

# ATTOCHEM 2023



## Book of abstracts

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## Program overview

	Monday (Sept 18.)	Tuesday (Sept 19.)	Wednesday (Sept 20.)
<b>8:10-8:30</b>	<b>opening</b>		
<b>8:30-10:15</b>	<b>Plenary 1.</b> Chair: F. Martin	<b>Plenary 2.</b> Chair: T. Weinacht	<b>Plenary 3.</b> Chair: T. Baumert
8:30-9:05	<b>Francesca CALEGARI</b>	<b>Luis DIMAURO</b>	<b>Jens BIEGERT</b>
9:05-9:40	<b>Thomas WEINACHT</b>	<b>Thomas BAUMERT</b>	<b>Nirit DUDOVICH</b>
9:40-10:15	<b>Hans Jakob WÖRNER</b>	<b>Alexander Kuleff</b>	<b>Jon MARANGOS</b>
<b>10:15-10:30</b>	break	break	break
<b>10:30-12:10</b>	<b>Invited 1.</b> Chair: R. Baker	<b>Invited 4.</b> Chair: F. Calegari	<b>Invited 5.</b> Chair: V. Despré
10:30-10:55	<b>Markus KITZLER-ZEILER</b>	<b>Fabien GATTI</b>	<b>László VEISZ</b>
10:55-11:20	<b>Stefanos CARLSTRÖM</b>	<b>Torsha MOITRA</b>	<b>Giulio M. ROSSI</b>
11:20-11:45	<b>Saikat NANDI</b>	<b>Jesús GONZÁLEZ VÁZQUEZ</b>	<b>Maurizio REDUZZI</b>
11:45-12:10	<b>Laura REGO</b>	<b>Bernd SCHÜTTE</b>	<b>Vincent WANIE</b>
<b>12:10-14:10</b>	lunch	lunch	lunch
<b>14:10-15:25</b>	<b>Invited 2.</b> Chair: S. Borbély	<b>Free time for discussions and networking</b>	<b>Invited 6.</b> Chair: L. Veisz
14:10-14:35	<b>Robert BAKER</b>		<b>Victor DESPRÉ</b>
14:35-15:00	<b>Paolo A. CARPEGGIANI</b>		<b>Csaba FÁBRI</b>
15:00-15:25	<b>Davide FACCIALÀ</b>		<b>Mathieu GISSELBRECHT</b>
<b>15:25-15:40</b>	break		<b>closing remarks</b>
<b>15:40-16:55</b>	<b>Invited 3.</b> Chair: M. Kitzler-Zeiler		
15:40-16:05	<b>Sándor BORBÉLY</b>		
16:05-16:30	<b>Darya GORELOVA</b>		
16:30-16:55	<b>Giulia MANCINI</b>		
<b>17:00-19:00</b>	<b>poster session</b>	<b>poster session</b>	

## Monday – September 18.

<b>8:10-8:30</b>	<b>opening</b>	
<b>8:30-10:15</b>	<b>Plenary 1.</b> Chair: F. Martin	
8:30-9:05	<b>Francesca CALEGARI</b> <i>UV-induced charge migration in chiral molecules: a new route for attochemistry</i>	<b>PT-1</b>
9:05-9:40	<b>Thomas WEINACHT</b> <i>Long Lived Electronic Coherences in Molecules</i>	<b>PT-2</b>
9:40-10:15	<b>Hans Jakob WÖRNER</b> <i>Advancing attochemistry to the liquid phase and to chiral molecules</i>	<b>PT-3</b>
<b>10:15-10:30</b>	break	
<b>10:30-12:10</b>	<b>Invited 1.</b> Chair: R. Baker	
10:30-10:55	<b>Markus KITZLER</b> <i>Carrier envelope phase sensitivity of photoelectron circular dichroism</i>	<b>IT-1</b>
10:55-11:20	<b>Stefanos CARLSTRÖM</b> <i>Spin-Polarized Photoelectrons in Strong- and Weak-Field Ionization</i>	<b>IT-2</b>
11:20-11:45	<b>Saikat NANDI</b> <i>Coherent light-matter interaction at XUV wavelength</i>	<b>IT-3</b>
11:45-12:10	<b>Laura REGO</b> <i>Studying chirality using ultrashort laser pulses with structured polarization</i>	<b>IT-4</b>
<b>12:10-14:10</b>	lunch	
<b>14:10-15:25</b>	<b>Invited 2.</b> Chair: S. Borbély	
14:10-14:35	<b>Robert BAKER</b> <i>Visualizing Electron Dynamics at Interfaces Using XUV Light: Applications in Photocatalysis and New Capabilities at NSF NeXUS</i>	<b>IT-5</b>
14:35-15:00	<b>Paolo A. CARPEGGIANI</b> <i>HHG at the Carbon K-Edge Directly Driven by SRS Red-Shifted Pulses from an Ytterbium Amplifier</i>	<b>IT-6</b>
15:00-15:25	<b>Davide FACCIALÀ</b> <i>Polarization- and time-resolved high-order harmonic spectroscopy in condensed media</i>	<b>IT-7</b>
<b>15:25-15:40</b>	break	
<b>15:40-16:55</b>	<b>Invited 3.</b> Chair: M. Kitzler	
15:40-16:05	<b>Sándor BORBÉLY</b> <i>Photoelectron holography: an interplay between different interference mechanisms</i>	<b>IT-8</b>
16:05-16:30	<b>Darya GORELOVA</b> <i>Theoretical description of attosecond x-ray imaging of electron dynamics in molecules and crystals</i>	<b>IT-9</b>
16:30-16:55	<b>Giulia MANCINI</b> <i>Multi-purpose Ultrafast Microscopy with a Compact High-Harmonic Source</i>	<b>IT-10</b>
<b>17:00-19:00</b>	<b>poster session</b>	

## UV-induced charge migration in chiral molecules: a new route for attochemistry

CALEGARI, Francesca (DESY, francesca.calegari@desy.de)

Attosecond science is nowadays a well-established research field, which offers formidable tools for the realtime investigation of electronic processes. In this context, we have demonstrated that attosecond pulses can initiate charge migration in aromatic amino-acids [1] as well as in the DNA nucleobase adenine [2]. These pioneering investigations have been done in ionized molecules and there is still a long path towards attochemistry and the control of the reactivity of neutral molecules via electronic coherences. Here, I will show our most recent work devoted to the investigation of charge migration in neutral molecules and its applications to manipulate the outcome of photochemical and photophysical processes. We exploited our new light source delivering few-femtosecond UV pulses [1] in order to photoexcite below the ionization threshold and trigger electronic dynamics in the chiral molecule methyl-lactate. We used time-resolved photoelectron circular dichroism (TR-PECD) to image charge migration and disclose - for the first time - its impact on the molecular chiral response. We show that charge migration enables an ultrafast chiroptical switching effect where the amplitude and direction of the photoelectron current generated by PECD can be controlled on a sub-10 fs timescale [7]. These results provide important perspectives to exploit charge-directed reactivity for controlling the chiral properties of matter at the electron time scale.

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### **Long Lived Electronic Coherences in Molecules**

Thomas Weinacht (Stony Brook University, Department of Physics and Astronomy, New York, USA), Brian Kaufman (Stony Brook University, Department of Physics and Astronomy, New York, USA), Tamás Rozgonyi (Wigner Research Centre for Physics, Budapest, Hungary), Philipp Marquetand (University of Vienna, Faculty of Chemistry, Institute of Theoretical Chemistry, Vienna, Austria)

I will discuss experiments and calculations that demonstrate long lived electronic coherences in molecules using a combination of measurements with shaped octave spanning ultrafast laser pulses, 3D velocity map imaging and calculations of the light matter interaction. Our pump-probe measurements prepare and interrogate entangled nuclear-electronic wave packets whose electronic phase remains well defined despite vibrational motion along many degrees of freedom. The experiments and calculations illustrate how coherences between excited electronic states survive even when coherence with the ground state is lost, and may have important implications for light harvesting, electronic transport and attosecond science.

## Advancing attochemistry to the liquid phase and to chiral molecules

Hans Jakob Wörner, ETH Zürich

Attochemistry has the potential of identifying approaches for transferring charge across molecular structures on electronic time scales and for electronically controlling the outcome of chemical reactions. Underlying this potential are electronic coherences that can drive charge migration in molecules [1]. Under the effects of nuclear motion, charge migration can decohere, but it can also revive, demonstrating that electronic coherence can survive for more several tens of femtoseconds, even in the presence of a dense manifold of intersecting electronic states [2]. Most remarkably, electronic coherence can also be transferred through conical intersections, which can switch the spatial character of charge migration [2]. Finally, by resolving charge transfer mediated by a conical intersection on the attosecond time scale, we have found an unexpected *delay* of  $1.46 \pm 0.41$  fs, which is attributed to a two-step process mediated by electron correlation [3]. However, most relevant charge-transfer processes and most (bio)chemical reactions take place in the liquid phase, calling for the development of liquid-phase attosecond spectroscopy. The development of liquid-jet attosecond photoelectron spectroscopy has revealed a delay of 50-70 attoseconds between photoemission from liquid and gaseous water, which is dominated by the effect of the first two solvation shells around the ionized molecule [4]. The demonstration of attosecond size-resolved cluster spectroscopy has further supported this interpretation and has suggested a linear relationship between photoionization delays and the spatial extension of the electron hole [5]. Most recently, we have successfully extended attosecond X-ray absorption spectroscopy to liquid flat jets and have observed a remarkably selective proton transfer between urea dimers following ionization of concentrated aqueous urea solutions [6]. Since most molecular of biochemical interest are chiral, the development of chiroptical attosecond spectroscopy is highly desirable. To this end, we have recently reported the first measurement of circularly polarized attosecond pulses [7]. We have applied them to the creation and attosecond manipulation of chiral photoelectron vortices [8]. Applying these pulses to chiral molecules, we have demonstrated attosecond switching of the chiroptical response known as photoelectron circular dichroism. These advances open the door to studying the chiral sensitivity of charge migration in solvated biomolecules.

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### **Carrier envelope phase sensitivity of photoelectron circular dichroism**

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The ionization of chiral molecules by circularly polarized light leads to a forward-backward asymmetry in the generated photoelectron distributions. This phenomenon is known as photoelectron circular dichroism (PECD). With respect to PECD, strong-field ionization with ultrashort intense laser pulses is particularly interesting since there the electron emission timing is linked to the laser field oscillations. This opens up the possibility to control and image molecular processes using the carrier-envelope phase (CEP) as a parameter. However, the sensitivity of PECD to the sub-cycle variations of electron emission introduced by the CEP of few-cycle pulses has so far been neglected.

Using coincidence momentum imaging we have studied the CEP-dependence of PECD using the methyloxirane molecule as the example. We could show for the first time, to our knowledge, a dependence of the PECD strength on the CEP. We show that both electrons emitted during a specific ionization-fragmentation reaction starting from the doubly charged molecular cation carry a CEP-dependent chirality.

By comparison to the results of simulations we trace back the mechanism that determines the PECD strength during double ionization and propose the following mechanism: As the CEP is a laboratory-frame-defined quantity, it sets a preferential direction for the first ionization step, selecting a molecular orientation. The instant of the second ionization step is then linked to the first one by the CEP and the molecular-orbital-defined ionization probability. As the observed PECD is determined by the chirality of the contributing molecular orbitals it is, thus, sensitive to the CEP.

## Spin-Polarized Photoelectrons in Strong- and Weak-Field Ionization

Dr CARLSTRÖM, Stefanos (Lund University, Sweden & Max Born Institute, Berlin); Dr DAHLSTRÖM, Marcus (Lund University); Prof. IVANOV, Misha Yu (Max Born Institute, Berlin, Humboldt University, Berlin, & Imperial College, London); Dr PAPOULIA, Asimina (Lund University, Sweden); Dr PATCHKOVSKII, Serguei (Max Born Institute, Berlin); Prof. SMIRNOVA, Olga (Max-Born Institute, Berlin & Technical University, Berlin); Ms TAHOURI, Rezvan (Lund University)

The production of the spin-polarized photoelectrons is of fundamental physical interest, as well as of practical importance for experiments such as in high-energy physics where the scattering cross-section are highly sensitive to the spin of the incoming projectile. It has been the topic of research for a long time; recently Trabert et al [1] measured spin-polarized photoelectrons in above-threshold ionization (ATI) of xenon using driven by circularly polarized light at 395 nm, with alternating spin polarization of the ATI peaks. Their results have proven notoriously difficult to reproduce, using standard single-active electron calculations with J-dependent pseudopotentials. Recently, we succeeded in reproducing the observed spin polarization using our implementation of time-dependent configuration interaction singles [2] that accounts for spin-orbit interaction ab initio.

In weak-field ionization, it has long been known that it is possible to produce spin-polarized photoelectrons using circularly polarized light [3]. Here we demonstrate for the first time, that is possible to achieve high degrees of spin polarization using linearly polarized light, as long as the photoelectron is measured in coincidence with the ion. In the weak-field case, we investigate the spin polarization in the vicinity of the Cooper minimum in argon, where we achieve close to 100% spin polarization [4]. In the strong-field case, we investigate spin-flipping of the photoelectron from xenon as it re-encounters the ion, and link this to the intrinsic spin-orbit clock of the ion [5].

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## Coherent light-matter interaction at XUV wavelength

NANDI, Saikat (Institut Lumière Matière, CNRS)

The periodic transfer of population between two levels in a quantum system interacting with an external electromagnetic field is known as Rabi oscillations [1]. Usually studied using long wavelength light pulses, ranging from infrared to ultraviolet radiation, these oscillations are central to our understanding of the nature of the coherent light-matter interaction. Here, we use intense femtosecond extreme ultraviolet (XUV) pulses from a seeded free-electron laser (FERMI in Elettra Synchrotron Trieste) to drive Rabi oscillations in bound-bound transitions in helium atoms [2]. The high instantaneous intensity and degree of coherence available from FERMI, allowed us to use photoionization as an in-situ tool to probe Rabi oscillations in the neutral helium atoms. The measured photoelectron spectra display an Autler-Townes (AT) doublet [3], which becomes asymmetric with respect to the change in photon energy of the XUV pulses. A clear avoided crossing emerges with the photon energy detuning, showing that it is possible to observe and study ‘photon + atom’ dressed-state in the short wavelength domain [4]. In addition, the photon energy of appearance of the doublet is blue-shifted with respect to the exact energy of the  $1s^2 \rightarrow 1s4p$  transition in helium atoms. To explain the observations, we developed an analytical model based on perturbation theory on top of the Rabi model. It shows that due to the high intensity of the XUV pulses from FERMI, the two-photon ionization pathway from the ground state can become almost equally probable to the one-photon ionization pathway from the excited state. These two pathways interfere, resulting in the observed blue shift of the experimental AT doublet. Our results pave the way towards using short-wavelength pulses to control the outcome of light-matter interactions in various systems, ranging from atoms and molecules to nano-objects.

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## Studying chirality using ultrashort laser pulses with structured polarization

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Distinguishing between the left- and right-handed versions of a chiral molecule (enantiomers) is vital, but also inherently difficult. Traditional optical methods using elliptically/circularly polarized light rely on linear effects which arise beyond the electric-dipole approximation, posing major limitations for ultrafast spectroscopy.

