## Monday, January 14

### New PI Presentation

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:10</td>
<td>Adrian Cavalieri</td>
<td>Self-referenced attosecond spectroscopy at XFELs</td>
<td>4</td>
</tr>
</tbody>
</table>

### Terahertz Spectroscopy

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:30</td>
<td>Philipp Krauspe (Banerji)</td>
<td>Effective detection of weak THz pulses in electro optic sampling</td>
<td>5</td>
</tr>
<tr>
<td>14:50</td>
<td>Andrey Shalit (Hamm)</td>
<td>Multidimensional spectroscopy at low-frequency regime – progress in 2D Raman-THz spectroscopy</td>
<td>6</td>
</tr>
<tr>
<td>15:10</td>
<td>Sarah Houver (Johnson)</td>
<td>Exploring the band curvature of low-bandgap semiconductors using few-cycle 2D THz spectroscopy</td>
<td>7</td>
</tr>
</tbody>
</table>

### Solvent Processes

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:00</td>
<td>Anuradha Das (Feurer)</td>
<td>Probing excited state dynamics of charge transfer reactions in ionic deep eutectic solvents</td>
<td>8</td>
</tr>
<tr>
<td>16:20</td>
<td>Thomas Gartmann (Signorelli)</td>
<td>Lifetimes and Energetics of the First Electronically Excited States of NaNH2O from Time-Resolved Photoelectron Imaging</td>
<td>9</td>
</tr>
<tr>
<td>16:40</td>
<td>FP-RESOMUS Kick-off</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Tuesday, January 15

### Tutorials

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30</td>
<td>Carlos Silva, Georgia Tech</td>
<td>Ultrafast optical probes of exciton-phonon and exciton-exciton correlations in hybrid semiconductors. 1: Excitons, phonons, polaron: quasi-particles in matter and how femtosecond lasers give us a window into their properties</td>
<td>2</td>
</tr>
<tr>
<td>10:30</td>
<td>Volker Engel, Uni Würzburg</td>
<td>I: Infinite Jest: Dynamics of nuclei and electrons in molecules</td>
<td>3</td>
</tr>
</tbody>
</table>

### Attosecond processes

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00</td>
<td>Benjamin Willenberg (Keller)</td>
<td>Linear momentum transfer in multiphoton strong-field ionization with sub-cycle time resolution</td>
<td>10</td>
</tr>
<tr>
<td>14:20</td>
<td>Giovanni Vanacore (Carbone)</td>
<td>Attosecond coherent control of a free-electron wave function via semi-infinite light fields and plasmon polaritons</td>
<td>12</td>
</tr>
</tbody>
</table>

### Theoretical approaches

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:40</td>
<td>Uxia Rivero (Meuwly)</td>
<td>Computational insights into a Diels – Alder reaction</td>
<td>13</td>
</tr>
<tr>
<td>15:00</td>
<td>Swarnendu Bhattacharyya (Röthlisberger)</td>
<td>Understanding Photoionization Induced Hydrogen Abstraction of Acetylene Through Nonadiabatic Molecular Dynamics Simulations</td>
<td>14</td>
</tr>
</tbody>
</table>

### Condensed matter and nanomaterials

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:50</td>
<td>Serhane Zerdane (Beaud)</td>
<td>Ultrafast magnetic and orbital phase transitions in a 4D correlated system</td>
<td>15</td>
</tr>
<tr>
<td>16:10</td>
<td>Michaela Gazzetto (Cannizzo)</td>
<td>Unraveling emission mechanism and electron mobility in fluorescent carbon nanodots by mean of 1D and 2D ultrafast transient absorption spectroscopy in various solvents</td>
<td>16</td>
</tr>
</tbody>
</table>

### Biologically relevant systems

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:30</td>
<td>Malte Oppermann (Chergui)</td>
<td>Ultrafast Broadband Circular Dichroism in the Deep-UV</td>
<td>17</td>
</tr>
<tr>
<td>16:50</td>
<td>Elena Grossenbacher (Häner)</td>
<td>Energy Transfer Processes in DNA-Organized, Multi-segmental Chromophore Stacks</td>
<td>18</td>
</tr>
</tbody>
</table>

## Wednesday, January 16

### Tutorials

<table>
<thead>
<tr>
<th>Time</th>
<th>Name</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30</td>
<td>Volker Engel, Uni Würzburg</td>
<td>II: Settin’ the Pace: Preparation, detection and control of molecular motion with ultrashort laser pulses</td>
<td>3</td>
</tr>
<tr>
<td>10:30</td>
<td>Carlos Silva, Georgia Tech</td>
<td>Ultrafast optical probes of exciton-phonon and exciton-exciton correlations in hybrid semiconductors. 2. The choreography of particles during earthquakes in condensed matter</td>
<td>2</td>
</tr>
</tbody>
</table>
Ultrafast optical probes of exciton-phonon and exciton-exciton correlations in hybrid semiconductors

