Second Annual Workshop of the AttoChem COST action CA18222

(13 – 15 October 2021)

Book of Abstracts

Second Annual Workshop of the AttoChem COST action CA18222

The 2nd Annual Workshop of the COST action AttoChem is organized by CFEL/DESY (Hamburg) online from the 13th until the 15th of October 2021, 9:00–17:00 CEST.

https://conferences.cfel.de/attochem_workshop_2021/
https://portalapp.brightelm.eventsair.com/VirtualAttendeePortal/attochem-webinar-series-2021/platform

Local organizing committee

Francesca Calegari, Andrea Trabattoni, Erik Månsson and Vincent Wanie

Poster award committee

Francesca Calegari, Andrea Trabattoni, Fernando Martín, Erik Månsson, Caterina Vozzi and Vincent Wanie.

The AttoChem network (https://attochem.qui.uam.es/) coordinates experimental and theoretical efforts to exploit the large potential of attosecond techniques in chemistry, with the aim of designing new strategies for the control of charge migration in molecules by directly acting on the attosecond time scale. This ability will also be used to selectively break and form chemical bonds, thus opening new avenues for the control of chemical reactions. The results of the Action are expected to have a significant impact in several areas of chemistry, such as photovoltaics, radiation damage, catalysis, photochemistry, or structural determination. AttoChem also acts as a liaison with the relevant stakeholders to bridge the gap to industrial applications. The purpose of the meeting is to revise the current status and future directions in this field, and to promote the exchange of ideas between participants.

This event is based upon work from the COST Action AttoChem, https://www.cost.eu/actions/CA18222, supported by COST (European Cooperation in Science and Technology). COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.

Program

All times are in the Central European Summer Time zone (CEST, UTC+0200).

Wednesday 13 October

8:50 – 9:00	Introduction
Attosecond photoionization dynamics in atoms & molecules	
9:00 – 9:30	**Anne L'Huillier**: Phase measurements by attosecond interferometry
9:30 – 10:00	**Pascal Salières**: Imaging resonant photoemission dynamics in real time
10:00 – 10:30	**Carlo Callegari**: Opportunities for Few-Femtoseconds and Sub-Femtosecond AMO Science with a Temporally-Coherent Seeded FEL
10:30 – 11:00	Discussions (one room per speaker)
11:00 – 11:30	Break
High harmonic generation in gases and solids	
11:30 – 12:00	**Carlos Hernandez Garcia**: Shaping high-order harmonic combs through phased-necklace drivers
12:00 – 12:30	**Katalin Kovacs**: Space-time coupling in high-harmonic generation – two case studies
12:30 – 13:00	**Michael Chini**: New Platforms for Generating and Characterizing Few-Cycle Optical Waveforms
13:00 – 13:30	Discussions (one room per speaker)
13:30 – 15:00	Lunch break
15:00 – 17:00	Poster session 1: P01 to P18 Carles Serrat, Isabella Merritt, Taran Driver, Jessica Harich, Jorge Delgado Guerrero, Ritika Dagar, Adrián Jesús Suñer Rubio, Saikat Nandi, Adhip Pattanayak, Vincent Loriot, Francisco Fernández Villoria, Nicola Mayer, Mrudul Muraleedharan Shylaja, Heloise Chomet, Sebastian Carrasco, Sergei Riabchuk, Coleman Cariker and Gabriele Crippa.

Thursday 14 October

Attosecond spectroscopy of polyatomic molecules	
9:00 – 9:30	**Yann Mairesse**: Chiral sensitivity of tunnel-ionization dynamics
9:30 – 10:00	**Davide Faccialà**: Probing ultrafast chiral dynamics in complex molecules with chemical sensitivity
10:00 – 10:30	**Csaba Fabri**: Quantum-light-induced nonadiabatic phenomena in the absorption spectrum and quantum dynamics of polyatomic molecules
10:30 – 11:00	Discussions (one room per speaker)
11:00 – 11:30	Break
Theory of attosecond electronic dynamics in molecules	
11:30 – 12:00	**Alicia Palacios**: Time-resolved images of electron dynamics in atoms and molecules using the new capabilities of FEL and XFEL sources
12:00 – 12:30	**Benjamin Lasorne**: On the preservation of coherence in the electronic wavepacket of a neutral and rigid polyatomic molecule
12:30 – 13:00	**Kalyani Chordiya**: Decoding the Response of Correlated Electrons to Photo-Ionization
13:00 – 13:30	Discussions (one room per speaker)
13:30 – 15:00	Lunch break
15:00 – 17:00	Poster session 2: P19 to P37 Lorenzo Colaizzi, Mattias Bertolino, Gilbert Grell, Gaia Giovannetti, Arturo Sopena Moros, Sucharita Giri, Ianina Kosse, Dominik Hoff, Alexie Boyer, Sivarama Krishnan, Abbie Bray, Saad Mehmood, Tomasz Wasowicz, Edvin Olofsson, Max Waters, Eva Vandaele, Andrea Annunziata, László Biró and Daria Gorelova.

Friday 15 October

Ultrafast photochemistry	
9:00 – 9:30	**Majed Chergui**: Ultrafast dynamics of chemical systems probed by X-rays and optical pulses
9:30 – 10:00	**Marc-Oliver Winghart**: Soft X-Ray Absorption Spectroscopy of Aqueous Solutions and Gases Using a Table-Top Femtosecond Soft X-Ray Source
10:00 – 10:30	**Nadja Doslic**: Strategies for Modelling and Monitoring Photochemical Processes: Progress and Challenges
10:30 – 11:00	Discussions (one room per speaker)
11:00 – 11:30	Break
Ultrafast dynamics in clusters & nanostructures	
11:30 – 12:00	**Daniela Rupp**: Ultrafast dynamics in clusters followed with CDI
12:00 – 12:30	**Tais Gorkhover**: X-ray imaging at the nanoscale with attosecond time resolution
12:30 – 13:00	**Zsuzsanna Papa**: Ultrafast Probing of Electron States after Plasmon Excitation
13:00 – 14:00	Lunch break
14:00 – 14:30	Discussions (one room per speaker)
14:30 – 15:00	Poster awards & closing remarks

Abstracts of invited talks

Phase measurements by attosecond interferometry

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One of the prominent methods for the study of ultrafast electron dynamics using attosecond pulses is the reconstruction of attosecond beating by interference of two-photon transition (RABBIT) technique, combining an attosecond pulse train, a weak time-delayed infrared dressing field and photoelectron detection [1]. Originally applied to the characterization of the attosecond pulses, it has then been successfully used for the measurement of photoionization time delays in atomic and molecular photoionization [2], as well for the determination of the phase and amplitude of a resonant transition, allowing the temporal reconstruction of attosecond electron wavepackets [3].

This presentation will describe two recent developments of the RABBIT technique, towards high spectral precision and multiple angular channels.

High spectral precision is obtained by a narrow spectral bandwidth dressing field, combined with a high-resolution electron spectrometer. It is useful in the study of electron wavepackets created by resonant absorption of XUV radiation close to discrete resonances in He and Ar [4]. The obtained spectral precision allows us to determine the quantum coherence of the wavepackets.

The determination of photoionization time delays by the RABBIT technique assumes that there is only one angular channel contributing to the photoionization, as in He, or that one channel is dominant. We will present a new method to extract the phase and amplitude of the angular channels involved in the photoionization of Ne in the 2p shell, in the 20-50 eV energy range. This method [5] is based on RABBIT experimental results obtained with angular resolution, as well as on theoretical knowledge of the influence of the continuum-continuum transitions.

[1] P.M. Paul, E.S. Toma, P. Breger, G. Mullot, F. Augé, Ph. Balcou, H.G. Muller, and P. Agostini, "Observation of a train of attosecond pulses from high harmonic generation" Science, **292**, 1689 (2001)

[2] M. Isinger, R. J. Squibb, D. Busto, S. Zhong, A. Harth, D. Kroon, S. Nandi, C. L. Arnold, M. Miranda, J. M. Dahlström, E. Lindroth, R. Feifel, M. Gisselbrecht and A. L'Huillier, "Photoionization in the time and frequency domain" Science **358**, 893 (2017)

[3] V. Gruson, L. Barreau, A. Jiménez-Galan, F. Risoud, J. Caillat, A. Maquet, B. Carré, F. Lepetit, J.-F. Hergott, T. Ruchon, L. Argenti, R. Taïeb, F. Martín and P. Salières, "Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron" Science **354**, 734 (2016)

[4] D. Busto, L. Barreau, M. Isinger, M. Turconi, C. Alexandridi, A. Harth, S. Zhong, R. J. Squibb, D. Kroon, S. Plogmaker, M. Miranda, A. Jimenez-Galan, L. Argenti, C. L. Arnold, R. Feifel, F. Martin, M. Gisselbrecht, A. L'Huillier, P. Salières, "Time-frequency representation of autoionization dynamics in helium" J. Phys. B **51**, 044002 (2018), and to be published.

[5] J. Peschel, D. Busto, M. Plach, M. Bertolino, M. Hoflund, S. Maclot, J. Vinbladh, H. Wikmark, F. Zapata, E. Lindroth, M. Gisselbrecht, J. M. Dahlström, A. L'Huillier, and P. Eng-Johnsson, "Complete characterization of multi-channel single-photon ionization" https://arxiv.org/abs/2109.01581

Imaging resonant photoemission dynamics in real time

A. Autuori[1], D. Platzer[1], M. Lejman[1], G. Gallician[1], L. Maëder[1], A. Covolo[1], L. Bosse[1], M. Dalui[1], D. Bresteau[1], J.-F. Hergott[1], O. Tcherbakoff[1], H.J.B. Marroux[1], V. Loriot[2], F. Lépine[2], L. Poisson[1,3], R. Taïeb[4], J. Caillat[4], and P. Salières[1]

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Imaging in real time the complete dynamics of a process as fundamental as photoemission has long been out of reach due to the difficulty of combining attosecond temporal resolution with fine spectral and angular resolutions. It is only recently that orientation-resolved spectral phase measurements could be performed, using cold target recoil ion momentum spectroscopy (COLTRIMS) [1-3], or velocity-map imaging spectroscopy (VMIS) [4-7].

In the present study, we combine Rainbow RABBIT attosecond spectral interferometry with VMI momentum spectroscopy to record the modulus and phase variations of the photoelectron quantum state with high spectral resolution and angular sensitivity. This is performed in the test case of two-photon XUV+IR photoionization of helium through the intermediate resonant states 1*s*3*p* and 1*s*4*p*. The resulting structured photoelectron wavepacket is fully characterized by measuring quasi-continuously the spectral and spatial variations of the final quantum state over a 0.8-eV spectral range (see Fig. 1). This allows reconstructing the attosecond photoemission dynamics strongly impacted by the sudden phase jumps of up to π rad measured *in both dimensions* [8].

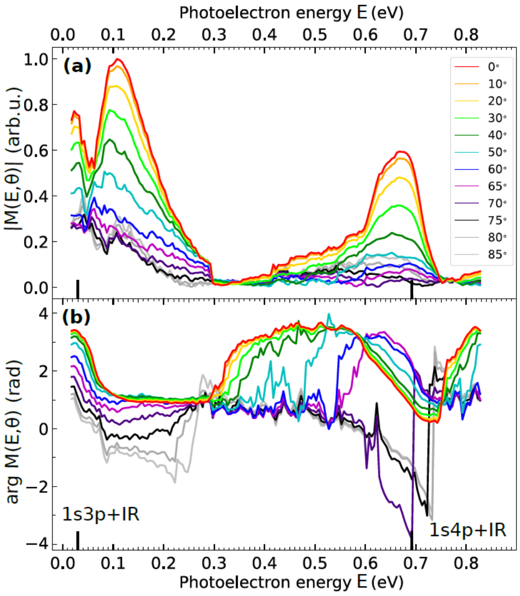

Figure 1: Spectral and angular variations of the modulus (a) and phase (b) of the two-photon transition resulting from a Rainbow RABBIT analysis of the angularly-resolved spectrogram measured in the VMIS.

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[2] J. Joseph *et al., J. Phys. B: At. Mol.Opt. Phys*. **53** (2020) 184007.

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[4] S. A. Aseyev *et al., Phys. Rev. Lett*. **91** (2003) 223902.

[5] S. Beaulieu *et al., Science* **358** (2017) 1288–1294.

[6] D. M. Villeneuve *et al., Science* **356** (2017) 1150–1153.

[7] D. Busto *et al., Phys. Rev. Lett*. **123** (2019) 133201.

[8] A. Autuori *et al., submitted* (2021).

Opportunities for Few-Femtoseconds and Sub-Femtosecond AMO Science with a Temporally-Coherent Seeded FEL

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Free-Electron-Lasers (FELs) in the EUV and XUV photon energy range have greatly expanded the feasibility range of experiments at the crossroad between tabletop lasers and synchrotrons. The FERMI facility in Trieste (Italy) is unique in the FELs landscape because it has been designed as a seeded source, resulting in superior performances in terms of control and reproducibility of its light pulses [1]. Of particular interest for spectroscopic applications are its broad tunability, wavelength purity (approaching the Fourier-transform limit, with sub-linewidth stability), short pulse duration and timing jitter. Transverse and temporal coherence are those characteristic of a true laser, and have been exploited in a series of pioneering AMO experiments [2].

The duration of the pulses produced by FERMI is restricted by the finite-gain bandwidth of the FEL process, which at EUV wavelengths implies values above 10 fs, and I will present the ongoing efforts to approach or even beat that limit [3]. An elegant way of circumventing the pulse duration limit for a certain class of experiments is that of performing interferometric measurements, that is: use multicolor beams and monitor an observable as a function of their relative phase(s) [2,4].

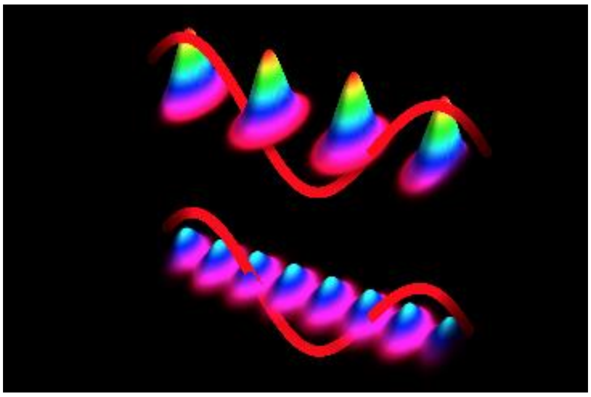

Figure 1: Artist's view of an attosecond pulse train (rainbow) phase-locked to a reference infrared beam [4]. The two configurations correspond to two different settings of the relative phase of the harmonics in the train.

As in laboratory High-Harmonic-Generation, FERMI harmonics are mutually coherent, but in contrast, they are produced with much higher pulse energy and independent control. At EUV wavelengths it is impossible to achieve the desired phase stability and control via conventional optical techniques, and at FERMI the goal is instead attained by imprinting the information into, and manipulating, the electron bunch that generates the light. RABBITT-type experiments with an external reference laser are also possible, in which case the phase reference is retrieved in post-processing via correlation techniques [4].

The results presented here originate from the joint effort of many international laboratories and of a large number of researchers, whose work is gratefully acknowledged.

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[2] K. C. Prince et al., *Nat. Photon.* **10** (2016) 176–179; D. Iablonskyi et al., *Phys. Rev. Lett.* **119** (2017) 073203; M. Di Fraia et al., *Phys. Rev. Lett.* **123** (2019) 213904; A. Wituscheck et al., *Nat. Commun.* **11** (2020) 883; D. You et al., *Phys. Rev. X* **10** (2020) 031070.

[3] D. Gauthier et al., *Nat. Commun.* **7** (2016) 13688; N. S. Mirian et al., *Nat. Photon.* **15** (2021) 523–529.

[4] P. K. Maroju et al., *Nature* (2020) **578** 386–391; P. K. Maroju et al., *New J. Phys.* **23** (2021) 043046.