Here, we will propose several schemes to study chirality using ultrashort laser pulses with tailored polarization to drive non-linear laser-matter interactions. In these works, we take advantage of spatially structured light to discriminate between the two enantiomers or even to imprint chirality in atomic systems.

First, we will show how to turn an ultrashort elliptical pulse into an efficient chiro-optical tool: by tilting its polarization plane towards its propagation direction [1]. This forward tilt is achieved by focusing the beam tightly, and it reveals the enantio-sensitive component of the molecular response, which otherwise would be parallel to the propagation direction of the laser. Our field realizes an efficient interferometer that separates the nonlinear optical response of opposite enantiomers in space.

Second, we will introduce an ultrafast all-optical approach for efficient chiral recognition which relies on the interference between two low-order nonlinear processes: sum-frequency generation and third-harmonic generation [2]. We show that we can force one molecular enantiomer to emit bright light while its mirror twin remains dark.

These works provide a simple way of spatially structuring the polarization of light to image molecular chirality, with extreme enantio-efficiency and on ultrafast timescales.

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## **Visualizing Electron Dynamics at Interfaces Using XUV Light: Applications in Photocatalysis and New Capabilities at NSF NeXUS**

Prof. BAKER, L. Robert (Ohio State University); Prof. DIMAURO, Louis F. (Ohio State University); Mr GAJAPATHY, Harshad (Ohio State University); Dr HRUSKA, Emily (Ohio State University); Dr LESHCHENKO, Vyacheslav (Ohio State University); Dr RONNINGEN, T.J. (Ohio State University); Dr SCARBOROUGH, Timothy (Ohio State University)

Directly observing electron dynamics at surfaces is required to understand and control the material properties that determine performance of many applications ranging from efficient solar energy conversion to ultrafast information processing. Toward this goal, my group has developed extreme ultraviolet reflection-absorption (XUV-RA) spectroscopy as a surface-specific analog of XUV transient absorption. This method combines the benefits of traditional X-ray absorption spectroscopy, such as element, oxidation, and spin state resolution, with surface sensitivity and ultrafast time resolution. Using this technique, we investigate charge and spin dynamics in materials capable of highly efficient photocatalytic water splitting. Last, I will also describe the development of the NSF National eXtreme Ultrafast Science Facility (NeXUS) at Ohio State University. The NeXUS Facility provides unique capabilities in ultrafast XUV and attosecond science and will soon be open for proposals from the international user community.

## HHG at the Carbon K-Edge Directly Driven by SRS Red-Shifted Pulses from an Ytterbium Amplifier

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High harmonic generation (HHG) in gases, driven by near-infrared (NIR) femtosecond laser pulses, has been widely used for time-resolved investigations of ultrafast electronic and molecular dynamics with a variety of techniques. More recently, the generation of soft X-ray pulses in the water-window spectral region [1,2] has been used for time-resolved investigations of molecular dynamics by transient absorption at the near edge (K or L edge) of the constituting elements of organic molecules in the gas [3,4] or liquid phase.

In this contribution, we will discuss the technological challenge of driving HHG at high photon energy and with enough photon flux. Also, we introduce a simplified approach [5] to efficiently extend the high harmonic generation (HHG) cutoff in gases without the need for laser frequency conversion via parametric processes. Instead, we employ postcompression and red-shifting of a Yb:CaF<sub>2</sub> laser via stimulated Raman scattering (SRS) in a nitrogen-filled stretched hollow core fiber. This driving scheme circumvents the low-efficiency window of parametric amplifiers in the 1100–1300 nm range. We demonstrate this approach being suitable for upscaling the power of a driver with an optimal wavelength for HHG in the highly desirable XUV range between 200 and 300 eV, up to the carbon K-edge. Due to the combination of power scalability of a low quantum defect ytterbium-based laser system with the high conversion efficiency of the SRS technique, we expect a significant increase in the generated photon flux in comparison with established platforms for HHG in the water window. We also compare HHG driven by the SRS scheme with the conventional self-phase modulation (SPM) scheme.

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## **Polarization- and time-resolved high-order harmonic spectroscopy in condensed media**

FACCIALÀ, Davide (CNR-IFN)

High-order harmonic generation (HHG) spectroscopy is a well-established technique for probing real-time dynamics [1] and sub-nanometer structures [2] in atoms and molecules. Its application in solids has opened new possibilities for characterizing ultrafast processes and structures in condensed media, enabling for example the band structure reconstruction [3] and the measurement of photoinduced dynamics in correlated materials [4]. However, the interpretation of these results is still difficult and requires advanced spectroscopic tools that go beyond the current state-of-the-art.

To make this step forward, we developed a setup for polarization- and time-resolved HHG spectroscopy. This setup allows us to excite the sample through an electronic transition induced by a pump pulse and characterize the following dynamics by HHG driven by an intense probe pulse. Finally, the HHG polarization state can be fully characterized with a polarimeter.

I will show HHG polarimetry results in bulk germanium, where the harmonic polarization state strongly depends on the intensity and polarization of the driving field. In particular, when the driving field polarization is not parallel to a crystal axis symmetry direction, the polarization of the harmonic emission deviates from the one of the driving field, which is indicative of a coherent ballistic motion of the electrons over the landscape of the curved band structure.

Then I will present preliminary HHG pump-probe results in a topological chiral compound, tellurium. Here, the strong structural sensitivity of HHG is used to probe the topological phase transition initiated by the pump through electron-phonon coupling. Time-resolved HHG has the potential to unveil the strong interplay between the symmetry of the lattice, the spin, the electronic properties, and the topology of such systems.

Finally, I will show how HHG spectroscopy can also be applied to mesomorphic states of matter, presenting the first experimental observation of HHG from Thermotropic Liquid Crystals (TLCs). Here HHG spectroscopy serves as a unique tool for characterizing phase transitions in liquid crystals and their structural properties when they are aligned by an external AC field.

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## **Photoelectron holography: an interplay between different interference mechanisms**

**BORBÉLY**, Sándor (Faculty of Physics, Babeş-Bolyai University); Prof. **NAGY**, Ladislau (Faculty of Physics, Babeş-Bolyai University); **TÓTH**, Attila (ELI-HU Non-Profit Ltd.)

During the interaction of ultrashort laser pulses with atoms and molecules the electronic wave packets following different spatial and temporal paths interfere leading to the formation of photoelectron holograms [1,2]. In our previous investigations [3,4] we have studied the photoelectron hologram induced by few-cycle time-symmetric laser pulse with sine-square envelope. Due to the particular shape of those laser pulses, in the observed hologram the dominant component was attributed to the spatial interference (wavepackets emitted at the same time moment but following different paths), while the component attributed to the temporal interference (wavepackets emitted at different time moments of the laser pulse) was barely visible.

In the present study we performed ab initio calculations for the ionization of the hydrogen atom in interaction with few-cycle flat-top laser pulses, each half-cycle having the same amplitude. The parameters of the driving laser field are chosen in such way, that the intensity of the continuum wave packets created by the different half-cycles of the driving field are similar. By doing so, we have ensured that both the spatial and temporal interference patterns are visible and their coherent superposition can be studied.

The formation of the spatial and temporal interference patterns, and their coherent superposition were investigated in details using the wave-function splitting technique [3].

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## Theoretical description of attosecond x-ray imaging of electron dynamics in molecules and crystals

GORELOVA, Daria (University of Hamburg)

We explore how attosecond x-ray and extreme ultraviolet pulses can be employed for imaging electron dynamics in molecules and materials in real time. In the first part of my talk, I will review our recent theoretical developments to describe pump-probe experiments following molecular as well as solid-state excitons. I will present our results of time-resolved momentum microscopy of molecular excitons [1,2] and attosecond x-ray absorption spectroscopy of Frenkel excitons [3]. I will present our theoretical framework developed within the Bethe-Salpeter equation for the description of x-ray absorption spectroscopy of solid-state excitons. In the second part of my talk, I will present our theoretical description of attosecond x-ray diffraction experiments from laser-dressed materials [4-6].

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## Multi-purpose Ultrafast Microscopy with a Compact High-Harmonic Source

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We developed an innovative EUV ultrafast compact microscope with 13nm and 30nm HHG beams, characterized by high spatial resolution and high throughput, while retaining flexibility and facility-scale beam diagnostics. Ultrafast microscopy is carried out with a technique for diffractive imaging called Ptychography [1], where multiple diffraction patterns from overlapping fields of view are processed by iterative algorithms [2, 3] to reconstruct the real-space image of the sample. The ultrafast multipurpose microscope design was carried out by in depth analysis of EUV source size, divergence, and high-order aberrations effects through ray tracing simulations, using the open-source ShadowOui through the OrAnge SYNchrotron Suite (OASYS). It is characterized by a simple and robust off axis  $z$ -fold XUV focusing scheme, to filter the probe EUV beam to a narrow bandwidth and to focus it onto the sample, allowing for a geometry demagnification of 10. Accounting for a  $1/e^2$  diameter between 30-50 $\mu\text{m}$  and a divergence in the range 0.7-2mrad at the EUV beam generation point, we obtain a variable 4 - 10 $\mu\text{m}$  beam diameter at the image plane. The automated motion of the detector allows for the flexible selection of Numerical Apertures (NA) from 0.04-0.6, supporting wavelength-scale spatial resolutions, with  $\approx 40\text{fs}$  time resolution.

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## Tuesday – September 19.

<b>8:30-10:15</b>	<b>Plenary 2.</b> Chair: T. Weinacht	
8:30-9:05	<b>Luis DIMAURO</b> <i>Building a Quantum Trajectory Selector for Studying Strong Field Physics</i>	<b>PT-4</b>
9:05-9:40	<b>Thomas BAUMERT</b> <i>Laser based photoelectron circular dichroism</i>	<b>PT-5</b>
9:40-10:15	<b>Alexander Kuleff</b> <i>Ultrafast charge migration in molecules initiated by ionization and excitation</i>	<b>PT-6</b>
<b>10:15-10:30</b>	break	
<b>10:30-12:10</b>	<b>Invited 4.</b> Chair: F. Calegari	
10:30-10:55	<b>Fabien GATTI</b> <i>Hydrogen Migration in the Photoionized Glycine by a Mixed Quantum-Classical Dynamics</i>	<b>IT-11</b>
10:55-11:20	<b>Torsha MOITRA</b> <i>Relativistic real-time TDDFT for pump-probe processes</i>	<b>IT-12</b>
11:20-11:45	<b>Jesús GONZÁLEZ VÁZQUEZ</b> <i>Time-resolved ionization close to the threshold: RABBIT N2 with XCHEM</i>	<b>IT-13</b>
11:45-12:10	<b>Bernd SCHÜTTE</b> <i>Two-color all-attosecond pump-probe spectroscopy at 1 kHz</i>	<b>IT-14</b>
<b>12:10-14:10</b>	lunch	
<b>14:10-17:00</b>	<b>Free time for discussions and networking</b>	
<b>17:00-19:00</b>	<b>poster session</b>	

### **Building a Quantum Trajectory Selector for Studying Strong Field Physics**

PIPER, Andrew J.; LIU, Qiaoyi; TANG, Yaguo; CAMACHO GARIBAY, Abraham; KIESEWETTER, Dietrich; AGOSTINI, Pierre; DIMAURO, Louis F. (Department of Physics, The Ohio State University, USA); BÆKHØJ, Jens E.; SCHAFER, Kenneth J. (Department of Physics & Astronomy, Louisiana State University, USA)

Nearly thirty years ago, a simple and intuitive unified view of intense laser-atom interactions was introduced. The model is based on a semi-classical description where a bound electron is tunnel ionized by the strong optical field, followed by propagation under the influence of the strong field and finally driven back to interact with the core. This simple view has become known as the three-step or rescattering model and is responsible for the production of high energy electron & photons, multiple ionization and the formation of attosecond light pulses. The coherent process is started by the initial step of tunnel ionization which defines the physical observables for steps (2) and (3).

Feynman has taught us that the outcome of a quantum process is dictated by the sum over all the quantum trajectories that contribute to it. Naturally, when analyzing experiments, we often refer to these individual trajectories even though they have not been measured individually. In this talk we will describe a fully functioning Quantum Trajectory Selector (QTS) which allows us to directly measure the outcome of “single” trajectories that summed together make up a quantum process. Our QTS operates in the strong field domain, where the simple semiclassical model described above is ubiquitously used to describe individual quantum trajectories.

The talk will describe elements of the semi-classical 3-step model. We will then describe the construction of the QTS experiment by reverse engineering using attosecond XUV pulse trains with a sculpted bandwidth phase-locked to an intense near infrared (NIR) optical field. In essence we replace the tunneling step by single-photon ionization. In essence, we select the moment the electron is launched into the continuum and measure the ensuing delay-dependent rate of electron emission and double ionization driven by near infrared field. The QTS provides a new paradigm for expanding our understanding of recollision-driven physics.

## Laser based photoelectron circular dichroism

BAUMERT, Thomas (Universität Kassel)

Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantioselective spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multiphoton ionization [3]. In the latter case resonance enhanced multiphoton ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of the coupled electron and nuclear motion in enantiomers. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution I will report on our investigations on PECD with coherent light sources whose pulse durations span from femtoseconds to nanoseconds [4]. By this we address impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation in mixtures with the help of high resolution nanosecond laser techniques [5]. The reflection of the number of absorbed photons in the PECD [6] will be discussed as well as subcycle effects in bichromatic fields [7].

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### Ultrafast charge migration in molecules initiated by ionization and excitation

KULEFF, Alexander I. (Theoretical Chemistry, PCI, Heidelberg University, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany)

Exposing molecules to ultrashort pulses results typically in a coherent population of several and even many electronic states. This triggers ultrafast electron dynamics, which may lead to a redistribution of the charge even before the nuclei start to move and adjust – a process often referred to as charge migration [1,2]. The non-adiabatic coupling between the electronic and nuclear motion will eventually destroy the initial electronic coherence and trap the migrating charge. The time during which the electron coherence is maintained is an important parameter. This time can be used to modulate the charge migration process and thus predetermine the succeeding nuclear rearrangement in the molecule – the paradigm of attochemistry. In this talk, fully quantum simulations of ultrafast charge dynamics initiated by both ionization [3,4] and excitation [5] of polyatomic molecules will be presented, and the possibility to trace these dynamics by attosecond transient-absorption spectroscopy [6] will be discussed. Examples of decoherence and revival of coherence will be shown, as well as a transfer of electronic coherence through conical intersections [5]. The possibility for a laser control of the electron-coherence time [7] will also be discussed.

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## Hydrogen Migration in the Photoionized Glycine by a Mixed Quantum-Classical Dynamics

K. Kety,<sup>1</sup> J. G. Vasquez,<sup>2</sup> A. Mitrushchenkov,<sup>1</sup> P. Decleva,<sup>3</sup> L. J. Doriol,<sup>1</sup> R. Cireasa,<sup>4</sup> D. Pelaez Ruiz,<sup>4</sup> F. Gatti,<sup>4</sup> (fabien.gatti@universite-paris-saclay.fr) and F. Martin<sup>2</sup>

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<sup>4</sup>*Université Paris-Saclay, Institut des Sciences Moléculaires d'Orsay ISMO, UMR CNRS 8214, F-91405 Orsay, France*

We have theoretically investigated the intra-molecular hydrogen migration in the glycine molecule ionized by XUV attosecond pulse train of duration 1.5 fs to explain previous experiments by R. Cireasa et al [The journal of physical chemistry letters 9 (2018) 6012-6016]. The interaction of the glycine molecule with the XUV pulse leads to a superposition of coherent electronic states which dynamics is coupled to the nuclear one. We have combined the Correlated Single Channel Approach to evaluate the ionization amplitudes with the trajectory surface hopping to describe the coupled electron-nuclear dynamics. A statistical analysis is then performed to evaluate the theoretical hydrogen migration time in order to compare with the experimental one which is approximately 48 fs. We do observe a hydrogen migration often occurring from the electronic ground state of the ionized ground state. In this first simulation, we do not include the quantum coherence of the electronic wavefunction, but work is in progress to include it and to understand the interplay between electronic and nuclear motions at a quantum level using the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package.

