaging. The observed temporal profiles of the transient mass signals exhibit a complex, multi-exponential decay behaviour (Figure 1a). Most prominently, all transients feature a pronounced and very long-lived coherent oscillation with 75–78 cm^{-1} frequency and its overtone. Photoelectron spectra (Figure 1b) recorded at a temporal delay corresponding to an oscillatory maximum clearly show two distinct bands that we assign to the aforementioned $\pi\pi^*$ and $\pi\sigma^*$ states. Moving the time delay towards a minimum, these bands decay in phase with each other until a weak, broad and structure-less band remains. The oscillation between these two configurations is observed for over 10 ps. We conclude that the modulation of the transient mass spectra gives the frequency of the vibrational coupling mode. The underlying mechanism will be discussed.

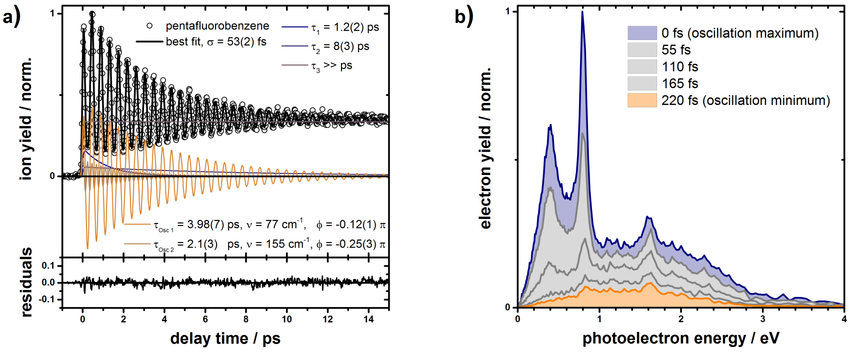

Figure 1: a) The transient mass spectrum of pentafluorobenzene excited with femtosecond pulses centered at 265 nm. b) Transient photoelectron spectra recorded in 55 fs-steps from an oscillatory minimum (orange curve) to a maximum (blue curve).

Spectral lineshape in nonlinear electronic spectroscopy: a practical approach based on a single trajectory

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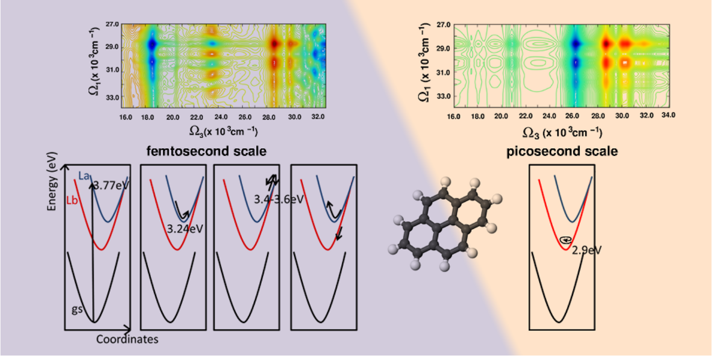
We outline a computational approach for generating nonlinear spectra, which accounts for the electronic fluctuations due to nuclear degrees of freedom, thereby explicitly considering the fluctuations of higher excited states, induced by the dynamics in the photoactive state(s)[1]. The approach is based on mixed quantum-classical dynamics simulations, tedious averaging over multiple trajectories is avoided by introducing the linearly displaced Brownian harmonic oscillator model. The presented strategy couples accurate computations of the high-lying excited state manifold to dynamics simulations. The protocol is applied to generate bi-dimensional electronic spectra of pyrene, a polycyclic aromatic hydrocarbon characterized by an ultrafast decay from the bright S_2 state to a dark S_1 state on a time scale of few tens of femtoseconds. Comparison of theoretical and experimental[2] spectra for different waiting times shows remarkable agreement allowing to unambiguously assign the detected signals.



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Time-Resolved Imaging of Molecular Dynamics Using Free-Electron Lasers

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Tracing the forming and breaking of molecular bonds in real time, watching chemistry in action on atomic length and time scales is a longstanding dream in science. The ultrafast reaction pathways that molecules undergo upon photoexcitation evolve along multidimensional potential energy surfaces, and for complex molecules, a multitude of different processes can happen. By combining energy and angle resolved (3d) electron and ion spectroscopy techniques with the element specificity of X-ray photoionization, a consistent picture of photoreactions may be retrieved. Electron holography approaches even hold the promise of imaging molecular structure directly, without need of detailed calculations. Results of first FEL experiments at FLASH and LCLS on halogenated benzene derivatives will be presented, where the molecules were actively fixed in space by adiabatic laser alignment, and then studied with angle resolved photoelectron and ion spectroscopy using soft X-rays [1,2,3]. These data are complemented with ion-electron coincidence measurements obtained at the PETRA III synchrotron [2], and in this context, possibilities for future studies at high repetition rate FELs are discussed.

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Intramolecular coupling of porphyrin chromophores studied with two-dimensional electronic spectroscopy

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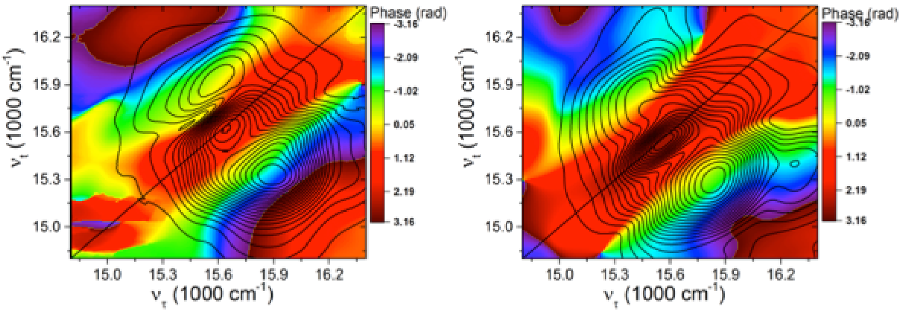
Two-dimensional electronic spectroscopy (2D ES) has emerged as a valuable new method to investigate inter- and intramolecular coupling. [1] 2D ES reveals coherences between different vibrational and/or electronic states through cross-peaks in the absorptive 2D ES spectra which oscillate as a function of population time. The assignment of the oscillations as of vibrational, electronic or mixed origin has proved difficult, and a clear understanding of their amplitude and phase behavior is still evolving. [2,3] In this work we report 2D ES studies of a zinc porphyrin monomer which has its lowest singlet-singlet electronic transition coupled to a single vibration. This allowed us to test theoretical predictions of interferences between different oscillatory contributions across the excitation-detection plane, as well as the possibility of distinguishing vibrations in the excited and ground electronic state. These results are also used to study the oscillatory dynamics in the 2DES of a conjugated zinc porphyrin dimer.



Experimental (left) and simulated (right) amplitude and phase of the rephasing 2D ES oscillations corresponding to the porphyrin monomer's vibration at 380 cm^{-1}.

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Time Resolved Ion- Spectroscopy of Iodine Containing Molecules

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Using the intense soft x-ray laser pulses from FLASH, we have studied the photofragmentation and ionization behavior of small iodine containing molecules to investigate the charge redistribution as well as the time scales of the involved dissociation processes [1]. The molecules iodomethane CH_3I and diiodomethane CH_2I_2 have been chosen as model systems, as a strong local core hole excitation can easily be applied at one or two different iodine sites of the molecules by exciting the strong 4d-4f shape resonance. The photoionization- and dissociation process is studied on a fs-timescale by ion time-of-flight-spectroscopy. We present first results of measurements performed at FLASH with a XUV-pump-XUV-probe setup. By using a split-and delay-autocorrelator setup it is possible to track the development of the different ionic charge states of the molecule fragments depending on the time delay between two XUV pulses. Delay-dependent intensity changes in the iodine ion charge states are a clear indication of charge migration processes within the molecule. The time scales differ for the different molecules. Performing first ab initio calculations, we analyze the charge redistribution of CH_3I and CH_2I_2 considering the charge dynamics within a molecular Auger decay before the dissociation proceeds. This work is supported by the collaborative research center SFB 925.

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Calculation of resonance Raman intensities of azobenzene using TDDFT and EOM-CCSD methods

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The calculation of excited state properties for large molecules remains a challenge in quantum chemistry. In particular, limited knowledge is available concerning the accuracy of quantum chemistry methods concerning the estimation of the excited state gradients. Because excited state gradients are fundamentally important for a correct evaluation of excited state geometries and potential energy surfaces and for the subsequent treatment of excited state dynamics, a better knowledge of the performance of standard computational approaches is highly desirable. Within the so-called short-time approximation, the resonance Raman (RR) intensities are directly related to the gradients of the excited state in resonance. Hence, the calculation of RR intensities and their comparison with experimental data offers an opportunity to gain more knowledge about the ability of standard quantum chemistry methods to determine excited state gradients and related properties [1,2]. This contribution provides such an investigation by considering the molecule of azobenzene. The RR spectra of the two isomers (*trans*-azobenzene and *cis*-azobenzene) are calculated assuming resonance with the two first transitions to the singlet excited states. Then, the accuracy of time dependent density functional theory as well as of coupled-cluster (EOM-CCSD) methods is estimated with respect to experimental results taken from the literature [3,4].

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Photoionization and Dissociation of Molecular Nitrogen

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Recent advances in atto second technology have made it possible to gain new insights into ultra-fast electron dynamics after sudden ionization [1,2]. In particular we investigate the photo induced dissociation of N_2 after interaction with XUV radiation. This process was studied experimentally by recording the kinetic energy release (KER) in an XUV-pump/IR-probe setup, observing a sub-femto second dependence of the N^+ yield on the XUV/IR time delay. In this contribution, we present a theoretical model that describes the ionizing effect of the XUV pulse using Dyson Orbitals [3,4] as well as the subsequent dissociation process (probed by IR pulse), which is modeled using a large set of potential energy curves (PECs), including non-adiabatic effects, on which to propagate by means of Split Operator and Fast Fourier techniques [5,6]. A small subset of PECs is extracted allowing for the identification of one and two photon processes chiefly responsible for the experimentally observed features in the KER.