Shaping high-order harmonic combs through phased-necklace drivers

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Precise coherent control over the frequency and divergence properties of high-frequency combs is fundamental for applications of high-harmonic generation (HHG) sources, such as high harmonic spectroscopy or imaging. During the recent years, manipulation over the angular momentum of the infrared driving beam has enabled exquisite control over the HHG to for example shape the polarization or orbital angular momentum (OAM) properties of the high-harmonic attosecond sources [1-3]. Here, we show that by harnessing the OAM of the driving beam, we can generate a transverse necklace-shaped beam that offers unique opportunities to manipulate the HHG process. In particular, it allows to create a spatial phased array of harmonic emitters that allow us to tune the frequency line spacing and the divergence of the emitted harmonic combs [4] (see Fig. (1)). This kind of control provides a new degree of freedom for the design of harmonic combs—particularly in the soft X-ray regime, where very limited options are available.

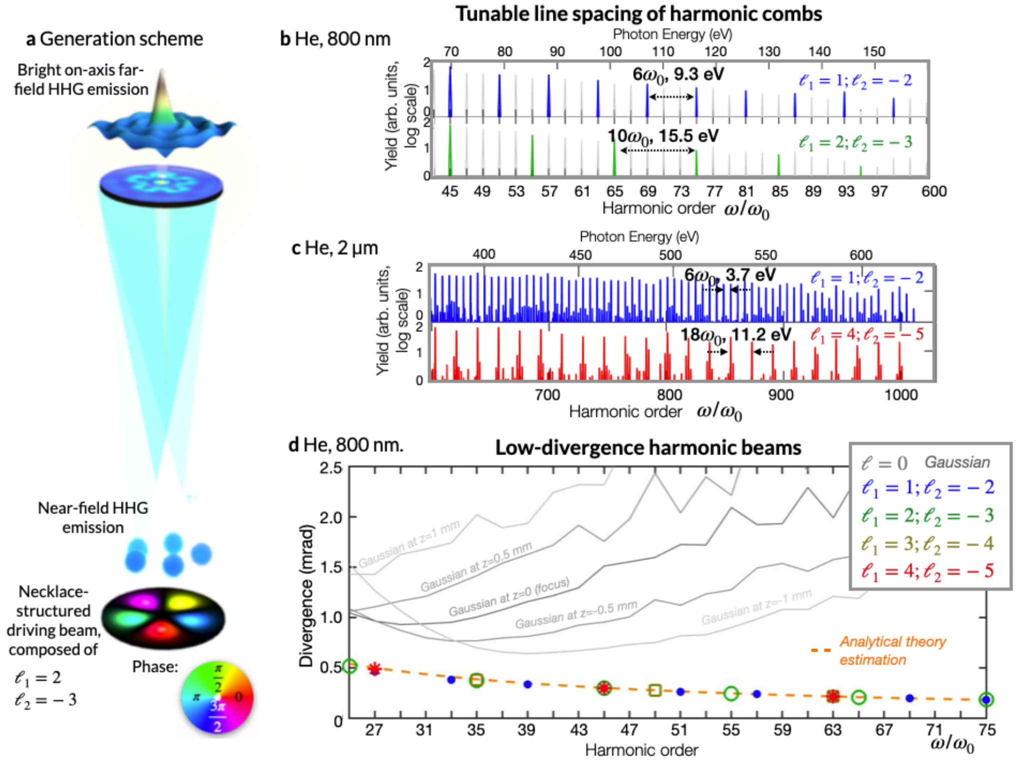

Figure 1: a) Generation scheme of necklace-structured HHG, where the driving field is composed of two collinear linearly polarized vortex beams with opposite—and different—OAM content (ℓ_1, ℓ_2) and same frequency (ω_0). Panels b) and c) show the tunability of the on-axis HHG spectra driven in He for 800 nm and 2 μm drivers, respectively. Panel d) shows the divergence of the on-axis harmonic beams which is lower than that obtained with Gaussian driving fields, and it also decreases with frequency.

[1] K. M. Dorney, et al. Controlling the polarization and vortex charge of attosecond high-harmonic beams via simultaneous spin-orbit momentum conservation. *Nat. Photon.* **13**, 123-130 (2019).

[2] L. Rego, et al., Generation of extreme-ultraviolet beams with time-varying orbital angular momentum. *Science* **364**, eaaw9486 (2019).

[3] L. Rego, et al. Trains of attosecond pulses structured with time-ordered polarization states, *Opt. Lett.* **45**, 5636 (2020).

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Space-time coupling in high-harmonic generation – two case studies

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We give an overview of the macroscopic aspects of the high-order harmonic generation (HHG) process. A 3D non-adiabatic model is presented [1]: in the framework of this model the driving pulse propagation is calculated; the elementary dipole response of an atom in the presence of a strong laser pulse is calculated using the strong-field approximation, while the modifications of the driving pulse due to propagation effects are intrinsically taken into account. Finally, the generated harmonic radiation is propagated in the same medium. The spatial, temporal and spectral properties of the macroscopic harmonic field are analyzed.

We give two examples of the space-time coupling in the macroscopic HHG:

(1) The attosecond lighthouse [2]: we show an experimentally feasible configuration based on HHG with a mid-IR driver, where the attosecond lighthouse effect is produced due to the macroscopic propagation effects, without the need to insert a dispersive element in the setup. We study in detail the specific propagation conditions of the laser beam, and describe the exact mechanism of the sensitive space-time variation of the medium's refractive index that lead to the dynamic wavefront rotation. This basic requirement for the lighthouse phenomenon is transmitted to the harmonic bursts, which are emitted with different divergence in successive optical half-cycles, thus can be detected in the far field at increasing distances from the optical axis. In this configuration, spectral filtering of the harmonics is not necessary, therefore the total harmonic pulse power might be used in further pump-probe experiments.

(2) The spectral separation of successive attosecond pulses [3] is another example of the space-time coupling, where the spectral content of two successive attosecond pulses is naturally separated. We demonstrate that two different single attosecond pulses (SAP) can be obtained from naturally separated spectral domains formed during high-order harmonic generation and propagation in a gas medium. We propose a feasible experimental configuration in which one can obtain an SAP in a lower energy domain (<300 eV), or another SAP in a higher energy domain (>300 eV). Without filtering, a double attosecond pulse emission with fixed temporal separation is obtained. The gap between the two spectral domains is close to the onset of the water window.

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[2] K. Kovacs, M. Negro, C. Vozzi, S. Stagira, V. Tosa, *J. Opt*. **19** (2017) 104003.

[3] K. Kovacs and V. Tosa, *Sci. Rep.* **10** (2020) 7392.

New Platforms for Generating and Characterizing Few-Cycle Optical Waveforms

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Advances in attosecond science have been tied to advances in our ability to generate, characterize, and control the electric field waveforms of intense, few-cycle laser pulses [1]. Generating such pulses has relied upon state-of-the-art laser systems accessible in only a few laboratories worldwide, while characterization of their electric field waveforms has required complex pump-probe setups [2-4]. In this talk, I will discuss two simple platforms based on commercially-available technologies which have the potential to advance attosecond sources. I will discuss how the delayed rotational nonlinearity of molecular gases can be harnessed for extreme pulse compression of ytterbium-doped lasers, as well as for frequency conversion from the near-infrared to the short-wave infrared [5]. Using a single stretched hollow-core fiber filled with N_2O gas and a chirped mirror compressor, pulse compression from 280 fs to below 6 fs can be achieved. In addition, I will present an "optical oscilloscope" capable of resolving the electric field waveform of few-cycle mid-infrared pulses in a single shot measurement [6].

[1] T. Brabec and F. Krausz, *Review of Modern Physics* **72** (2000) 545–591.

[2] E. Goulielmakis, et al., *Science* **305** (2004) 1267–1269.

[3] S. Keiber, et al., *Nature Photonics* **10** (2016) 159–162.

[4] S. B. Park, et al., *Optica* **5** (2018) 402-408.

[5] J. E. Beetar, et al. *Science Advances* **6** (2020) eabb5375.

[6] Y. Liu, et al. *arXiv* preprint (2021) 2109.05609.

Chiral sensitivity of tunnel-ionization dynamics

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D. Descamps[1], B. Fabre[1], S. Petit[1], D. Rajak[1], R. Taïeb[3], A.J. Uzan[2],
V. Blanchet[1], N. Dudovich[2], B. Pons[1], Y. Mairesse[1]

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Photoelectron circular dichroism, which occurs when chiral molecules are ionized by circularly polarized light, is one of the most sensitive chiroptical phenomena. It appears as a strong forward/backward asymmetry in the number of ejected electrons, and occurs in all regimes, from single-photon to multiphoton and strong-field ionization [1,2]. In the strong field regime, the ionization process can be decomposed in two steps. An electron wavepacket tunnels through the potential barrier lowered by the laser field, before being accelerated in the continuum (Fig. 1 (a)). The chiroptical response is conventionally seen as being imprinted during this second step, through scattering off the chiral ionic potential in the continuum. Could the first step also imprint a chirosensitive response?

We introduce two complementary approaches, using sub-cycle shaped ionizing laser fields. First, we photoionize chiral molecules with a field composed of co-rotating circularly polarized fundamental and second harmonics (Fig. 1(b)). The angular streaking by rotating field encodes information on the ionization dynamics. Second we combine a linearly polarized fundamental and its orthogonality polarized second harmonic to manipulate the instantaneous chirality of the ionizing radiation [3] and perform sub-cycle gated photoelectron interferometry (Fig. 1(c)). These two approaches enable us to disentangle the two steps in strong-field ionization. They show that tunnel-ionization from chiral molecules in a rotating laser field is a chirosensitive process, imprinting a sub-barrier phase and amplitude modulation of the electron wavepacket.

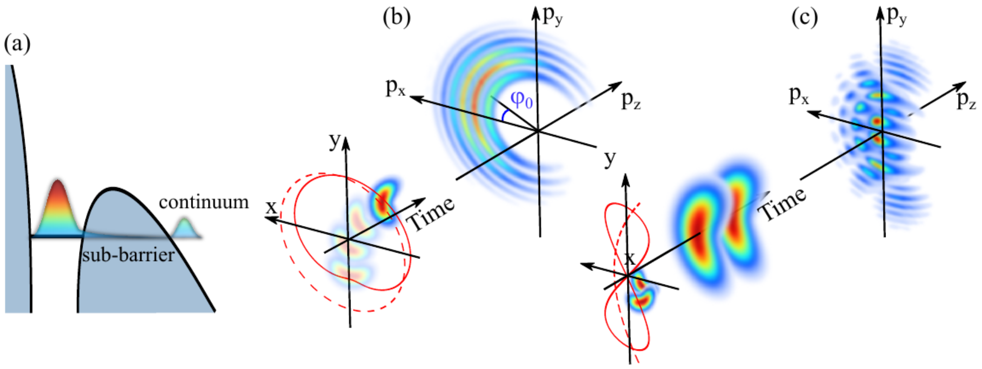

Figure 1: (a) The two steps of strong -field ionization. (b) Angular streaking in a bicircular laser field. (c) Photoelectron interferometry in a bilinear laser field.

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Probing ultrafast chiral dynamics in complex molecules with chemical sensitivity

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Chirality, or handedness, is the property of an object to be not superimposable to its mirror image. One of the most significant manifestations of chirality is the existence of pair of chiral isomers with opposite handedness, called enantiomers or optical isomers. Despite having identical properties in an achiral environment, most enantiomers exhibit very different chemical and physical properties when interacting with other chiral objects, such as other chiral molecules or circularly polarized light. As a result, chirality governs most biochemical interactions, playing a fundamental role in science and nature, from drug development to the formation of life itself. For this reason, the study of time-dependent dynamics in chiral molecules on the femtosecond and attosecond time scale represents one of the key steps for unraveling and controlling the evolution of chirality during a chemical reaction. In this perspective, time-dependent photo-electron circular dichroism (TR-PECD) constitutes one of the most promising techniques for studying these dynamics in real-time. In conventional PECD, a circularly polarized pulse ionizes a randomly oriented enantiomer, and the chirality emerges from a strong forward-backward asymmetry of the photoelectron distribution along the laser propagation direction. In TR-PECD, the chiral relaxation dynamics initiated by a femtosecond pump pulse is tracked with a time-delayed circularly polarized femtosecond probe pulse.

Recently, TR-PECD from the electronically exited state of a molecule has been demonstrated [1,2]. In this speech, I will show how it is possible to perform TR-PECD from the highly localized core-levels of a molecule, with soft X-rays and extreme ultraviolet (XUV) circularly polarized Free Electron Laser (FEL) radiation. This approach combines the chemical sensitivity of core excitation [3] with the chiral sensitivity of circularly polarized light, allowing us to gain a better understanding of the underlying processes. In particular, I will present an experiment where we probed, at the core level, the femtosecond chiral dynamics occurring in a photo-excited randomly oriented sample of a selected fenchone enantiomer, exploiting the circularly polarized XUV light source provided by the FEL FERMI. These results represent one of the first observations of chiral femtosecond dynamics probed with core-level excitation and pave the way towards the extension of this technique to more complex molecular and electronic chiral dynamics, and to the study of these dynamics on the attosecond time scale.

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Quantum-light-induced nonadiabatic phenomena in the absorption spectrum and quantum dynamics of polyatomic molecules

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The interaction of a molecule with the quantized electromagnetic field of a nano-cavity gives rise to polaritonic (hybrid light-matter) states and light-induced conical intersections between polaritonic potential energy surfaces. Strong nonadiabatic effects associated with quantum-light-induced conical intersections have substantial impact on the absorption spectrum and quantum dynamics of the coupled molecule-cavity system. We choose the four-atomic formaldehyde molecule, lacking any natural nonadiabatic effects, as target of our examinations and consider the coupling between the molecule and a cavity mode which is in near resonance with the S_0–S_1 electronic transition of formaldehyde.

In the first part of the lecture we investigate the validity of the Born–Oppenheimer approximation, neglecting nonadiabatic coupling between polaritonic surfaces, in relation to spectroscopy. We show that the Born–Oppenheimer approximation may fail even if one vibrational degree of freedom is treated and generally fails for two- or more-dimensional vibrational models due to conical intersections induced by the cavity [1]. In the second part, inspired by the idea presented in [2], we demonstrate that the time-resolved ultrafast radiative emission of the cavity enables to follow both nuclear wavepacket dynamics on and nonadiabatic population transfer between polaritonic potential energy surfaces without applying a probe pulse. The latter provides an unambiguous (and in principle experimentally accessible) dynamical fingerprint of quantum-light-induced conical intersections [3].

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Time-resolved images of electron dynamics in atoms and molecules using the new capabilities of FEL and XFEL sources

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Free electron lasers (FELs) and X-ray FELs facilities are nowadays capable to provide ultra-short pulses, as short as a few tens of attoseconds [1], and with unprecedented intensities (10^{20} W/cm^2), over a large range of photon energies going from VUV to the hard X-ray domain. These light sources provide new avenues to explore non-linear response in atoms and molecules [2], such as direct two-photon ionization of atoms [3] or non-linear Raman and Compton scattering processes [4]. In the present talk, we discuss our most recent theoretical developments and simulations performed to investigate highly non-linear processes occurring in atoms and molecules when subject to these sources, physical phenomena that can only be access experimentally with the newest capabilities at FEL facilities. First, the high brilliance of these sources is employed to induce above threshold two-photon ionization in He atom in the XUV frequency region, allowing one to uncover distinct two-photon direct and sequential mechanisms in the electron emission depending on the specific energy region [5]. Secondly, a hardly explored scenario is investigated in the hydrogen molecule: stimulated Compton scattering (SCS) [6] using soft X-ray frequencies, ranging from 0.5 to 1.6 keV [7]. At these frequencies the commonly employed dipole approximation breaks down and non-dipole corrections are required to describe the SCS process. Interestingly, we found that as result of this mechanism an asymmetric electron emission is induced in the homonuclear molecule, favoring a specific direction of the electron emission depending on the relative orientation of the molecule with respect to the polarization and the propagation directions of the light (see Fig. 1). Finally, on-progress applications to extract time-resolved images of electron dynamics in small biomolecules exploiting the capabilities of FEL will be discussed.