## Relativistic real-time TDDFT for pump-probe processes

MOITRA, Torsha (UiT The Arctic University of Norway)

We present fundamental insights on pure electron dynamics captured by pump–probe attosecond transient absorption processes, within the realms of relativistic real–time time-dependent density functional theory [1-3], where both scalar and spin-orbit relativistic effects are included variationally using modern atomic mean-field eXact two-component (amfX2C) Hamiltonian [4]. We address how this technique records the signature of the transient dynamics triggered by the pump pulse imprinted onto the molecular response to probe pulse, including effects of additional degrees of freedom (pump pulse features and pump–probe time delay) absent in conventional spectroscopy. Non-equilibrium response theory will be used to lend further mathematical interpretation of the simulated spectral observations. Furthermore, given the remarkable agreement of the highly accurate yet order of magnitude computationally cheaper amfX2C Hamiltonian with respect to Dirac- Coulomb Hamiltonian, makes our framework consistently applicable for all elements across the periodic table and for both core and valence energy regions.

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## Time-resolved ionization close to the threshold: RABBIT N<sub>2</sub> with XCHEM

Jesús González-Vázquez<sup>1,2</sup>, Vicent J. Borràs<sup>1</sup>, Luca Argenti<sup>3</sup> and Fernando Martín<sup>1,4,5</sup>

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The theoretical description of observables in attosecond pump-probe experiments requires a good representation of the ionization continuum. For poly-electronic molecules, however, this is still a challenge, due to the complicated short-range structure of correlated electronic wave functions. Whereas quantum chemistry packages designed to compute bound electronic molecular states are well established, comparable tools for the continuum are not widely available yet. To tackle this problem, we have developed a new approach [1] that, by means of a hybrid Gaussian-B-spline basis [2], interfaces existing multi-reference quantum chemistry packages with close-coupling scattering methods. In this talk, we will describe the ingredients of the method, already implemented in the XCHEM code, and illustrate its focusing of the N<sub>2</sub> molecule [3], including time-resolved simulations of its RABBIT spectrum [4].

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## Two-color all-attosecond pump-probe spectroscopy at 1 kHz

KRETSCHMAR, Martin; SVIRPLYS, Evaldas; VOLKOV, Mikhail; WITTING, Tobias; NAGY, Tamás; VRAKKING, Marc J. J.; SCHÜTTE, Bernd (Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin, Germany, Bernd.Schuette@mbi-berlin.de)

The development of femtochemistry has enabled the observation of the processes during a chemical reaction in real time. In a typical femtochemistry experiment, a femtosecond pump pulse initiates the dynamics in a chemical reaction, and a second femtosecond probe pulse interrogates these dynamics at different time delays. For his pioneering contributions in the field of femtochemistry, Ahmed Zewail was awarded with the Nobel Prize in 1999.

The development of attosecond science at the beginning of this century has raised expectations that the concept of femtochemistry may be transferred to the attosecond domain, meaning that one attosecond pump pulse initiates dynamics in a system and that a second attosecond probe pulse interrogates this system at different time delays. However, it soon became obvious that this is a very challenging goal, since the conversion efficiencies in high-harmonic generation (HHG) are very small. Instead, attosecond pulses have been used in combination with femtosecond near-infrared (NIR) pulses in the vast majority of experiments. Using the oscillation period of the NIR pulses as a clock, exciting insights into electron dynamics on extremely fast timescales were obtained in atoms, molecules, liquids, solids and at the nanoscale.

Attosecond-pump attosecond-probe spectroscopy (APAPS) remains a highly attractive goal, because the application of strong fields can be avoided and because APAPS allows the selective pumping and probing from valence and core levels using attosecond pulses in both the pump and the probe step. Pioneering work on APAPS has been carried out by the groups of Charalambidis [1] and Midorikawa [2]. In these experiments two copies of extreme-ultraviolet (XUV) pulses have been used to perform auto-correlation type of measurements, enabling an estimation of the XUV pulse durations of 1.5 fs [1] and 500 as [2]. The large setups and low-repetition-rate laser systems (10 Hz) used in these experiments offer a potential explanation for why the number of APAPS experiments that have been reported is very limited.

We will present two approaches for APAPS developed in our laboratories, which have in common that they are optimized for a high XUV intensity instead of a high XUV pulse energy: (1) Using an 18-m-long HHG beamline, an XUV peak intensity of  $7 \times 10^{14}$  W/cm<sup>2</sup> was demonstrated, enabling the investigation of highly non-linear dynamics in atoms, which resulted in the generation of ion charge states up to Ar<sup>5+</sup> [3]. By generating two pairs of short attosecond pulse trains, it became further possible to study XUV multi-photon ionization with attosecond resolution [4]. Recently, this lab was upgraded with a kHz laser system. (2) In our second approach, high harmonics are generated away from the focus of the driving laser using a compact setup [5] and resulting in a focused XUV beam waist radius on the order of 1  $\mu$ m. In addition, a transient blueshift of the driving laser is exploited [6], thereby boosting the HHG conversion efficiency. This configuration allowed us to demonstrate for the first time two-color APAPS at a kHz repetition rate, studying the sequential two-photon double ionization of Ar [7]. We will discuss possible applications of our APAPS approaches. Moreover, features of our HHG-based approaches and the exciting new APAPS capabilities reported from LCLS will be compared.

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### Wednesday – September 20.

<b>8:30-10:15</b>	<b>Plenary 3.</b> Chair: T. Baumert	
8:30-9:05	<b>Jens BIEGERT</b> <i>Attosecond spectroscopy of the electronic and vibrational dynamics in Furan</i>	<b>PT-7</b>
9:05-9:40	<b>Nirit DUDOVICH</b> <i>Attosecond Interferometry</i>	<b>PT-8</b>
9:40-10:15	<b>Jon MARANGOS</b> <i>Probing electron-nuclear coupling dynamics and non-linear interactions with ultrashort x-ray pulses</i>	<b>PT-9</b>
<b>10:15-10:30</b>	break	
<b>10:30-12:10</b>	<b>Invited 5.</b> Chair: V. Despré	
10:30-10:55	<b>László VEISZ</b> <i>A 100 TW quasi-single-cycle light source for attosecond physics</i>	<b>IT-15</b>
10:55-11:20	<b>Giulio M. ROSSI</b> <i>OP(CP)A-based pulse synthesis and its possible applications in attosecond science</i>	<b>IT-16</b>
11:20-11:45	<b>Maurizio REDUZZI</b> <i>Towards attochemistry of gas-phase organic molecules</i>	<b>IT-17</b>
11:45-12:10	<b>Vincent WANIE</b> <i>Real-time tracking of electron-driven dynamics in chiral molecules</i>	<b>IT-18</b>
<b>12:10-14:10</b>	lunch	
<b>14:10-15:25</b>	<b>Invited 6.</b> Chair: L. Veisz	
14:10-14:35	<b>Victor DESPRÉ</b> <i>Ab-initio simulations of ultrafast electron-nuclear dynamics: Paving the way to attochemistry</i>	<b>IT-19</b>
14:35-15:00	<b>Csaba FÁBRI</b> <i>Cavity-modified ionization spectrum of a polyatomic molecule</i>	<b>IT-20</b>
15:00-15:25	<b>Mathieu GISSELBRECHT</b> <i>Young-slit experiments in time</i>	<b>IT-21</b>
<b>15:25-15:40</b>	closing remarks	

### **Attosecond spectroscopy of the electronic and vibrational dynamics in Furan**

**BIEGERT**, Jens (ICFO); **SEVERINO**, Stefano; **ZIEMS**, Karl Michael; **SUMMERS**, Adam; **REDUZZI**, Maurizio; **SUN**, Hung-Wei; **CHIEN**, Ying-Hao; **GRÄFE**, Stefanie

We apply attosecond time-resolved carbon K-edge spectroscopy to investigate the ultrafast nonadiabatic relaxation pathways of furan after strong field excitation [1]. Disentangling the inter-play of the various mechanisms, and how they lead to a specific flow of energy inside a molecular system, is extremely challenging since many of these effects occur on overlapping temporal scales. I will show, however, the extreme temporal resolution along with state and conformational sensitivity of AttoXAFS allows to disentangle the intricate interplay between of the electronic and nuclear wavepackets and extract a detailed picture of the rich dynamics that involves several parallel pathways, multiple CIs, electronic coherences and transiently populated dark states. Our method detects electronic-nuclear correlations, the dephasing of electronic coherence due to nuclear motion, and identifies the ring-opened isomer as the dominant product. These results demonstrate the efficacy of attosecond core level spectroscopy as a potent method to investigate the real-time dynamics of photochemical reaction pathways in complex molecular systems.

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### **Attosecond Interferometry**

DUDOVICH, Nirit (Weizmann Institute of Science)

High harmonic generation (HHG) spectroscopy has been successfully applied over the past two decades to resolve fundamental strong-field phenomena in atoms, molecules and solids. An important aspect of HHG spectroscopy lies in its coherent nature. The strong-field interaction directly transfers the coherence of the laser field into the coherent properties of the electronic wavefunction that interacts with the field, and back into the optical properties of the emitted harmonics. Resolving the internal coherence is key to reconstructing the internal dynamics, being one of the primary challenges in HHG spectroscopy. As in many other branches of physics, the presence of coherence is determined through interferometry.

In this talk, I will describe advanced schemes for attosecond interferometry. The application of these schemes provides direct insights into a range of fundamental phenomena in nature. The first part of my talk will be dedicated to the study of phenomena in atomic systems. By using two interfering phased-locked attosecond sources, we resolved the scattering phase associated with the basic mechanism underlying photoionization. Next, we resolve one of the most basic strong field phenomena – field induced tunnel ionization. Applying interferometry resolved the barrier's modifications during the tunneling mechanism as well as the excitation of the electron as it propagates under the tunneling barrier. Interferometry can be induced in the spatial domain as well. By shaping of 2D electron trajectories, we have induced a microscopic spatial interferometer, and probed the spatial properties of molecular systems. Finally, we have applied attosecond interferometry to explore subcycle dynamics in condensed matter systems, resolving field induced band gap dynamics or probing the Berry phase accumulated during the strong field interaction.

## Probing electron-nuclear coupling dynamics and non-linear interactions with ultrashort x-ray pulses

MARANGOS, Jon (Imperial College London)

I will discuss the application of ultrafast x-ray pulses from both HHG sources and XFELs to study dynamics in matter through time-resolved x-ray spectroscopy that provides sensitivity to both the localized electronic excitation and electron-nuclear couplings. Using a HHG source to generate water window sub-femtosecond pulses [1] we have probed the exciton dynamics in the organic semiconductor polythiophene (P3HT). We observe the signature of atomically resolved electron density changes following exciton formation, and also a transient pre-edge feature attributed to the initial delocalization of the exciton across neighboring polythiophene chains [2]. Electronic dynamics in inner valence states of molecular cations of isopropanol and glycine are probed using an x-ray pump-probe methodology at LCLS and FLASH using few-fs pulses. In isopropanol we capture breathing mode charge migration dynamics of the excitation formed in a superposition of single hole and 2 hole- 1 particle states [3] which is a signature of frustrated Auger-Meitner decay. In glycine we observe oscillatory signatures of charge migration at early times (to 20 fs) that apparently couple to vibrational motion over longer timescales [4].

The use of enhanced SASE (XLEAP) pulses at LCLS to provide unprecedentedly high attosecond pulse energies will then be discussed. These were used to study coherent electronic wavepackets of core excited states in NO [5]. The large coherent bandwidth laser permits the electronic excitation through impulsive x-ray Raman which was observed in NO gas [6] and recently in liquid water with the Raman signature observed in the transmitted x-ray spectrum. We will conclude with an overview of recent X-ray pump-probe measurements of electronic dynamics in the aminophenol molecule using the two-pulse XLEAP capability.

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## A 100 TW quasi-single-cycle light source for attosecond physics

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Laser-plasma physics at ultrahigh intensities is normally driven by lasers with few-10 fs or longer pulse duration, while attosecond physics utilizes few-femtosecond sub-TW lasers. Certain applications involving the generation of intense and isolated attosecond x-ray or electron pulses, however, require much shorter or higher peak power pulses that are not available from lasers. We report on the optical parametric synthesis of quasi-single cycle waveforms that can reach ultra-relativistic intensities up to  $10^{21}$  W/cm<sup>2</sup>. A pulse duration below 4.5 fs is achieved by amplifying the spectrum between 580 – 1020 nm in two separate spectral regions in two consecutive optical parametric chirped pulse amplifiers. One stage pumped by 355 nm is optimized below 700 nm, while another pumped by 532 nm is optimized above 700 nm. This combination of amplifiers is called optical parametric synthesizer (OPS) [1], which serially synthesizes the spectrum (full spectrum propagates through all amplifiers). Three such OPS double stages provide 440-500 mJ energy in the short light pulse corresponding to 100 TW peak power. Typical applications in attosecond physics will be shortly introduced, such as high-harmonic generation from relativistic laser-plasmas [1,2], high-harmonic generation in gases [1,3], and nonlinear attosecond x-ray interaction [4].

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### **OP(CP)A-based pulse synthesis and its possible applications in attosecond science**

ROSSI, Giulio Maria (CFEL-DESY); KUBULLEK, Maximilian (CFEL-DESY); Prof. KÄRTNER, Franz X. (CFEL-DESY); Dr MAINZ, Roland (CFEL-DESY); Dr SCHEIBA, Fabian (CFEL-DESY); SILVA-TOLEDO, Miguel Angel (CFEL-DESY)

The coherent synthesis of ultrashort pulses generated via optical parametric (chirped-pulse) amplification (OP(CP)A) opened a path to tailor the electric field waveform of intense optical pulses with unprecedented freedom. OP(CP)A allows for the generation of broadband pulses with scalable pulse energy, few-cycle duration, stable carrier-envelope phase (CEP) and spectrum tunable almost continuously over the visible-to-mid-IR region. The synthesized optical waveforms can be tailored by two key-parameters: the common CEP and the relative phases (or relative delay) among the constituent pulses. Controlling these synthesis parameters allows to access a large variety of peak intensities and half-cycle field shapes and at the same time allows to fully characterize the electric field shape of all available waveforms in a fast and in-situ fashion.

In its current implementation, the synthesis of field-controlled  $\sim 3$  fs long pulses covering the 650- 2200 nm range with  $\sim 0.5$  mJ of energy made it possible to gain control over the high-harmonic generation (HHG) process. In HHG, the use of non-sinusoidal waveforms shorter than a single optical cycle has a twofold advantage: (i) it ensures the generation of isolated attosecond pulses (IAPs) in a robust manner and without the need for spectral filtering (ii) it allows control over the central photon-energy, bandwidth and duration of IAPs in real-time by controlling the synthesis parameters. This allowed generating IAPs tunable over the 30-400 eV range and to adjust their duration (and bandwidth) between 80 and 240 as.