Carlos Silva
School of Chemistry and Biochemistry, School of Physics, Georgia Institute of Technology

Tutorial 1: Excitons, phonons, polarons: quasi-particles in matter and how femtosecond lasers give us a window into their properties

Tutorial 2: The choreography of particles during earthquakes in condensed matter

Ultrafast spectroscopies are now very powerful and reliable tools to probe, with a high degree of precision and reliability, complex photoexcitation dynamics in condensed matter. I will take stock of non-linear electronic spectroscopies that stand out as tools in materials science, including both incoherent techniques such as transient absorption spectroscopy and coherent ones such as multidimensional spectroscopies. I will focus my tutorial on excitons and multiexcitons in hybrid organic-inorganic metal-halide perovskites. Owing to both electronic and dielectric confinement effects, two-dimensional (2D) hybrid perovskites sustain strongly bound excitons at room temperature. In these systems, organic cations not only serve as spacers between slabs consisting of corner-sharing metal-halide octahedra, but also determine lattice structure by inducing varying degree of distortion of the octahedra via the organic-inorganic interactions. Perovskite crystal structures thus involve strongly interacting organic and inorganic sub-lattices with drastically different normal-mode frequency spectra, imposing complex lattice dynamics across the organic-inorganic interface. The structure exhibits excitonic correlations that are specific to the lattice structure and its polar fluctuations, both of which are controlled via the chemical nature of the organic counter-cation. Dynamic disorder is dominant in defining exciton energies, for example, due to strong electron-phonon coupling. Yet excitons and biexcitons experience extremely high binding energies. An analogy would be that of a perfectly choreographed set of dancers in perfect harmony and intimate contact during a high-magnitude earthquake. Excitonic correlations (exciton and biexciton binding energies) and exciton dynamics (e.g. uni- and bimolecular population decay mechanisms, pure dephasing processes, excitation-induced dephasing, etc.) reflect the polar solvation-like processes induced by organic cation components of the hybrid lattice in a broad structural space. I will address how ultrafast nonlinear spectroscopies yield deep insight on the multiparticle properties in complex semiconductor materials.
I. Infinite Jest:
Dynamics of nuclei and electrons in molecules

II. Settin’ the Pace:
Preparation, detection and control of molecular motion with ultrashort laser pulses

V. Engel
Institut für Physikalische und Theoretische Chemie,
Universität Würzburg, Emil-Fischer Str. 42, 97074 Würzburg, Germany

(Dated: January 2, 2019)

In lecture I basic concepts to describe the dynamics of electrons and nuclei in molecules are reviewed. In a first example the Born-Oppenheimer (BO) approximation holds and many observables can be calculated accurately within the frame of time-independent quantum mechanics [1]. Here, the use of wave packets often is numerically more efficient and provides direct insight into the dynamics [2, 3]. Next, it is discussed that there are fundamental problems in calculating certain quantities within the BO-approximation [4, 5]. More seriously, in excited electronic states of molecules this approach usually breaks down. Examples will be discussed which involve avoided crossings [6] and conical intersections [7].

The second lecture is concerned with wave-packet motion in molecules which is prepared and detected using ultrashort laser pulses. This involves different spectroscopic techniques like time-resolved photoelectron spectroscopy or two-dimensional (2D) optical spectroscopy. Examples are discussed which range from the gas-phase dynamics of small molecules [8–10] to the exciton dynamics in molecular aggregates [11, 12]. Eventually, as a final topic, the quantum control of molecular motion will be touched.

1. V. Engel, V. Staemmler, R. L. V. Wal, F. F. Crim, R. J. Sension, B. Hudson, P. Andresen, S. Hennig, K. Weide, and
Self-referenced attosecond spectroscopy at XFELs

Intense few-femtosecond and attosecond X-ray pulses at free electron lasers will allow time-domain access to electronic and structural dynamics through a variety of spectroscopic and scattering methods. However, immediate application of attosecond or otherwise tailored X-ray pulses is not yet possible, as an external laser required for triggering events cannot be phase-locked to the X-rays. To overcome this limitation, we developed a self-referenced, tandem streaking measurement using phase-shifted fields.

When observing prompt photo emission, as well as subsequent Auger emission, there is a slight delay between the appearance of the two electrons in the streaking field. This delay results in an effective phase shift between the measurements. By collecting a set of measurements made over a random distribution of absolute phases, the relative phase shift between the pairs of measurements can be determined. With this information, the single-shot amplitude and phase of the streaking laser can be recovered.

On the other hand, quantification of the relative phase shift itself constitutes a time-domain measurement of the delay between the prompt photoemission and Auger emission. In turn, this provides direct access to the core-hole lifetime. We demonstrated this approach using few-femtosecond X-ray pulses at the Linac Coherent Light Source at Stanford. Our initial analysis shows that the Auger decay time in neon is 2.7 fs with an accuracy that appears to be well below a single femtosecond.