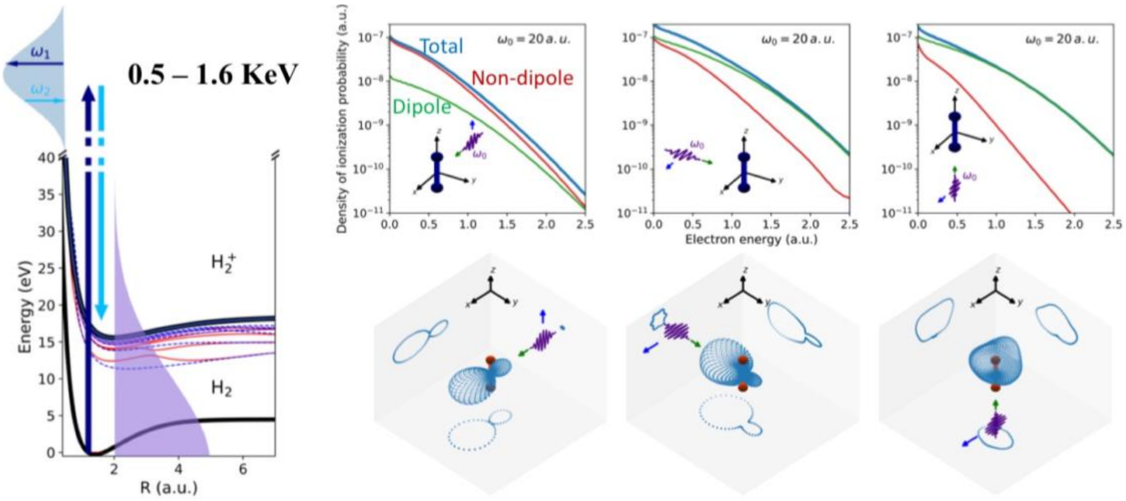

Figure 1: Stimulated Compton Scattering scheme. (Upper row) Photoelectron spectra including the contributions of the dipole (**A**·**p**) and non-dipole correction terms (**A**^{2}). (Bottom row) Angular distributions.

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On the preservation of coherence in the electronic wavepacket of a neutral and rigid polyatomic molecule

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We present [1] a rigid model of five nuclear dimensions and three electronic states for the pyrazine molecule to investigate the time evolution of electronic coherences. By an ultrafast optical pump- ing in the ground state (11Ag), we prepare a coherent superposition of the 11B2u and 11B1u excited states and reveal the effect of the nuclear motion on the preservation of the created electronic co- herence. More specifically, two aspects are considered: the anharmonicity of the potential energy surfaces and the coordinate-dependence of the transition dipole moments (TDM). To this end, we define an ideal model by making three approximations: (i) only the five totally symmetric modes move, (ii) which correspond to uncoupled harmonic oscillators, and (iii) the TDMs from the ground electronic state to the two bright states are constant (Franck-Condon approximation). We then lift the second and third approximations by considering, first, the effect of anharmonicity, second, the effect of coordinate-dependence of the TDMs (first-order Herzberg-Teller contribu- tion), third, both. Our detailed numerical study confirms long-term revivals of the electronic coherence even for the most realistic level of the presented model.

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Decoding the Response of Correlated Electrons to Photo-Ionization

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Realization of the ultrafast charge migration in molecular systems has been a long-awaited dream for many researchers in the field of chemistry, material science and biology. The extracted information on charge migration dynamics, will ultimately assist in engineering of new materials for photo-voltaic applications, photo-responsive drugs, photo-catalysis, determining fragmentation channel and understand radiation damage or photo-protective response to radiation therapy. To move in this direction, using the single particle Green's function Non-dyson ADC(3) method [1], we study the influence of tautomeric sites and methyl group on the charge migration dynamics in Uracil and Thymine nucleobases. Our results manifest that, the charge migration dynamics can be influenced and tailored by the site of tautomeric hydrogen, presence of methyl group and by targeting highly correlated molecular orbitals. Tautomerisation is important for the biologically important systems as it is interpreted to be one of the photo-protective response mechanism to radiation [2], in living organisms. The analysis also reveal that the maximum flux time (within 100 as) i.e., time when atomic site starts to donate or receive electronic density, shows the influence of electronegativity of atoms in the molecular systems. Thus, present study could be utilized to understand the possible response to post-radiation, and hence may be of interest to design photo-responsive or photo-protective materials, to reveal the subsequent nuclear dynamics.

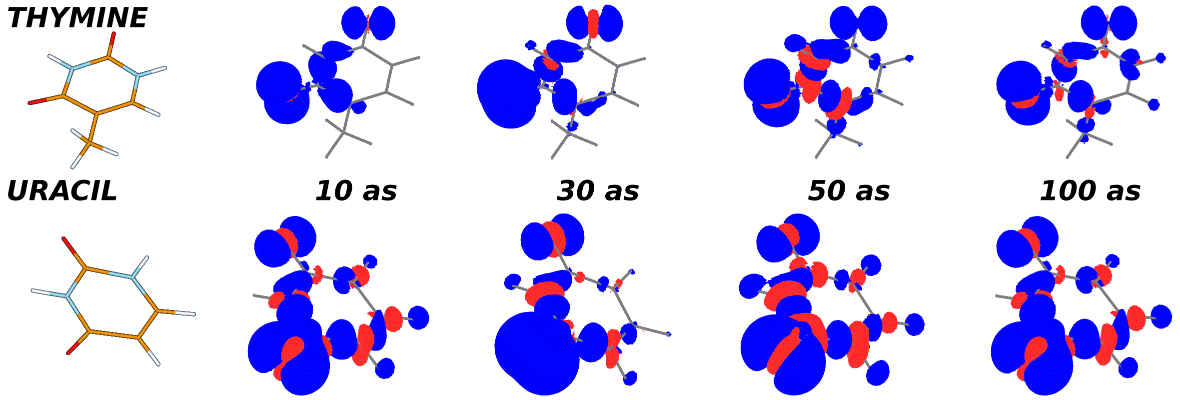

Figure 1: Charge migration dynamics after sudden ionization of HOMO-2 orbital of Uracil and Thymine.

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Ultrafast dynamics of chemical systems probed by X-rays and optical pulses

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The combination of ultrashort optical and X-ray pulses has and is still opening fascinating opportunities in the study of the dynamical behaviour of (bio)chemical systems. It is also bringing us to the core electron processes that trigger nuclear dynamics in these systems. In this presentation, I will dwell on some examples that point to the occurence of extremely fast electron and nuclear dynamics in the case of transition metal complexes and metallo proteins. I will then discuss some recent developments in the field of non-linear X-ray phenomena and elaborate on future developments in the study of chemical systems.

Soft X-Ray Absorption Spectroscopy of Aqueous Solutions and Gases Using a Table-Top Femtosecond Soft X-Ray Source

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Time-resolved X-ray absorption spectroscopy has become a method of choice to investigate the local electronic structure of molecules under non-equilibrium conditions. With recent developments of broadband table-top soft X-ray sources, the technique is no longer limited to large-scale facilities and can supply photon energies covering the K-absorption edges of the three biologically most abundant chemical elements (O, N, C). The method has successfully been applied by multiple groups to study molecular photochemical reactions in the gas phase [1-3], while the adaptation to the classical chemical reaction of a solute in the liquid phase has remained a challenge. In my talk I want to showcase our efforts in this direction using liquid flatjet technology [4] in synchrotron based experiments and present recent developments with our high-order harmonics setup [5,6].

The focus of our scientific work at large scale facilities has been on proton transfer reactions. Employing the local probe character of soft X-ray spectroscopy we investigate proton-donating molecules, so-called photoacids after UV excitation. The observed electronic structural changes allow conclusions to be drawn about the driving force for photoacidity i.e. for the increase in deprotonation rates upon photoexcitation. We were also able to follow the proton uptake of the proton-receiving reaction partner, paving the way for studies of the microscopic mechanism of proton transport through solutions.

In the second part I will present the current status of our table-top high-order harmonics setup for soft X-ray spectroscopy on liquid jets. With the implementation of a reflective zone plate spectrometer a 12% efficiency at the nitrogen K-edge, with a resolving power $\Delta E/E = 890$, clearly better than what typically has been achieved with commercially available spectrometers based on variable line space gratings was reached [6]. Using the higher photon flux, we performed first transient soft X-ray absorption experiments investigating the strong field ionization dynamics of molecular nitrogen by intense near infrared 50 fs laser pulses. The initially created distribution of multiple ionic states of N_2^+ and the subsequent fragmentation to neutral and single charged nitrogen atoms is directly mapped onto the transient N K-edge absorption spectrum. We rationalize the observed dynamics on a timescale of a few tens of picoseconds with dissociative excitation of N_2^+ in the dense plasma formed in the focus of the laser pulse. Our study highlights the capability of high-order harmonics based setups to simultaneously probe multiple coexisting species in complex photoinduced reactions by means of a broadband X-ray probe pulse.

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Strategies for Modelling and Monitoring Photochemical Processes: Progress and Challenges

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The theoretical study of chemical processes involving excited electronic states is a subject of fundamental and practical importance. This talk presents our strategies for modelling these processes.

One usually starts with the theoretical assignment of electronic spectra. In complex molecules this is a challenging problem which requires the determination of the diabatic character of a large number of electronic states. We will discuss a procedure for automatically determining the characters of electronic transitions and apply it for the assignment of UV absorption spectra of the five nucleobases in the gas phase and in aqueous solution. [1,2]

In photochemical reactions, the time-dependent population probabilities of electronic states are the observables of interest. By comparing a range of methods for solving the time dependent Schrödinger equation we show that trajectory-based mixed quantum-classical methods which account for switching between electronic states, but otherwise neglect nuclear quantum effects, are well suited to deliver this information. The methodology is illustrated for photophysical and photochemical processes of recent interest.[3,4]

We focus then on methods for monitoring photochemical reactions and discuss a theoretical framework for the simulation of femtosecond time resolved transient absorption and photoionization spectra using trajectory-based methods.[5,6]

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Ultrafast dynamics in clusters followed with CDI

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With coherent diffraction imaging (CDI), "snap-shot" images of individual isolated nanoscale specimen can be recorded [1]. In CDI, the intense pulses from short-wavelength free-electron lasers (FELs) or high harmonic generation (HHG) sources scatter off a free-flying nanostructure and form an interference pattern on a large-area detector. With computer-based iterative phase-retrieval [2] or forward-fitting methods [3,4] the structure can be retrieved from the pattern. CDI has enabled the in-situ imaging of such fragile specimen as single viruses [5] or superfluid spinning helium nanodroplets [4,6].

In the field of laser-cluster interaction studies, the possibility to image a single cluster in a single laser pulse and to measure at the same time the residuals from the interaction, i.e. ions, electrons or fluorescence light, opened up a new class of quantitative experiments [7,8,9]. The usual averaging over cluster sizes and laser intensities in experiments on ensembles is avoided. In post-processing, the single shot data can even be sorted for cluster size and X-ray intensity by the information gained from the CDI pattern.

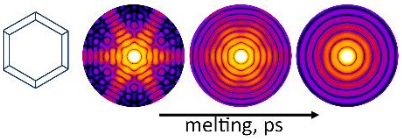

Figure 1: Sketch of coherent diffraction images tracing laser-induced melting of the facets of individual silver nanoparticles.

Light-induced structural dynamics such as melting of metal clusters (sketched in Fig. 1, Dold, von Issendorff et al., in preparation), can be studied in a time-resolved manner using pump-probe schemes: The cluster is brought to an excited state by pre-irradiation with an optical laser before imaging with an X-ray pulse. Furthermore, not only structural changes can be observed with CDI. Also electronic processes which occur during irradiation with a sufficiently intense laser pulse, such as ionization and the formation and evolution of a nanoplasma, change the diffraction response [10,11]. However, these processes happen so fast that they are not approachable with the typical 100 fs pulses at FELs. In this context, the current leap of FELs and HHG sources towards intense attosecond pulses is a promising prospect for our research.

In my talk I will discuss recent results on the light-induced dynamics in single clusters on different time scales from sub-femto- to picoseconds.

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X-ray imaging at the nanoscale with attosecond time resolution

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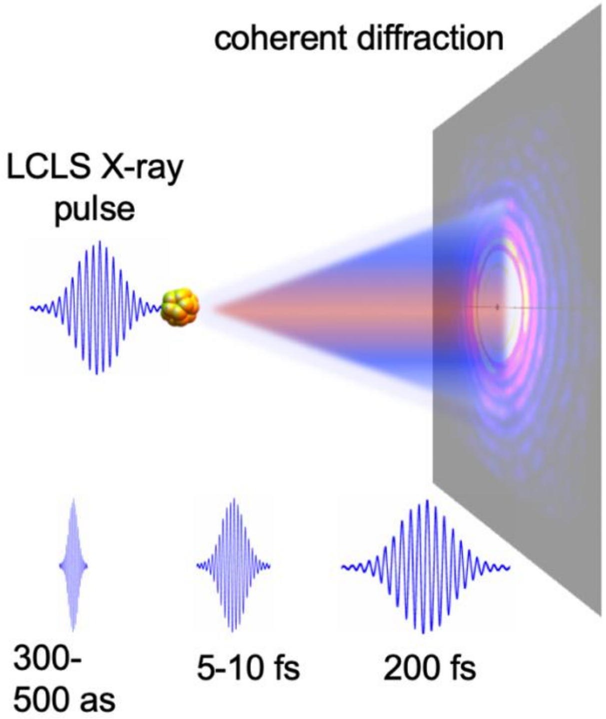

Most of our high-resolution imaging methods compromise between temporal or spatial resolutions akin to a pinhole camera. This still limits our capabilities to observe fast processes at the nanoscale, especially as the required brightness often damages the sample. Examples of such processes include chemical and catalytic reactions, nucleation dynamics and growth of nanoparticles, as well as other fragile/intermediate states of matter. One idea to overcome this obstacle is to use Free Electron Lasers (FELs), which are capable of producing very bright bursts of coherent X-rays within a few femtoseconds. X-ray FELs help to visualize transient processes in “frozen” time steps via single shot coherent X-ray diffractive imaging (CDI). Currently, the resolution of single CDI images is around ten of nanometers, which is limited by the brightness of the images [1-3]. Our recent study at LCLS suggests that transient ionic resonances (TR) above an absorption edge can enhance diffraction efficiency before significant structural damage can occur. This is surprising as TRs are usually regarded as a signature of increased X-ray absorption/damage and thus, detrimental to image quality [4-6]. We recorded a large data set of single exposure diffraction patterns with 200 fs, 5 fs and sub-fs FEL pulse durations from Xe nanoparticles by scanning the FEL energy in the vicinity of the 3d absorption edge. Our experimental results and a theoretical simulation suggest, that TRs provide a pathway to increase the quality of CDI with soft and hard X-ray FELs. Particularly, newly available sub-fs FEL pulses will play a crucial role to outrun the structural damage. We demonstrate that intense FEL pulses can combine nanometer with attosecond resolutions at the single nanoparticle level which opens a novel route to study ultrafast non-equilibrium dynamics at the nanoscale.

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Ultrafast Probing of Electron States after Plasmon Excitation

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We demonstrate an experimental method for monitoring the distribution and temporal evolution of the available electron states upon the excitation and decay of surface plasmon polaritons (SPP). Our method is based on the measurement of the dielectric function of the plasmonic system with ultrafast ellipsometry. Exploiting the correlation between the dielectric function and the electron distribution function, pump-probe ellipsometric approach with <100fs resolution enabled us to determine electron distributions belonging to different processes after SPP generation when energetic electrons are generated, scattered among each other and interact with the lattice.

For the excitation of SPPs, we applied the Kretschmann-geometry involving a glass right angle prism coated with 45 nm gold by thermal evaporation. SPPs were excited from the backside of the film using the 35 fs pump pulses at 800 nm of an amplified Ti:sapphire laser (Coherent Astrella). Simultaneously, spectral fingerprints of SPP-related changes were monitored by spectroscopic ellipsometry, illuminating the sample from the top side with white light continuum probe pulses generated from a part of the fundamental beam under 55° angle of incidence.