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Photoinduced dynamics in cyclic dienes: How the ring size influences the reaction channels

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The reaction dynamics of cyclic dienes with ring sizes of n = 5-8 have been investigated upon photoexcitation to their lowest lying valence state using femtosecond time resolved photoelectron spectroscopy and linear response TD-DFT fewest switches surface hopping computations. We found that the dynamics of all dienes take place on a single excited potential energy surface, opposite to earlier analyses. In the gas phase, the major reaction channel is to return to the ground state within about 100 fs by passing through an ethylene-type conical intersection (dynamophore). For all molecules, a competitive reaction channel was found. For n = 6 (cyclohexa-1,3-diene), the alternative pathway is most pronounced and leads to the well-known ring opening to form hexatriene. For this molecule, we also found the fastest dynamics which slowed down toward smaller and larger ring sizes from (70 ± 20) to (130 ± 20) fs for cyclo-1,3-octadiene. For n = 5, 7, and 8, we found a [2+2] ring closure leading to a bicyclic complex with a significantly reduced quantum yield as compared to the ring-opening in cyclohexa-1,3-diene.

Nuclear Wave Packet Dynamics in Strong-Field Ionized Iodomethane Studied by Coincident Ion Momentum Imaging

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Iodomethane (CH_3I) is a prototypical polyatomic system with well-studied photodissociation dynamics that has recently been used, e.g., to test novel quantum control schemes via light-induced conical intersections [1] and to investigate charge transfer processes after X-ray absorption [2]. These applications require a detailed understanding of the CH_3I fragmentation mechanisms by short, intense laser pulses. Here we present the results of a time-resolved Coulomb explosion imaging experiment that maps the dynamics of both bound and dissociating nuclear wave packets in singly and doubly charged ionic states of CH_3I. Measuring kinetic energies and emission angles of coincident ionic fragments as a function of time delay between two 25 fs, 800 nm pump and probe pulses, we visualize the propagation of different dissociation pathways, vibrational motion of the molecule and its impulsive alignment. In particular, a periodic (~ 130 fs) feature in the delay-dependent ion energy spectra can be assigned to C-I stretching vibrations in the lowest cationic state. This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

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Study of Molecular Electronic and Rotational Coherences by High-Harmonic Generation: Theory

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Measuring and controlling electronic and nuclear motion is one of the core interests of ultrafast atomic, molecular physics. As recently demonstrated in nitric oxide High-Harmonic Spectroscopy (HHG) is a sensitive tool to unravel coupled electronic spin-orbit and rotational wave-packet dynamics [1,2], that was induced by a Raman scattering of an ultrashort optical pump pulse. The sensitivity of the HHG signal to electronic wave packets stems from a cross channel, that coherently connects strong-field ionization from a specific electronic state to recombination into another electronic state. We treat this process theoretically by a generalized density matrix approach [3] that describes the pump process on the level of the rotational Hamiltonian of the system. For the probe process, the density matrix is extended by the electronic degrees of freedom and a semiclassical quantitative rescattering approach was applied to determine pump-probe HHG spectra. The theory allows for quantitative comparison with the experimental results and a detailed analysis of the influence of the different tensorial components of the Raman scattering to the coupled electronic rotational wave packet. Results for parallel and perpendicular linear polarizations of the pump and probe laser pulses will be presented, together with an analysis of the combined rotational-electronic density matrix in terms of irreducible components, which facilitates interpretation of the results.

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Femtosecond Nonlinear Resonant Auger Spectroscopy

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Ultrashort intense x-ray pulses available from X-ray Free-Electron Laser (XFELs) allow the study of nonlinear optical processes in a variety of systems, ranging from atoms and molecules in the gas phase to solids. A potentially promising new nonlinear all x-ray technique is based on a sequence of stimulated electronic x-ray Raman scattering processes close to resonant transitions [1]. The extremely small Raman scattering cross section in the x-ray domain will, however, make it extremely challenging to detect coherent Raman scattering signals by homodyne or heterodyne detection, that are usually applied in the visible spectral domain. Here we propose to read out coherent signals by Auger-electron spectroscopy and present a case study for the CO molecule. An ultrashort weak pump pulse resonantly creates the core excited ($1s\text{-}1\pi^*$) vibrational states that are coupled to valence excited vibrational states by a second ultrashort x-ray pulse. The second pulse is strong and can induce a complete Rabi cycle back to the core-excited vibrational state manifold. By changing the time delays between the two x-ray pulses, one can effectively change the vibrational dynamics on the core-excited manifold, which is manifested in a change of the Auger-electron spectra. We present a comparison of the one dimensional Auger spectra to the optical nonlinear response functions and the pros and cons of both methods will be assessed for this simple model system.

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Electron Pulse Compression with Radio Frequency for Ultrafast Electron Diffraction

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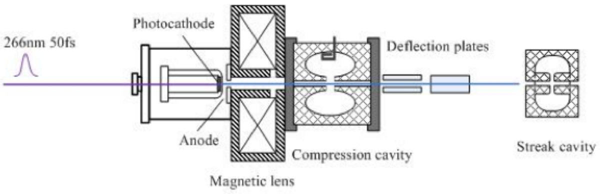
Ultrafast electron diffraction (UED) technique, which is equipped with both the high temporal resolution of femtosecond laser and the high spatial resolution of electron diffraction, can provide an effective approach to study the structural change of matter in atomic scale [1]. Space - charge forces in multi-electron packet largely broaden the pulse duration [2], thus limiting the temporal resolution of the bright pulse with many electrons. We demonstrate the duration of an electron bunch with 1.0×10^5 electrons per pulse can be maximally compressed to 500fs by means of the oscillatory electric field of a 3.2 GHz radio-frequency cavity[3], which imposes a linear velocity chip inversely to the broaden effect on the electrons.



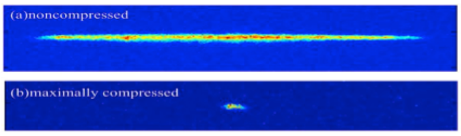


Fig.1 Schematic of electron gun Fig.2 Streak of (a)an uncompressed and (b) a maximally compressed bunch with 1×10^5 electrons

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Ultrafast Electron Diffraction on nano-crystalline Graphene

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In carbon layered materials (graphite, graphene or carbon nanotubes) the electronic subsystem, stimulated by high currents or optical excitations, is strongly coupled to a small set of optical phonons which limits the ballistic conductance. A detailed understanding of phonon decay mechanism is thus essential in improving the performance of carbon based future electronic devices [1,2]. Time-resolved diffraction experiments using x-rays or electrons probes, has become a promising technique to directly provide insights into fundamental dynamics in solids at the microscopic level and on the pico- to subpicosecond timescale [3,4]. In this contribution we present results on photo-induced structural dynamics in single layer nano-crystalline graphene [5] obtained with our compact and well characterized Ultrafast Electron Diffraction setup [6] and discuss the influence of the main structural properties for our results [7].

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Valence-Shell-Photoelectron Imaging of Controlled Biomolecules

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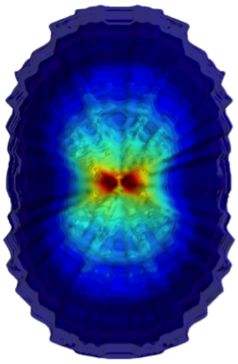
A molecule's chemical behavior is governed by its electronic properties. Thus, a view at the evolution of the involved molecular orbitals during a reaction lures with insight into the fundamentals of chemistry. In our experiments molecules are investigated by means of photoelectron imaging. State-selected molecular ensembles are laser aligned or mixed-field oriented inside a velocity map imaging spectrometer [1, 2]. The resulting velocity maps display the projected three-dimensional distributions of both, the photoelectrons' kinetic energy and their release angle, in the molecular frame (MFPADs) [3]. MFPADs of various molecules will be presented, which were obtained through tomographic reconstruction of the projected 2D images. These experimentally obtained MFPADs will be discussed using two different theoretical models, i.e., first, an approach based on strong-field approximation and, second, a computational advance employing time-dependent density functional theory.



Reconstructed MFPAD of Indole ionized with linearly polarized light

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Single Shot Mapping Atomic Motions Based on Space-Time Correlation

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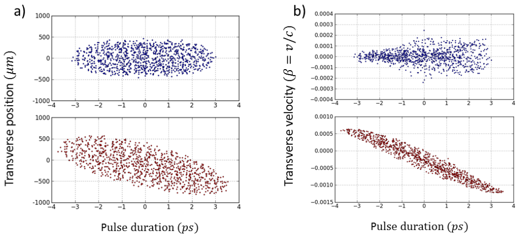
A major challenge in time-resolved electron diffraction is acquiring sufficient time resolution [1]. One can transversely streak the electrons after diffraction to determine arrival time of electrons via a streak camera, thus time-stamping the diffraction spots and improving time resolution [2]. Conventional streak cameras use a time gradient electric field that streaks the electrons based on arrival time [2]. However, this requires active synchronization between the electron pulse arrival and triggering of the electric field, limiting the maximum achievable time resolution. Here we present an alternative method that uses passive uniform magnetic and electric field for velocity-dependent streaking of electrons. We show the effectiveness of this method through simulations from particle tracking software (General Particle Tracer) [3] and by analyzing equations of motion. This approach provides an extremely robust solution that increases the effective source brightness by two orders of magnitude, to provide full movie mode capabilities for atomically resolved structural dynamics in a single shot with time resolution expected to be 300 fs, limited only by the camera spatial point spread function.



GPT simulation of Wien field streaking. a) Cross-sectional side view of electron bunch before (top) and after (bottom) streaking. b) Transverse velocity vs temporal position of electron bunch before (top) and after streaking (bottom).

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Femtosecond Electron Diffraction Study of the Spin Crossover Dynamics of Single Crystal Fe(PM-AzA)$_2$(NCS)$_2$

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Spin crossover (SCO) molecules undergo a reversible conversion from low spin (LS) ground state to high spin (HS) excited state due to temperature change, light absorption, etc. [1,2]. For Fe(II)(3d^6) compounds, the LS $^1A_1(t_{2g}{}^6)$ ground state switches to the HS $^5T_2(t_{2g}{}^4 e_g{}^2)$ excited state, and the Fe-N bond distance in the HS state is elongated by ~0.2 Å because of the transfer of two electrons to the antibonding e_g orbital and loss of π-backbonding from the t_{2g} orbital [2]. Here, we use Femtosecond Electron Diffraction (FED) to study the structural dynamics of single crystal Fe(PM-AzA)$_2$(NCS)$_2$ [3]. Within the present time resolution, we observe structural dynamics that are in effectively perfect agreement with optical studies [4]. There appears to be a faster initial relaxation phase that is currently under study with finer time steps. Changes in diffraction intensities, followed with 100 fs time steps, gave fully resolved time constants for the nuclear displacements of 2 ps that are effectively in perfect agreement with transient optical studies of the spin cross over dynamics and the structural changes correlate with that expected from the thermal spin crossover [5].