The availability of tailored optical waveforms with sub-cycle durations and tunable IAPs opens up interesting possibilities in attosecond science. The control of electron trajectories obtained in HHG can be extended to e.g. laser-induced electron diffraction or HH-spectroscopy, where the delay between ionisation and collision/recombination could be adjusted, thus obtaining (as) time resolution. On the other hand, by independently tuning the bandwidth and central photon energy of the IAPs one could precisely control the coherent superposition of electronic states of the molecular cation (hole wavepacket) following ionization, or control the Coulomb interaction between the hole wavepacket and the emitted electron, that is the decoherence due to interchannel couplings.



## Towards attochemistry of gas-phase organic molecules

REDUZZI, Maurizio (Politecnico di Milano)

Since their demonstration, attosecond pulses have been exploited for time-resolved investigations of ultrafast processes in atoms, molecules, and solid-state materials. Attosecond pulses are extremely sharp photo-triggering tools: as such, they have been used in the last decade as pump pulses in order to create electron wave packets in highly excited cationic states of molecules [1].

At the same time, the broad bandwidth of attosecond pulses makes them valuable probing tools, because of the element, charge, and electronic state sensitivity gained by accessing the inner valence and core levels of chemical elements [2]. Furthermore, narrowing the bandwidth of attosecond pulses via appropriate monochromatization [3] also results in exquisite probing tools, allowing for few-fs-resolved photoemission spectroscopy. Focusing on gas-phase organic molecules, both these broadband and narrowband probes allow to follow with unprecedented time resolution the ultrafast relaxation of such systems after UV photoexcitation to the first electronically excited states. The relevance of the ensuing ultrafast dynamics (radiation damage and charge transfer are two prominent examples) calls for thorough experimental and theoretical efforts towards their full understanding.

In my talk, I will present our recent efforts towards few-fs to sub-fs resolved ultrafast dynamics investigations of gas-phase organic molecules by exploiting the above paradigms.

First, I will present our results on the ultrafast dynamics of attosecond photoionized nitroaniline, a prototypical donor-acceptor molecular system. We show that a concerted nuclear and electronic motion drives electron transfer from the donor group on a sub-10-fs timescale.

Then, I will move to our investigation of the ultrafast non-adiabatic dynamics of acetylacetone with sub-20 fs resolved UV-XUV photoelectron spectroscopy. The temporal resolution allows us to resolve for the first time the ultrashort lifetime (15 fs) of the S<sub>2</sub> state.

Finally, I will present our results on the generation of sub-3-fs tuneable UV pulses via Resonant Dispersive Wave Emission. We believe that the combination of such pulses with attosecond sources in a variety of spectroscopic implementations will constitute an important step towards attochemistry.

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## Real-time tracking of electron-driven dynamics in chiral molecules

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Molecular chirality has a pivotal role in biological processes as well as for numerous technological applications [1]. In ultrafast science, exploiting the electronic motion triggered by photoexcitation of chiral molecules is a promising avenue to manipulate the outcome of enantio-sensitive photophysical and photochemical processes [2]. I will showcase a combined experimental and theoretical investigation of *coherent electron dynamics in neutral chiral molecules* via time-resolved photoelectron circular dichroism (TR-PECD) [3], revealing its impact on the molecular chiral response [4].

We used ultrashort UV pulses [5,6] to photoexcite just below ionization threshold and trigger electronic coherences in the Rydberg states of chiral methyl-lactate molecules. The dynamics is probed by a delayed circularly polarized near-infrared probe pulse through TR-PECD with an exceptional time resolution of ~3 fs. We observe that the preferential photoemission direction that is intrinsic to PECD can reverse in less than 10 fs. Calculations allow us to identify the Rydberg states responsible for the periodic modulation of the chiroptical response. I will also discuss new perspectives regarding how the chiral currents generated in our experiment can be exploited for enantio-selective charge-directed reactivity, leading to oriented fragmentation.

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## **Ab-initio simulations of ultrafast electron-nuclear dynamics: Paving the way to attochemistry**

DESPRÉ, Victor (CNRS)

The advent of attosecond physics allowed the observation and manipulation of dynamic processes occurring within the intrinsic time scale of the charge motion in atoms and molecules. This has opened the door to the realization of the dream of attochemistry, namely to control chemical reactions through the manipulation of the pure electron dynamics taking place in the first instants after the excitation of the system.

Thereby, the existence of long-lasting electronic coherences in molecular systems is the first key prerequisite to its realization. Furthermore, understating the mechanism leading to or preventing the loss of coherence is necessary for its development.

The first measurement of decoherence and revival in attosecond charge migration will be presented. This dynamics occurs after excitation of silane ( $\text{SiH}_4$ ) by an IR pulse. Simulations treating quantum mechanically both the electronic and nuclear degrees of freedom permitting the interpretation of the experimental results will be discussed. Using these simulations, the behavior of the coherence and the possibility to conserve coherence through conical intersection will be rationalized.

The second key prerequisite of the realization of attochemistry is the understanding of how charge migration can impact the reactivity of a molecular system. Recently, an XUV-pump IR-probe experiment performed on adenine has demonstrated a sub 3 fs delay in its dicationic signal. It will be shown, using multielectron wave-packet propagation, that this delay is due to a correlation-driven charge migration occurring in the correlation band region of the molecule that stabilizes the system. The stabilization is due to the delocalization of the created hole and its change from  $\sigma$  to  $\pi$  character. The generality of the observed dynamics makes correlation bands a promising playground for the exploration of the possibilities offered by attochemistry.

### Cavity-modified ionization spectrum of a polyatomic molecule

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We investigate the combined impact of natural and light-induced conical intersections (CIs) on the ionization spectrum of the butatriene ( $C_4H_4$ ) molecule. It is well known that in the butatriene cation a natural CI is formed between the two lowest electronic states, which gives rise to an unexpected and well-separated band in the photoelectron spectrum termed the “mystery band” [1,2]. In addition to the natural CI one can create a (quantum) light-induced CI (LICI) by placing the molecule into a cavity which couples the two lowest electronic states of the cation. In contrast to natural CIs, the position of the LICI and the strength of the light-induced nonadiabatic coupling can be controlled by changing the cavity frequency and the cavity coupling strength, respectively, which allows us to study the interplay of natural and light-induced nonadiabatic effects with different cavity setups. Changes in the ionization spectrum due to the cavity will be demonstrated by presenting numerical results for different cavity parameters [3].

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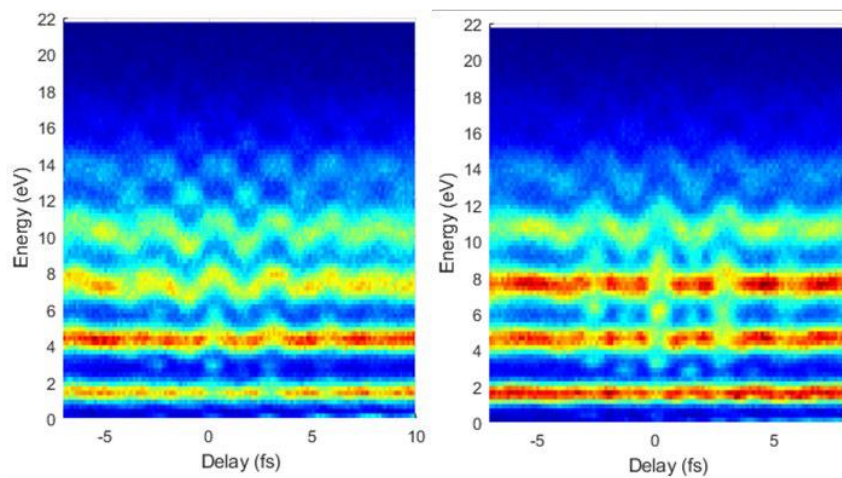
### Young-slit experiments in time

HOFF, D.; OUAHIOUNE, N.; MAROJU, P. K.; MIKAELSSON, S.; GUO, C.; RAAB, A.-K.; ANOLD, C. L.; L'HUILLIER A.; GISSELBRECHT, M; (Department of Physics, Lund University, P. O. Box 118, SE-22100 Lund, Sweden, mathieu.gisselbrecht@sljus.lu.se); VOGELSANG, J.; (Institut für Physik, Carl von Ossietzky Universität Oldenburg, 26129 Oldenburg, Germany)

Single-photon photoionization is one of the fundamental processes in nature, whose temporal aspects have attracted much attention the recent years [e.g. 1,2]. We recently demonstrated the ability to perform photoionization studies in a regime where only a small number of attosecond pulses are produced [3]. Under these conditions, photoemission can be interpreted as a Young's slit experiment in time, and we present here our progress in understanding the photoionization dynamics with a few attosecond pulses.

The experiment was carried out using high order harmonic generated from a 200 kHz optical parametric chirped pulse amplification laser emitting CEP-stabilized few-cycle pulses ( $\leq 6$ -fs) around 800 nm. The resulting attosecond pulse trains consist of 2-3 pulses with controllable phase difference [4]. When the ultrashort XUV light pulses impinge on atoms together with a weak IR dressing field ( $< 10^{11}$  W/cm<sup>2</sup>), multiple coherent ultrabroadband electron wave packets are created. The IR field allows to modulate the individual phases of the electron wave-packets, and to control how they interfere in the frequency domain. The photoelectrons are analysed with a 3D momentum electron-ion spectrometer [5].

As shown in Figure 1, the spectrograms representing the photoelectron signal emitted along the polarization axis as function of the kinetic energy and the delay between the attosecond pulses. These spectrograms exhibit non-trivial behaviour, which depends on the number of pulses. One can identify continuous energy shifts ("streaking-like"), or the formation of discrete energy peaks ("sideband-like").



**Figure 1.** Spectrograms recorded in helium with two attosecond pulses (left) and three attosecond pulses (right)

In general we observe that photoionization is no longer ruled by energy quantization and parity conservation. Instead, the emission is asymmetric with respect to the polarization axis. Time-frequency analysis of the electron wave-packets allows us to provide a quantum mechanical description of the different processes, uncovering the details of the light-matter interaction.

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## Gauge-invariant absorption of light from a coherent superposition of states

STENQUIST, Axel (Lund University); Dr DAHLSTRÖM, Marcus (Lund University); Dr ZAPATA, Felipe (Lund University)

Attosecond transient absorption spectroscopy (ATAS) is used to study electron dynamics with the aim of unravelling ultra-fast phenomena in atoms and molecules. There have been many investigations on ATAS between bound states [1], but few works has focused on the coupling of a prepared bound wave packet to both bound and continuum states [2]. A recent experimental investigation of the physical phenomena in this regime is presented in Ref. [3]. In order to disentangle the fundamental processes in this rich transient absorption regime, we establish a gauge invariant formulation of ATAS based on Yang's energy operator [4]. In the present work [5], perturbation theory is used to study the absorption of a hydrogen atom in an initial superposition state interacting with an attosecond pulse. Absorption is studied both in the time and the energy domain, resolved over the relative phase of the superposition. The model is validated by numerically solving the time dependent Schrödinger equation. The model allows for disentangling the absorption into fundamental processes of resonant and off-resonant nature, being symmetric and anti-symmetric over phase, respectively. The off-resonant contribution is found to be significant for states with dipole-allowed transitions to states of lower energy. This yields large regions of emission in the absorption profile of the  $2p+3p$  superposition, not present in the  $2s+3s$  case. Additionally, agreement with simulations of helium and neon atoms indicate the applicability of our model to more complex atoms. Using the model we have fully disentangled the ATAS spectra of two-state superpositions in atoms, with resonant and off-resonant coupling to continuum states as well as off-resonant coupling to bound states.

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## Reversible Systems in Photochemistry: Beyond Photoisomerization

SLANINA, Tomáš (IOCB Prague)

The traditional approach for achieving photochemical reversibility is the use of photoswitches. These molecules can be interconverted between two forms by the light of different wavelengths. Formally, two forms of a photoswitch are the products of photoisomerization (e.g., electrocyclization or isomerization). While this strategy has been utilized in many applications, such as smart materials, photopharmacology and molecular electronics, we believe that many other modes of photoinduced reversible systems are possible.

We combine redox and photochemical processes to selectively manipulate photoswitches and develop novel systems capable of reversible transformation upon irradiation. We focus on (i) programmable gated photoswitches, such as fulgides and diarylethenes, (ii) photoinduced manipulation with electrons (“electron ping-pong”) and (iii) reversible formation and cleavage of covalent bonds between two molecules (“catch-and-release” strategy). We also reversibly modulate the luminescence of molecular systems by the light of a specific wavelength.

While these approaches diversify in terms of potential applications, the fundamental design principles are analogic to the development of photoswitches, namely optimization of wavelength orthogonality, quantum yields, dark stability and photostationary state composition. Combined, these next-generation reversible photochemical systems broaden the scope of photoactivatable molecules applied in chemical biology, molecular electronics, photovoltaics, and material chemistry.

## Ultrashort laser pulse reconstruction from FROG traces using deep neural networks

Dr TOTH, Istvan-Ferenc (National Institute for Research and Development of Isotopic and Molecular Technologies); Dr GHERMAN, Ana Maria Mihaela (National Institute for Research and Development of Isotopic and Molecular Technologies); Dr KOVACS, Katalin (National Institute for Research and Development of Isotopic and Molecular Technologies); Dr TOSA, Valer (National Institute for Research and Development of Isotopic and Molecular Technologies)

SHG-FROG (Second Harmonic Generation - Frequency Resolved Optical Gating) [1] can be used for a complete temporal and/or spectral characterization of ultrashort laser pulses. Although SHGFROG does not directly measure attosecond duration pulses, femtosecond pulses are routinely used to generate attosecond pulses, and a good knowledge of these driving fields is required. In a SHG-FROG measurement a delayed replica of the original pulse and the pulse itself overlap in a non-linear medium and the spectrum of the second harmonic is recorded for a number of delay points. The resulting collection of spectra is a spectrogram image (trace), from which the amplitude and phase can be recovered by different inversion algorithms [2-3]. In the present work we present a pulse retrieval (amplitude and phase) method, based on CNNs (deep convolutional neural networks), with the aim to be faster than classical algorithms. The near instantaneous reconstruction of ultrashort pulses would be of great benefit to laser facilities like ELI-ALPS, ELI-NP or other laboratories. The deep neural network we employed in our work is a modified version of the DenseNet neural network [4]. We train the neural network on computationally generated FROG traces, and monitor the error between the original and the retrieved laser fields. The CNN layer parameters are adjusted according to this error. The performance of the CNN is evaluated by calculating the average reconstruction error on a test set, distinct from the training set. We generate our dataset by a semi-empirical method, which uses the Taylor-expansion of the spectral phase. In the expansion we calculate the higher order terms (third, fourth, fifth order) using experimentally viable ranges for parameters like the grating distance or incident angle of a laser system located at ELI-NP in Magurele, Romania. Our results show a good and fast reconstruction of the simulated laser pulses with low values of the reconstruction error on the test set.

This work was supported by a grant of the Romanian National Authority for Scientific Research, ANCS-UEFISCDI, project PN-III-P5-ELI-RO, project number ELI\_03/01.10.2020. This project is funded by the Ministry of Research, Innovation and Digitalisation through Programme 1 - Development of the National Research and Development System, Subprogramme 1.2 - Institutional Performance - Funding Projects for Excellence in RDI, Contract No. 37PFE/30.12.2021.