For the interpretation of the measured changes in the dielectric function, we exploited its proportionality with the joint density of electron states and electron occupancies [1]:

$\varepsilon_2(\omega) = \varepsilon_{2,\,intra}(\omega) + \frac{A}{(\hbar\omega)^2}\int_{E_{min}}^{E_{max}} D(\hbar\omega,\, E)\big(1 - f(E)\big)dE$, where $\varepsilon_{2,intra}$ is the contribution of the intraband electronic transitions, $D(\hbar\omega,E)$ denotes the energy distribution of the joint density of states (EDJDOS), and $f(E)$ describes the electron energy distribution. To determine $\varepsilon_{2,intra}$ a Drude function was applied, while to calculate the EDJDOS parabolic band structures were assumed at the L and X points in the Brillouin zone according to [1].

To describe the changes of the measured dielectric functions, we assumed different electron distributions belonging to the different mechanisms following the SPP excitation. During the first 100fs, the photon absorption perturbs the Fermi-Dirac distribution at energies matching with the excitation energy. Later, a high temperature electron distribution develops. When the energetic electrons interact with the lattice, slight changes are expected near the Fermi energy level accounting for the phonon excitation, and finally the system reaches a thermalized state. By introducing these changes into the electron distribution function, we can compute the corresponding dielectric function using the equation above. Good agreement between the measured and simulated changes in the dielectric function supports the applicability of our method (Fig. 1).

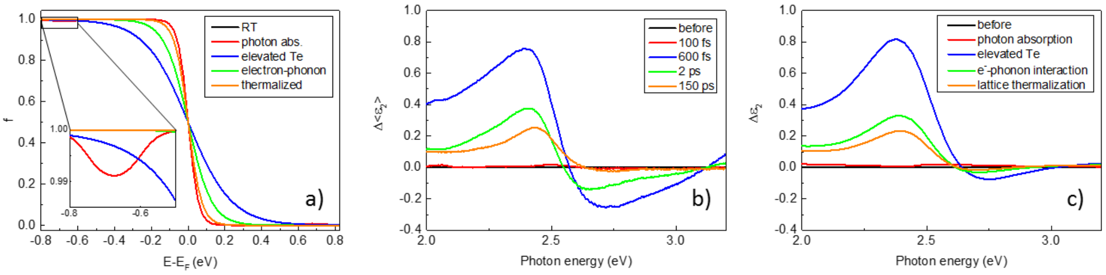

Figure 1: a) Simulated electron distributions belonging to different processes. b) Measured and c) simulated changes in the dielectric function of the plasmonic gold layer.

In summary, we could detect the different stages of the plasmonic system following the SPP excitation and the corresponding electron distributions. The signatures of these transient electronic states were revealed with the help of spectroscopic ellipsometry.

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Abstracts of posters

Selective core excitation of molecules by X-ray resonantly-enhanced difference-frequency generation

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Using real-time time-dependent density functional theory simulations I show how an oxygen atom in a water gas molecule is excited at its K-edge by resonantly-enhanced difference-frequency generation (re-DFG) involving intense ultrashort two-color coherent X-ray pulses [1]. The duration of the two-color pulses determine the spectral selectivity that can be achieved by the nonlinear re-DFG effect.

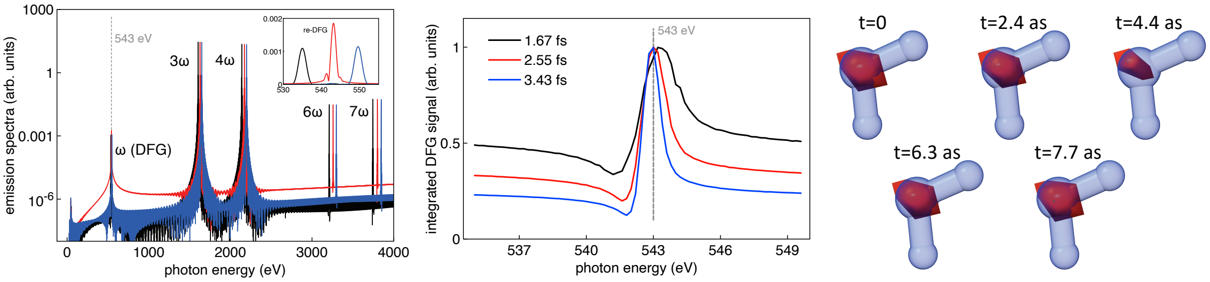

Figure 1: Left: Spectral signal resulting from the interaction of two-color (3ω, 4ω) pulses with a water molecule, for three different values of the photon energies and 10^{12} W/cm^2. The inset is a zoom of the spectra near the oxygen K-edge showing the enhancement of the DFG signal at resonance (the calculated oxygen K-edge is in this case ω_0=543 eV). Center: DFG spectral signal integrated around the oxygen K-edge as a function of the incident photon energy ($\hbar\omega$) of two-color (3ω, 4ω) pulses. Right: Snapshots of the density-difference 46 as after the exciting two-color field is over, in the case of resonance ($3\omega_0$, $4\omega_0$). The period of the calculated oxygen K-edge is 7.6 as. The illustration shows a complete cycle of the core oxygen excitation, the temporal resolution of the numerical integration is 0.48 as.

Resonant excitation near a core atomic ionization edge in a molecule can follow a rapid redistribution of charge and the molecule might become unstable and dissociate. In this regard, considering that a spectral fingerprint of the particular state of a molecule can generally be obtained by its XANES/EXAFS linear absorption spectra, the selectivity of the re-DFG process that I outline could be further optimized using a combination of several synchronized two-color (ω_1, ω_2) pulses producing $\omega_2 - \omega_1$ signals resonant with several molecular core absorption lines. I therefore anticipate the potential of extending this technique to larger molecules and to higher photon energies following the rapid advances in FEL sources, by considering two-color hard X-ray pulses to core excite higher atomic number atoms by re-DFG. The essential in this hard X-ray approach is that the two-color (ω_1, ω_2) pulses can be highly penetrating in bulk, while the core resonant re-DFG signals $\omega_2 - \omega_1$ are not. In this perspective, it was recently reported that exposure to laser-produced hard X-rays pulses with relatively high peak intensities - such as the ones used in the present simulations, does not lead to increased harm to mammalian cells exposed in vitro compared with the harm induced from exposure to hard X-rays with the same dose from conventional medical sources, concluding that the use of high-power laser facilities for medical imaging is justified [2]. Extensions of the present results are hence in progress to study the optimal pulse parameters such as photon energies, peak intensities and durations to attain a harmless dose in different tissues and materials using coherent hard X-ray pulses producing sufficiently intense re-DFG signals to dissociate molecules. Extensive potential applications of the nonlinear X-ray re-DFG effect can be envisaged, which include, in general, the local and selective manipulation of atoms and molecules in bulk matter, and in particular in medicine, it might be significant for local and selective cancellation of the active center of biomolecules maybe combined with molecule labellings.

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Cis → *Trans* Photoisomerisation of Azobenzene [1]

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The *cis-to-trans* photo-isomerisation mechanism of azobenzene, after excitation to the $n\pi^*$ and $\pi\pi^*$ states, is revisited using *ab initio* surface hopping mixed quantum-classical dynamics in combination with multi-reference CASSCF electronic structure calculations. A reduction of photoisomerisation quantum yield of 0.10 on exciting to the higher energy $\pi\pi^*$ state compared to the lower energy $n\pi^*$ state is obtained, in close agreement with the most recent experimental values [2] which re-examined larger changes in quantum yield found in prior literature. By direct comparison of both excitations, we have found that the explanation for the decrease in quantum yield is not the same as the one of the *trans-to-cis* photoisomerisation.

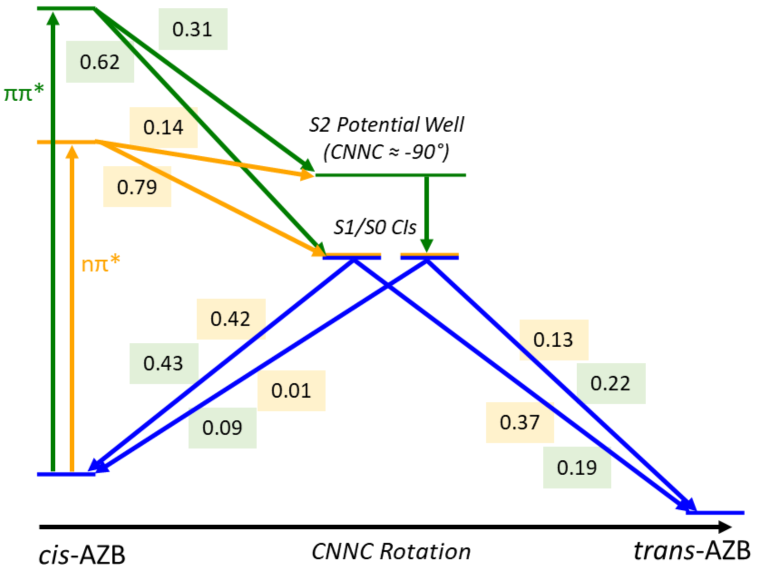

Figure 1:. Summary of the major pathways accessible to cis-AZB, and fraction of photochromes which follow each pathway, after both nπ * (yellow) and ππ* (green) excitation

In contrast to *trans-to-cis*, decay from the S_1 state does not occur at 'earlier' C−N=N−C angles along the central torsional coordinate after $\pi\pi^*$ excitation: in the *cis-to-trans* case, the rotation about this coordinate occurs too rapidly. The wavelength dependency of the quantum yield is instead found to be due to a potential well on the S_2 surface, from which either *cis* or *trans*-azobenzene can be formed. The combination of two factors results in the reduction of 0.10 of the quantum yield of photoisomerisation on $\pi\pi^*$ excitation of *cis*-azobenzene, compared to $n\pi^*$ excitation. Firstly, the potential well is more easily accessed after $\pi\pi^*$ excitation - an additional 15-17% of photochromes, which under $n\pi^*$ excitation would have exclusively formed *trans*-azobenzene, are trapped in this well after $\pi\pi^*$ excitation. Secondly, the probability of forming *cis*-azobenzene when leaving this well is also higher after $\pi\pi^*$ excitation, increasing from 9% to 35%.

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Attosecond Coherent Electron Motion in Molecules Measured with Ultrashort X-ray Pulse Pairs

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Attosecond soft X-ray pulse pairs from a free-electron laser [1] offer the opportunity to probe valence electron dynamics in molecules, with elemental specificity, on the natural attosecond timescale of coherent valence electron motion. We present two recent measurements performed at the Linac Coherent Light Source employing ultrashort X-ray pulse pairs [1,2] to probe few- to sub-femtosecond coherent electron dynamics.

A coherent superposition of electronic states is prepared in a molecule by impulsive valence ionization [3] by an ultrashort first (pump) X-ray pulse. The resulting valence electron dynamics are probed by a second (probe) ultrashort X-ray pulse, tuned to the manifold of O 1s → inner valence transitions in the molecule and arriving at a controlled time delay after the pump pulse. We measure the delay-dependence of the cross section for this resonant absorption process, which maps to the transient valence electron density in the proximity of the O atom. These measurements are performed by collecting the Auger-Meitner (AM) electrons emitted following decay of the O 1s → valence excitation. By scanning the X-ray photon energy, we spectrally resolve the time-dependence of different O 1s → inner valence transitions. This provides access to the varied dynamics triggered by coherent removal of different valence electrons.

In the first experiment [4], we use few-fs pulse pairs [2] to make the first time-resolved measurement of frustrated Auger-Meitner decay in a photoionized molecule. By spectrally resolving the resonant X-ray probe step, we experimentally observe the electron hole lifetimes associated with removal of an electron from different inner valence orbitals. In the second experiment we use attosecond pulse pairs [1] to interrogate the coherent electron dynamics of valence ionized para-aminophenol. We observe the pump pulse opening a new transient resonant absorption channel whose delay dependence provides access to the attosecond coherent electron dynamics in the molecule. We also perform time-resolved X-ray photoelectron spectroscopy on the three atomic edges in the molecule.

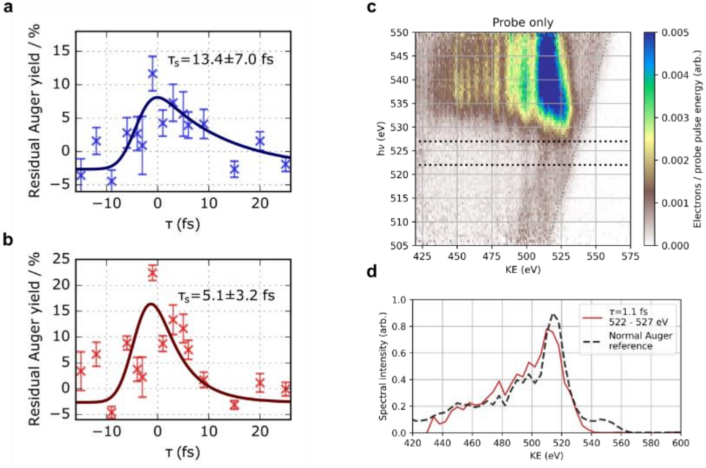

Figure 1. **a** & **b** time-resolved electron hole dynamics in isopropanol following ionization from the 7*a* (**a**) and 6*a* (**b**) orbitals. **c**) resonant Auger-Meitner (AM) absorption of para-aminophenol measured with attosecond X-ray pulses. At the photon energy indicated by the horizontal dashed lines, a new resonant feature appears at very short delays when the molecule is pumped by an X-ray attosecond pulse. The associated kinetic energy spectrum of these AM electrons matches the normal (*KLL*) AM spectrum in the ground state molecule (**d**).

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Probing the UV-induced photochemistry of the L-Cysteine disulfide in aqueous solution via femtosecond X-ray absorption spectroscopy

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The disulfide bond motif is an important structure-making moiety in proteins, whereby two spatially adjacent L-cysteinyl residues in an amino acid chain can react to form a covalent disulfide bond. These disulfide bonds stabilize the proteins tertiary structure and can act as a UV radiation shield and as radical scavengers.

However, many of the underlying processes are still unknown. This is especially true for the earliest timescales where the initial disulfide bond breakage occur. Therefore, the UV photochemistry of sulfur-containing amino acids and in particular of the disulfide bond are of interest in the field of ultraviolet photochemistry in proteins. Such reactions have therefore been studied extensively with both conventional and time-resolved methods. We demonstrated that time-resolved X-ray absorption spectroscopy (TRXAS) at the sulfur K edge is a chemically sensitive tool to observe the UV photochemistry of simple organosulfur compounds in nonpolar solvent environments [1–2]. However, for a better understanding of the photochemistry under physiological conditions, these model systems need to be extended to the natural amino acid L-Cysteine in aqueous solution.

Herein, we report the first results of the photodissociation dynamics of L-Cystine, the disulfide dimer of L-Cysteine, in aqueous solution upon UV irradiation with 267 nm light using TRXAS at the sulfur K-edge with femtosecond time resolution. We observe the emergence and subsequent decay of the photoproduct on timescales of hundreds of femtoseconds up to 800 ps [3].

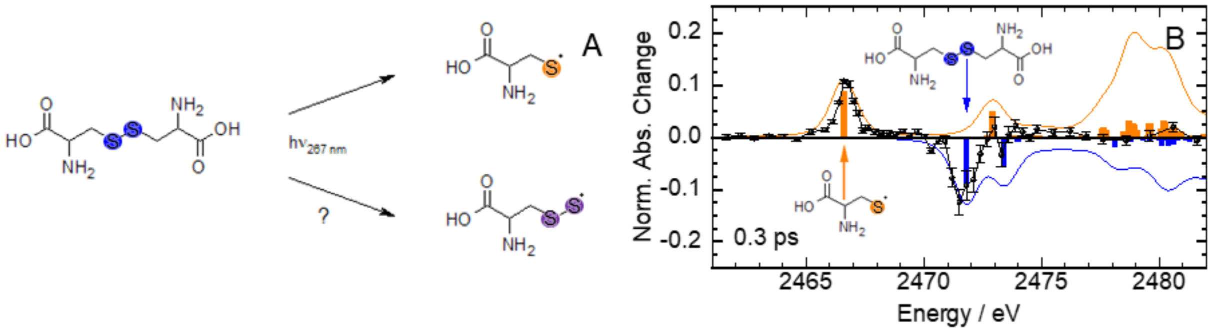

Figure 1: Panel A shows possible reaction pathways of L-Cystine after UV-excitation. In panel B is the differential X-ray absorption spectrum of L-Cystine at 0.3 ps after 267 nm excitation is displayed. The negative absorbance change at 2471.8 eV signals the emergence of either excited state parent molecules or new sulfur-containing species. The characteristic absorption lineshape of the sulfur radical at 2466.5 eV suggests ultrafast generation of thiyl radicals.