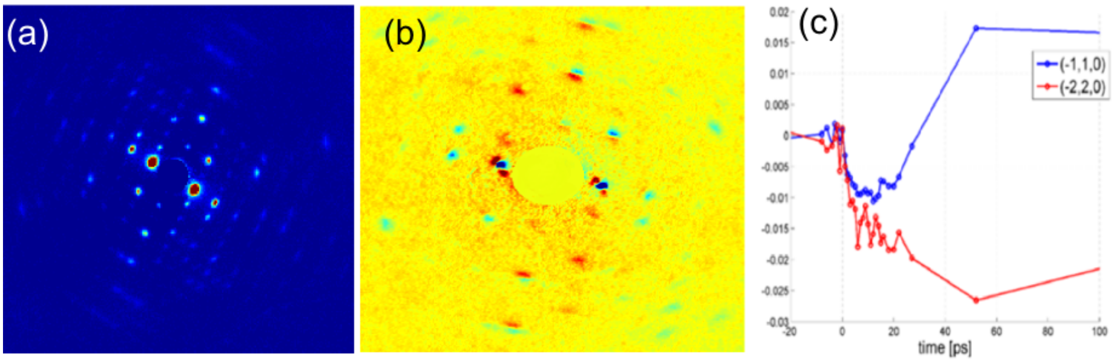

Figure 1. a) Electron diffraction pattern in 170 K, b) Time resolved intensity change, c) relative intensity change [5].

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Diffraction effects in the Recoil-Frame Photoelectron Angular Distributions of Halomethanes

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Synopsis We have measured the Recoil Frame - Photoelectron Angular Distributions (RF-PADs) for inner-shell photoionization of CH_3F, CH_3I and CF_3I halomethane molecules for photoelectron energies up to 300 eV detected within a 4 solid angle in the gas-phase. For high kinetic energies, the RF-PADs are dominated by diffraction effects that encode information on the molecular geometry. Recoil frame - photoelectron angular distributions supply deep insights into the molecular photoionization process and provide access to an unparalleled level of detailed information such as phases of photoelectron waves [1, 2], localization of core holes [3], and double- slit interference [4, 5]. RF-PADs can also be interpreted in terms of photoelectron diffraction [6, 7] and direct information on the geometric and electronic structure of the molecule can be obtained, e.g., by comparing the measured diffraction patterns and RF-PADs to single and multiple scattering calculations [8, 9, 10, 11, 12]. For high kinetic energies of 50eV and above, the RF-PADs contain diffraction effects that encode information on the molecular geometry in the RF- PADs. In order to illustrate this in more detail, we are comparing our experimental results to single and multiple scattering calculations similar to those used in earlier studies [10, 11, 12] and to DFT calculations [13, 14].

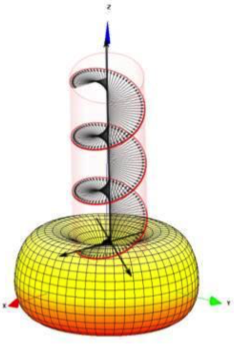

Figure 1: RF-PADs after F(1s) photoionization of CH3F at 875eV photon energy, i.e. 180eV photoelectron energy. Light propagation axis and molecular F-C axis are parallel.

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A testing platform for coherent imaging with ultrabright electron pulses

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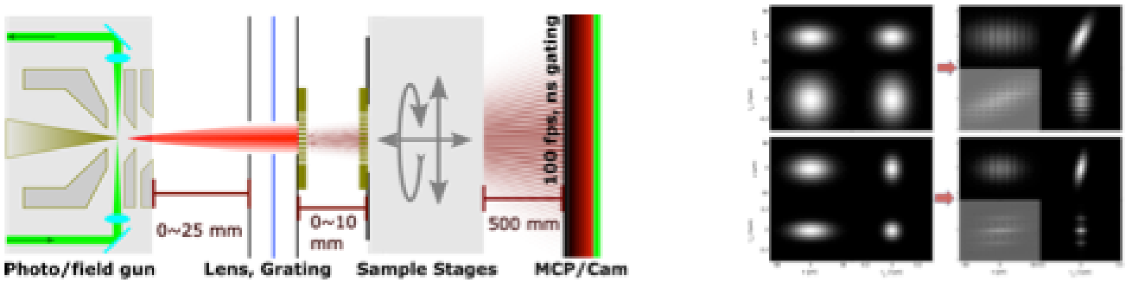
High-brightness electron pulses as an ideal probe for structural dynamics are employed in a variety of experimental schemes spanning orders of magnitude in their accessible spatial and temporal scales, from mapping atomic motions driving phase transitions1 to real-space movies on the nano scale2. Further extending this scope – in particular into the realm of complex and fragile biomolecules – will require improvement of electron sources in terms of current and coherence, as well as exploration of coherent imaging techniques that maximize the information gathered from each scattered particle. In this contribution, we will present a new 12 keV electron beam apparatus, designed for characterization of pulsed electron sources, as well as proof-of-principle demonstrations of coherent diffractive imaging schemes. As a first test sample, a grating interferometer is placed in the electron beam. The resulting near-field (Talbot) and far-field (Lau) fringes will allow directly measuring the coherent brightness on the sample3, as well as characterizing the impact of Coulomb interaction on the information stored in the electron wave. Sources to be studied will comprise optically and electrically gated field emitters with or without thermionic enhancement, as well as fiber- and nanotube-based emitters4,5.



Left: Sketch of the interferometer beam line. Right: Wigner phase space distributions for different initial beams (top/bottom) at source (left) and after gratings (right)

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Time-Resolved Serial Femtosecond Crystallography based on a Solid Target Crystallography Chip

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Novel ultrabright x-ray sources such as the LCLS allow for a detailed study of molecular structures with the highest spatial and temporal resolution, enabling the experimental study of ultrafast protein dynamics on the atomic level. Current experiments with protein samples are performed with nano- and microcrystals due to radiation damage from the high intensity x-ray pulses. Crystallography using these small crystals is carried out in a serial approach (known as Serial Femtosecond Crystallography, SFX), requiring a steady supply of samples. We report here on a novel approach for the delivery of crystalline protein samples using a solid target. A crystallography chip has been developed to implement rapid and reliable access to individual crystalline samples [1]. This crystallography chip contains 10^4 features to trap protein crystals and is fabricated from silicon. The crystals are trapped in place and can be hit individually. The precision of the microfabrication process minimizes the positioning error, making this approach far more accurate compared to competitive methods, like using a liquid jet. Furthermore, it is possible to take reference data of the same crystal in a time-resolved experiment. Crystals trapped in the chip are mapped using a homebuilt absorption spectrometer. Mapping the positions on the chip which are loaded with crystals enhances the hit rate to approximately 90%. This crystallography chip has been successfully used for studying time resolved structural dynamics of carboxylated myoglobin recently at the LCLS. The resulting data suggests that the crystallography chip is well-suited and promising for time-resolved SFX experiments.

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Few-cycle phase effects in atoms/molecules; steps toward Laser Induced Electron Diffraction

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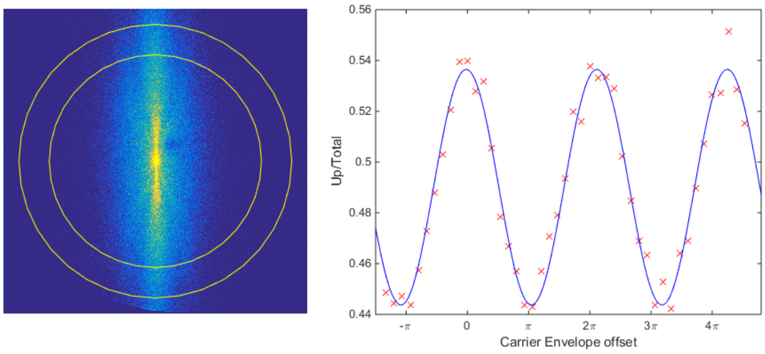
Using a recently established few-cycle mid-IR ultrafast laser source, based on [1], we present carrier envelope phase effects measured on both atoms (argon) and molecules (naphthalene and carbonyl sulfide). The atom/molecules are strong-field ionized using a 1850nm, <12fs laser pulse characterized by a dispersion-free SHG-FROG. The resulting ions/electrons are mapped onto a MCP using a VMI spectrometer and the ratio of up/total electrons are measured as a function of the carrier envelope phase and a variation of 10% is observed. The carrier envelope phase offset is under full control and monitored with a f-2f interferometer. The next step is to adiabatically align/orient the molecules using a Nd:YAG laser. The long wavelength and short duration of the mid-IR beam places the ionization in the tunnel regime and due to the large ponderemotive energy the electrons will obtain wavelengths shorter than the intermolecular distances thereby opening possibilities for ultrafast structural studies using laser induced electron diffraction.



Left: VMI image of electron distribution for a carrier envelope offset of 0. Right: Up/total amount of electrons extracted from region as shown on the VMI image to the left as a function of the carrier envelope offset.

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Molecular dynamics traced with single-shot Autocorrelation in the VUV

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For the investigation of atomic and molecular dynamics on the sub 10 fs time scale a combined single-shot autocorrelation pump-probe experiment in the VUV is presented. The scheme is based on wave-front splitting and a colliding pulse geometry, thus mapping the temporal delay onto a spatial coordinate. A high harmonic source with a spectral range from the ultraviolet to the extreme ultraviolet provides the pump and probe pulses for the experiment [1, 2]. The 5^{th} harmonic of the Ti:Sa laser at 161.8 nm is selected as single-color pump and probe pulses. While the instantaneous two-photon ionization of atomic Kr and Xe gas targets yields the 2^{nd} order autocorrelation of the pulse, the dynamics of photo reactions, such as the VUV-induced dissociation of O_2 or H_2O with time constants below 10 fs, are accessible.

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Collinear two-dimensional spectroscopy via fluorescence detection with rapid phase cycling

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Coherent multidimensional spectroscopy is a powerful tool to study electronic couplings and coherences of molecular systems. We present a novel all-collinear setup to perform pulse-shaper-assisted two-dimensional electronic spectroscopy with fluorescence detection. The pulse shaper (Dazzler, Fastlite) allows the variation of the interpulse delays and their relative phases with 1 kHz rate, enabling a rapid scan and shot-to-shot 27-fold phase cycling. We show preliminary data of a 4-pulse excitation of cresyl violet in the liquid phase. Rephasing and non-rephasing contributions can be extracted from one single measurement session via phase cycling [1].