Recently, we have generalized this self-referenced streaking for use with arbitrary sample systems by engineering the requisite phase shift. Rather than relying on the intrinsic delay provided by Auger decay, we exploit the Gouy phase advance of a focused laser beam. In this way, we can extract amplitude and phase information from a single, prompt photoemission peak. Once the streaking pulse has been "clocked," it can then be used as an effectively phase-locked pump pulse to realize the full potential for time-resolved studies – Dynamics driven with an optical laser pulse can be probed with sub-cycle resolution using synchronized attosecond X-rays.
Effective detection of weak THz pulses in electro optic sampling

Philipp Krauspe, Gonzague Rebetez, Natalie Banerji, and Julien Réhault

Weak electric fields in the THz frequency range are challenging to detect. In the standard non-contact detection scheme the THz pulse mixes with an optical probe in an electro-optic crystal. This detection mechanism known as electro optic sampling (EOS) can be improved in its sensitivity by biasing the probe beam polarization. Using (EOS) to investigate organic semiconductors is particularly challenging due to the long lifetimes of the generated charges limiting the repetition rate down to the kHz range\[1\]. This method to enhance the sensitivity without extra optics can be applied to any electro optic sampling system that has excess photons available in the probe and is based on previous work in the same direction [2-5], while here we focus on weak fields. For typical few kHz amplified systems this is the case since the limiting factor are the photo detectors. They saturate at a few nJ while hundreds of μJ can be available in the probing beam. We describe the source of typical distortions using these methods and how to avoid them in common experiments. Our description is based on the propagation of stokes’ vectors through the system. We apply this theoretical approach to describe the measured amplified signal depending on the input signal and the polarization state of the probing light pulse. The comparison to our measured data presents convincing evidence on the mechanism how distortions are introduced and how one can avoid them in a standard measurement. Exemplary we present how we measure weak pulses emitted from a thin layer of an organic semiconductor and discuss the applicability of this modification used in typical optical pump THz probe setups.

Multidimensional spectroscopy at low-frequency regime – progress in 2D Raman-THz spectroscopy

A. Shalit, G. Ciardi, A. Berger, D. Sidler, and P. Hamm

Institut für Chemie, Universität Zurich,
Winterthurerstrasse 190, CH-8057 Zurich, Switzerland, peter.hamm@chem.uzh.ch

Over last two decades, multidimensional spectroscopy in the mid-infrared and visible spectral ranges has been established as a powerful technique for studying structural dynamics and correlations between coupled vibrational and electronic transitions in various chemical and biological systems ranging from water to light-harvesting complex. At the same time, much slower progress has been made in the development of multidimensional approaches in the low-frequency spectral range. The low-frequency equivalent of multidimensional spectroscopy can be realized either by means of third-order THz techniques, where low-frequency vibrations are interrogated resonantly by a sequence of short THz pulses [1] or by fifth-order Raman spectroscopy [2], where vibrational coherences are excited by two pairs of non-resonant field interactions.

Here we will describe an alternative, hybrid approach that has been developed in our lab in which low-frequency vibrational modes below 300 cm\(^{-1}\) consecutively interrogated through impulsive Raman and direct THz excitations - 2D Raman-THz spectroscopy [3]. It will be demonstrated that the new technique can uncover features that are hidden in one-dimensional spectra such as line broadening mechanisms and couplings between interrogated low-frequency vibrational modes thus providing an equivalent information accessible by conventional multidimensional vibrational spectroscopies such as 2D-IR.

Specifically, the extent of the inhomogeneity of intermolecular motions of liquid can be monitored through the relaxation dynamics of the vibrational echo signal measured along the correlated coordinate \(t_1=t_2\) in the 2D response. Correlation of the extent of the echo signal with temperature in various isotopologues forms of liquid water (\(\text{H}_2\text{O}, \text{D}_2\text{O}, \text{H}_2\text{\(^{18}\text{O}\)}\)) reveals the impact of the nuclear quantum effects on the lifetime of local structures. Series of 2D Raman–THz spectra in various aqueous salt solutions uncover how the ability of a given salt to increase/decrease bulk viscosity of water is connected to microscopic hydrogen bond networks dynamics [4]. In addition, the ability of 2D Raman–THz spectroscopy to reveal couplings between various inter- and intramolecular degrees of freedom by observing cross-peaks in the 2D spectrum of liquid halogen compounds will be demonstrated. Finally, the aspects of polarizable water model calibration against experimental THz, Raman, and 2D-Raman-THz spectra of bulk water will be discussed [5].