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## NEW DATASET FOR ELECTRON-IMPACT PROCESSES INVOLVING HYDROGEN AND ALKALI MOLECULAR IONS

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The new data for electron-impact processes involving some small molecular ions have been reported. Collisional processes under consideration may have an effect on the atom excited-state populations i.e. Rydberg state populations, ionization level, and optical properties of various environments [1]. Rate coefficients for electron-impact processes involving potassium, sodium, lithium and hydrogen molecular cations in domains of higher principal quantum numbers and temperatures up to 10 000 K are presented. The outcomes, i.e., the data gathered, could be used for various applications, such as plasma chemistry or experiments, for modelling atmospheres of diverse environments such as the interstellar medium, planets, and dwarf stars, and also in the plasma fusion area [2,3].

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## Spectrally separated attosecond pulse pairs

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Based on numerical calculations, which include macroscopic propagation effects, we propose an experimentally feasible configuration for high-order harmonic generation (HHG) with mid-infrared few-cycle driving pulse [1]. The advantage of the proposed configuration is that it allows the generation of a pair of attosecond pulses having separate spectral content, both in the XUV regime. We demonstrate that the spectral separation results from macroscopic propagation effects in Helium gas.

The experimentally feasible parameters are based on the setup presented in [2]:  $\lambda = 1700$  nm,  $\tau = 6$  fs FWHM,  $L_{\text{cell}} = 9$  mm filled with He gas at  $p = 200$  Torr pressure placed in the converging beam such that it ends in the nominal laser focus position ( $f = 50$  cm). A pulse of 1 mJ energy creates  $I_{\text{peak}} = 9 \cdot 10^{14}$  W/cm<sup>2</sup> peak intensity at the beginning of the gas cell. The Gaussian beam waist is  $w_0 = 90$   $\mu\text{m}$ , the Rayleigh range is 15 mm. This initial configuration produces 2.3% ionization of the neutral He medium.

With the proposed experimental parameters a pair of attosecond pulses can be generated. The temporal separation between them is constant, but the two bursts are characterized by different spectral content and spatial distribution. The earlier attosecond pulse is concentrated close to the propagation axis, and contains the cutoff harmonics which are above 300 eV. The second attosecond pulse is predominantly emitted off-axis, and spectrally contains harmonics below 300 eV. There is a natural spectral gap between the two attosecond emissions close to the onset of the water window (282 eV).

Based on the simulation results we propose three scenarios:

- (1) With the use of a low-pass spectral filter the attosecond pulse below 300 eV is kept with its total flux.
- (2) With a high-pass filter the attosecond pulse above 300 eV is kept with its total flux.
- (3) Without spectral filtering a double attosecond pulse emission with fixed temporal separation is obtained.

The spectral separation of successive attosecond pulses is an example of space-time coupling in nonlinear optics, good candidate to be further explored and exploited both theoretically and experimentally.

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## Laser Induced Breakdown –importance, possibilities and limitations

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The development of high-powered lasers in the 1960 opened a new area of research - Laser-Induced Breakdown (LIB). This phenomenon occurs due to the interaction of laser with a matter regardless of its physical state, being it solid, liquid or gas, involving different ways for plasma creation. The physical effects associated with LIB are intensive heating and explosive expansion in the focal volume and the emission of shock waves that may cause severe damage. This limits the great potential of laser application in medicine [1, 2], industry [3, 4]. To control the LIB process, the theoretical modelling of the underlying physical picture is required. The common approach starts with description of plasma formation, i.e. from the temporal evolution of free electron density,  $\rho(t)$ . To describe it the following expression can be used:  $\frac{\partial \rho(t)}{\partial t} = \sum_1^n a_i \rho_i^n(t) - \sum_1^m b_j \rho_j^m(t)$ . Here, the first sum denotes all contributing processes, while the second sum corresponds to the processes leading to the electron loss. Coefficients  $a_i$  and  $b_j$  are rates for given processes, while  $\rho_i^n(t)$  denotes the reciprocal degree of the electron density.

In the present study, we report on how different laser parameters influence the electron density and LIB threshold. After a comprehensive analysis, we found that, for a given medium, the threshold laser intensity depends on the laser beam characteristics. In addition, based on the presented results, one can conclude that the usage of femtosecond pulses minimizes energy deposition and, at the same time, mechanical and thermal effects that lead to collateral damage. The presented findings can be highly valuable in the photoacoustic applications.

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## Investigations of electron correlation dynamics at ELI Beamlines

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Multielectron processes and electron correlation play a key role in many photochemical events, autoionization, or formation of different material properties. The electron correlation can manifest itself in the population of satellite states of atoms. Satellite states have been largely investigated by synchrotron radiation. However, their dynamics, which typically occurs on femtosecond to attosecond timescale, can be inferred only indirectly from these studies. The temporal evolution of populated satellite states can be investigated using XUV pulses of femtosecond duration coming from the high harmonic generation (HHG).

In our study we follow, and to some extent control, the ionization dynamics of atomic krypton satellite states [1]. We use a single high harmonic selected by a monochromator to prepare  $\text{Kr}^+$  ion in an excited state, which is then probed by a synchronized femtosecond NIR pulse. Detection of transient  $\text{Kr}_2^+$  ion yield provides a background-free signal to unravel the ongoing dynamics. The experiment was performed at the MAC end-station [2] at HHG beamline [3,4] of the ELI Beamlines facility, operated within the Extreme Light Infrastructure ERIC. The MAC end-station is a multipurpose station dedicated to investigations of ultrafast electron and ion dynamics in atoms, molecules and nanostructures employing synchronized XUV and NIR/Vis beams.

To follow particular processes in excited  $\text{Kr}^+$  we carefully manipulate the NIR probe intensity. Using this technique, we can (i) control the ratio of sequential and non-sequential two-color double ionization, (ii) selectively monitor quantum beating oscillations of multiple states coherently excited within the bandwidth of the XUV pulse and (iii) precisely follow the relaxation dynamics of doubly excited decay channels. Our work demonstrates a practical way to control ionization mechanisms in multielectron systems.

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## Field-driven electron-molecule correlation resolved on attosecond time-scale

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In our work we employ the molecular multi-photon R-matrix method [1] to show that the IR field in a typical RABITT-like experiment can interact strongly with the initial and/or ionized molecule, not only with the photoelectron. This interaction leads to new components of the RABITT delay which therefore measure field-driven electron-molecule correlation. We demonstrate these effects by calculating accurate above-threshold multi-photon ionization amplitudes from the leading order perturbation theory. This enables us to reproduce low-intensity interference experiments without resorting to the commonly used high-energy limits (asymptotic approximation).

At the same time our approach provides a transparent physical interpretation while avoiding the need for the computationally expensive solution of the full time-dependent Schrödinger equation. The first new delay component is the “coupling delay” [2] caused by absorption of the IR photon by the residual ion. We illustrate this effect on ionization of CO<sub>2</sub> into the strongly dipole-coupled states B  $^2\Sigma_u^+$  and C  $^2\Sigma_g^+$  separated by 1.3 eV, where it contributes tens of attoseconds. Another effect not investigated in the context of RABITT so far is the dipole-laser coupling (dLC). We show [3] that polarization of neutral or final states of polar molecules by the IR field gives rise to additional one-photon pathways contributing to the RABITT interference scheme. In the highenergy limit the interplay between the one- and two-photon amplitudes reduces to the well-known dLC streaking formula. Accounting for the IR dressing in the multi-photon approach reproduces the streaking delays calculated by RMT [4] almost perfectly.

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## Resonance formation and photoionization of formic acid and ammonia dimers

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Photophysics of nucleobases triggered by ultraviolet light (UV) have been largely studied, motivated by the light-driven mutagenic DNA damage, with special focus on the investigation of long-lived charged-transfer (CT) states in stacked nucleobase pairs [1]. The alternative electron impact and photoionization processes may lead to generation of CT states but have not been extensively explored. In our research, we have been focusing on the formation of resonant states in molecular dimers, which are known to enhance elastic and inelastic collision processes. However, modeling of continuum states in such systems leads to an exponential increase in the computational demands due to the doubling of the number of electrons, and it requires developments of efficient configuration-interaction approaches to make the calculations feasible. In this work we compare and characterize resonance formation in photoionization of formic acid monomer (FAM) and dimer (FAD), a simple prototype for nucleobases and a precursor of amino acids. FAM has two sites that support hydrogen bonds leading to a highly stable dimeric structure. FAD is suitable for the development of general dimer scattering models and to initiate studies of biomolecule pairs [2]. We employed the R-Matrix method implemented in the UKRmol+ suite [3] to calculate scattering and photoionization cross sections, as well as the time-delay matrix to study resonance formation. To describe the molecular electronic states, we used different models: Static-Exchange (SE), Polarization-Consistent Coupled Hartree-Fock (PC-CHF) [4], CASSCF and its variant restricted to single and double (SD) excitations and discuss their differences and computational affordability. This work introduces an efficient computational framework we developed to investigate temporary states in dimers. We benchmarked our approach on ammonia dimer for which both large and reduced models can be employed and use them to support the experimental findings concerning proton transfer [5]. We also discuss our findings concerning the population of CT states in the dimers and the employment of this framework for nucleobase pairs.

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## **Towards probing multi-electron effects in high-harmonic generation in xenon**

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Our understanding of atomic processes induced by strong laser fields is largely based on effective single-particle or mean-field models, which are often well suited to provide a qualitative understanding of the underlying process. For a quantitative understanding, the inclusion of multielectron effects is crucial, all the more so since they can have a dramatic impact. One prominent example is the giant dipole resonance in Xe, which strongly enhances the yield in high-harmonic generation (HHG) yield at around 100 eV, as has been experimentally observed [1] and theoretically described [2]. However, an accurate description of this multi-electron effect, in a strong-field driven system, is still lacking due to the considerable challenge posed by the many-body dynamics in this 54-electron system. Recently, we have shown that the time-dependent two-particle reduced density matrix theory (TD2RDM) is able to capture the multi-electron dynamics during HHG in atoms with high accuracy, while avoiding the exponential barrier that typically plagues wavefunction based methods [3]. Accurate ground states of Xe are required to initialize the propagation. The ground state of Xe is computed using imaginary time-propagation within the time-dependent complete active space self-consistent field (TDCASSCF) method [4]. We will present first results on HHG generation in Xe within TD2RDM.

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## The Impact of Early Coherences in Ultrafast Photochemical Reactions

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The manipulation of quantum interference plays a crucial role in coherent control, one that has been used in applications ranging from quantum-state preparation, photochemical reactions and quantum information [1]. As in most quantum effects, a seemingly necessary requirement for coherent control is the existence of two or more pathways that connect the initial state with the final target state, which leads to the following question: Can the yield of a simple, direct, ultrafast photodissociation reactions be enhanced by quantum effects?

To answer the question, we maximize the yield of photodissociation in the first absorption band of  $H_2^+$  starting from the ground state, using a semiclassical model based on the Ehrenfest approximation [2], by optimizing the parameters of a transformed-limited ultrashort pulse, with time-durations smaller than 10 fs. The control mechanism is apparently simple: it maximizes the absorption in the Franck-Condon window. Qualitatively similar results are obtained using a full-quantum model. While very intense, ultrashort (attosecond) pulses are in principle preferred, a balance must be struck to avoid multi-photon dissociation and ionization.

Can the yield of photodissociation be further improved? To do so we apply the geometrical optimization method [3] to variationally improve the initial wave function. We show how, in the semiclassical limit, the yield of photodissociation relies on maximal use of the Franck-Condon window, for which the initial momentum must be correlated to the position of the trajectory. In the quantum case, the correlation can be clearly observed in the initial Wigner distributions, while the dynamical mechanism behind the absorption relies on wave packet squeezing.

The geometrical optimization is general and can be used to maximize differential scattering or photo-dissociation cross sections in complex photochemical reactions involving intersystem crossing and competing chemical channels, as in the photodissociation of  $CH_3I$ .

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## Ultrafast and Conformer-Specific Imaging of Molecular Chirality

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Chiral molecules are non-superimposable with their mirror image. Oppositely handed versions of a chiral molecule, or enantiomers, have identical properties, except when interacting with another chiral object. The ubiquity of chiral molecules in living organisms makes chiral recognition vital. However, traditional optical methods are not efficient since they rely on weak linear effects which arise beyond the electric dipole approximation.

We have recently developed [1] an ultrafast and all-optical approach for chiral discrimination based on chiral sum-frequency generation (SFG), and demonstrated how it can drive strongly enantiosensitive optical signals in the chiral molecule propylene oxide.

SFG [2] uses two incident lasers with frequencies  $\omega_1 \neq \omega_2$ , wave vectors  $k_1$  and  $k_2$ , and polarisations  $\hat{e}_1$  and  $\hat{e}_2$ , which drive a second-order response with frequency  $\omega_3 = \omega_1 + \omega_2$  and polarisation  $\hat{e}_3 = \hat{e}_1 \times \hat{e}_2$ , leading to light emission at  $k_3 = k_1 + k_2$ . SFG is exclusive to chiral media, and driven by purely electric-dipole interactions, but produces a signal which lacks enantiosensitive intensity – the molecular handedness is hidden in the phase of the signal. We have recently shown how, by making the driving field locally chiral, we can generate an achiral third-harmonic response that turns the enantiosensitive phase into a strongly enantiosensitive intensity [1].

Unlike propylene oxide, more complex bio-molecules often exist not only as left- and right-handed, but also have different conformers under standard conditions. Indeed, large organic molecules usually present several stable conformations with identical chemical connectivity, but with different spatial arrangements of their nuclei. Different conformers have different physical and chemical properties, such as molecular potentials or energy levels. However, conformer interconversion does not involve breaking or making chemical bonds, and thus the energy barriers separating them are typically small. It is therefore common that several conformers of a chiral molecule coexist in standard conditions.

Using state-of-the-art computational modelling, we are investigating how the ultrafast optical response of the chiral molecule carvone in enantiosensitive SFG is affected by the presence of multiple conformers. Indeed, each enantiomer of carvone has several conformers which coexist under standard conditions. These differ by orientation of the substituent propen-2-yl moiety relative to the molecule's cyclohexene ring [3].

Here we will present our results on the ultra-fast electronic response of the three most abundant conformers of carvone [3]. We will show that, while the enantio-sensitive response of the molecule is affected by the stereochemical arrangements of their nuclei, it remains strong upon conformational averaging in the macroscopic optical response.

We believe that this work creates exciting opportunities for measuring not only molecular chirality, but also relative abundances of different conformations, and conformer-dependent ultra-fast chiral electronic dynamics – with atto-second time resolution. Because, in our approach, the enantiosensitive response of the molecules is driven by low-order nonlinear interactions, one can apply laser fields with moderate intensities, which simplify the experimental realisation of our proposal.

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## Photoelectron signature of dressed-atom stabilization in intense XUV field

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We consider non-perturbative resonant multiphoton ionization (1+1) from atoms, for parameters accessible to a free-electron laser [1]. This is studied using the resolvent operator technique, enabling the description of non-perturbative effects such as Rabi oscillations. In addition to ionization from the excited state, non-resonant contributions also have to be considered at intensities on the order of  $10^{13} - 10^{14}$  W/cm<sup>2</sup> [1,2]. The interference of these pathways is responsible for the dressed-atom stabilization effect predicted by Beers and Armstrong [3].