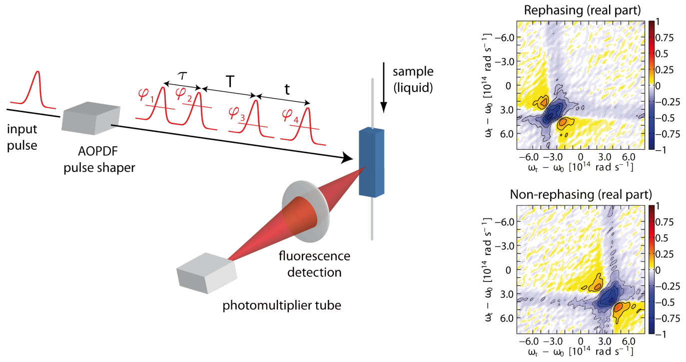

Figure: Pulse-shaper-assisted multidimensional spectroscopy in collinear geometry. The response of the molecule under study to the multi-pulse excitation is obtained via fluorescence detection.

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Ultrafast charge-transfer of a valence double-hole in glycine driven by nuclear motion

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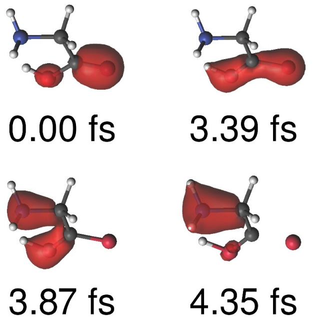
We theoretically investigate the hole transfer dynamics in doubly ionized glycine after Auger decay. The hole dynamics starts from electronic states with two electron holes localized in the same valence orbital, namely $O(2s^{-2})$ or $N(2s^{-2})$. We find that the two holes can redistribute within less than five femtoseconds from the carboxyl to the amino group driven exclusively by small atomic displacements of the carboxyl group and in complete absence of electronic coherence between the electronic states involved, in contrast to hole-migration mechanisms involving electronic wavepackets [1,2]. The preparation and probing of these charge dynamics can be accomplished with ultrashort x-ray pulses and electron-ion coincidence measurements at XFELs [3].



Snapshots of the positive charge density in di-cationic glycine following ionization from one of the O1s orbitals and the subsequent Auger decay. Initially the two positive charges are localized in the COO group and later evolve towards the NH$_2$ group.

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Standoff explosives trace detection and imaging by selective stimulated Raman scattering

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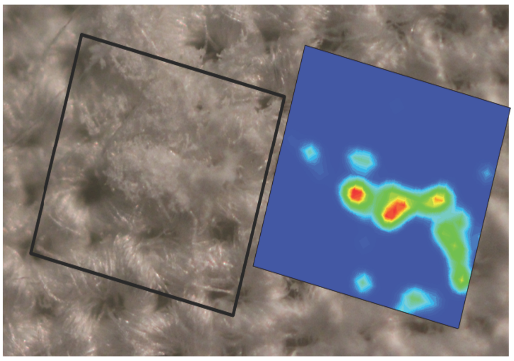
We introduce a sensitive method for laser based standoff detection of chemicals based on stimulated Raman scattering [1]. Selective excitation of a particular Raman transition is detected by measuring the diffusely reflected laser light from a distant surface. The method simultaneously measures stimulated Raman loss and gain within a single laser shot and is insensitive to the optical properties (reflectivity/absorptivity) of the substrate. We demonstrate the specificity and sensitivity by detecting and imaging nanogram explosives microcrystals on paper, fabric, and plastic substrates at 7 to 10 m standoff distance using only 10 mW of laser power from a single broadband femtosecond laser.



Standoff SRS images of RDX (cyclotrimethylenetrinitramine) on cotton. With 20 laser shots per pixel in the 30x30 images, the distribution of the explosive is recorded by observing SRL. Statistics were used to eliminate points less than 0.8 standard deviations of the mean above zero. Signal was collected at 7.5 m standoff distance. Inset shows the distribution of RDX micro-particles within the inscribed square.

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Femtosecond Nanoplasmonic Dephasing of Individual Silver Nanoparticles and Small Clusters

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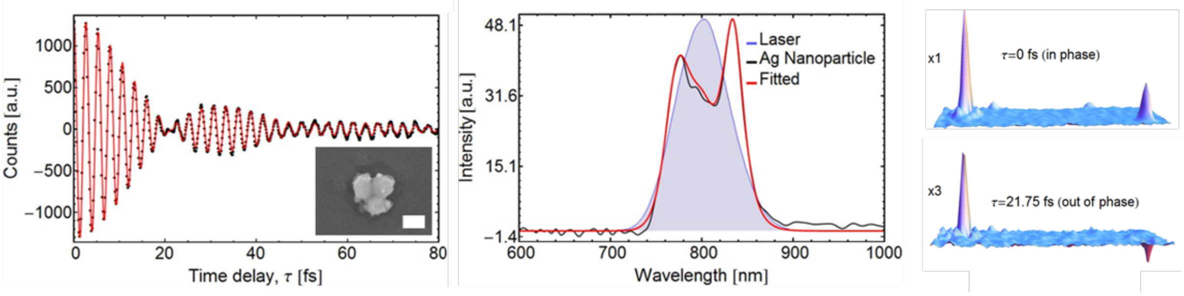
We present experimental measurements of localized surface plasmon (LSP) emission from individual silver nanoparticles and small clusters via accurately delayed femtosecond laser pulses [1]. Fourier transform analysis of the nanoplasmonic coherence oscillations reveals different frequency components and dephasing rates for each nanoparticle or small cluster. We find three different types of behavior: single exponential decay, beating between two frequencies, and beating among three or more frequencies. Our results provide insight into inhomogeneous and homogenous broadening mechanisms in nanoplasmonic spectroscopy that depend on morphology and nearby neighbors. In addition, we find the optical response of certain pairs of nanoparticles to be at least an order of magnitude more intense than the response of single particles. Our measurements track the linear response unlike previous measurements based on second harmonic [2,3], or photoelectron detection [4].



Plasmonic response of a three silver nanoparticle cluster (SEM image with 100nm scale bar) in the time and frequency domains. Shown in the frequency domain is the FT (black), the fit (red), and the laser spectrum (shaded in blue). The 3D plots show the plasmonic response from two different particles 18.6 μm apart.

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Quantifying noise in ultrafast laser sources and its effect on nonlinear applications

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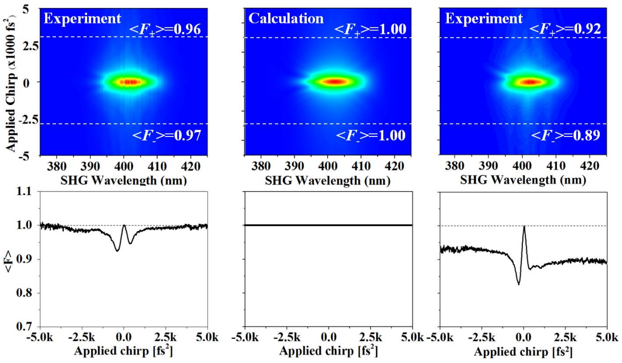
Nonlinear optical applications depend on pulse duration and coherence of the laser pulses. Characterization of high-repetition rate pulsed laser sources can be complicated by their pulse-to-pulse instabilities. Here, we introduce and demonstrate experimentally a quantitative measurement that can be used to determine the pulse-to-pulse fidelity of ultrafast laser sources [1]. The method relies on the effect of linear chirp on the laser source. Numerical simulations and experiments on titanium sapphire and Yb-fiber lasers illustrate the effect of spectral phase and amplitude noise on second and third harmonic generation. We will also show how the fidelity measurement can also be used to identify pre-/post-pulses in amplified laser sources.



Experimental 2D MIIPS trace for a titanium sapphire oscillator producing 27.5fs pulses (left), and the corresponding calculated MIIPS trace assuming perfect coherence (middle). (Right) Experimental 2D MIIPS trace for the same laser with destabilized temperature control. Bottom, fidelity curves based on integrated SHG intensity corresponding to each case above.

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Theoretical and experimental studies of femtosecond CARS quantum beat

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The quantum beats are often observed in the femtosecond time-resolved coherent anti-Stokes Raman spectroscopy. In this paper, we present theoretical expression of quantum beats and discuss the effects of vibrational mode parameters on quantum beats. The effects of nonresonant background on the performance of the quantum beats are discussed as well. It is the conclusion that the bigger the nonresonant background is, the smaller the signal to noise ratio in the fast Fourier transform power spectrum of the quantum beats signal will be. If the quantum beats in time domain are Fourier transformed with a little or little nonresonant background, the signal to noise ratio in the fast Fourier transform power spectrum of the quantum beats signal will be enhanced. In our simulation, the effects of different ranges in time-domain quantum beats signal on Fourier transformation were discussed. The best range of time-domain quantum beats signal was obtained, which is used to analyze our experimental results of BBO crystal and PMMA sheet.

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From Photophysics to Photochemistry: Ultrafast Hydrogen Atom Abstraction Inside A Self-assembled Nanocage

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Photosystem II (PSII) has evolved to carry out visible light-initiated multi-electron catalysis within its protein matrix. A specialized set of chromophores, arranged spatially in the protein matrix, achieve kinetic stabilization of photogenerated redox intermediates thereby lowering the rate of charge recombination. In order to mimic the process of intermediate stabilization carried out by PSII, we used a water soluble electron deficient Pd_6L_4-nanocage[1] to host water insoluble photoreactive aromatic amines[2]. Upon incarceration of the amine, a charge transfer (CT) band due to donor-acceptor interaction arises in the visible region. Upon photoexcitation at the CT band, an ultrafast hydrogen atom abstraction occurs with >80% quantum yield through a stepwise proton-coupled electron transfer (PCET) reaction within ~900 fs. The phenoxyl photo-intermediate generated inside the nanocage is kinetically stabilized till diffusion timescales (>10 ns) thereby providing an opportunity to use this new paradigm for visible-light induced photocatalysis from the singlet manifold.

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Modeling ultrafast exciton deactivation in organic photovoltaic materials.