Exploring the band curvature of low-bandgap semiconductors using few-cycle 2D THz spectroscopy

Sarah Houver1*, L. Huber1*, M. Savoini1, E. Abreu1, S. L. Johnson1
1 Institute for Quantum Electronics, ETH Zürich, 8093 Zurich, Switzerland

2D spectroscopy has been recently extended to frequencies between 1 THz to 25 THz, showing the potential of this technique for probing and exciting low-energy excitations, including electronic and lattice coupling [1], 2-phonon coherence [2], magnon nonlinearities [3].

Here we present 2D-THz experiments in the range between 1-10 THz in a reflective geometry (see Fig. 1) investigating nonlinearities in the electronic bands of InSb, using THz electric fields generated from a 2-colour plasma source (up to 100 kV/cm) and optical rectification in an organic crystal (up to 250 kV/cm). In the very first picoseconds after excitation, coherent motion dominates the nonlinear response, as previously observed in GaAs [4]. Subsequently, electron-electron scattering effects, i.e. impact ionization, start to dominate. Using 2D THz spectroscopy, we show that we can follow the continuous ballistic trajectory of the out-of-equilibrium electron population in the (Γ → X, K)-plane of InSb. By using cross-polarized beams and polarization control to separate contributions to the nonlinear response of different parity (see Fig. 2), we observe distinct features in the 2D spectra.

To better understand the system response at times when the pulses overlap, we simulate our results using the finite-difference time-domain technique (FDTD). The simulations show that the nonlinear response is dominated by deviations of the conduction band dispersion from the radially symmetric, parabolic bands expected from a simple free electron gas model.

In conclusion, we demonstrate that the nonlinear observations result from ballistic transport of electrons along an anharmonic and anisotropic conduction band. The spectra contain information regarding the local band curvature sufficient to identify the symmetry of the valley in which the carriers reside.

Fig. 1: Measurement geometry of reflective 2D-THz spectroscopy on InSb and InAs.

Fig. 2: Odd and even parity 2D-spectra of InSb. Broken lines indicate the plasma-edge (1.9 THz) and phonon features (5.7 THz).

References
An interesting puzzle of the Nature is how do plants in extreme condition (droughts or frozen zones) sustain the important chemical and physiological reactions. Recent developments show that plants contain solvents composed of various sugars, ions, amides and water (1). These naturally occurring solvents are quite similar to the deep eutectic solvents (DES) which are formed by mixing two or more room temperature solids at a certain molar ratio to get a liquid at a temperature much below their individual melting points. Typically, at least one of the constituents is a Hydrogen bond participant (2). Characteristically these DES are similar to ionic liquids, only more feasible and cheap to synthesise. Also, the constituents are environment friendly and thus, popular as green solvents in several industrial applications. A few naturally occurring DES examples are honey (major constituents- sucrose, glucose, maltose, water) and the metabolite of barley seeds during germination (major constituents- choline and sucrose) (1).

The main driving force of bringing all the constituents to a liquid state is extensive interspecies H-bonding, besides the Coulombic and van der Waals forces. Various experimental techniques (like time resolved fluorescence, Kerr effect spectroscopy, dielectric relaxation spectroscopy) and simulations have indicated that these systems have micro domains which are spatially and temporally heterogeneous (3). Therefore, these systems are inherently different from typical organic solvents and are highly customisable. With the change of constituents and temperature, one can tune the physical and transport properties of these DES to a great extent to suit a chemical reaction. However, how efficiently DES can house chemical reactions, have not been explored extensively.

Here we report one of our recent studies on 4-(N, N' dimethylamino) benzonitrile [DMABN] investigated in a DES consisting of (0.75 Acetamide+ 0.25 Potassium thiocyanate) using transient absorption spectroscopy (femtosecond- picosecond timescale). Subsequently measured reaction times of the photoexcited intramolecular charge transfer molecule (DMABN) in the DES have been compared with reaction times obtained from conventional solvents like n-hexane and acetonitrile. A strong dynamic solvent control over reaction time is noticed in DES. From steady state fluorescence, a dual emission from the locally excited (LE) and intramolecular charge transfer (CT) states of the molecule has been observed in DES, similar to polar solvents. The distribution of dual emission (LE/CT) as well as the reaction time changes considerably in the studied temperature range. The observed change at higher temperature is an effect of faster rotation of the N(Me2)-CH bond of DMABN. The LE/CT ratio and position change with excitation wavelength which is due to the presence of microheterogeneous domains in DES.