The Rabi oscillations lead to an Autler-Townes (AT) doublet structure in the photoelectron spectrum [1,4], that can be interpreted in terms of the dressed states of the atom. Using a model based on time-dependent perturbation theory, we showed that interference between the resonant and non-resonant pathways leads to a detuning-dependent asymmetry between the two components of the doublet [1]. The model was able to explain observations made at FERMI for the  $1s^2 - 1s4p$  resonance in He, and agreed with simulations performed using the time-dependent configuration interaction singles method [1].

Here we extend the model used in Ref. [1], by accounting for depletion and AC-Stark shifts in the two-level system through an effective Hamiltonian. This is used to study photoelectrons resulting from resonant ionization with linearly or circularly polarized light. We show how the stabilization effect predicted by Beers and Armstrong depends on the number of available ionization continua, and that only circular polarization allows for stabilization in the case of ionization via  $1s2p$  in He [2]. Our main result is that a signature of stabilization should be present in the photoelectron spectrum, with the component of the AT doublet associated to the stabilized dressed state vanishing for certain laser parameters. At the point of stabilization the spectrum will therefore be nearly completely asymmetric, with regards to the components of the AT doublet.

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### **Carrier-envelope-phase measurement of sub-cycle UV pulses using angular photofragment distributions**

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Carrier-envelope-phase (CEP) of sub-cycle ultraviolet (UV) pulse strongly influences the dynamics of quantum systems, but its characterization is not accessible experimentally. Here we investigate photodissociation of a diatomic molecule from its ground-rovibrational state in a linearly polarized weak sub-cycle UV pulse with a controlled CEP. The angular distribution of photofragments shows an asymmetric profile deviating from the well-known  $\cos^2$ - or  $\sin^2$ -like ones, which can be identified as a way to imprint CEP [1]. We unveil that such an effect stems from the temporal neighboring rotational excitation by molecular permanent dipole interaction through the joint contributions between counter-rotating and rotating terms. This in turn, opens different pathways in photodissociation dynamics. Given that the temporal excitation between various states with close energies can be manipulated by CEP of sub-cycle UV pulses, our results pave ways for understanding and manipulating electron, nuclear and their joint dynamics with variation of CEP of attosecond pulses.

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### Electron-rotation coupling in diatomics by intense UV pulses

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The electronic angular momentum projected onto the diatomic axis, naturally couples with the angular momentum of the nuclei rotations. Such an electron-rotation coupling is safely neglected in weak-field regime, and rightly not included in the conventional model for pulse-molecule interactions. However, under strong field excitation, the electron-rotation coupling must be taken into account for observables related directly to the rotational dynamics, such as molecular alignment and angular distribution of photofragments [1, 2]. Stronger probe pulse intensity and larger degrees of alignment increase the influence of the electron-rotation coupling [3]. A UV pump-probe scheme is proposed to study the electron-rotation coupling effects, simulations of the rovibrational dynamics unravel clear fingerprints of the electron-rotation coupling effects that can be observed experimentally [4]. These theoretical results advance our in-depth understanding of intense pulse molecule interactions.

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**Time-resolved resonant Auger scattering clocks distortion of a molecule**

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Resonant Auger scattering (RAS) provides information on the core–valence electronic transition and impresses a rich fingerprint of the electronic structure and nuclear configuration at the time-initiating RAS process. Here, we suggest using a femtosecond X-ray pulse to trigger RAS in a distorted molecule, which is generated from the nuclear evolution on a valence excited state pumped by a femtosecond ultraviolet pulse [1]. With the time delay varied, the amount of molecular distortion can be controlled and the RAS measurements imprint both their electronic structures and changing geometries. This strategy is showcased in H<sub>2</sub>O prepared in an O–H dissociative valence state, where molecular and fragment lines appear in RAS spectra as signatures of ultrafast dissociation. Meanwhile, we observed the coherent vibrational dynamics on the dissociative fragment [2]. Given the generality of this approach for a broad class of molecules, this work opens a new alternative pump–probe technique for mapping the core and valence dynamics with ultrashort X-ray probe pulses.

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## **Experimental Setup for Ultrafast X-ray Spectroscopy of Coherent Superpositions of Valence States with Few-Femtosecond Tuneable Pump Pulses from Resonant Dispersive Wave Emission**

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The first step in an attochemistry experiment is the creation of a coherent superposition of valence states in the vicinity of a conical intersection. The current bandwidth of UV pump pulses is typically insufficient to cover multiple electronic states and create a coherent wavepacket. Additionally, many probing techniques lack the time resolution to capture dynamics before they decohere, which is typically on the scale of a few femtoseconds [1].

Here, we report an experimental setup that combines intense tuneable pump pulses produced in a hollow core fibre (HCF, stretched capillary) using soliton self-compression and RDW emission with our robust soft x-ray probe from HHG [2]. This will allow us to perform UV pump – x-ray probe absorption experiments with a time resolution an order of magnitude better than previously reported and allow the creation and direct observation of electronic coherences as they travel along a potential energy surface.

Here we will present the tabletop optical setup that we have developed. We use ~1m-long stretched HCFs to compress the signal (1.45  $\mu\text{m}$ , 1.6 mJ, 45 fs) and idler (1.75  $\mu\text{m}$ , 1.2 mJ, 40 fs) outputs of a 1 kHz Ti:Sapph-pumped OPA down to 2 optical cycles. The idler beam is used to generate isolated ~500 attosecond soft x-ray pulses with energy spanning beyond the carbon K edge [3]. The signal beam is used to generate compressed, tuneable pump pulses (230–700 nm, 2-10 uJ, ~4 fs). Our combination of a few-femtosecond pump, zero-dispersion mirrors and attosecond probe pulses means we anticipate a time resolution of ~5 fs.

The tunability of the pump pulses allow us to select the exact energy to best create a superposition between two states in a given molecule, in contrast to traditional fixed pumping wavelengths. We also combine the laser pulses with a home-built target system capable of delivering solid, liquid and gaseous targets with which we will study a wide range of important photochemical molecules in their natural environments. This is a tabletop experimental setup capable of measuring charge transfer dynamics in neutral molecules by the creation of coherent superpositions of valence excited states. We plan to resolve the first steps in the ultrafast ring opening of thiophene which is thought to occur on the 20 fs timescale.

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## Time-resolving molecular tunneling dynamics with Free-Electron-Laser-pump and High-Harmonics-Generated-probe transient absorption spectroscopy

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We combine XUV-FEL-pump with XUV-HHG-probe pulses in a transient absorption spectroscopy experiment to investigate the dissociation of molecular oxygen. We time-resolve the tunneling of the  $O_2^+$  ( $c4\Sigma_u^- v=0$ ) state into two channels within picoseconds by identifying absorption resonances of the neutral and ionic fragments.

We introduce an all-XUV FEL-pump—HHG-probe transient absorption spectroscopy scheme, which allows to investigate XUV-initiated molecular dynamics with electronic-state-resolved sensitivity to neutral and ionic fragments. For a first benchmark of this new measurement scheme, we consider the tunneling and pre-dissociation dynamics in oxygen molecules from a specific FEL-excited state by measuring the broadband HHG-probe absorption spectra, covering 10s of characteristic absorption lines from 23 to 35 eV. The FEL-excited  $O_2^+$  ( $c4\Sigma_u^- v=0$ ) state, which exhibits a local potential-energy minimum in the Franck-Condon region, can dissociate along two parallel pathways, with the rates  $R_{1,2}$ , respectively, 1st: the  $O(3P) + O+(4S_o)$  channel or 2nd: the  $O(1D) + O+(4S_o)$  channel including the electronically excited state  $O(1D)$ . We identify these fragments in the time-resolved absorption spectrum ( $\Delta OD$ ) from well-known resonant atomic transitions and find, in agreement with a rate equation model and theoretical expectations [1–4], all fragments to appear with a common 280 ps time constant.

In the future, this scheme can be applied to molecular systems, allowing both precision tests of state-of-the-art quantum dynamics theory in small molecules as well as time-resolving statespecific molecular dynamics in more complex systems with a broad dynamic range from nanoseconds to femtoseconds and beyond.

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### **Studying internal conversion dynamics in strong-field molecular ionization**

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We investigate the coupled electronic and nuclear dynamics during strong-field molecular ionization in CH<sub>2</sub>BrI by measuring the momentum-resolved photoelectron yield in different ways: i) as a function of the delay or ii) of the relative phase for a pair of strong-field laser pulses and also iii) as a function of the chirp of a single pulse. The measurements are compared with and interpreted by ab initio electronic state calculations and model quantum dynamics simulation of the strong-field ionization dynamics, which include multiphoton resonance, dynamic Stark shifts, as well as 1D vibrational dynamics and internal conversion during the ionization process. The measurements and calculations illustrate how the light-matter coupling can compete with the coupled motions of electrons and nuclei in strong-field laser-molecule interactions and demonstrate coherent control over internal conversion during the resonantly enhanced multiphoton ionization process with shaped, few-cycle laser pulses.

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## **Analysis of Autler-Townes patterns in photoelectron energy spectra at resonant two-photon ionization of atom by laser pulses of different shapes**

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Using the method of time-dependent amplitudes we analyze the fingerprints of the Rabi dynamics between the ground and excited 2p states of the hydrogen atom, induced by an intense short laser pulse which resonantly couples the two states, in the energy spectra of photoelectrons produced in the subsequent ionization of the atom from the excited state. It is found that for Gaussian, half-Gaussian and rectangular pulses, characterized by the same pulse area, the spectra consist of similar patterns having the same number of peaks between the prominent edge (Autler-Townes) peaks [1]. The analysis in terms of dressed states performed within the minimal three-level model showed that the mechanism of formation of multiple-peak structures during the photoionization process is the same regardless of the pulse shape. This fact disproves the hypothesis proposed in earlier studies [2] that the multiple-peak pattern appears due to dynamic interference of the photoelectrons emitted with a time delay at the rising and falling sides of the pulse, because, in contrast to the Gaussian pulse, the pulses of other two shapes do not have one or both sides. This conclusion is in agreement with the analysis of the conditions for dynamic interference [3], where it was found that they are not always fulfilled.

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## Mapping the UV-induced dynamics of CH<sub>3</sub>I with 5 fs resolution

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Methyl iodide (CH<sub>3</sub>I) has become a benchmark molecule for time-resolved ultraviolet (UV) spectroscopy [1]. The lowest-lying states of the molecule, forming the A-band, are accessible by single UV photon absorption in the energy range between 4.1-5.4 eV [2]. The prompt dissociation of the band is accompanied by a passage through a conical intersection (CI) along the C–I reaction coordinate. The CI crossing is expected to be reached in ~ 10-20 fs timescale, imposing difficulties in being observed experimentally [3, 4].

In this work, we use our recently developed light source delivering broadband UV pulses with central energy of 4.9 eV [5] to populate the A-band. The UV-induced dissociative dynamics were probed via multiphoton ionization induced by ultrashort near-infrared (NIR) pulses with 5-fs time resolution.

The extreme time resolution provided by the use of few-cycle pulses allows us to benchmark a full-dimensional classical trajectory simulation that has been used to predict the neutral evolution through the formation of CH<sub>3</sub>I<sup>+</sup>, CH<sub>3</sub><sup>+</sup> and I<sup>+</sup> cations. In turn, the benchmarked theoretical model allows us to extract the time to reach the conical intersection and analyze its dependence on the excitation energy. Notably, a 5-fs decay time observed in the time-dependent yield of the parent ion reveals that the probability for the UV-induced cleavage of the C-I bond can be manipulated by adjusting the delay of the NIR probe pulse in a narrow time window after excitation (illustrated in Fig. 1) [6], therefore offering a new control scheme for the photoprotection of the molecule against dissociation.

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## haCC-M: a general purpose solver to study multiphoton processes in small molecules

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We introduce haCC-M (hybrid anti-symmetrized coupled channels method for molecules) for investigating multi-photon and strong field processes in molecules. The intricate nature of these phenomena, characterized by high-dimensional multi-electron effects, the absence of spherical symmetry, and the significant involvement of continuum states, surpasses the realm of standard quantum chemistry. In haCC-M we address these challenges by an expansion of the wave function into a hybrid basis composed of quantum chemical CI functions and a numerical basis in the form:

$$|\psi\rangle = \sum_{I,\alpha_{\perp}} c_{I\alpha_{\perp}} \mathcal{A}|I\alpha_{\perp}\rangle + \sum_{I,i} c_{Ii} \mathcal{A}|Ii\rangle + \sum_{\mathcal{N}} c_{\mathcal{N}} \mathcal{A}|\mathcal{N}\rangle$$

Here,  $|I\alpha_{\perp}\rangle$  represents the channel functions, which are formed by taking the anti-symmetrized product of ionic states denoted by  $I$  and a numerical one-electron basis. The numerical one-electron basis consists of multi centered molecular orbitals  $i$  and a single-centred DVR expansion  $\alpha_{\perp}$ . The terms  $|\mathcal{N}\rangle$  represent the neutrals. The neutral and ionic states are obtained as linear combinations of Slater determinants built from molecular orbitals, utilizing the multi-reference configuration interaction theory implemented in the COLUMBUS quantum chemistry package [1].

The haCC-M method extends the coupled channels approach previously introduced by Majety et al. [2], where the numerical one-electron basis was limited to a single-centred expansion. However, with the inclusion of a multi-centred basis, the convergence properties of the current method are significantly improved.

Solving the TDSE with the haCC-M basis involves solving a set of coupled ordinary differential equations, requiring the computation of Hamiltonian matrix elements. The two-electron integrals, appearing in various combinations of Gaussians and DVR functions, are computed efficiently using carefully designed algorithms.

The haCC-M implementation is realized within the tRecX (time-dependent Recursive indexing) framework [3], a general-purpose TDSE solver that handles arbitrary discretizations and associated operators using Tree data structures. The tRecX package incorporates methods such as tSurff (time-dependent surface flux method) and irECS (infinite-range exterior complex scaling), which are particularly valuable for studying multiphoton processes.

In this work, we present the theoretical framework of haCC-M, discuss key implementation details, and showcase its initial applications in computing molecular photoemission time delays. Combining advanced computational techniques and a comprehensive basis representation, haCC-M offers a promising avenue for investigating multiphoton phenomena in atomic and molecular systems.

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## **The parametric optical waveform synthesizer as a platform for future attosecond-pump attosecond-probe experiments**

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Optical waveform synthesis allows for generating optical transients with durations down to the sub-cycle timescale allowing for strong field pumping to be confined to only one event per pulse.

We present our parametric waveform synthesizer, capable of producing waveforms with durations down to 3fs and a spectrum from 690nm to 2200nm, as well as our in-situ detection method to determine their full electric field.

The synthesis of the waveforms is achieved by coherently combining two few-cycle pulses produced in parallel channels based on optical parametric amplifiers. Active stabilization of the system offers us great control and long-term stability of the waveforms.

Using these waveforms, we could show the direct generation of isolated attosecond pulses (IAPs) with variable duration, central energy, and bandwidth reaching up to  $\sim 400\text{eV}$ .

Many strong field processes studied in attosecond science are highly field sensitive. Therefore, knowing the precise electric fields of the waveforms used to generate the IAPs and pump the system under investigation is paramount.