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The understanding of the electronic structure at the D/A interface and exciton deactivation in organic materials, plays key role in organic photovoltaics.[1] Accurate predictions of D/A electronic structure, ultrafast relaxation and charge transfer mechanisms, are as much valued as urgent. We investigate these aspects adopting DFT calculations and nonadiabatic excited states dynamics. Excited states of D/A blends (Figure 1a) are computed and classified. The size of D/A molecular clusters affect the interplay between charge transfer vs. localized states, and their spatial delocalization. Exciton relaxation dynamics and charge transfer processes are investigated in a series of oligothiophenes. Photorelaxation is modeled *via* TD-DFT and TDA nonadiabatic surface hopping, considering single molecules and aggregates. We predict exciton localization and ultrafast charge transfer mechanisms within 150 fs, in perfect agreement with the experimental data.[2]

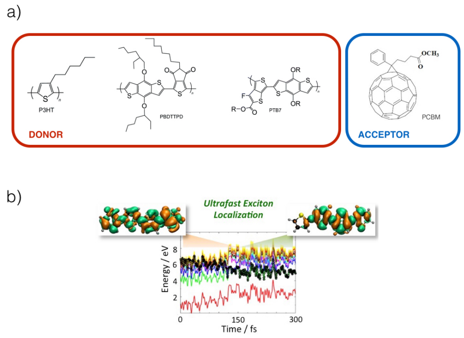

Figure 1: a) donor/acceptor organic materials for OPV applications. b) Ultrafast exciton localization in oligothiophene computed via TDDFT surface hopping methods.

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Exciton Dissociation in Ordered Donor-Acceptor Assemblies

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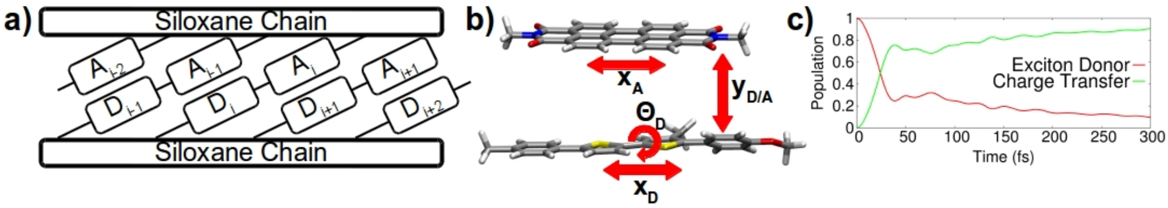
We present electronic structure and quantum dynamical studies of novel thiophene-perylenediimide donor-acceptor (DA) systems that are prospective precursors for a new class of organic solar cells [1]. As revealed by time resolved spectroscopy, smectic liquid crystalline (LC) phases show the formation of charge transfer states on a sub-100 femtosecond timescale, followed by rapid recombination. To explain these observations, we use a theoretical approach combining (i) a site-based vibronic coupling Hamiltonian, (ii) Time-Dependent Density Functional Theory (TDDFT) calculations on an isolated DA system [2] as well as selected D_n and A_n fragments, and (iii) quantum dynamical calculations employing the Multilayer Multi-Configurational Time-Dependent Hartree (ML-MCTDH) approach [3].



a) Sketch of the investigated LC phase. b) Molecular structures of the D and A units with the relevant modes used in our quantum dynamics simulations. c) Population plot of the excitonic and charge transfer states.

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Short-time dynamics at a conical intersection in high-harmonic spectroscopy

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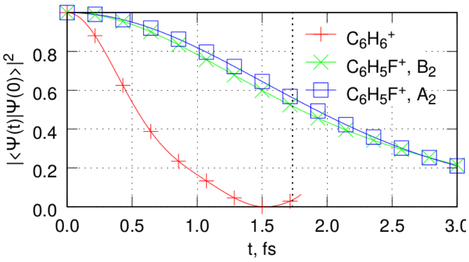
High-harmonic spectroscopy probes molecular dynamics using electrons liberated from the same molecule earlier in the laser cycle. It affords sub-Ångstrom spatial and sub-femtosecond temporal resolution. Nuclear dynamics in the intermediate cation influence the spectrum of the emitted high harmonic photons through autocorrelation function. Recently, we developed an analytical approach for computing short-time nuclear autocorrelation functions in the vicinity of conical intersections, including laser-induced and non-adiabatic coupling between the surfaces[1]. We apply the technique to two molecules of current experimental interest C_6H_6 and C_6H_5F. In both molecules, high-harmonics generated within the the same electronic channel are not sensitive to non-adiabatic dynamics, even in the presence of substantial population transfer. Calculated autocorrelation functions exhibit significant deviations from the expected Gaussian decay, and may undergo revivals at short (1.5 fs) times. The associated phase of the nuclear wavepacket provides a possible experimental signature.



Autocorrelation decay in C_6H_6 and C_6H_5F.

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Accurate, efficient, and simple implementation of 1-electron TDSE in spherical coordinates

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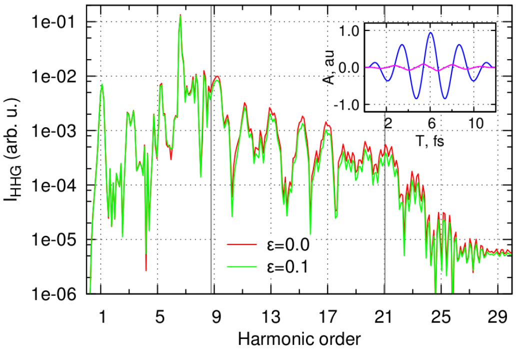
Modelling atomic processes in intense laser fields often relies on solving time-dependent Schroedinger equation. For processes involving ionization, such as above-threshold ionization (ATI) and high-harmonics generation (HHG), this is a formidable task even if only one electron is active. I present a computationally efficient, yet highly accurate implementation of the atomic time-dependent Schrödinger equation. The code is based on several ideas introduced by H.G. Muller some time ago [1]. The TDSE is propagated in a non-inertial reference frame, chosen such that the vector-potential of the laser field remains parallel to the local Z axis. The Hamiltonian is split into many individual terms. Each of these terms can be implemented in a linear-scaling fashion. By carefully combining the forward [1 - i H k dt] and inverse $[(1+ \mathrm{i\,H\,k\,dt})^{-1}]$ parts of the Crank-Nicholson's propagator for each term, one obtains a stable, time-reversible overall propagator. Implicit representation of the derivative operators allows highly-accurate numerical results, without sacrificing numerical efficiency or employing unduly-dense radial grids. The accuracy and efficiency of the implicit representation of the derivative operators come at the cost of making the overall Hamiltonian matrix non-Hermitian, with the non-Hermiticity becoming prominent for non-uniform grids. As the result, both the left and right wavefunctions are required to evaluate the observables, and must be propagated explicitly.



High-harmonic spectrum of H atom (1s initial state) driven by 800 nm, 4.8 fs FWHM, 10^{14} *W cm*$^{-2}$ *light. Red: linear polarization (run time: 5 min). Green: Elliptical polarization (run time: 40 min).*

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Second order interferometric gas-phase autocorrelation in the VUV

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We demonstrate a Michelson-type all-reflective interferometric autocorrelator in the VUV realized with two moveable interdigitated reflective gratings. An imaging time-of-flight spectrometer is used for separating ions formed in different diffraction orders in the focal plane. In the setup, 18 fs VUV pulses centered at 161.8 nm are created in a variable-length gas cell driven by a Ti:Sa laser and selected for non-resonant two-photon ionization processes of Kr atoms [1,2]. With the fringe-resolved 2nd order autocorrelation the pulse duration of the VUV pulses was determined, since the 2nd order autocorrelation yields information about the temporal phase. With well-characterized VUV pulses, photo-reaction dynamics of molecular gas targets like O_2 and C_2H_4 were studied.

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Bimolecular reactions on the fs- to μs-timescale

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We investigate nucleophilic substitution reactions of a photo-generated highly reactive carbocation intermediate that can react with nucleophiles like alcohols or amines. The carbocation is generated on a 300 fs time scale by UV absorption of diphenylmethylchloride or on a low ps time scale for a phosphonium leaving group. A fs-pump-probe setup [1] is used to measure the ultrafast reaction of the cations. Usually, the intrinsic speed of a bimolecular reaction in diluted solutions is masked by the diffusion limit. To study the "real" reaction rate the precursor is dissolved in a pure nucleophile as the solvent. Depending on the reactivity of the nucleophile and the cation, the reaction time varies from a few hundred ps down to a few hundred fs. This is much faster than the diffusion limit and on the order of rotational relaxation times. For the pump-probe measurements on the ns- to μs-timescale we use a tunable ns-laser system which is synchronized with the probe pulse and can be electronically delayed. This setup is used to measure the cation reaction in solvent mixtures of a non-reactive and a reactive solvent. We observe a linear increase with the reactant concentration. That hints to a statistical diffusional encounter and not to a specific solute-solvent interaction like selective solvation. The different time regimes therefore provide insight into the reaction dynamics as well as the solvent environment.

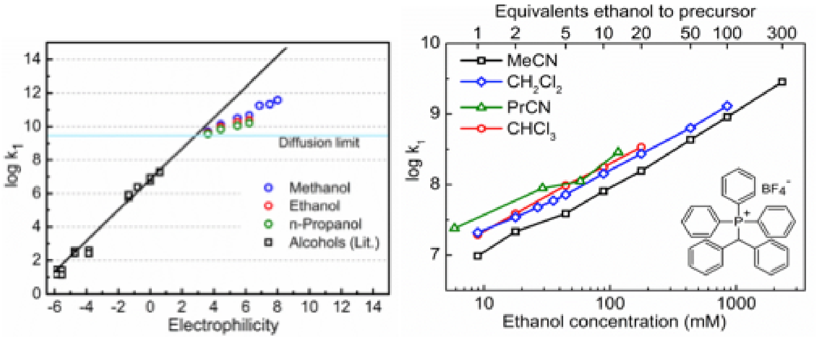

Figure1: (left) Reaction rates for the bimolecular reaction on the fs-timescale (see [2] for lit. values). (right) Reaction rates in solvent mixtures on the ns-timescale

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Detection-energy dependence of coherent phonon signal considering material group velocity dispersion.