References:
Lifetimes and Energetics of the First Electronically Excited States of NaH$_2$O from Time-Resolved Photoelectron Imaging

T. E. Gartmann$^{1*}$, S. Hartweg$^1$, L. Ban$^1$, B. L. Yoder$^1$
E. Chasovskikh$^1$, R. Signorell$^1$

$^1$Laboratorium für physikalische Chemie, ETH Zürich, 8093 Zürich, Switzerland

Anion water clusters as well as sodium-doped water clusters are prototype systems to investigate electron solvation dynamics [1-3]. In this context, we have studied the lowest electronically excited states of NaH$_2$O and NaD$_2$O with time- and angle-resolved photoelectron spectroscopy. Two different bands in the photoelectron spectrum with similar lifetimes and photoelectron anisotropies were observed. By comparison with calculations (MP2/aug-cc-pVTZ and CIS(D)), these two bands were assigned to excitations via p-states with qualitatively different potential energy curves [4].

For a thorough interpretation of photoelectron spectra of larger water clusters and liquid water microjets, it is crucial to account for the scattering of the electrons in the solvent [5-9]. To this end, we have recorded angle-resolved photoelectron spectra of neutral water clusters over a large cluster size range from clusters with only a few to a few hundred molecules. A pronounced decrease of the photoelectron anisotropy with increasing average cluster size was observed as a result of electron scattering in the clusters. Comparison with predictions from a scattering model revealed that electron scattering in larger clusters behaves differently from that in the liquid bulk [6,8,10]. Dielectric screening seems to play a major role here.

References:
Linear momentum transfer in multiphoton strong-field ionization with sub-cycle time resolution

Benjamin Willenberg, Jochen Maurer, Benedikt W. Mayer, Ursula Keller
Department of Physics, ETH Zurich, 8093 Zurich, Switzerland

How the incoming photons transfer their energy to the ion and the photoelectron during multiphoton ionization of an atom is well studied in theory and experiment. However, the linear momentum transfer from the photon during the ionization process, i.e. the momentum transfer along the laser propagation direction, is still not fully understood. Here, we present the first sub-cycle time-resolved measurement of the linear momentum transfer along the laser pulse propagation direction in strong-field ionization. Within the dipole approximation no transfer of linear momentum onto the photoelectron occurs in this direction [1]. Beyond the long-wavelength limit of this approximation, however, we observe a time-dependent linear momentum transfer [2, 3]. We can show that the time-averaged photon radiation pressure picture [4] is not applicable for the case of strong-field ionization with elliptical polarization and that the linear momentum transfer to the photoelectron depends on the ionization time within the electromagnetic cycle of the laser pulse. Furthermore, we show that the Coulomb interaction of the outgoing photoelectron with its parent ion induces a measurable attosecond time delay between the ionization times with minimal linear momentum transfer and maximum ionization rate, respectively.

Fig. 1 (a) Isosurface of a reconstructed 3D photoelectron momentum distribution (PMD) together with the polarization ellipse for strong-field ionization from xenon. (b) Cut of the 3D PMD in the polarization plane visualizing the definition of the streaking angle \( \alpha \) and the effect of the interaction with the residual ion on an outgoing photoelectron ionized at the peak of the electric field. In a perturbative picture, the final momentum of the photoelectron gains a contribution \( p_{iL} \) from the interaction with the parent ion on top of the momentum \( p_{fL} \) acquired by the propagation in the laser field. This gain happens mostly in the direction of the electric field of the laser. (c) Illustration of the streaking angle \( \alpha_i \) where the ionization rate is maximum and the angle \( \alpha_M \) in the polarization plane where the linear momentum transfer \( (p_x) \) is minimum for an ellipticity \( \epsilon = 0.6 \) of the driving laser field. The angle difference \( \Delta \alpha \) corresponds to a sub-cycle attosecond time delay.

To access the non-dipole regime, we use laser pulses in the mid infrared with a central wavelength of 3.4 \( \mu \)m and a pulse duration of 50 fs from an OPCPA source [5]. These pulses are focused into a velocity-map imaging spectrometer to peak intensities of \( \sim 6 \cdot 10^{15} \) W/cm\(^2\) yielding a Keldysh parameter \( \gamma \approx 0.4 \) for our target gas xenon. We recorded full three-dimensional photoelectron momentum distributions (PMDs) with elliptical polarization. We extract the linear momentum transfer onto the photoelectron from the 3D PMDs as a function of the streaking angle \( \alpha \) using elliptical coordinates in the polarization plane.

For the linear momentum transfer in the laser pulse propagation direction we observe a minimum at an angle \( \alpha_M \) close to the streaking angle \( \alpha_i \) for the most probable photoelectron. Based on the attoclock principle [6], where the rotating electric field vector serves as a time reference, we can...
translate the angle difference $\Delta \alpha = \alpha_2 - \alpha_3$ into a sub-cycle time delay. We observe that the electron trajectory with the lowest linear momentum transfer is advanced with respect to the most probable electron trajectory.

Our results demonstrate new possibilities to obtain a fully time-resolved picture of laser-induced momentum transfer during the ionization process.