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Attosecond Spectroscopy of Small Organic Molecules: XUV pump-XUV probe Scheme in Glycine

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The availability of coherent light sources with attosecond resolution (1 as=10^{-18} s) has opened the door to resolve electron dynamics in excited and ionized complex molecules. The early electron dynamics triggered in a biomolecule is at the heart of biological processes which are essential to life. Therefore, understanding the ultrafast charge dynamics that steer these processes has become a hot topic in the field of attosecond science. Attosecond time-resolve experiments allow us to retrieve images of this charge dynamics in molecules. The first experiment retrieving a sub-femtosecond ultrafast dynamics in a biomolecule was performed by using an as UV-pump/ fs IR-probe scheme in phenylananine [1]. The sub-fs charge fluctuations where associated with electronic coherences initiated by the as pump pulse. Theorical calculations to describe this experiment were initially performed considering that the nuclei of the molecule remained fixed in space [1], [2]. How long these electronic coherences can survive when nuclear motion comes into play is a question that has yet to be solved.

In the present study, we pursue to shed some light on this matter by theoretically describing the outcome of an attosecond two-color XUV-pump/XUV- probe scheme in glycine. The broadband pump pulse ionizes the molecule, creating a coherent superposition of cationic states, which evolve in time coupled to the nuclear motion until it is probed by the second XUV pulse. An explicit evaluation of the full-electron wave function in the continuum and the inclusion of non-adiabatic effects are carried out [3]. Both aspects have been addressed in this work by combining a multi-reference static-exchange method and a surface hopping approach, respectively. We have found that, in the absence of the probe pulse, ionization can lead to fragmentation of the glycine cation through the C-C or the C-N bonds. The lower electronic states of the cation are more likely to induce elongation of the C-C bond, while the higher excited states favor elongation of the C-N bond, both of which can ultimately break. We have found that by simply varying the central frequency of the pump pulse by a few eVs, one can alter the cation dynamics favouring specific fragmentation pathways. We have also investigated the role of the probe pulse in capturing the above dynamics, first by looking at the photoelectron spectra and then at the fragmentation yields, both as a function of the pump-probe delay.

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Spatial control of molecular dissociation on the surface of nanoparticles with tailored laser fields

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The use of nanoparticles in catalysis to boost chemical reactions is expanding. The role of aerosolized silica nanoparticles to serve as catalysts in the formation of H_3^+ via unconventional ways in intense-femtosecond laser fields has recently been indicated [1] using the reaction nanoscopy (NanoTRIMS) [2,3]. The aforementioned technique is based on three-dimensional ion momentum spectroscopy and in the present work, with its assistance, we manifest the control of molecular adsorbate reactions on the surface of SiO_2 nanoparticles with nano-meter resolution. We demonstrate spatial control of the reaction yield landscape on the nanoparticle surface, by tailoring the near-fields using waveform-controlled two-color laser (1μm and 2μm) pulse.

First, we investigate the phase-dependent proton emission and field-induced propagation effects with relative phase delays between linearly polarized two-color pulses and using two differently sized (300 nm and 600 nm) silica nanospheres. For 300 nm particles, we observe a large asymmetry (~80%) in H^+ emission from the nanoparticle surface. In addition to a high asymmetry (though comparatively smaller than 300 nm particles), the proton signal from larger particles also exhibits the signature of field-propagation effects. Then, using bicircularly polarized laser pulses, we observe a 3-lobed proton momentum distribution with counter-rotating two-color pulses whereas a semi-lunar like proton momenta distribution is observed with co-rotating bicircular pulses. A relative phase-delay between the two-color pulses results as change in the angular distribution of the observed proton momenta distribution. The momentum distribution for both the cases is believed to change in accordance with the pointing direction of the electric-field vector as the field propagates and thus the generated near-field hotspots in real-time. Therefore, the liberty of shaping and controlling the near-field direction, translates into the control of the reaction sites on the nanoparticle surface.

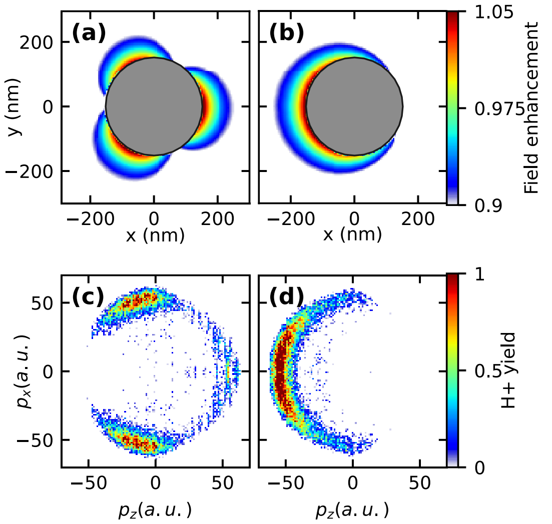

Figure 1: Calculated near-field enhancement for bicircular counter-(a) and co-(b) rotating laser pulses and the corresponding proton momentum distribution (c) and (d) respectively.

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Molecular photoionization time delays

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The observation of electronic motion in real time has been a dream over the years, which opens unforeseen ways to track and manipulate matter. In the last decades, the first light pulses with durations comparable to the time scale of electronic motion, *i.e.* a few attoseconds (1 as $= 10^{-18}$ s), were generated [1-3]. Thus, it is nowadays possible to obtain real-time images of the formation and breaking of chemical bonds or to quantify the electron dynamics upon excitation or ionization processes. In a photoionization event, the electron is ejected from an atom or a molecule after the interaction with an electromagnetic field. However, the emission is not instantaneous. How long does the electron wave packet require to escape? This is defined as photoionization time delay. One of the most successful experimental strategies to extract these photoionization time delays in atoms is the attosecond electron streaking [4-6]. This technique uses a pump-probe scheme to characterize the electronic wave packet, accessing the dynamical information. However, scarce works have been performed in molecules [7-10] and a solid theoretical ground to define the concept of photoionization time delays when the electronic dynamics is coupled to the nuclear degrees of freedom is still to be developed. This is the goal of the current project. We employ as benchmark system the simplest molecule, the hydrogen molecular ion. The dependencies with the nuclear degrees of freedom are investigated by performing, for the first time, full dimensional simulations to extract molecular photoionization time delays.

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Ultrafast dissociation in a molecule and its isotopologue upon ionization by attosecond pulse trains

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Following the pioneering works of A. H. Zewail, femto-chemistry experiments have provided many important insights about photo-induced dynamics in complex molecules. These experiments usually involve resonant excitation using ultraviolet or, visible laser pulses, allowing the study of relaxation processes in the neutral molecule. With the advent of high-order harmonic generation (HHG) based sources providing ultrashort coherent pulses in the extreme ultraviolet (XUV) domain, it is now posible to investigate similar dynamical processes in highly excited photo-ionized species. Pioneering examples include small diatomic molecules [1] as well as large polyatomic molecules [2,3].

Here, we use an attosecond pulse train (APT), produced via HHG in Krypton, as a pump pulse to ionize and excite ethylene molecule (C_2H_4) and its deuterated counter-part (C_2D_4). The subsequent relaxation dynamics is probed using a near-infrared (NIR) pulse. The ionic fragments were collected as a function of the delay between the XUV-pump and NIR-probe pulses, using a velocity map imaging spectrometer operating in the time-of-flight mode.

The H^+ and D^+ fragments collected in this manner show a fast decay of a few tens of femtoseconds in their delay-dependent ion-yields. However, the extracted time-constants (τ) show that τ_{H^+} is faster by almost 7±2 fs compared τ_{D^+} [see Fig. 1(a)], independently of the NIR-probe intensity. Our findings are supported by advanced trajectory surface hopping based calculations which show that the number of H-loss trajectories increases at a much faster rate compared to the number of D-loss trajectories [see Fig. 1(b)]. This is because, the heavier D-atom takes longer time compared to the lighter H-atom to reach a sufficient enough distance where it can be considered fully dissociated. The use of XUV APT allowed us to study light-induced sturctural changes in molecules taking place within only a few femtoseconds [4].

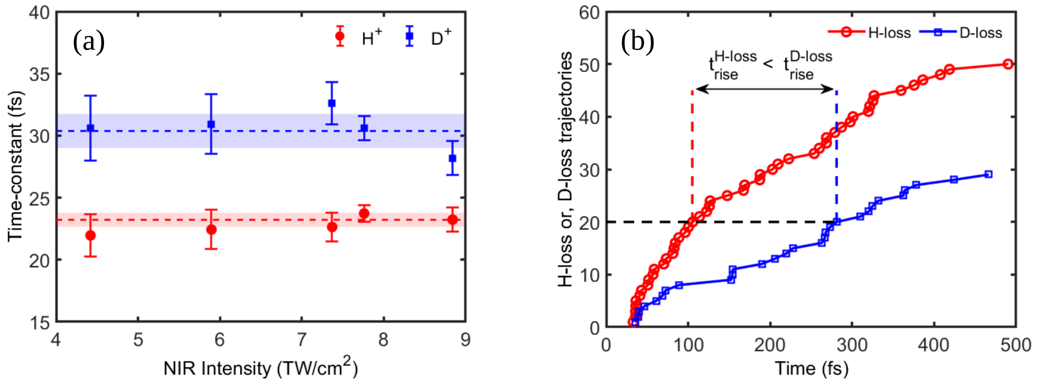

Figure 1: (a) Time-constants for H^+ and D^+ fragments at different probe intensities. (b) The number of trajectories for H-loss in C_2H_4 and D-loss in C_2D_4 following ionization by an ultrashort XUV pulse.

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Fingerprints of Majorana fermions in high-harmonic spectroscopy

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Majorana fermions [1], due to the equivalent character of their particle and antiparticle, have found applications in various scientific areas like solid state physics, nuclear and particle physics. Till date, the presence of Majorana fermions in solid state systems is under vigorous debate. HHG in solids became a method of choice to probe different aspects of solids such as examining the dynamics of the defects in solids [2,3] and probe localisation-delocalisation phase transition [4] in condensed matter systems. In this work, we provide an alternative method to see the signatures of the Majorana fermions without ambiguity using ultrashort laser pulses and high-harmonic spectroscopy. We show that the nonlinear optical response of a system is able to sense the presence of Majorana fermions. The one-dimensional superconducting chain originally proposed by A. Kitaev that hosts Majorana edge modes in its topological phase is considered as the model system. We show non-resonant light fields probe topological–trivial superconducting phase transition in a system with edges, i.e., open boundary conditions. The sensitivity of high-harmonic spectroscopy to the superconducting phase transition to trace the signature of Majorana edge modes as their population dynamics are different than other modes in the bulk. Moreover, the high-harmonic spectroscopy becomes insensitive to the phase transition with similar harmonic profiles in both phases for systems with periodic boundary conditions when Majorana-zero-modes (MZMs) are absent. Moreover, we show that the harmonic spectra obtained from Bogoliubov-de Gennes (BdG) form of the Hamiltonian and from the many-body Kitaev superconducting Hamiltonian are same.

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Attosecond time delay sensitivity to the atomic arrangement in a molecule

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Photoionization time delays result from the scattering of electrons in a quantum potential [1]. Protocols such as RABBIT allow to measure such photoionization time delays down to the attosecond timescale maintaining the spectral resolution [2]. Its principle is presented in Fig.1(a) an electronic state (orange line) is ionized by XUV photons (purple arrows), the excitation is coupled with infrared photons (red arrows) leading to the same final electron kinetic energy. This result in an interference where the yield oscillates with the time delay between the XUV and IR pulses. The phase of the oscillation carries the ionization time delay information [2,3]. This method has already successfully been applied to atoms, small molecules, clusters, solids and liquid systems unraveling a large diversity of physical mechanisms.

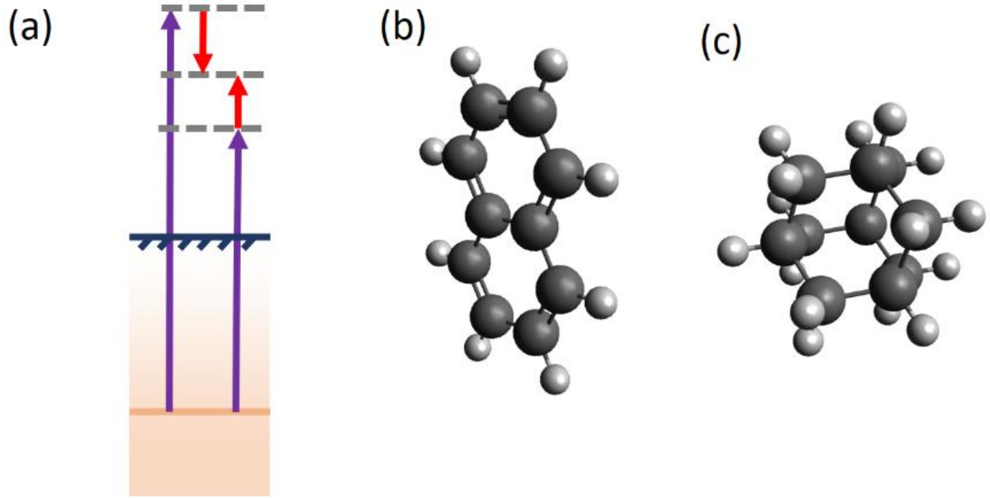

Figure 1: (a) Sketch of the RABBIT protocol that is applied to (b) naphthalene and (c) adamantane.

In this work, the RABBIT technique is used to compare the photoionization time delay as a function of the atomic arrangement in the molecular potential. Naphthalene ($C_{10}H_8$, Fig. 1b) and adamantane ($C_{10}H_{16}$, Fig. 1c) principally differs by their geometry (planar and diamantoid respectively). This poster presents the experimental results of RABBIT measurements performed on such molecules. Several tens of attosecond difference in photoionization time delay are observed out of resonances. This difference can be attributed to the geometrical arrangement of the atoms in the molecular potential [4].

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Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules

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Ever since the first models of organic solar cells were proposed more than 40 years ago, the search for new materials with the ability to produce a charge separation, necessary for photovoltaic applications, has kept drawing the scientific community's attention.

Organic photovoltaic devices usually achieve charge photogeneration by using charge transfer complexes, which act as an intermediate step between exciton dissociation and charge extraction.

In order to capture the real time evolution of such electronic process, which takes place in the time range between tens of attoseconds to a few femtoseconds, a sub-femtosecond time-resolution is required. Therefore, in this work we propose the use of a pump-probe scheme employing ultrafast laser sources to track the charge transfer process using as target a typical donnor-acceptor molecule in the gas phase. In particular, we investigate the ultrafast dynamics following the excitation of para-nitroaniline (PNA), which has been extensively studied in a solvent, both theoretically [1] and experimentally [2], while scarcer works have been performed in gas phase to date.

We thus propose the use of a pump-probe scheme, using a few-fs UV pulse to excite the target. The ensuying electron-nuclear dynamics will be later probed by a time-delayed attosecond XUV pulse which will ionize the molecule. The time-varying ionization yields are expected to capture the complex dynamics triggered in the excited molecule.

In a first approach, using the fixed nuclei approximation, we retrieve the time evolution of the excited wave packet by analyzing the electron density variation, computed through a transition density matrix formalism. The imprint of these dynamics is later retrieved into the cation with the time-delayed absorption of the probe pulse.

We later explored how these electron dynamics evolved when coupled with the nuclear degrees of freedom, when non-adiabatic couplings come into play. The coupled electron-nuclear motion is described by means of a surface-hopping method, i.e. within a semi-classical picture. In short, the time-dependent wave function is retrieved at each time step, computing the electronic structure on-the-fly by means of a quantum mechanical description, while the nuclear dynamics follows the classical equations of motion.