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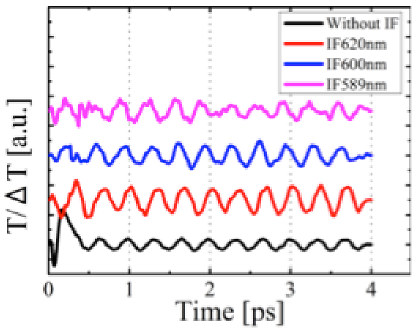
Pump-probe technique has been used to investigate the dynamics of coherent atomic vibration in many molecules or solids. In transparent media, such vibrations change a refractive index, which causes a spectral modulation in the probe pulse. Therefore signal amplitude increases by filtering a part of probe spectra [1, 2]. Conversely, if probe spectra are not filtered, the signal should be weak in the case of no group velocity dispersion (GVD) of media and no chirp of the probe pulse. However, in many studies, coherent phonons were observed without filtering techniques. For a deep understanding of the coherent phonon properties, the effects of GVD and chirp on the signals should be clarified. In this study, we used a ZnO single crystal as a large GVD medium and investigated spectral filtering effect of the probe pulse in coherent phonon detection (Fig. 1). The detection-energy dependence of the phase of the coherent phonon signal was measured by changing interference filters (IF) in front of the detector. We have succeeded in explaining the observed phase change of the probe pulses using a model including GVD and chirp, as shown in Fig. 2. Details will be shown in the presentation.



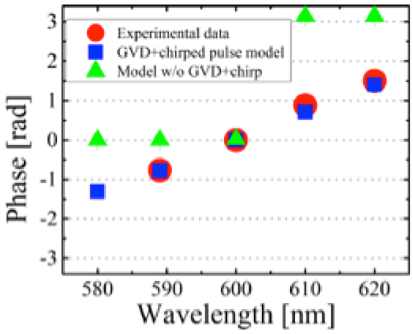


Fig. 1 (Left) Filtered-spectrum dependence of coherent phonon signal in ZnO. The probe central wavelength is 600nm. Fig. 2 (Right) Detected wavelength dependence of the phase of the coherent phonon signal. Circles: experiments, Squares and triangles: calculations

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Field Emission Beam Characteristics and Collimation Property of a Double-Gate Single Nanoemitter

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Double gate metal nano-tips combining the extremely high beam brightness of field emission with the capability of beam collimation and enhancing the tip-laser coupling by on-chip electrodes have been studied intensively for high current and high brightness applications such as free electron lasers and THz vacuum electronic devices. While previous works focused on array characteristics, exploring intrinsic brightness and coherent characteristics of single emitters is important fundamentally as well as for applications that demand ultrabright and ultrafast electron sources such as time-resolved electron diffraction study of protein crystals. Therefore, in this work, we study the field emission characteristics of a molybdenum single nanotip, which was fabricated by the same method as the previously reported 40,000-tip array device. We prepared two single emitter devices, both of which are equipped with a stacked on-chip extraction G_{ext} and collimation G_{col} gate aperture but possess different structural features in terms of size, shape, and alignment of the apertures. Our results suggested that a high shielding structure and a good alignment between G_{ext} and G_{col} aperture are the major factors for the excellent collimation capability of the device with minimal loss of emission current. We will discuss the results in detail in the meeting.

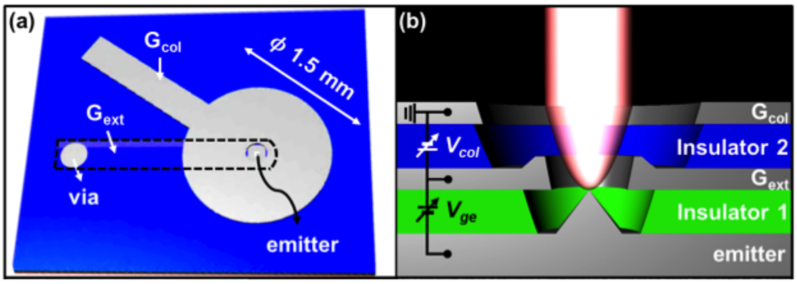

Figure 1. (a) Top-view and (b) cross-sectional-view schematic diagram of the double-gate single nanotip emitter device.

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Optical focusing of isolated particles for diffractive imaging experiments

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The short, intense, and coherent x-ray pulses produced by x-ray free-electron lasers (XFELs) have the potential for major advances in macromolecular structure determination. Serial femtosecond crystallography (SFX) is among the most successful emerging new paradigms. It consists of directing a stream of randomly oriented protein microcrystals across the focus of the XFEL beam. Three-dimensional electron density maps can be constructed from exposures of many identical crystals at room temperature. Efforts are underway to extend this approach such that high-resolution structures can be determined from isolated molecules, multi-protein complexes, viruses or cells without the need for growing well-ordered crystals (often the principal bottleneck to structure determination). However, delivering these nanoparticles to a sub-micrometer x-ray focus at higher efficiency and hit rate remains a considerable challenge. Current sample delivery efficiencies (fraction of particles that are intercepted by an x-ray pulse) for single-particle imaging based on aerodynamic-lens systems are on the order of 10^{-7} on average, which renders experiments infeasible for samples that cannot be obtained in high abundance. In order to confront this challenge, we are developing techniques for guiding aerosolized nanoparticles to the X-ray focus with specially shaped laser illumination [1, 2]. Our current experiments aim at transversely confining streams of aerosolized particles as they exit an aerosol injector [3] with a counter-propagating "hollow" quasi-Bessel beam. The experiment exploits radiation pressure and thermal (photophoretic) forces arising from the interaction of the particles with surrounding gas molecules. [1] Eckerskorn, Li, Kirian, Küpper, DePonte, Krolikowski, Lee, Chapman, Rode, *Opt. Express* 21, 30492-30499 (2013).

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Femtosecond to nanosecond dynamics of 2,2′-bipyridine-3,3′-diol inside the nano-cavities of molecular containers

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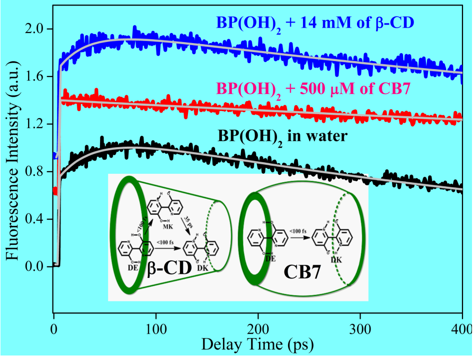
Molecules exhibiting excited state intramolecular proton transfer (ESIPT) have received lot of interest owing to their current cutting-edge applications in science, such as molecular probes, logic gates and light-emitting diodes.[1] Among them, [2,2′-bipyridyl]-3,3′-diol ($BP(OH)_2$) is of special interest, since it contains two protons, which can involve in double proton transfer (ESIDPT) process.[2] The ESIDPT can be concerted directly from dienol (DE) to diketo (DK) and/or sequential via monoketo (MK). In this work, femtosecond fluorescence measurements are employed to elucidate the mechanism of ultrafast double proton transfer dynamics of $BP(OH)_2$ inside molecular containers (cucurbit[7]uril (CB7) and β-cyclodextrin (β-CD)). The up-converted signals of $BP(OH)_2$ in water consist of growth followed by a long decay component of a two-step sequential proton transfer process of $BP(OH)_2$ in water. Surprisingly, inside the CB7 nano-cavity diol does not exhibit any growth component characteristic of a two-step sequential process. Meanwhile, presence of growth component inside the nano-cavity of β-CD, infers the presence of a two-step sequential process inside the β-CD nano-cavity. The different PT dynamics of $BP(OH)_2$ in two macrocyclic hosts may be attributed to the presence and absence of water solvation network inside the nano-cavities of β-CD and CB7, respectively.



Fluorescence decays of $BP(OH)_2$ in water, CB7 and β-CD (λ_{ex} = 380 nm: λ_{ob} = 465 nm).

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Ultrafast Energy Transfer from Solvent to Solute induced by Sub-ps Highly Intense THz Pulses

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Temperature-jump (T-jump) experiments in liquid water have a long history in the study of chemical kinetics. With the advent of femtosecond lasers a couple of decades ago, ultrafast T-jump experiments became possible and have since been used to study the very fast kinetics of fundamental steps in chemical reactions and many aspects of the hydrogen bond (H-bond) dynamics as well as energy transfer in liquid water. A widely used technique for T-jumps in water is to target the O-H vibrational mode of liquid water at about 3400 cm^{-1} with an infrared (IR) laser, thus providing T-jumps in the nanosecond to femtosecond timescales. T-jump with such methods has been limited to only few tens of K. Here we present a new method to produce T-jump up to ~1000 K in a ps timescale by using a sub-ps highly intense THz pulse and able to create a high temperature and high-pressure liquid environment. Such aqueous environment transfers a large amount of energy to solute molecule. These are insensitive to such THz pulse directly. This THz pump heating mechanism is not mode-selective, which makes it a general technique for T-jump experiments in thermally activated chemical processes.

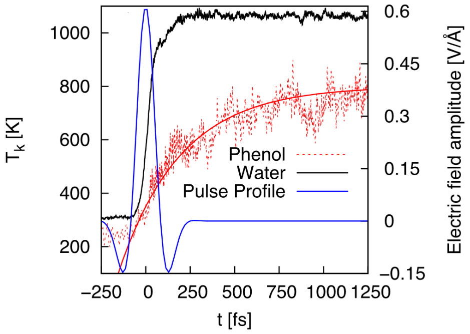

Figure: Kinetic Temperature of water and the dissolved solute (phenol, as an example) molecule. Water molecules gain energy only for the duration of the THz pulse. The solute molecule keeps increasing its temperature after the THz pump pulse.

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Photolysis of peroxynitrite

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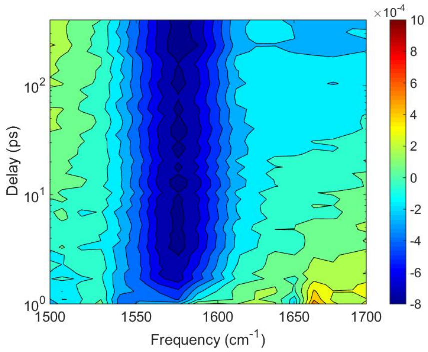
The primary photolysis of aqueous peroxyitrite, $ONOO^-$(aq) is explored by UV-VIS and UV-IR transient absorption spectroscopies. The measurements show that 90 ± 10 % of the photolysed $ONOO^-$ anions remain dissociated for more than the experimental time range of 400 ps. The photolysis products are explored using steady state absorption spectra and electron structure calculations on potential photoproducts in clusters of water molecules. In addition, calculations of all excites states of $ONOO^-$(g) below the excitation energy helps to identify the reaction channels. The dominant reaction channel is $h\nu + ONOO^- \rightarrow O_2^- + NO$.