References
Attosecond coherent control of a free-electron wave function via semi-infinite light fields and plasmon polaritons

G. M. Vanacore, I. Madan, G. Berruto, E. Pomarico, and F. Carbone
Institute of Physics, Laboratory for Ultrafast Microscopy and Electron Scattering (LUMES), Ecole Polytechnique Federal de Lausanne, Station 6, CH-1015 Lausanne, Switzerland
E-mail: giovanni.vanacore@epfl.ch

The interaction between light and electrons can be exploited for generating radiation, such as in synchrotrons and free electron lasers, or for controlling electron beams in applications such as time-resolved electron microscopy for the dynamical investigation of materials and molecules. Using electromagnetic fields the coherent control of the electron wave-function can be pushed to unexplored timescales, even below the attosecond regime, which would enable new applications in light-assisted quantum devices and diagnostics at extremely small timescales, such as those governing intramolecular electronic motions and nuclear processes.

In this contribution, we report on a generalized method for the coherent phase manipulation of free electrons with attosecond precision, and show that it can be pushed down to the zeptosecond regime with existing technology. A relativistic pulsed electron beam was made to interact with an appropriately synthesized electromagnetic field. The field was generated either by a sequence of two fs laser pulses reflected at the surface of a mirror (semi-infinite field), or by the coherent superposition of the surface plasmon polaritons (SPPs) optically-generated from nanofabricated structures (near field). The energy-momentum exchange resulting from the electron-field interaction was directly mapped via momentum-resolved ultrafast electron energy-loss spectroscopy. When the two phase-locked light pulses were delayed by fractions of the optical cycle, we observed coherent oscillations in the electrons energy-momentum states. This effect is the result of coherently constructive and destructive phase modulation of the electron wave-function while varying the relative phase between the two driving optical pulses.

Furthermore, our method offers the possibility to manipulate the phase-controlled combination of the electron interaction with both a semi-infinite light field and a plasmon polariton propagating on a plasmonic waveguide. The non-local interference between the traveling plasmon wave and the light field, as mediated by the electrons, creates a standing wave distribution which can perturb the electron wave-function in a controlled manner. Here, we describe the case of SPPs generated at the edge of a circular nanocavity carved in a Ag layer deposited on a Si3N4 thin film, and demonstrate that the resulting near-field distribution transiently creates a vortex plasmon carrying a defined orbital angular momentum (OAM), which can be efficiently transferred to the interacting electrons as a result of the coherent interaction.

The potential of our approach to reach the attosecond timescale and below should pave the way to achieve unprecedented insights into non-equilibrium phenomena in advanced materials, and should play a decisive role in the rational design and engineering of future applications.
Computational insights into a Diels – Alder reaction

Uxía Rivero, Markus Meuwly and Stefan Willitsch
Chemistry Department, University of Basel

The Diels-Alder reaction, in which a diene reacts with a dienophile forming a cyclic product, is widely used for the synthesis of organic rings. There has been many studies about whether or not this is a concerted process and, if so, whether it happens in a synchronous or an asynchronous manner [1, 2]. The (a)synchronicity is usually defined from the (a)symmetry of the transition state structure but recent simulations show that both, synchronous and asynchronous additions are present even for symmetric transition states [3,4].

Recent advances in molecular-beam experiments allow now conformational separation of isomers by electrostatic deflection of a molecular beam based on their different dipole moments [5]. Hence, the separation of the s-cis and s-trans conformers of a diene is possible as long as they meet the experimental requirements for this technique.

We aim to experimentally and computationally explore the detailed mechanism of the Diels-Alder reaction between conformationally selected 2,3-dibromo-1,3-butadiene and maleic anhydride. We have recently found that the reaction goes through a symmetric transition state [6] and we are now using multi-surface adiabatic reactive molecular dynamics (MS-ARMD) [7] to understand which initial conditions will lead to a reactive event. With this method it is possible to simulate a crossed molecular beam experiment where the two molecules start approaching each other to then collide. A van der Waals complex can be formed and live for several picoseconds, dissociate or lead to the Diels-Alder product.

Understanding Photoionization Induced Hydrogen Abstraction of Acetylene Through Nonadiabatic Molecular Dynamics Simulations

Swarnendu Bhattacharyya1, Nadja Hartmann2, Fabian Schlaepfer2, Mikhail Volkov2, Zeno Schumacher2, Matteo Lucchini3, Lukas Gallmann2, Ursula Keller2 and Ursula Röthlisberger1

1Laboratory of Computational Chemistry and Biochemistry, Ecole Polytechnique Fédérale de Lausanne, Switzerland
2Department of Physics, ETH Zuerich, 8093 Zuerich, Switzerland
3Physics Department, Politecnico di Milano, 20133 Milan, Italy