We will present our pulse characterization technique based on the observation of the perturbative nonlinear response in gas.

The extremely broad spectra of our pulses lead to the overlap of different nonlinear signals. When performing a relative delay scan of the constituent pulses, fringes sensitive to the overall carrierenvelope phase of the waveform are observed in the recorded spectrogram.

From these spectrograms we can determine the entire fields of both constituent pulses and therefore the synthesized waveform up to one global sign using a custom genetic algorithm.

This allows us to determine the complete set of possible waveforms from a single measurement and the precise temporal overlap of the two pulses.

The pulse characterization is performed fully in-situ utilizing the same gas target used for HHG and can be carried out in parallel to an attosecond experiment.

This enables us to monitor the temporal overlap and thus the waveform stability during a measurement.

To perform advanced pump-probe experiments the optical waveforms must be independently optimized for IAP generation and the strong-field pumping of the target. We will realize this with an additional dispersion control setup inside our beamline's pump arm. Additionally, we are investigating ways to independently control the intensities in both arms, which requires attenuating our multi-octave spanning spectra.

## Isolated Attosecond Pulse Generation in a Semi-Infinite Gas Cell

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In the last decade, Isolated Attosecond Pulses (IAP) production has become of paramount relevance for investigating ultrafast electron dynamics in atoms and molecules, giving birth to the new field of Attosecond Chemistry. In this work, we explore a non-conventional and versatile scheme for IAP generation employing a semi-infinite gas cell geometry (SIGC). With the support of a newly developed numerical simulation tool, we investigate, as a function of pressure, how the isolation of an attosecond pulse is affected by the change in the phase-matching time window of a few-cycle driving field. The role of the spatio-temporal reshaping of the driving field, as well as the key role of the gas-profile distribution, are addressed to identify the conditions for optimized IAP production.

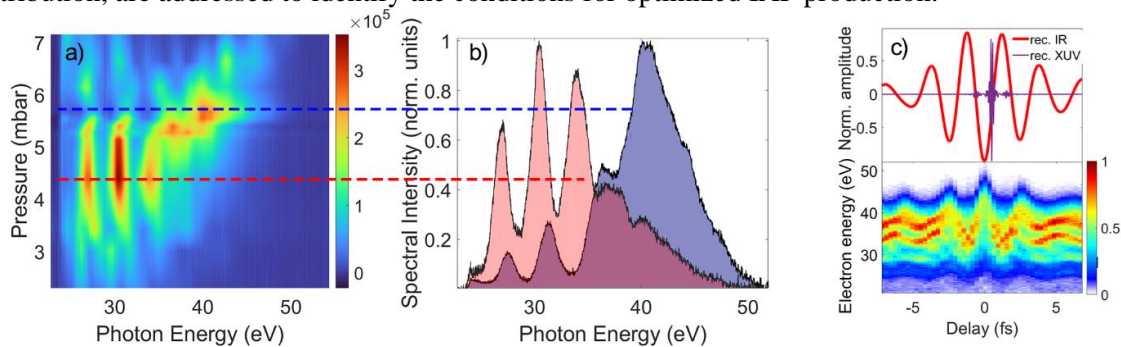


Figure 1: a) Experimental XUV spectra in Argon as a function of different gas pressures obtained by optimizing the CEP value. b) Details of experimental XUV spectra for 5.8 mbar (blue curve) and 4.3 mbar (red curve) c) Lower panel: Streaking trace of the 140-as IAP at 5.8 mbar Upper panel: reconstructed XUV (purple) and IR (red) fields.

The experiments were performed using 3.8-fs CEP-stable driving pulses, centered at 730 nm, generated by the hollow-fiber compression technique, injected in a SIGC filled with Argon [2,3]. Figure 1(a) shows the experimental XUV spectra obtained as a function of the input pressures. As the pressure increases, the generated XUV spectrum shifts from a discrete structure (Fig. 1(b) red curve) to a more continuous one (Fig. 1(b) blue curve) ultimately meeting the conditions necessary for the generation of an IAP. Temporal characterization of the XUV pulses, generated at 5.8 mbar, has been achieved by measuring the streaking trace in an Ar gas target (Fig. 1(c), lower panel). Isolated pulses with a duration of  $140 \pm 23$  as were reconstructed (Fig. 1(c), upper panel). To validate this phenomenon, we performed numerical calculations using as inputs of simulations the experimentally characterized parameters. The simulations include spatio-temporal nonlinear propagation of the driving field through the cell, TDSE calculations of HHG emissions combined with propagation through realistic gas profile distribution. The presented results expand our practical understanding of IAP generation, addressing the impact of driving field reshaping in the HHG process, the role of time-gated phase matching in long-medium geometry, and the influence of low-order harmonic re-absorption employing gas filters.

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## Relativistic treatment of hole alignment due to autoionization processes and Cooper minima in noble gas atoms

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The recent developments in attosecond physics allow us to study the temporal dynamics of photoelectrons and corresponding ions in photoionization experiments. In noble gases, the ion consists of several “holes” characterized by the properties of the missing electron. The alignment of a hole refers to the population ratio of different magnetic quantum numbers,  $m_j$ , with the same  $j$  [1]. In this work, we tune the field frequency to use particular spectral properties of absorption cross-section, like Fano profiles of autoionizing states and Cooper minima, to control this alignment. Since holes are coupled to the total angular momentum,  $j$ , a consistent treatment of relativistic effects should be employed.

Here, we use the Relativistic Time-Dependent Configuration-Interaction Singles (RTDCIS) method [2]. The RTDCIS method can be used to study partial cross-sections and photoelectron fluxes in noble gas atoms when interacting with ultra-fast pulses. This method, which is based on the Dirac-Fock spin-orbitals, accounts for electron correlation effects at the level of single excitations. In this way, photoelectron and hole pairs can be simulated in a relativistic framework. Here, we focus on reduced ion channels, which correspond to unresolved photoelectrons, by incoherently summing the outgoing electrons’ population corresponding to a given hole state.

In previous studies, the photon energy was tuned to autoionizing states [1]. As Fano resonances are spectrally narrow, they demand long XUV pulses (hundreds of fs) to achieve high alignment ratios. Here, we consider the Cooper minimum of argon and xenon, which gives the possibility of employing shorter pulses (hundreds of as) to obtain a high degree of alignment. Thus, Fano resonances and Cooper minima present promising avenues to hole alignment studies for a wide range of pulses.

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**Continuously tunable monochromatic intense HHG source for exciting He nanodroplets.**

JURKOVIČOVÁ, Lucie (ELI Beamlines)

HHG is a well-established tabletop source of radiation spanning from VUV region up to XUV. Applicability of the source is, however, not so straightforward. For many applications, like an excitation of distinct electronic states, there is a need for intense and monochromatic radiation at a very specific resonant photon energy. If the mismatch occurs, the interaction signal is weak and cannot be increased just by delivered photon flux.

To produce monochromatic radiation, a grating monochromator is usually used. This approach is, however, for many photon-hungry applications not applicable due to its high losses and pulse lengthening. Also, particular frequencies of a harmonic comb are defined by the spectral properties of the driving laser. If the narrowband spectral resonance is in between harmonic comb frequencies, using a grating monochromator will not solve the situation and spectral tuning of the spectral comb is necessary.

In this contribution we demonstrate experimentally the ability of precise spectral tuning across the resonance of He nanodroplets excitation energy (21.4 eV) in high-intensity interaction regime allowing nonlinear processes inside the droplet.

For the experiment we used a home-built broadband (750-950nm) OPCPA system capable of delivering 20 mJ pulse energy compressed below 15 fs pulses at a repetition rate of 1 kHz. High-order harmonic generation photon energy tuning is based on conversion of IR laser pulse into its second harmonic in the nonlinear BBO crystal (type I). Broad IR laser spectrum allows for a continuous tuning of the central wavelength of the generated second harmonic component within the available laser bandwidth without losing conversion efficiency.

Generated second harmonic pulse is then filtered from the residual IR radiation to drive the high-harmonic generation in a Kr gas jet. Tuning the phase-matching of the crystal (by its rotation) in the broad spectrum of the OPCPA system allows broadband tuning of the central wavelength of the UV pulse keeping very high efficiency of the HHG.

Along with continuous tunability of generated photon energy, there is the benefit of increased photon flux per harmonic order thanks to the driver wavelength scaling law. Another advantage is the doubled separation between adjacent harmonic orders. For applications, where this energy gap between adjacent orders is large enough, so that the only one harmonic order is within the resonance (as is the case of He clusters), no further monochromator is needed allowing to reach very high VUV intensities on the target.

Generated VUV radiation is then focused to the target of He clusters by a spherical mirror with broadband multilayer coating operating close to normal angle of incidence. High VUV intensity regime is demonstrated by observing nonlinear processes inside He nanodroplet like collective autoionization of multiply excited pure He nanodroplets recently found upon irradiated He nanodroplets with intense pulses from seeded FEL, FERMI.

## **The Relativistic Time-Dependent Configuration Interaction Singles Method**

Dr PAPOULIA, Asimina (Lund University); Dr DAHLSTRÖM, Jan Marcus (Lund University); Ms TAHOURI, Rezvan (Lund University); Dr ZAPATA, Felipe (Universidad Autónoma de Madrid)

Attosecond physics aims to unravel the electron motion and coherence in atoms and molecules. Major contributions to this field are the real-time observations of the motion of electrons in ions and atoms through attosecond transient absorption spectroscopy (ATAS) [1-3]. Despite the great success of ATAS, all studies have so far been based on non-relativistic ATAS theory. Seeking a compromise between computational cost and accuracy, the Relativistic Time-Dependent Configuration Interaction Singles (RTDCIS) method is proposed for studying atoms and ions [4]. This novel method opens up the possibility to describe the electron spin dynamics by means of spin-resolved ATAS experiments, far beyond the perturbative regime. Similarly, it can be applied to other strongfield processes, such as high-order harmonic generation, above-threshold ionization, laser-assisted photoionization, hole alignment, and the study of complex Rabi dynamics.

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## Use Angular Streaking to Measure Attosecond Delays with X-ray Free-Electron Laser

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We report the angular streaking [1] measurements of attosecond delays at the Linac Coherent Light Source (LCLS). In angular streaking measurements, we use attosecond soft X-ray Free-Electron Laser (XFEL) pulses [2] to ionize photoelectrons in the presence of a circularly polarized IR laser. The circularly polarized IR laser maps the temporal profile of the electron emission onto the measured electron momentum spectrum, providing the time-resolved information within one laser period. However, the large laser/X-ray relative arrival time jitter (~500 fs) at LCLS makes the streaking direction of each electron emission feature highly random from shot to shot. The information of attosecond delays is only encoded in the relative angular difference in momentum shifts of electron emissions on a single-shot basis.

To overcome this challenge, we have developed two independent data analysis methods to retrieve the attosecond delay information in angular streaking measurements. In the first method, the streaking direction of one photoemission feature is sorted on a single-shot basis to determine the relative X-ray arrival time within one IR laser period. In the second method, we employ a correlation-based method that directly exploits the shot-to-shot variations in streaking-induced momentum shifts in photoemission features. The second method does not rely on any singleshot streaking direction determination. Two methods have been cross validated on the time delay measurements between attosecond XFEL pump/probe pulse pairs at LCLS, which is the first measurement of XFEL group velocity. These methods have also been applied to time-resolve the near edge photoemission delays in molecules.

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## Probing Vibronic Coherence in Charge Migration in Molecules Using Strong Field Sequential Double Ionization

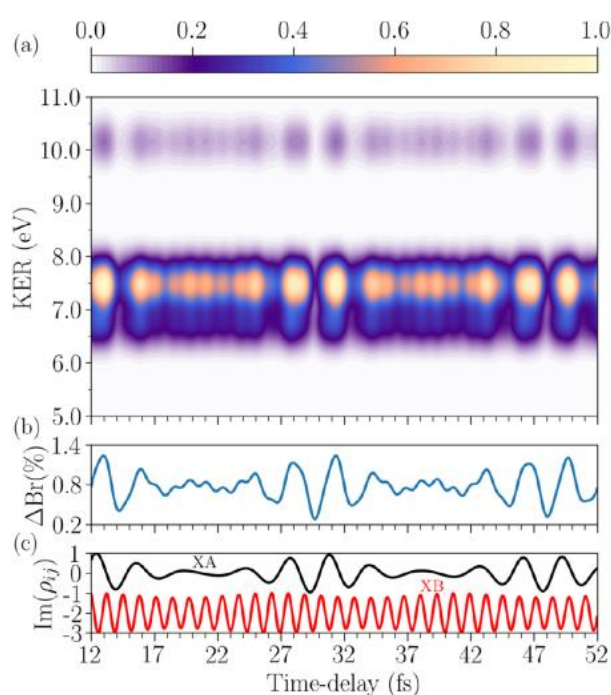
Chi-Hong Yuen and Chii-Dong Lin (J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA, [iyuen@phys.ksu.edu](mailto:iyuen@phys.ksu.edu))

**Synopsis:** We propose a novel scheme for probing vibronic coherence in charge migration of molecules utilizing strong field sequential double ionization. Full simulations of a pump-probe scheme employing few-cycle intense infrared pulses are performed for  $N_2$  and  $O_2$ . We predict that the vibronic coherence between the pumped states will be directly imprinted in experimental observables such as kinetic energy release spectra and branching ratios of the dissociative dications. Our findings strongly encourage the use of this probing scheme in future charge migration experiments.

Charge migration is a subject of intense theoretical and experimental investigations in recent years. A critical problem in charge migration studies is that the nuclear motion will set in after a few femtoseconds, and could lead to the decoherence between different electronic states. While there have been some successful experiments [1, 2], the types of the target molecules and the probing mechanisms greatly varied, and it is uncertain whether a particular probing scheme will work on other targets. The search for a general and experimentally accessible probing scheme for charge migration of molecules is therefore of great importance.

In this work, we propose a novel and general scheme for probing the coherence in charge migration of molecules using strong field sequential double ionization (SDI). This process is partly driven by the laser couplings between the pumped states, such that the change of their coherence will influence their population, and will thereby change the dication yield. As a result, the time dependence of the coherence will be directly imprinted in the observables such as kinetic energy release and branching ratio at different pump-probe delays.

We perform complete simulations of a few-cycle intense infrared light pump-probe scheme for nitrogen and oxygen molecules utilizing our recently developed DM-SDI model [3, 4]. For the first time, we demonstrate that the SDI process can effectively probe the vibronic coherence in charge migration of the pumped molecules (see Fig. 1). Our theoretical approach is general and can extend to other molecular targets. As the experiment setups for this probing scheme are widely available, our findings can be directly verified in future experiments, therefore stimulating new directions for studying charge migration as well as other molecular dynamics.



**Figure 1.** Simulated KER spectra for  $N^+ + N^+$  (a) as a function of pump-probe delays, subtracted by the respective probe-only signal. (b) The branching ratio of  $N^+ + N^+$  over their respective total dication yield as a function of pump-probe delay, subtracted by the probe-only ratio. (c): Imaginary part of the angular-averaged off-diagonal density matrix elements between the  $X^2\Sigma_g^+$  and  $A^2\Pi_u$  states (black) and the  $X^2\Sigma_g^+$  and  $B^2\Sigma_u^+$  states (red) of  $N_2^+$ .