Contour plot of the transient absorption pertaining to the $ONOO^-$(aq) groundstate at 1574 cm^{-1}. The constant bleaching of the ground state indicates that nearly all photolysed $ONOO^-$ anions remain dissociated after 400 ps.

Water solvation dynamics near hydrophobic groups probed by fs fluorescence Stokes shift measurements

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Hydrophobic solvation dynamics in aqueous solution were obtained by analyzing the time-dependent Stokes shift of fs broadband fluorescence spectra. Specially designed dyes based on the well-established water dynamics probe *N*-methyl-6-oxyquinolinium betaine differ only in the hydrophobic and not in the hydrophilic side of the solute making it possible to assign any difference in environmental response to water molecules in the hydration shell of the hydrophobic groups. The resulting solvation dynamics show a moderate retardation with increasing hydrophobic group, which could be explained by volume exclusion effects. No ice-like enhanced water structures near unpolar groups were monitored.

Ultrafast excited state dynamics of apocarotenals: Identifying the S* state with vibrationally excited molecules in the ground electronic state S_0*

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The three terminally aldehyde-substituted carotenes β-apo-12′-carotenal, β-apo-4′-carotenal and 3′,4′-didehydro-β,ψ-caroten-16′-al ("torularhodinaldehyde") were investigated by ultrafast pump-supercontinuum probe (PSCP) spectroscopy in the range 350-770 nm in *n*-hexane. The increasing conjugation length of the apocarotenals results in a shorter S_1 lifetime of 192, 4.9 and 1.2 ps, respectively. Consequently, for torularhodinaldehyde, having the longest conjugation length among three, a large population of highly vibrationally excited molecules in the S_0 state is generated by internal conversion from S_1 already within the first picosecond of relaxation. As a result, clear S* signals are visible which bear characteristic spectral fingerprints of highly vibrationally excited molecules in the ground electronic state S_0*: an $S_0 \rightarrow S_2$ red-edge absorption and a "finger-type" structure in the $S_0 \rightarrow S_2$ bleach region. Similarly, we also observed S_0* features for β-apo-4′-carotenal, however, they are not detected for β-apo-12′-carotenal, because of the very low concentration of S_0* resulting from the long S_1 lifetime. We therefore conclude that spectral features assigned to the so-called S* signal of carotenoids arise from vibrationally hot molecules in the ground electronic state S_0* and not from an electronically excited state.[1]

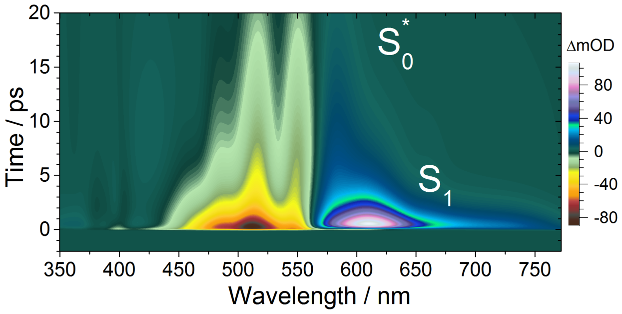

Figure 1. Contour plot of transient absorption spectra of torularhodinaldehyde in the solvent n-hexane after photoexcitation at 500 nm.

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Spin crossover in Fe^{II} complexes by XES and WAXS

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Iron-based spin crossover (SCO) complexes have lately received vast attention as they offer a wide range of attractive functionalities for technology, e.g. for data storage and displays. The optically induced transition to HS quintet state takes place via excitation of the ^{1,3}MLCT manifold, which in hundreds of fs decays into the HS state through a two-step intersystem crossing [1]. In the HS state two d-electrons are promoted from the non-bonding t_{2g} to anti-bonding e_g orbital (O_h) that leads to elongation of the Fe-ligand bonds typically by ~0.2 A. The relaxation dynamics of the HS state is defined by the multidentate ligand type (symmetry) and the host matrix or solvent. In this contribution we present studies on a set of three solvated SCO systems in order of increasing structural complexity. All the compounds are investigated by means of combined time-resolved Fe K-edge x-ray emission spectroscopy (XES) and wide angle x-ray scattering (WAXS) at a synchrotron. While XES allows for tracking the electronic spin configuration, WAXS provides transient structural information on both the solute molecule and its solvation [2]. The first two studied molecules $[Fe(tpen)]^{2+}$ (tpen = N,N,N′,N′-Tetrakis(2-pyridyl methyl)-1,2-ethylene- diamine) [3] and $[Fe(btpa)]^{2+}$ (btpa = N,N,N,N-tetrakis (2-pyridylmethyl)-6,6-bis (aminomethyl)-2,2-bipyridine) [4] have similar structures, but the O_h symmetry is distorted to D_{3h} and C_2 respectively. The $[Fe(btpa)]^{2+}$ exhibits the second HS state with C_1 symmetry where the Fe ion is additionally coordinated with an extra pyridyl ring. The structural changes upon the transition were obtained from the WAXS data fitting and the DFT calculations. The cooperativity effect of the HS transition was studied in a di-nuclear SCO complex $[Fe\text{-}Fe(pmk)_3]^{4+}$ (pmk = 2-pyridylmethyl ketazine). The XES results indicate that both Fe centers were converted to the HS state at relatively low laser excitation intensity suggesting the cooperativity of transition. The structural coupling of the excitation between the two centers and the solvation dynamics were elucidated by means of WAXS.

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A Multi Target Approach to Control Chemical Reactions in Their Inhomogeneous Solvent Environment

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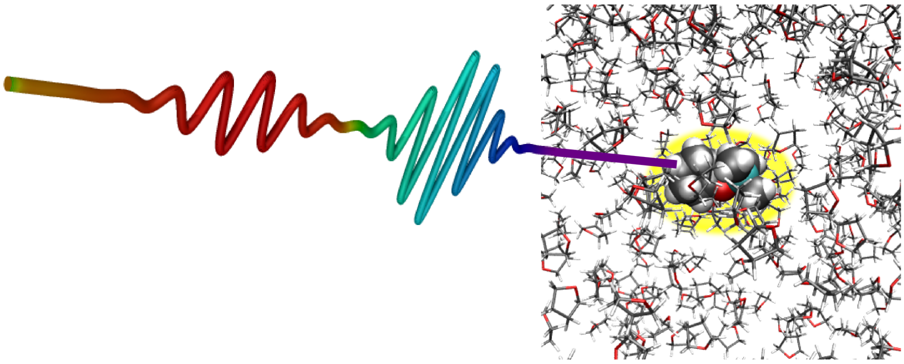
Influencing the outcome of chemical reactions is an everyday struggle for chemists. A powerful and constantly improving tool to manipulate molecular quantum systems is available with shaped laser pulses. Their application to chemical reactions in solution is a promising concept to redesign chemical synthesis. Along this road, theoretical developments are necessary to understand the underlying mechanisms. When investigating chemical processes in solution, an appropriate theoretical treatment becomes more challenging. Electrostatic as well as steric solvent effects influence the quantum dynamics during ultrafast reactions and have to be included in the description. We present a way to account for these effects in laser pulse optimizations conducted with optimal control theory (OCT). Therefor a QD/MD approach combining quantum dynamics (QD) and classical molecular dynamics (MD) is employed which simulates the solvent by randomly selected snapshots from MD trajectories [1]. Based on this, we use multi target OCT [2,3] to optimize pulses for the various arrangements of explicit solvent molecules simultaneously. These arrangements alter the potential energy surface for the chemical reaction in different ways. The resulting large inhomogeneity constitutes a major challenge for the control algorithm. We investigate how the algorithm handles the new challenges and how well the controllability of the system is preserved with increasing complexity. Additionally, we will discuss a way to statistically estimate the efficiency of the optimized laser pulses in the complete thermodynamical ensemble.



Multi target OCT is used to optimize laser pulses for various solvent arrangements simultaneously.

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Coherent oscillations expose a reactive mode in the ring-opening reaction of fulgides

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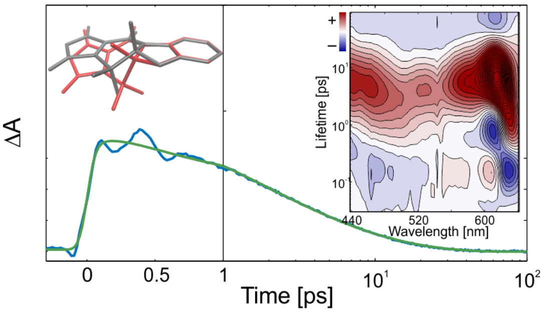
The ultrafast ring-opening reaction of photochromic fulgides [1] proceeds via conical intersections to the ground state isomers [2] involving activation barriers in the excited state [3]. The femtosecond transient absorption of a methyl-substituted indolylfulgide as well as of a water soluble dicarboxylic acid indolylfulgimide shows distinct coherent oscillations within the excited state absorption (ESA) band. The coherence was analyzed in the framework of vibrational excited state wavepackets [4]. The quantum chemical calculations in the Franck-Condon and relaxed excited state geometry revealed that the experimentally observed low-frequency vibrational mode (~80-90 cm^{-1}) has a dominant contribution to the relevant ring-opening reactive coordinate [5].



Transient absorption trace at the ESA band of the indolylfulgide with coherent oscillations at early times. The distortion of the molecule due to the vibrational mode is shown in the overlaid structures. The dynamics are presented as lifetime density map [6]

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Freezing of oil-in-water emulsions studied by sum frequency scattering spectroscopy

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We study the properties of dodecane and hexadecane oil droplets in water with broadband femtosecond sum-frequency scattering (SFS) spectroscopy over a wide range of temperatures, including the frozen state of the water matrix and the oil droplets. The SFS spectra contain vibrational bands that correspond to the symmetric and antisymmetric CH stretching vibrations of the methylene (CH_2) (d^+ and d^-) and methyl (CH_3) (r^+ and r^-) groups of the alkane molecules (Fig. left panel). The relative amplitudes of the vibrational bands provide important information on the surface structure and shape of the oil droplets.