With the advent of ultrafast lasers, small organic molecules in gas phase have been serving, more than ever, as prototypes to understand the subtleties of ultrafast photoinduced excited state dynamics of molecules and molecular ions. In close collaboration with the group of Prof. U. Keller (ETH, Zurich), we have simulated the photoionization induced hydrogen abstraction dynamics of the acetylene cation, studied experimentally by an extreme-ultraviolet (XUV) pump pulse, followed by a delayed infrared (IR) probe pulse [1]. Extensive static electronic structure calculations at SA-CAS(9,10)-SCF/CASPT2/cc-pVTZ level provided first hints about the importance of different vibrational modes on the overall dissociative dynamics. However, to achieve a more comprehensive understanding, we have performed ab initio nonadiabatic molecular dynamics simulations within a trajectory surface hopping (TSH) scheme, where the electronic energies, the nuclear gradients and the nonadiabatic couplings have been calculated on-the-fly at SA(5)-CAS(9,8)-SCF/6-31G** level. Besides the well-known excited state acetylene-vinylidene isomerization [2], our dynamic simulations have also revealed the possibility of a C-H bond dissociation directly on the excited or the ground state, which explains the presence of the peak corresponding to C2H+ in the experimental mass spectrum without probe pulse. To explain the dip of the C2H+ ion yield at ca. 30fs pump-probe delay, we propose an IR-induced resonant dumping mechanism, which potentially quenches C-H dissociation. To further investigate the influence of the IR pulse on the overall dynamics, full-dimensional quantum nonadiabatic dynamics will be performed with explicit light- matter interaction (in the dipole approximation). To this end, we have constructed a general 6-state 4-mode Renner-Teller (vibronic coupling) Hamiltonian [3], which might be useful for other linear systems as well.

References:


Ultrafast magnetic and orbital phase transitions in a 4d correlated system

S. Zerdane,¹ P. Beaud,¹ M. Braden,⁴ B. Burganov,³ V. Esposito,¹ N. Gurung¹ G. Ingold,¹ K. Jenni,⁴ S. Johnson,¹ P. van Loosdrecht,⁴ G. Mancini,² R. Mankowsky,¹ J.L. Mardegan,¹ B. Pedrini,¹ J. Rouxel,² F. Sekiguchi,⁴ U. Staub,³ C. Svetina,¹ and H.T. Lemke¹

¹Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland,
²Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland,
³Eidgenössische Technische Hochschule Zürich (ETHZ), CH-8093 Zurich, Switzerland,
⁴Universität zu Köln, 50923 Köln, Germany.

In the 4d correlated material Ca₂RuO₄, the interactions between lattice, charge, orbital and magnetic degrees of freedom (DOF) form stable states differing in magnetization or conductivity, with different magnetic and electronic phase transitions that can be triggered by temperature pressure and light. To understand the elementary mechanisms associated with the magnetic and orbital changes, it is necessary to study this process on the time scale of atomic motions. In this work, we investigated the ultrafast magnetic and orbital dynamics by time resolved resonant diffraction at the Ruthenium L-edge [1]. With SwissFEL Bernina, this tender energy regime becomes accessible at an FEL diffraction instrument for the first time. In order to study the ultrafast magnetic and orbital dynamics, we followed the intensity change of (100) reflection [1] after excitation by an ultrashort IR pulse (cf. Fig.1) at 80 K. Our results show a decrease of integrated Bragg intensity (100) which is due to the Antiferromagnetic (AF) transition.


FIG. 1: Top left: Temperature series of (100) reflection intensity as function of energy in the vicinity of the Ru L₂ edge (adapted from [1]). Bottom left: The L₂ edge feature (Q-integrated intensities) indicates magnetic and orbital order through decrease by one order of magnitude at the AF and insulator-metal phase transitions. Both can be investigated and their transitions caused by impulsive excitation by IR light.

FIG. 1: Top left: Temperature series of (100) reflection intensity as function of energy in the vicinity of the Ru L₂ edge (adapted from [1]). Bottom left: The L₂ edge feature (Q-integrated intensities) indicates magnetic and orbital order through decrease by one order of magnitude at the AF and insulator-metal phase transitions. Both can be investigated and their transitions caused by impulsive excitation by IR light.
Unraveling emission mechanism and electron mobility in fluorescent carbon nanodots by mean of 1D and 2D ultrafast transient absorption spectroscopy in various solvents

M. Gazzetto\(^1\), A. Sciortino\(^{1,2,3}\), M. Nazari\(^1\), A. Das\(^1\), E. Rohwer\(^1\), T. Feurer\(^1\), F. Messina\(^{2,3}\), A. Cannizzo\(^1\)

\(^1\)Institute of Applied Physics, University of Bern, Sidlerstrasse 12, 3012 Bern, Switzerland
\(^2\)Department of Physics and Chemistry, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy
\(^3\)Dipartimento di Fisica e Astronomia, Università degli studi di Catania, Via Santa Sofia 64, 95123 Catania, Italy.