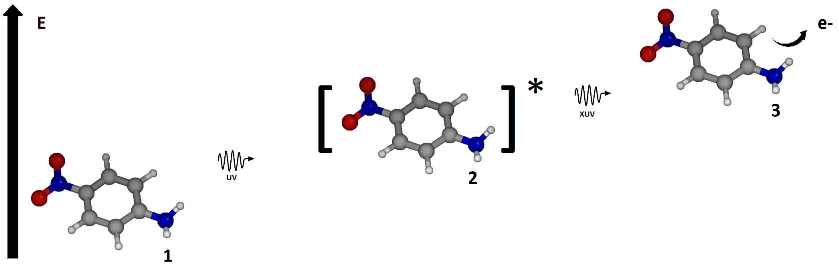

Figure 1: Diagram of the pump-probe scheme.

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Imprinting chirality on atoms using synthetic chiral light

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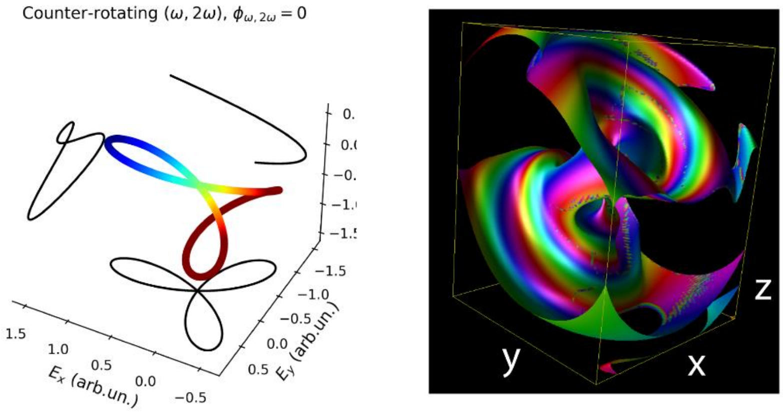
Chiral light fields in the dipole approximation can be synthetized by crossing two beams with different frequency and suitable polarization properties. The interaction of this particular type of lightwave with a chiral sample leads to giant enantio-sensitive responses [1]. While atoms are usually thought as achiral, there exists chiral superpositions of atomic states whose handedness can be probed by standard Photoelectron Circular Dichroism methods [2]. Here, we explore the link between chiral light and chiral atomic superpositions and show via state-of-art TDSE simulations that it is possible to imprint chirality on an achiral atomic target using chiral bicircular, co- and counter-rotating fields both in the low- and strong-field regime. We demonstate the existence of time-dependent chiral wavepacket exhibiting time-varying handedness as well as chiral Freeman resonances [3].



Bicircular chiral light Isosurface plot of a chiral wavefunction in sodium

Figure 1: Syntethic chiral light (left) and atomic chiral wavefunction (right).

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Light-control of Valley-polarization in Graphene

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Graphene, the first monolayer material, has achieved significant attraction in both applied and fundamental sciences in the past decade [1]. The charge carriers in graphene, also known as Dirac fermions, have peculiar properties from the linear dispersion and zero bandgap of the material.

One of the most exciting features of graphene and gapped graphene materials is the electron's extra degree of freedom, the valley pseudospin, associated with populating the local minima K and K' in the lowest conduction band of the Brillouin zone. This extra degree of freedom can encode, process and store quantum information, opening the field of valleytronics [2]. In gapped graphene materials, valley selectivity is achieved by a pump pulse resonant with the bandgap and with matching helicity to the Berry curvature of the material [2]. The vanishing bandgap makes graphene unsuited for such resonant valley-selective excitations - a disappointing conclusion given its exceptional transport properties.

In our recent work, we have illustrated how valley-selective excitation in graphene can be achieved in an all-optical-means [3]. This non-resonant valley-polarization mechanism uses a combination of two counter-rotating circularly polarized fields, the fundamental and it's second harmonic. The tailored field allows one to both break the symmetry between the adjacent carbon atoms and to exploit the anisotropic regions in the valleys, taking advantage of the fact that the energy landscape of the valleys are mirror images of each other.

In the present work, we explore how different laser parameters can be tuned to get optimum valley-polarization. We observe that this mechanism of valley-polarization contributes significantly for longer wavelengths and intense pulses. Moreover, the relative intensity of the two fields have a significant role in the valley-polarization mechanism. Furthermore, we investigated other tailored fields for which no significant valley-polarization could observe, showing the importance of inversion symmetry breaking in order to observe valley-polarization in pristine graphene.

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Quantum bridges in phase space – Interference and Non-Classicality in Enhanced Ionisation

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Our studies show that enhanced ionisation in H_2^+ stems from the interplay of at least two qualitatively different ionisation pathways, shown in Fig. 1 (a).

One of these pathways follows the field gradient and leads to tails along separatrices that 'spill' into the continuum, while the other does not obey field gradients or classical barriers in phase space. The former pathway may be associated with quasi-static tunnelling mechanisms [1, 2] as well as the semiclassical limit of Wigner quasi-probability distributions [3], with oscillatory tails around separatrices and equienergy curves. The latter pathway has been first identified in [4, 5] for oscillating driving fields. It consists of a cyclic motion performed by the Wigner function in phase space and the emergence of momentum gates, along which there is a direct quasiprobability flow from one well to the other. Therein, momentum gates were explained as resulting from strongly coupled states and the non-adiabatic response to the time-dependent field gradients.

We find, however, that this pathway occurs also for static fields, and even in the absence of driving fields altogether. On top of that, near quantum bridges the Wigner quasiprobability distribution exhibits non-classical evolution, shown in Fig. 2 (b), which we assess using the quantum Liouville equation:

$$\left(\frac{\partial}{\partial t}+\frac{p}{M}\frac{\partial}{\partial x}-\frac{dV_{\text{eff}}}{dx}\frac{\partial}{\partial p}\right)W(x,p,t)=Q(x,p,t).$$

By employing different types of initial bound states for the electronic wave packet, we show that the primary cause of the momentum gates in [4,5] is quantum interference. We also shed light on the behaviour observed for time dependent fields. The frequency of the quantum bridge being higher than that of the laser field, the quasiprobability distribution will sometimes counter-intuitively flow in the direction opposed to the electric-field gradient.

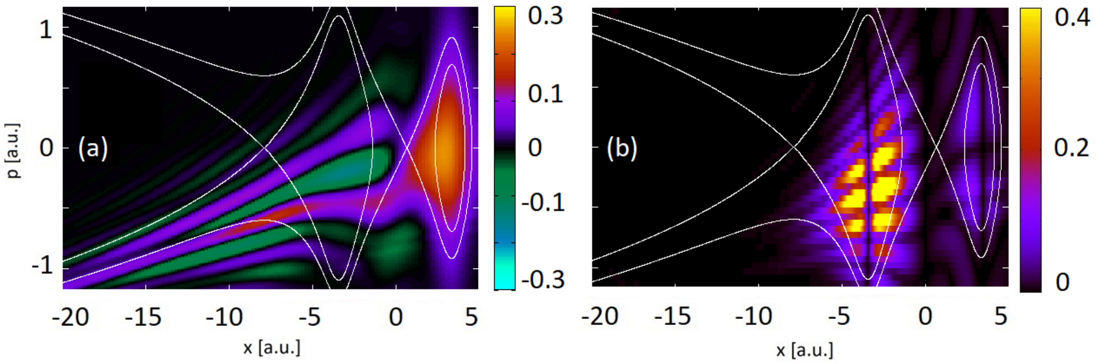

Figure 1: Comparison of (a) the Wigner quasi-probability distribution and (b) the quantum corrections Q(x, p, t), calculated for a model H_2^+ molecule of inter-nuclear separation R = 6.8 a.u. at time t = 24 a.u. in a static laser field of strength E = 0.0534 a.u. (intensity I = 1014 W cm^{-2}) using a Gaussian initial wave packet centred around the upfield potential well. The thin white lines in the figure give the equienergy curves (including the separatrices).

The fact that enhanced ionisation is an optimisation problem suggests that these ionisation mechanisms can be controlled by appropriate coherent superpositions of states, targets and driving fields. This opens up a wide range of possibilities for studying quantum effects in enhanced ionisation.

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Stabilizing the excited states of molecules with circularly polarized fields

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We study the dynamics of the excited state of the H_2^+ molecule under a strong circularly polarized field. Our analytical results show that under certain approximations a circularly polarized field allow the stabilization of this molecule, thus overcoming the anti-alignment dynamics that makes the stabilization impossible with a linearly polarized field [1, 2]. However, it is unclear whether the analytical approximations hold or not, and in what degree. To check this point, we numerically simulate the quantum dynamics of both electron and nuclei, by solving the three coordinates of the electronic motion expanding in prolate spheroidal coordinates while propagating the nuclear wavepacket using a second-order split-operator scheme over a square grid.

In Fig. 1(a), we show the average and standard deviation in R and θ under the circularly polarized field after radially perturbing the stabilized state by $+0.5a_0$. In agreement with our analytical calculations, we observe vibrations in the LIP with a 23 fs period during the 100 fs of simulation indicating a high degree of stability. Although the time scale of the field is much shorter than the one of the nuclei, it appears to be slow enough to induce an oscillatory dynamics in θ. At the same time, the wavepacket gradually spreads in θ, which agrees with the fact the pulse is symmetric respect orientation.

In Fig. 1(b), we present some snapshots from the wavepacket dynamics considered in Fig. 1(a). The snapshots illustrate the oscillation if the wavepacket in the light induced potential. However, we also spot a tiny amount of probability dissociating at t = 11.25 fs (see around θ = 0, R=6 a_0), which indicates a small degree of instability due to non-adiabatic couplings. Indeed, the vibrational motionleads to a slow decay in the continuum (a half-life of hundreds of fs), so that all eigenstates of the LIP are meta-stable.

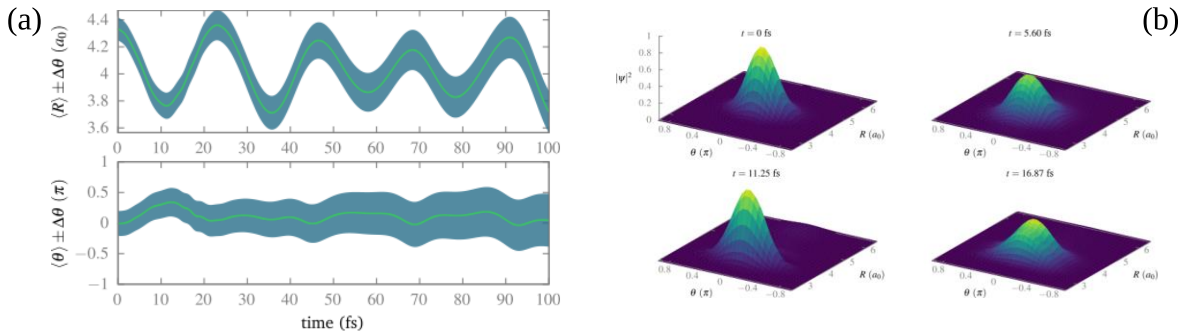

Figure 1: (a) Expected value of the interatomic distance and molecule orientation as function of time for a Gaussian wavepacket in the stabilized excited electronic state displaced from the equilibrium by $0.5a_0$. (b) Snapshots of the wavepacket dynamics at selected times.

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Interferometric measurements for ultrashort UV pulses characterization

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Ultraviolet (UV) light exposure provokes a variety of chemical reactions in biorelevant molecules [1]. The underlying mechanisms are based on electron rearrangements occurring on few femtoseconds (fs) or even attosecond time scales. Time-resolved spectroscopy methods utilizing ultrashort UV pulses can be applied for studying the involved electron dynamics with a possibility to open new perspectives for controlling photoinduced reactions.

Several groups have demonstrated the generation of few-fs UV pulses [2-4]. However, the temporal characterization of such pulses is not a trivial task. The main issue is associated with the ultra-broadband nature of the UV spectrum, over which any dispersion needs to be avoided. In this regard, characterization techniques should be implemented in dispersion-free schemes based on, e.g. reflective optics. One of the candidates fulfilling this requirement is the fringe-resolved interferometric autocorrelation (FRIAC) method as described in [5].

Here, we present the successful implementation of a second-order FRIAC approach for the characterization of ultrashort UV pulses generated by tripling a 10 fs infrared field in a neon medium. Two copies of the incident pulses are created using a reflective beam splitter formed by two intertwined comb-like mirrors. Each of them acts like a grating producing a clearly resolved diffraction pattern. Overlapping the single patterns spatially and temporally, e.g. in the focal plane of focusing optics, allows for recording the autocorrelation signal with interferometric contrast. To do so, the zeroth diffraction order was selected by a gold wire, acting as the non-linear medium by creating a photocurrent by 2-photon absorption (Au work function > 5.1 eV). By measuring the induced photocurrent as a function of the delay, second-order FRIAC traces were acquired.

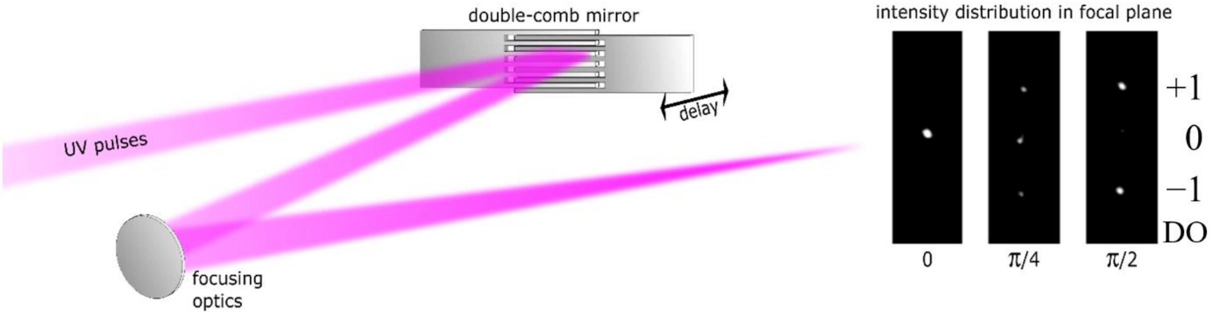

Figure 1: Schematic of the ultrashort UV pulses interacting with the double-comb mirror. By scanning the delay between the two combs, a phase shift is introduced between the superimposed diffraction patterns. On the right, the intensity distribution in the focal plane is depicted for exemplary phase shifts. DO means diffraction orders.

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Autoionizing polaritons in attosecond transient absorption

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An intense laser coupling metastable resonances can give rise to a pair of autoionizing polaritons, whose lifetime can be extended as a result of interference between radiative and Auger decay channels [1]. We explain this phenomenon using an extension of the Jaynes-Cummings model to autoionizing states [2,3], showing how this stabilization depends on the parameters of the dressing field. We perform *ab initio* simulations of attosecond transient absorption in argon, where multiple avoided crossings in the calculated spectra are observed between the $3s^{-1}4p$ autoionizing resonance and light-induced states originating from other resonances. These avoided crossings, characteristic of the formation of a polaritonic multiplet, clearly show a stabilization of some of the polaritonic branches. These theoretical predictions are in excellent agreement with experiments conducted in parallel, and point to a novel method of controlling electronic structure in the continuum.