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## Direct Referencing of Ionization Delays between Molecular Samples in Attosecond Interferometry

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Comparing Wigner ionization delays between different samples of a series with common characteristics allows for a systematic study of the physics at play that ultimately governs their chemistry, like increasing number of conjugated  $\pi$  bonds. This makes it possible to directly relate the extracted ionization delays to fundamental properties of the studied samples.

Previous studies on molecular samples [1] were unable to directly compare the obtained delays between the studied samples because they did not have a common reference between delays. Other studies [2], were able to obtain relative delays between atomic gases by measuring a mixture of the two sample gases. However, for more complex systems like molecules, which have dense photoelectron spectra with multiple broad features, such sample mixtures suffer from overlap of the individual component's photoelectron spectra [3]. This overlap makes the extraction of ionization delays difficult if not impossible because the phases of the  $2\omega$  oscillations cannot be separated.

We present a new technique of in-situ sample switching that circumvents this spectral overlap and allows for a direct comparison of Wigner ionization delays between different samples. Through the use of a custom nozzle with two separate feeds, one for each of the two gas samples that can be individually turned on or off, a fast switch from one sample to another is realized. This fast sample switch, done halfway through each measurement of the interferogram, manifests as a clear and sharp shift of the observed photoelectron spectrum from one sample to the other. Therefore, the measurements are inherently unaffected by the aforementioned spectral overlap. At the same time, we are able to directly compare the extracted delays between the two samples, because the  $2\omega$  oscillations occur on the same continuous XUV-dressing delay axis and therefore have the same phase reference.

We demonstrate the effectiveness of this new technique on the molecular system of ethylene and allene by extracting the ionization delays of the respective  $\pi$ -electron systems. This allows us to relate the extracted ionization delay to the delocalization of the ionized electron inside  $\pi$  systems of different spatial extensions.

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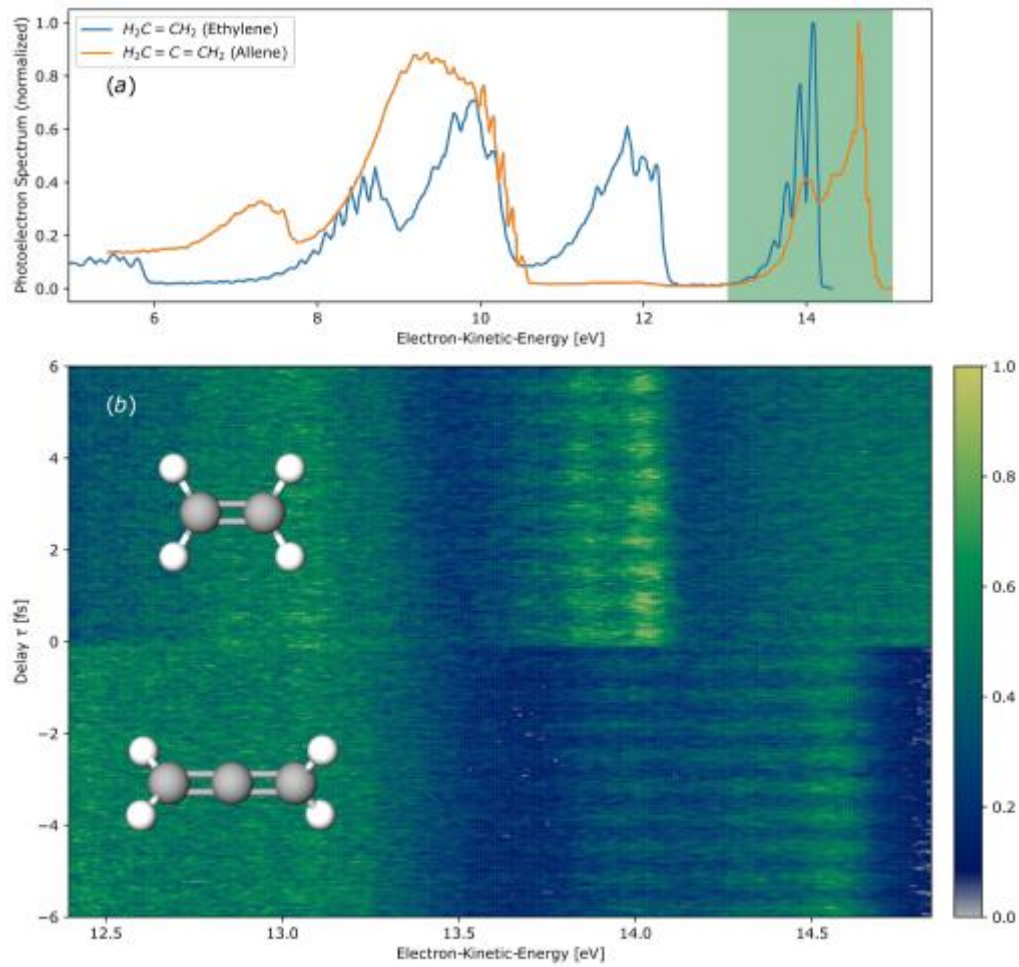


Figure 1: (a): Photoelectron spectra of ethylene (blue) and allene (orange), taken Ref [1]. The green highlight indicates the spectral region that is shown in the experimental data. (b): Experimental data of the measured interferogram. The gas was swapped from allene to ethylene halfway through the measurement.

## Yb-laser Driven High Harmonic Generation and Applications in Magnetic Imaging and to monitor the Electron Dynamics in complex systems

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High harmonic generation (HHG) in gases, driven by Yb-laser, is meanwhile widely used for many challenging experiments such as resonant magnetic diffraction imaging and to investigate complex electron dynamics in solids. By using a Yb:CaF<sub>2</sub> laser amplifier at 1030 nm delivering sub-picosecond laser pulses of up to 6 mJ at 500 Hz and exploiting the processes of Self-Phase Modulation and Stimulated Raman Scattering in a gas-filled hollow-core fiber [1] in combination with chirped mirrors, it is possible to produce strong laser pulses compressed to the femtosecond time-scale. These post-compressed fs-pulses are exploited to drive the HHG-process in a gas medium to obtain a broadband spectrum of harmonics reaching up to the extreme ultraviolet (EUV) or the soft X-ray regions, optimised to cover the energy interval 50 – 220 eV. This spectral range covers the ferromagnetic N and M absorption edges in magnetic targets as well as the inner-shell absorption edges of some metals such as Al and Cu, thus making it ideal for coherent magnetic domain imaging [2] and to follow the complex electron dynamics in metal surfaces.

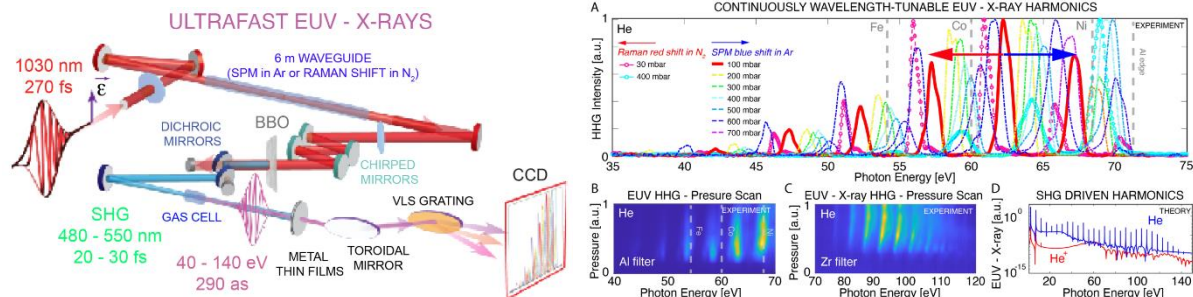


Figure 1. Continuously tunable, EUV – X-ray high harmonics from He, generated by a tunable VIS driving laser with wavelengths spanning the 480 – 550 nm range. Left – Schematic of the setup, Right - A. Blue-shift and red-shift wavelength-tunable harmonics. The arrows indicate the shift direction when atomic Ar (blueshift) or molecular N<sub>2</sub> gas (red-shift) is employed for spectral broadening (the color-coding denotes the corresponding pressure required for broadening). B. and C. Experimental pressure dependence of the high harmonics extending into the soft X-ray region for Ar-filled waveguide at 400 mbar. D. Single-atom estimate of the harmonic yield from neutral He atoms and He<sup>+</sup> ions at an intensity of >10AB W/cm<sup>2</sup>.

In a recent work, we generated high harmonics from He employing a tunable driving laser in the visible range, with wavelengths spanning between 480 – 550 nm, using a BBO type I crystal before the HHG gas medium. This approach allows to fine-tune the spectrum of harmonics, shifting it towards the “red” or “blue” wavelengths in the EUV regime including the generation of attosecond pulse trains (APT) exhibiting a characteristically low attosecond chirp (Fig. 1).

In another ongoing work [3], the same type of HHG-set-up is used to generate APT in the EUV-regime, suited for the temporal investigation of the photoelectron emission processes in Aluminium. The main objective of this ongoing project is to resolve the complete dynamics of a bulk plasmon using RABBITT (Reconstruction of Attosecond Beating By Interference of Two-photon Transition) and Attosecond Streaking techniques. In a first step, a comb of EUV-harmonics around 150eV is sent as a pump-signal onto the Al target, thus inducing photoelectron emission from the L-shell. The near-infrared seeding pulse (NIR) is used as a probe-signal reaching the Al-surface at various time-delays. The ejected photoelectrons (PEs) can either be directly detected or they can additionally undergo inelastic scattering events, thus transferring part of their energy to the surrounding solid-state electrons prior to their escape above the surface barrier. These inelastically scattered PEs are intimately linked to the excitation of the bulk plasmon in Al, exhibiting a characteristic resonant energy of  $\hbar\omega_{pl} = 15\text{eV}$ . By monitoring the RABBITT traces of these two PE-signals it will be possible to determine the time delay intercurring in between the direct emission of PEs and the rise of a bulk plasmon. To actually monitor the complete plasmon dynamics, it is necessary to detect – along the same time-scale – the so-called “secondary” electron, which is emitted from the target as a consequence of the bulk plasmon decay.

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## High repetition rate beamline for time- and angle-resolved photo-emission spectroscopy with high harmonics

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Time- and angle-resolved photoemission spectroscopy (Tr-ARPES) with high harmonic probe pulses has enabled studies of electron dynamics in a range of 2D materials, e.g. [1]. Many novel materials cannot be produced over large areas or have small domain sizes ( $<10\ \mu\text{m}$ ), and require a suitably small XUV spot to probe their dynamics. However, reducing spot size requires a reduction in the number of electrons generated (and hence number of photons per shot) to reduce space-charge effects that degrade the measured angular and spectral resolution. In order to obtain suitable statistics within a reasonable time, it is necessary to substantially increase the repetition rate. We have designed and commissioned a new beamline for Tr-ARPES running at 100 kHz repetition rate.

Our beamline is based on an optical parametric chirped pulse amplifier pumped by a Yb-doped laser, delivering 50 fs duration pulses at 1700 nm with 200  $\mu\text{J}$  energy per pulse at 100 kHz [2,3]. The laser or its second harmonic are focused into argon to produce high harmonics. A single harmonic is selected using a grazing incidence time-preserving monochromator [4], and the exit slit is imaged with demagnification using an aberration compensated double-toroid [5], giving a FWHM spot size of 20  $\mu\text{m}$ . We measured Tr-ARPES from a graphene sample at  $\sim 36\ \text{eV}$  probe energy and compared the results to measurements from our 1 kHz beamline. The new beamline has much finer angular resolution due to reduced space-charge.

We have upgraded our Tr-ARPES end-station with a new Fermi surface mapping analyser, enabling efficient acquisition of high-quality ARPES spectra of optically-pumped excitations close to the Fermi surface level. The beamline's capability to rapidly switch between high harmonics has also enabled us to demonstrate measurement of out-of-plane dispersing states.

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## Transition delays derived from interference of two-photon and one-photon transitions

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**Synopsis** We have developed an original interferometric technique to extract the transition delay associated with a two-photon transition through a bound state with both high accuracy and spectral resolution. By blue-shifting and blue-broadening the harmonic 15, we show its application in the case of He with the intermediate resonant states  $1sNp$  with  $N = 3, 4, 5, 6$ .

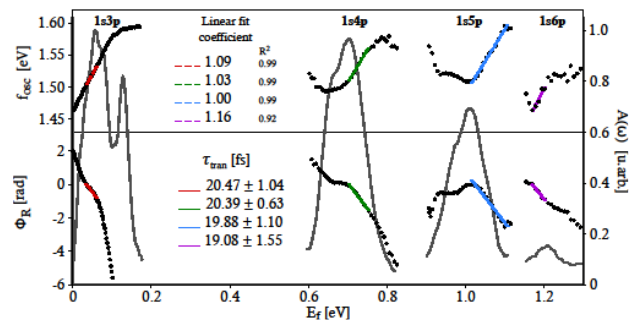
The ionization dynamics in the vicinity of resonances are specifically interesting as they reveal the electronic behavior at energies particularly relevant for the quantum system. They have been studied using interferometric schemes such as the RABBIT technique where measurements of the spectral phase evolution allowed reconstructing the corresponding rich dynamics.

In the present study, we develop an alternative interferometric scheme to access the spectral phase of resonant transition amplitudes. It relies on reference single-photon transitions (rather than reference two-photon transitions as in RABBIT-like approaches) leading to a number of advantages. This is demonstrated in the case of the two-photon XUV+IR ionization of helium through the intermediate resonant states  $1sNp$  with  $N = 3, 4, 5, 6$ .

We use a single harmonic beam (H15) overlapped with its generating IR field to induce two-photon transition towards the continuum, creating the free electron wavepacket (EWP) of interest. The latter is structured by the transient resonances with the intermediate  $1sNp$  states that lead to  $\pi$  rad spectral phase jumps [1,2]. The  $1sNp$  states are also coherently populated through one-photon transitions. After a variable delay  $\tau$ , an additional IR field transfers some population from these states to the continuum, again by one-photon transitions, creating reference EWPs centered at the same energies. In contrast to the resonant two-photon transition, the sequential one-photon transitions produce an EWP with a smooth phase evolution providing an ideal reference. The interferences between the probed and reference EWPs encode their relative phase that has two contributions: i) the difference of phases accumulated during the delay  $\tau$  by the  $1sNp$  and the continuum states, and ii) the

phase of the resonant two-photon transition. By measuring the  $\tau$ -dependent photoelectron spectrum over hundreds of femtoseconds, we can access the latter phase with both high accuracy and high spectral resolution. A further advantage of this interferometric scheme is that the reference EWP has a similar partial wave decomposition as the studied EWP, which maximizes the contrast of the interferences regardless of the electron emission direction.

In a first study, we investigated thoroughly the  $1s3p$  resonant transition. We here extend our study to the  $1s4p$ ,  $1s5p$  and  $1s6p$  resonant transitions, reached by blue-shifting and blue-broadening the harmonic 15 through ionization-induced driving-laser phase modulation. Figure 1 shows the spectral phase associated with each transition that encode the transition delay due to the trapping of the electron in one of the intermediate bound states before reaching the continuum.



**Figure 1.** Upper panel: Central oscillation frequency for the intermediate resonant states  $1sNp$   $N = 3, 4, 5, 6$ . Lower panel: Associated phase  $\Phi_R$ . The data used for the determination of the transition delay  $\tau_{\text{trans}}$  are respectively colored as red, green, cyan and purple for  $N = 3, 4, 5, 6$ .

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