Freezing of water is observed to lead to a strong increase in the disorder of the alkyl chains ($d^+/r^+ >$) and a distortion of the oil droplets ($r^-/r^+ >$) in case the droplets are liquid (case of dodecane), see Fig. 1 right panel. If the oil droplets have already solidified (case of hexadecane), the effects of water freezing are negligible. Freezing of the oil droplets increases the ordering of the alkyl chains at the surface ($d^+/r^+ <$), irrespective whether the water matrix is liquid or solid. For completely frozen emulsions a further decrease in temperature is observed to lead to a further disordering of the surface alkyl chains ($d^+/r^+ >$) and a further distortion of the solid oil droplets ($r^-/r^+ >$), probably because of the hardening of the ice matrix that encompasses the frozen oil droplets.

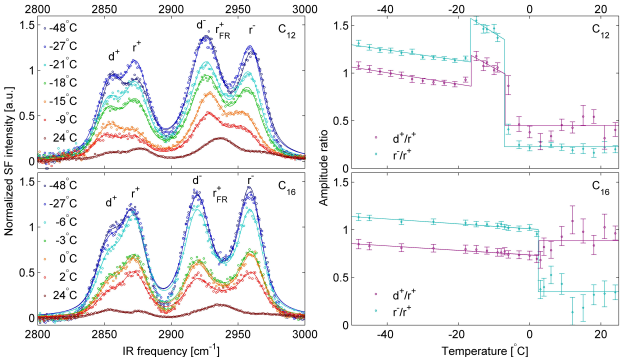

Fig. 1 SFS spectra of the dodecane in water emulsion (left) at 7 temperatures in the range -48 to 24 °C, and ratios of the different vibrational bands as a function of temperature (right panel).

Ultrafast photodynamics of multimetallic Ag(I) and Pt(II) complexes: gas phase and solution

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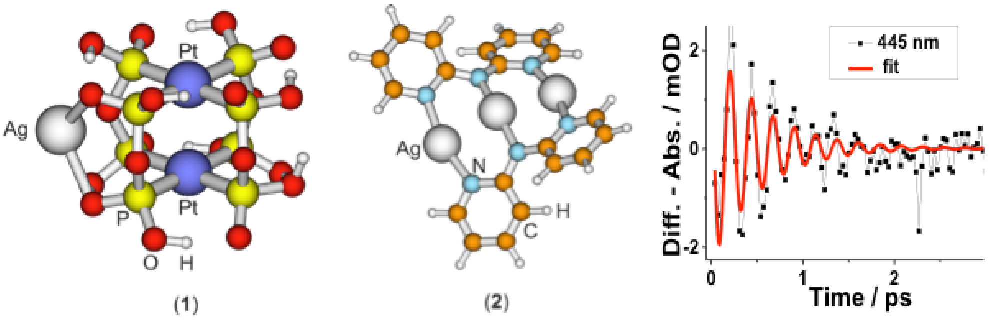
The optical properties and photodynamics of multimetallic ligand-stabilized complexes provide key information on their electronic structure and energy relaxation pathways and allow for the characterization of cooperative metal-metal interactions. We present recent data on silver aggregates of the Ptpop complex (**1**, $[Pt_2(\mu\text{-}P_2O_5H_2)_4 + H,Ag]^{2-}$) in solution and gas phase (ion trap) employing transient absorption (TA) and transient photofragmentation (tPF), respectively. Gas phase analysis and DFT calculations clearly show a preferential side-on coordination of the Ag(I) ions (**1**) but no indication for an axial structure. [1] The slightly red-shifted (compared to Ptpop) gas phase absorption band of **1** (375 nm) is assigned to a Pt_2-centered transition. tPF is dominated by loss of neutral Ag, supporting the involvement of charge transfer (CT), whereas uncomplexed Ptpop shows photodetachment. Gas phase excited-state dynamics on timescales of ~50 fs to tens of ps is observed, but no vibrational coherences are found. [2] The absorption band of Ptpop in aqueous solution (368 nm) is red-shifted by ~30 nm forming **1** upon silver aggregation. TA reveals vibrational coherences of period ~0.23 ps together with a significantly shorter coherence time (0.53 ps) than for uncomplexed Ptpop, attributed to interaction with a silver CT state. Additionally, we present first results on string-type complexes in gas phase $[(Hdpa)_2Ag_n{-}(n\text{-}1)H]^+$ (Hdpa=2,2′-Dipyridylamine, n=1,2,3; **2**) with electronic dynamics on a 100 fs - 10 ps timescale, depending on the number of Ag(I) ions.



(1) (2)

*DFT structures of $[Ptpop + H,Ag]^{2-}$ and $[(dpa)_2Ag_3]^+$. Vibrational coherences of **1**.*

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Ultrafast Time-Resolved Emission Studies of Nile Red Embedded In Metal Doped Mesoporous Materials

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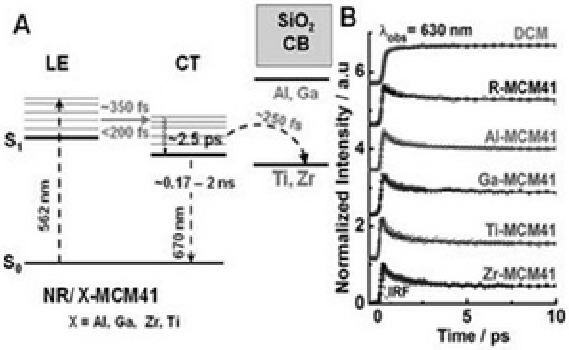
The development of ordered porous silica materials emerged as one of the most attractive alternatives to amorphous silica material, due to their unique physical and chemical properties.[1] Here, we present the steady state and femto- to nanosecond time-resolved study for Nile Red (NR) dye interacting with MCM41 mesoporous materials doped by Al, Ga, Zr and Ti. The results show that the presence of the silica materials leads to the formation of different NR populations, including monomers, J- and H-aggregates. The femtosecond results for R-MCM41, Al-MCM41 and Ga-MCM41 hosts indicate that the excitation of NR leads to the generation of the locally excited (LE) state followed by the internal charge transfer (ICT) within 340 – 420 fs. For the NR/Ti-MCM41 and NR/Zr-MCM41 samples, the ICT occurs in time shorter than 200 fs. Furthermore, the presence of transition metals results in the electron injection (EI) from organic dye to the trap states formed by the Ti or Zr in the host framework (~250 fs).



(A) Energy levels NR interacting with X-MCM41. (B) Emission transients of Nile Red interacting with MCM41 materials excited at 562 nm and observed at 630 nm.

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[2] **Acknowledgment:** This work was supported by the MINECO and UCLM through Projects Consolider Ingenio 2010 (CDS2009-0050), PRI-PIBIN-2011-1283, MAT2011-25472 and PEII-2014-003-P.

Absolute configuration of chiral molecules at aqueous interfaces probed with phase-resolved sum-frequency generation spectroscopy

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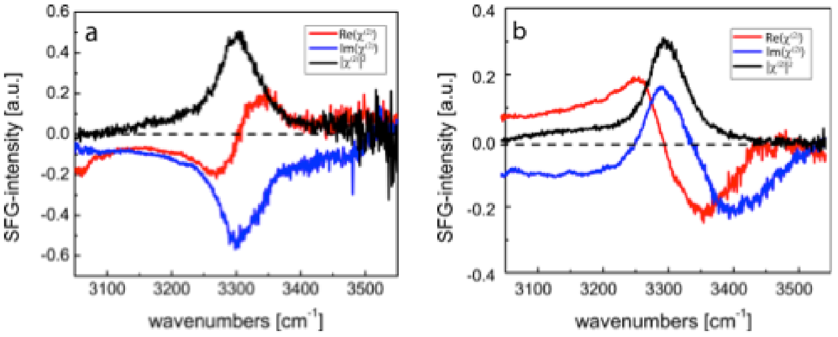
Chirality is a key aspect in the function and recognition of complex (bio)molecular systems and thus a topic of central interest for research fields ranging from macromolecular chemistry to structural biology. At present no spectroscopic technique is capable of determining the absolute configuration of chiral molecules with interface specificity. We perform femtosecond broadband vibrational sum-frequency generation spectroscopy (VSFG) with a polarization combination that selectively probes chiral molecular structures. By employing an interferometric detection scheme, the phase of the sum-frequency light generated by the chiral molecules is determined, allowing us to discriminate between right-handed (L-type) and left-handed (D-type) α-helical peptides at the water-air interface. By combining the surface-specificity of VSFG spectroscopy with phase-sensitive detection, we were able to determine for the first time the absolute configuration of a biomacromolecule at an aqueous interface with monolayer sensitivity. Figure 1 shows the real and imaginary $\chi^{(2)}$ of the L- and D-forms of the peptide *AFP1* in the spectral region of the NH-stretch vibration obtained under psp-polarization settings. The opposite phase of the backbone NH-vibration resulting from the different signs of $\chi^{(2)}{}_{\text{chiral}}$ for right-handed and left-handed α-helical peptides is clearly resolved. Our experimental approach is perfectly suited for the study of (bio)chemical transformations at interfaces, and may open up a novel route to study the conformational rearrangements of interfacial macromolecules.



a) Real and imaginary $\chi^{(2)}$ measured for L-type AFP1; b) As a) for D-type AFP1. Intensity VSFG-spectra (proportional to $\mid \chi^{(2)} \mid^2$) are shown in black for comparison.

Capturing Exciton to Polaron Splitting Dynamics in Low Bandgap Polymer Films

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Low bandgap conjugated polymers are potent low-cost materials for organic electronics. In order to improve their efficiency, it is critical to track the fate of photogenerated electron-hole bound pairs (*excitons*) to achieve higher charge transfer (CT) yields at the molecular interfaces. Recent studies on pristine conjugated polymers suggested that polaron pairs, formed within the polymer domains, are as significant as singlet excitons. Scherf & co-workers has reported structural correlations in direct generation of polaron pairs with optical excitation [1] but the temporal evolution of exciton to polarons in these polymers has not been explored. We have used transient absorption spectroscopy to probe sub-picosecond exciton decay dynamics in diketo-pyrrolopyrrole (DPP)-based low bandgap polymer film. The evolution of CT exciton to polaron pair is impaired due to fast recombination timescale of 3 ps limiting the yield of the polaron pair to 18 %. The importance of side chain engineering to control the flux of free polarons will be discussed. Our work demonstrates that the intermolecular interactions may be one of the key factors in determining the performance of these devices.

References:

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