Carbon nanodots (CDs) are a novel family of optically-active carbon-based nanomaterials discovered only a few years ago. They are 1-10 nm nanoparticles endowed with a rather appealing combination of properties: first of all a tunable and strong fluorescence in the visible, excellent solubility in aqueous environments and bio-compatibility, sensitivity to perturbations like the presence of metal cations and the capability of behaving as efficient photo-activated acceptors or donors of electrons and protons. Understanding their optical properties at a fundamental level and especially the interplay between core and surface groups is crucial to provide tailored samples for applications in many fields as optoelectronics, bio-imaging, nanosensors and markers.

Figure 1: A representative selection of 2D-TA UV spectra on N-rich CDs at different population times: 0.1, 0.4, 1.25, 20 and 200 ps showing the transient signals related to the two separate emissions. It is accompanied by a plot of the steady state emissions on the right.

We carried out an extensive study with 1D and 2D DUV-to-Vis femtosecond transient absorption (TA) spectroscopy on N-rich CDs in various solvents and pump-probe configurations. This family of dots is particularly interesting because of its high emission QY up to 80\%, the possibility to tune the nm core structure from crystalline to amorphous and the presence of dual emission with strong sensitivity to the environment. As the fundamental properties are subject of strong debate in literature, our TA studies allow to disentangle the dynamics of different bands contributing to the emission activity (Figure 1) and to address size-dependent effects on optical and physical properties. We also provide an unanticipated insight on the photocycle of CDs, unravelling the relaxation steps upon photo-excitation with the characteristic timescales. Moreover, anisotropy studies in different solvents as water, ethanol, DMF and deep eutectic solvents (DES) allowed us to study the rotational diffusion of the transition dipole moment on fast timescales (10s ps), much faster than the rotational diffusion of the entire nanoparticles (10s ns). This finding reveals a diffusional energy transfer occurring through surface electronic states of the nanodots assisted by solvent fluctuations. The extensive study in DES, newly studied bio-compatible solvents related to ionic liquids, allowed important findings on the nature of the emission efficiency thanks to the possibility of varying the amount of water in solution.
Ultrafast Broadband Circular Dichroism in the Deep-UV

Malte Oppermann*,1, Jasmin Spekowius2, Benjamin Bauer1, Thomas Rossi1, Francesco Zinna3, Jan Helbing2, Jérôme Lacour3 and Majed Chergui1

1Laboratory of Ultrafast Spectroscopy, EPFL, CH-1015 Lausanne, Switzerland
2Institut für Chemie, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
3Département de chimie organique, Université de Genève, Quai Ernest Ansermet 30, 1211 Genève 4, Switzerland

*malte.oppermann@epfl.ch

The measurement of chirality and its temporal evolution is crucial for the understanding of a large range of biological functions and chemical reactions. Steady-state circular dichroism (CD) is a standard analytical tool for measuring chirality in chemistry and biology. Nevertheless, its push into the ultrafast time domain has remained a challenge [1], with only some isolated reports of sub-nanosecond CD [2]. Here, we present the first broadband time-resolved CD spectrometer in the deep-UV spectral range with femtosecond time-resolution. The setup employs a photoelastic modulator to achieve shot-to-shot polarization state switching of a 20 kHz pulse train of broadband femtosecond deep-UV pulses (250–370 nm) [3]. The resulting sequence of alternating left- and right-circularly polarized probe pulses is employed in a pump-probe scheme with shot-to-shot dispersive detection and thus allows for the acquisition of broadband circular dichroism spectra of ground- and excited state species. Through polarization scrambling of the probe pulses prior to detection, artefact-free static and transient CD spectra of enantiopure [Ru(bpy)3]2+ are successfully recorded with a sensitivity of < 2•10^{-5} OD (≈ 0.7 mdeg). Due to its broadband deep-UV detection with unprecedented sensitivity, the measurement of ultrafast chirality changes in biological systems such as peptides and DNA oligomers is now feasible, which we demonstrate with recent studies on the photo-isomerisation of a chiral model peptide.

Figure 1: Static (left) and transient CD (right) of 1 mM aqueous solutions of enantiopure Λ- and Δ-[Ru(bpy)3]2+, pumped at 395 nm with a 50 ps delay. For the static CD, the TRCD setup is compared to a commercial CD spectrometer.

References
[3] M. Oppermann et al., Optica, manuscript accepted
Energy Transfer Processes in DNA-Organized, Multi-segmental Chromophore Stacks

Elena Grossenbacher, Nutcha Bürki, Simon M. Langenegger and Robert Häner
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, CH-3012, Switzerland

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

Fig.1 From segmented to multi-segmented multi-chromophoric systems. A: Multi-segmented duplex with light-harvesting phenanthrenes in both strands and the pyrene acceptor in one strand. B: Multi-segmented duplex with an unmodified complementary DNA strand; chromophores in only one strand.