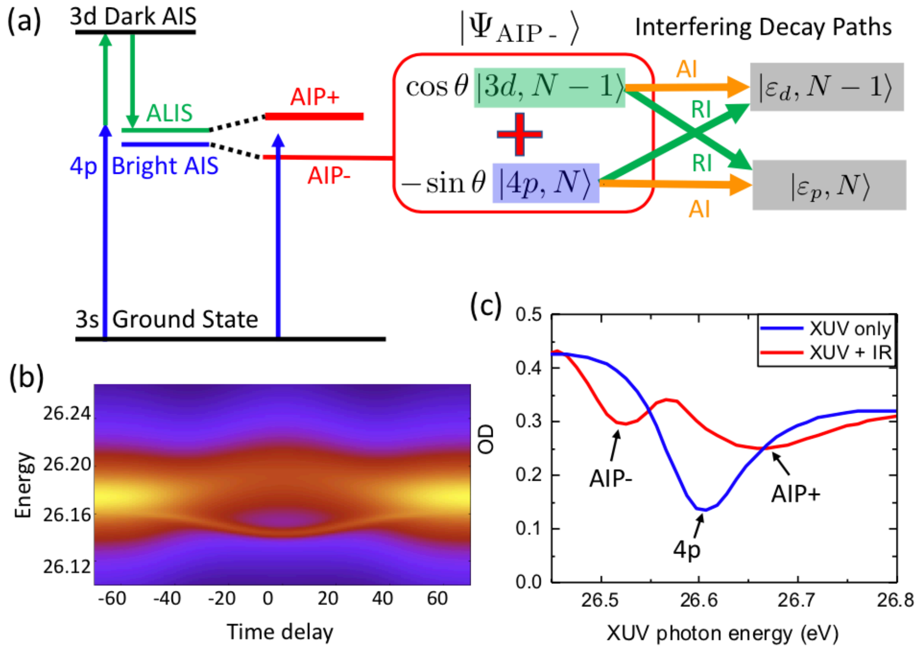

Figure 1: (a) Diagram showing the formation of autoionizing polaritons from the mixing of a bright resonance and a light-induced state, predicted by the model (b) and observed in experiment (c).

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A new Soft-X beamline for Transient Absorption Spectroscopy in solids

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High Harmonic Generation (HHG) arising from the interaction of intense laser pulses with noble gases led to the realization of table-top sources of coherent XUV and soft-X radiation. This allowed ultrafast spectroscopy experiments to be performed with extreme temporal resolutions, down to the attosecond regime, and chemical sensitivity [1, 2]. However, the full exploitation of these sources is hindered, even today, by their technological complexity and their low generation efficiency when moving towards higher photon energies.

Here we present a new soft-X beamline to perform transient absorption spectroscopy experiments in solids that aims at overcoming these limitations. HHG is performed in a microfluidic device, that grants a dramatic increase of the generation efficiency and the possibility to finely control the gas density in the harmonic generation region [3]. We foresee novel possibilities for the engineering of the generation process and the implementation of different functionalities on the same microfluidic device, leading to the realization of Lab-On-a-Chip (LOC) approaches in attosecond science.

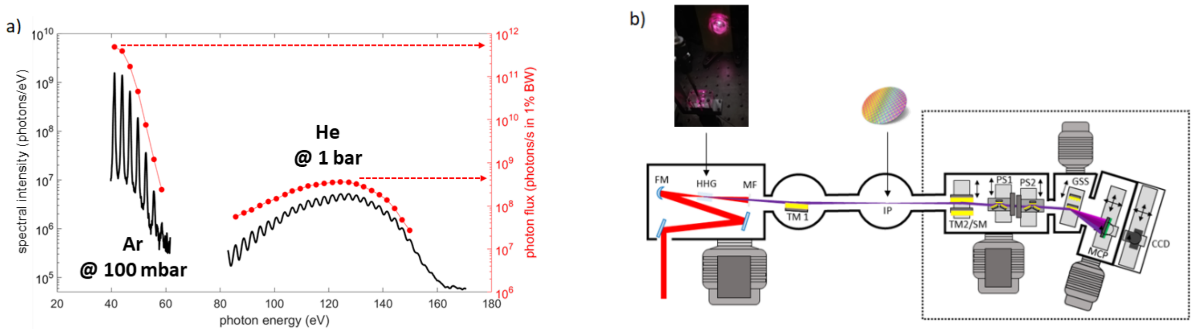

Figure 1: a) Spectra generated in 100 mbar of Ar and 1 bar of He inside the microfluidic device with photon flux calibration. b) Sketch of the beamline with the flexible spectrometer highlighted with dashed lines. FM, Focusing Mirror; HHG, microfluidic device; MF, metallic filter; TM, Toroidal Mirror; IP, Interaction Point; SM, Spherical Mirror; PS, Polarimeter Stage; GSS, Grating Selection Stage; MCP, Micro Channel Plate; CCD, Charge-Coupled Device.

The radiation is then focused on an interaction point where attosecond transient absorption spectroscopy in solids can be performed and analyzed by a flexible spectrometer. This can be remotely tuned, without any need to realign optical elements or to break the vacuum, to work in the 1-100 nm range both in stigmatic and astigmatic configuration. Moreover, an XUV polarimeter and a calibrated photodiode can be independently inserted, granting the full characterization of the radiation in terms of Stokes parameters down to 12 nm and absolute photon fluxes. We believe this flexible and user-friendly solution for the analysis of XUV radiation will facilitate the diffusion of HHG-based technologies and the realization of novel experimental schemes.

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Ultrafast molecular dynamics induced by few-femtosecond ultraviolet excitation

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Ultraviolet (UV) induced ultrafast processes in molecules are fundamental for their chemical and biological implications. In this context, they have been extensively studied on a time scale of hundreds of femtoseconds (fs) or longer, unravelling processes such as DNA photoreactivation [1] or isomerization process involved in vision [2]. However, the possibility of triggering and controlling electron dynamics with even shorter UV light pulses in molecules has been barely explored, mostly due to the technological challenge of producing few-fs pulses in this spectral region.

Here, we present the first benchmark pump-probe experiments employing few-fs UV pulses on acetone and iodomethane: a 3-fs UV pump, generated in a high pressure micro-machined gas cell filled with Neon [3], is combined with a 5-fs VIS/NIR probe to ionize the target. Electron Velocity Map Imaging (VMI) images and Time-of-Flight Mass Spectra (TOFMS) are simultaneously recorded as a function of the delay between the two pulses using a double-sided spectrometer [4].

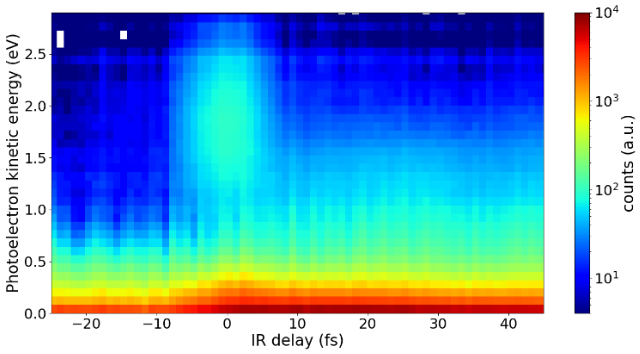

Figure 1: Angularly integrated photoelectron kinetic energy as a function of the IR delay obtained in acetone. Positive delay means NIR pulses come later. 75% of the first delay spectrum has been subtracted as background to enhance visualization.

In acetone, we observe the kinetic energy of the emitted electrons undergoing a few-fs long energy shift towards higher energy, probably related to an ultrafast reshaping of the phase of the electron wave packet; the subsequent decay (~ 280 fs) appears modulated by a 25 fs oscillation which starts immediately after the excitation. In iodomethane, instead, the few-fs temporal resolution of the experiment allows us to resolve the appearance of the iodine ion yield after 25 fs from the time overlap. The interpretation of the above-mentioned results is still preliminary and advanced calculations to simulate the UV-induced photo-fragmentation are ongoing.

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Multiphoton interaction phase shifts in attosecond science

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We study three recent attosecond and free-electron laser interferometric experiments from Ref. [2-4], using *ab initio* simulations and derive a simple rule of thumb for *interaction phases*, which accumulate for each interaction [1]. We find that RABBIT sidebands are exceptional since they are not affected by interaction phases. On the other hand, experiments with an unbalanced number of interactions in each arm are affected. By introducing the concept of interaction phases, we find that interferometric above-threshold ionization are shifted relative to RABBIT experiments and provide an explanation to why laser-assisted photoionization experiments with mixed parity express no RABBIT modulation.

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Charge migration in aminophenol following sub-fs X-Ray pulses: Influence of nuclear effects and the XFEL shot-to-shot variation

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Recently, X-Ray free electron laser (XFEL) facilities have been demonstrated to be capable of producing sub-fs soft X-Ray pulses, using the method of X-Ray laser-enhanced attosecond pulse generation (XLEAP) at the LCLS facility [1]. This makes it now possible to use tunable soft X-Ray pulses, carrying a much higher intensity than their respective high harmonic generation counterparts, enabling nonlinear spectroscopies to investigate attosecond electron dynamics in molecules.

We here present theoretical results describing the ultrafast charge dynamics induced in the 4-aminophenol molecule (OH - C_6H_4 - NH_2) ionized with a sub-fs 260 eV pulse, i.e. below the carbon K-edge. The ionization calculations have been carried out using the static exchange B-spline DFT method that has been successfully applied in related previous studies at lower photon energies [2,3]. In particular we scrutinize the influence of the shot-to-shot variation in terms of envelope, phase, and intensity by considering a set of 100 different X-Ray pulses generated from start-to-end simulations of the XFEL. Moreover, we examine the ground state nuclear effects in the resulting charge fluctuations. To this end we take into account an ensemble of molecular geometries sampled from the equilibrium Wigner distribution.

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A table-top Soft X-ray beamline for transient absorption experiments in liquid phase

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Transient absorption spectroscopy allows for studying primary relaxation processes in molecules. In particular, Soft X-ray absorption performed in the water window spectral range [1] offers the possibility of studying biologically relevant molecules in their physiological environment (liquid phase), with the advantage of site-selectivity. However, the real-time interrogation of the electronic dynamics in the valence and core molecular orbitals requires attosecond light pulses [2]. In the context of probing ultrafast molecular dynamics beyond the gas phase, liquid jets recently revealed to be exceptional sources to perform time-resolved spectroscopy in liquid phase. Indeed, key tools for interrogating aqueous systems, such as infrared and soft X-ray spectroscopy, cannot readily be applied in sub-fs spectroscopy because of strong absorption in water [3].

In this work we report the development of an attosecond Soft X beamline which combines high harmonic generation (HHG) with a liquid jet molecular source for aqueous phase experiments.

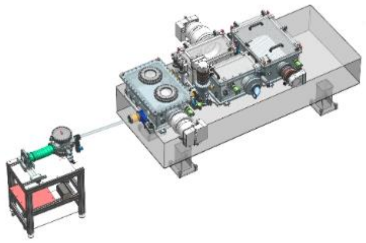

Figure 1: Design of our Soft X beamline.

The HHG process requires a MID-IR wavelength driving laser and a carrier-envelope phase (CEP)-stable driving field. Therefore, the beamline is driven by a two-stages optical parametric (OPA) source [4], which produces few-optical-cycle multi-mJ CEP-stable 1.8 µm carrier wavelength pulses.

Furthermore, we present the construction of a microjet source able to generate stable sub-micron liquid sheets, which are found to be tunable in thickness from over 1 µm down to less than 20 nm. The higher flexibility of our jet source with respect to traditional transmission cells allows aqueous sheets to transmit photons across the spectrum while containing pulse dispersion and sample damaging, paving the way to applications in infrared, X-ray and electron spectroscopies.

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Asymmetric electron emission in non-linear processes in the X-ray regime

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The last two decades have seen the rise of X-ray free electron lasers (XFELs) throughout the world, providing ultra-short pulses with unprecedented intensities (10^{20} W/cm^2), over a large range of photon energies going from VUV to the hard X-ray domain. Besides the achievements in terms of brilliance, tremendous activity has been also devoted to the generation and control of XFEL pulses with sub-fs and even attosecond durations [1]. Extending X-ray to the attosecond domain is of crucial interest in a wide range of fundamental problems such as, for instance, resolving in time the dynamics of electronic rearrangement in atoms after core excitation or ionization [2]. New avenues are also opened to explore non-linear response in X-ray regime, like direct two-photon ionization of atoms [3] or non-linear Raman and Compton scattering processes [4].

In this poster, we present a novel scheme of stimulated Compton scattering (SCS) on the hydrogen molecule using a highly intense ultrashort X-ray pulse with frequencies ranging from 0.5 to 1.6 keV (see Fig. 1a). We solve the time-dependent Schrödinger equation including the explicit evaluation of dipole and non-dipole terms. The short wavelength of the X-ray pulse breaks down the commonly employed dipole approximation and it is found that the coherent contributions of dipole and non-dipole effects lead to a symmetry breaking in the photoelectron emission, which strongly depends on the X-ray wavelength and the molecular orientation (see Fig. 1b). This is a pure non-linear effect captured in the low-energy lying electrons emitted after absorption and subsequent stimulated emission of photons within the energy bandwidth of the pulse.

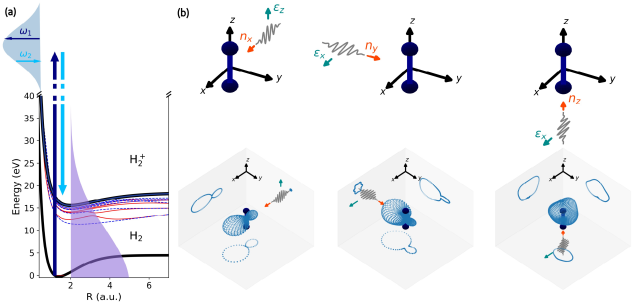

Figure 1: (a) Schematic representation of SCS using ultrashort pulses with H_2 potential energy curves. (b) MFPADs integrated over a range of electron energies [0-2.5 a.u.] for 1.1 keV pulse with a duration of 68 as and an intensity of 10^{18} W/cm^2.

Additionally, we present results for SCS simulations using two ultrashort pulses with different photon energies and propagation directions. As seen in atoms [5], non-dipole effects depend on the relative propagation angle of the pulses presenting a maximum in the SCS ionization probability for counter-propagating pulses. In this case, the direction of the photoelectron emission asymmetry can be related to the momentum transferred to the molecule by the absorption of a photon and the subsequent emission stimulated by the second field.

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Imaging charge migration in chiral molecules using time-resolved x-ray diffraction

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Chirality, which can be defined as the geometric property of a molecule being non-superimposable on its mirror image, is a general property observed in nature.

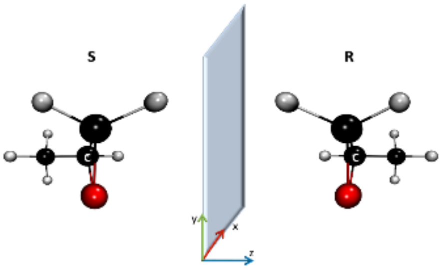

Figure 1: R- and S-enantiomers of epoxypropane in the molecular fixed frame.

A linearly polarised pulse is used to induce the charge migration [1], which is imaged by time-resolved x-ray diffraction. It is found that the total time-resolved diffraction signals are significantly different for both enantiomers as a function of pump-probe time delay [2].

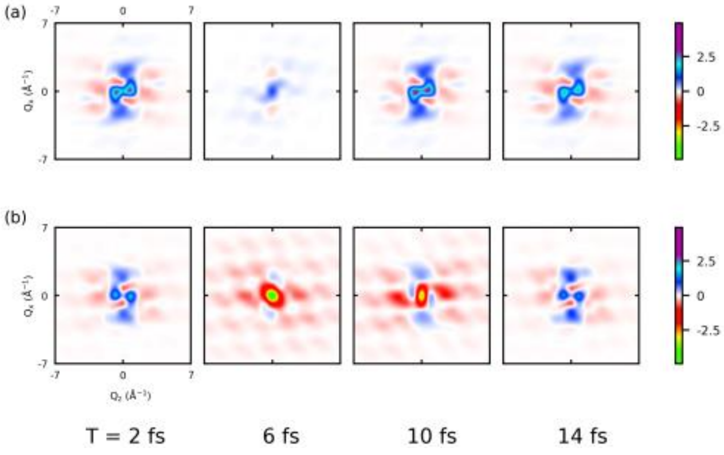

Figure 2: Time-resolved diffraction patterns for (a) R- and, (b) S-enantiomers of epoxypropane. Here, time-dependent diffraction signal at pump-probe time delay, T = 0 fs is subtracted to the subsequent delay times.

Furthermore, a connection between time-resolved x-ray diffraction and electronic continuity equation has been discussed by analysing time-dependent diffraction signal and the time-derivative of the total electron density in the momentum space [2].

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Generation and modulation of attosecond XUV pulses.

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Coherent phase modulated spectroscopy is a powerful tool for the investigations of dynamics induced by the interaction with visible and near-infrared pulses [1]. In order to perform coherent nonlinear spectroscopy two major requirements has to be fulfilled. First, in order to observe coherences high temporal stability between excitation pulses is necessary. Second, high sensitivity is required to isolate very weak nonlinear contributions from overall signal. Several experimental techniques (mainly interferometric) have already achieved high sensitivity and stability in visible and IR light [2,3,4]. However, the extension of these techniques to the XUV spectral range is difficult due to severe material limitations. Here, we present our approach to achieve phase modulation of attosecond extreme ultra-violet (XUV) pulses produced by high harmonic generation (HHG).

Driving highly nonlinear processes like HHG requires high intensity few cycle infrared (IR) pulses. Here, we use a Ti:Sa laser with 1 kHz repetition rate delivering CEP stabilized 5 mJ pulses with 35 fs pulse duration. Due to lack of the XUV interferometers one needs to use a new approach. In our case the XUV pulses are manipulated by phase modulating the driving IR field via two different interferometric setups. Thus, performing the phase-cycle on the fundamental wave of the driving laser collinear, phase-locked XUV pulse trains could be generated [5,6]. The goal of this project is to demonstrate novel and versatile experimental approach fostering nonlinear spectroscopy from HHG-based sources. We plan to perform all-XUV quantum interference spectroscopy on gas-phase samples combined with different detection mechanisms.

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Every single shot Carrier-Envelope Phase detection, control and tagging for attosecond science at repetition rates beyond 100 kHz

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To study interactions between electric fields of ultra-short laser pulses with atoms, molecules or solid state systems with attosecond resolution, a common approach is to use few-cycle laser pulses (FCP) for the generation of short trains or single pulses of attosecond duration [1]. For such FCP the shape of the electric field strongly depends on the relative position between the carrier wave and the pulse envelope which is described by the carrier-envelope phase (CEP). This parameter also strongly influences the generation of high order harmonic radiation and the interplay between a HHG pump and an FCP probe beam. The typically achievable temporal jitter between the electric field and the laser pulse maximum and thus the CEP also ranges well down on the attosecond time scale.

Here we present an enhanced way of measuring and controlling the CEP of individual few-cycle laser pulses and tagging this information to detected laser-matter interaction events, for instance in a coincidence ion/electron spectrometer like CIEL [2]. To achieve this, we use the established Stereo Above Threshold Ioniziation technique based on the detection of rescattered electrons emerging after ionization of Xenon [3]. This Stereo-ATI is capable to measure the CEP and asymmetry, i.e. the pulse duration, of each and every laser shot. We show that we can stabilize and control the CEP of an OPCPA laser amplifier at the full repetition rate of 200 kHz. By implementing an in-line measurement of the individual pulses in the beam, we characterize the very same pulse that is then used to generate high harmonics and also to probe the attosecond process of interest. The in-line approach additionally allows working with merely 10 µJ of pulse energy at 800 nm. The information about the wave form of every laser shot is used to tag each and every laser-atom interaction event by sending it simultaneously into standard RoentDek coincidence particle detection electronics.

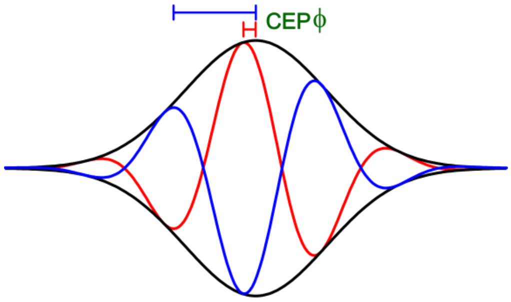

Figure 1: Few-cycle pulses with different CEP

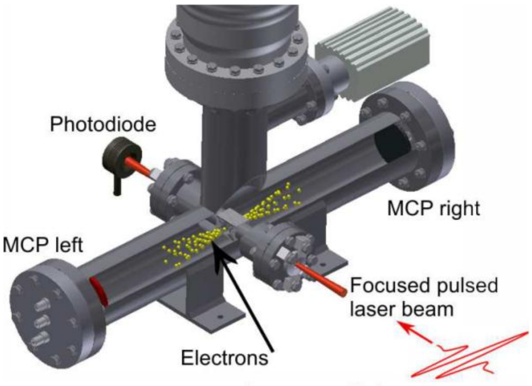

Figure 2: Stereo-ATI setup [3]

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Controlled ultrafast charge transfer in tryptophan-based peptides with tailored micro-environment

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Ultrafast dynamics in biomolecules induced by the absorption of light have major importance in nature. The understanding of these processes depends on the knowledge of the complex relaxation pathway following the excitation of the molecule. In this context, ultrafast technology offers tools to study in real time the dynamics involved in the relaxation steps [1]. Up to now, most of the studies have been performed on neutral molecules, unravelling significant processes such as DNA photoprotection for instance [2]. However, biomolecules usually exist either in deprotonated or protonated forms in biological condition and it has been shown that the charge state of molecules completely changes their electronic landscape, leading to a modification of their reactivity.

In this work, we investigate the effect of the charge and micro-environment on the dynamics of molecular ions. The experimental set-up combines ultrafast pump-probe technology with an electrospray source, allowing to probe charge transfer induced by UV light in small peptides: sodiated tryptophan (Trp.Na+), protonated tryptophan (Trp.H+) and sodiated alanine tryptophan (AlaTrp.Na+). Our results show that the change of the charged adduct atom leads to a change of the timescale of the charge transfer by more than one order of magnitude (see Fig.1.). To understand this drastically change, we performed calculations to extract the potential energy surfaces of the studied molecules. The energies of the states involved in the charge transfer, $\pi\pi^*$ and $\pi\sigma^*$, were found to evolve depending on the adduct atom. This change is explained by a Global-Local Stabilization Separation (GLoSS) model, in which the adduct atom has two main effects on the molecule: a global and a local contribution [3]. The global effect is defined by the global affinity between the adduct atom and the molecule and affects the energy of the $\pi\pi^*$ state while the local effect corresponds to the long range Coulomb attraction between the adduct atom and the NH_2 moiety and affects the energy of the $\pi\sigma^*$ state. The GLoSS model reproduces very well the shift in energy obtained in the calculation. These results bring new perspectives on the control of ultrafast dynamics such as charge transfer on the atomic length scale.

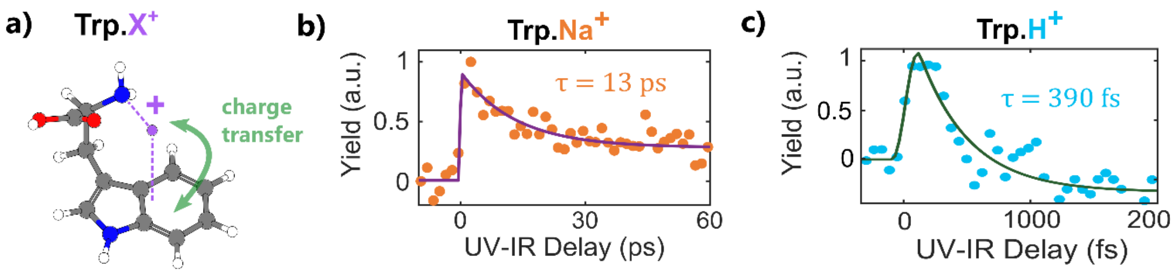

Figure 1: a) Representation of the charge transfer occurring in tryptophan-based peptides with a charged adduct atom X^+. b) Time-dependent signal recorded for $Trp.Na^+$. c) Time-dependent signal recorded for $Trp.H^+$.

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Extreme Ultraviolet Penning Ionization of Camphor Molecules in mK He Nanodroplets

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We will present intriguing observations of photoelectron spectroscopy on chiral camphor molecules embedded at sub-kelvin temperature (~ 0.4 K) of He nanodroplets. We have used a velocity map imaging (VMI) spectrometer to detect photoelectrons in coincidence with photoions detected by a time of flight (ToF) spectrometer. Using this PEPICO technique we are able to measure kinetic energy and angular distributions of the emitted photoelectrons. When photoexcited at photon energy $h\nu = 21.43\ eV,$ significant Penning ionization [1,2] occurs from the higher excited states of the dopant (Camphor) molecules leading to fragmentation of ions. We will discuss the details of these excited states of fragment ions and the photoelectron spectra associated with them.

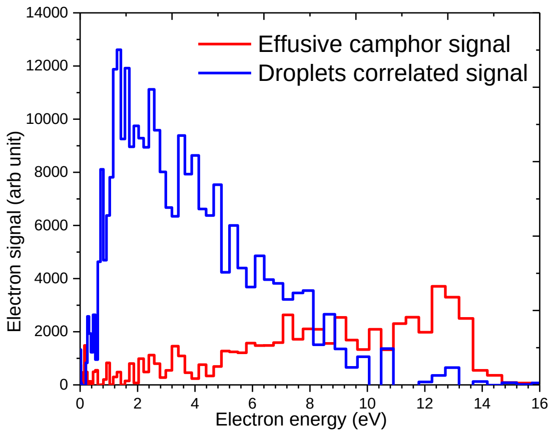

Figure 1: Photoelectron energy spectra measured in coincidence with camphor monomer ($[C_{10}H_{16}O]^+$) ion at photon energy hν = 21.43 eV. Here red line corresponds for effusive camphor and the blue line corresponds for Penning ionization electron spectrum (background subtracted droplet correlated signal). The He expansion conditions are stagnation pressure P_0 = 40 bar and nozzle temperature T_0 = 14K.

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Beyond Born-Type Methods: The Power of Potential

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Similarly, to light holography, ultrafast photoelectron holography makes use of a probe and a reference wave to reconstruct a target using phase differences. This makes use of the fact that different pathways for an electron in a strong laser field may be associated with specific interference patterns. Typically, the reference is a direct pathway, and the probe is associated to a laser-induced rescattering process. If traditional orbit-based approaches are employed, such as the strong-field approximation, for linearly polarised fields rescattering will occur near and on the polarisation axis. This will make it detrimental for probing targets whose geometry is oriented perpendicular to the field. In the present contribution, we employ a novel approach which goes beyond that and considers the residual binding potential and the external laser field on equal footing: The Coulomb Quantum Orbit Strong-Field Approximation (CQSFA) [1,2].

By studying a variety of atomic species prepared in excited states of different geometries, we show that, due to the presence of the Coulomb potential, rescattering will no longer be confined to this axis, which makes it possible to probe orbitals whose polarisation is perpendicular to that of the field. We also identify the main types of orbits responsible for a non-vanishing photoelectron signal within the CQSFA and initial momentum distributions of the instances of tunnelling and re-scattering. We further probe the interplay between the driving field and the binding potential by modifying parameters such as the field intensity and the binding energy. By comparing with ab initio models (such a Qprop and ADC BSplines [3,4]), we can assess core dynamics through the description of resonances from multi-electron effects, as well as provide a description of hybrid orbits through single electron effects from CQSFA [5].

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Control of Parent-Ion Coherence in Helium Ion Ensemble

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Attosecond pulses can ionize atoms in a coherent process. Since the emerging fragments are entangled, however, each preserves only a fraction of the initial coherence [1], thus limiting the chance of guiding the ion subsequent evolution. In this work, we use *ab initio* simulations of pump-probe ionization of helium above the *2s/2p* threshold to demonstrate how this loss of coherence can be controlled [2]. A broadband XUV pump pulse in association with an IR probe pulse with controllable delay activate several multi-photon paths to the shake-up ionization of the helium atom, some of which proceed through intermediate $2lnl'$ autoionizing states [3]. The Interference between direct and multi-photon ionization paths gives rise to a partial coherence between the *2s* and *2p* states of the ion, controllable via the pump-probe delay τ. The coherence between the ionic *2s* and *2p* states, which are degenerate in the non-relativistic limit, results in a stationary, delay-dependent electric dipole. From the picosecond real-time beating of the dipole, caused by the fine-structure splitting of the $N=2$ manifold, it is possible to reconstruct all the original coherences between the ionic states. The coherence between antiparallel-spin states, in particular, is a sensitive probe of relativistic effects in attosecond photoemission.

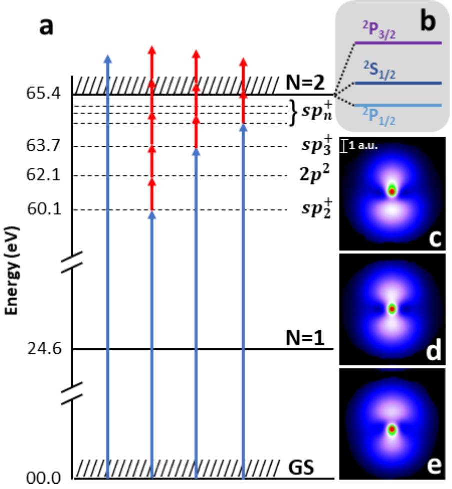

Figure 1: a) Multi-photon paths interact to give rise to *2s-2p* coherence. **c-e)** Ion electron density at τ=0, 1, and 2 fs exhibits asymmetry due to ionization in the presence of polarized IR field. **b)** Due to the FS splitting of the $N=2$ He^+ level, the ionic dipole fluctuates, thus mapping the attosecond dependence of initial ionic coherence.

We simulate this process by solving the time-dependent Schrödinger equation for the atomic system in the presence of the external pulses [3,4]. The density matrix of the system is computed at the end of the pulse from the partial photoionization amplitudes [3], as a parametric function of the pump-probe delay. The relativistic terms in the ionic Hamiltonian are considered for the subsequent evolution of the isolated ion. The slow fine-structure evolution, therefore, maps the attosecond modulation of the ionic density to a temporal domain three orders of magnitude larger.

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Formation of neutral high-Rydberg fragments following the ultrafast recapture processes to Rydberg states in the inner-shell fragmentation of molecules

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The states with the electrons excited to the high principal quantum number orbitals (high-Rydberg (HR) orbitals) having the energies below the ionization potential can be classified as long-living metastable states characterized by very long lifetimes. The HR molecules may be more reactive and behave considerably different than molecules excited to the normal states. Before they dissociate into the atomic and molecular excited fragments, molecular isomerization and/or H atoms migration may occur, leading to unexpected fragmentation pathways. For example, the formation of the excited NH($A^3\Pi$) fragments was observed in the collisions of pyridine molecules with the low energy cations applying the collision-induced luminescence spectroscopy [1]. Since the pyridine molecules consist of five CH units and one N heteroatom and have not got any NH structural components at all, the occurrence of the luminescence from the excited NH($A^3\Pi$) free radicals is the straightforward indicator of a chemical bond rearrangement process associated with the migration of one of the hydrogen atoms prior to the cation-induced dissociation. Such unusual free radicals were also observed in the studies on the photodissociation into higher-lying superexcited states of pyridine [2] and isoxazole [3].

In the present work, we investigate the production of neutral high-Rydberg fragments at the K edges of the molecules containing oxygen and nitrogen atoms, exploiting a combined soft x-ray excitation with pulsed-field ionization and ion time-of-flight (TOF) spectrometry. The experiments were performed at the Gas Phase beamline of the Elettra synchrotron radiation laboratory (Trieste, Italy) utilizing a TOF mass spectrometer modified for pulsed-field ionization measurements [4]. These measurements revealed the ultrafast photoelectron recapture process [4-6], where the photoelectron is pushed back to the HR orbital of the molecular ion. This reaction occurs via the population of $\text{val}^{-2}\text{HR}^1$ states, whose dissociation can then yield neutral fragments in HR states.

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Frustrated tunneling dynamics in ultrashort laser pulses

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In addition to the process of tunneling ionization, one also finds a nonzero Rydberg state population, when an atom is subjected to an intense, low frequency laser pulse. This process is known as frustrated tunneling ionization, and has been explained with a classical model where the electron tunnels close to the peaks of the electric field, and is later captured by the atomic potential [1]. We have studied frustrated tunneling in Hydrogen with ultrashort pulses using a theory based on the strong field approximation (SFA) [2], and compared it to results obtained by solving the time-dependent Schrödinger equation (TDSE) [3]. We used pulses of 800 nm wavelength, 2-4 cycle pulse duration and intensities on the order of 10^{14} W/cm^2.

The SFA model that was used relies on a saddle point approximation that is supplemented with additional constraints to ensure that the trajectory associated to a solution of the saddle point equation will have an energy and angular momentum that corresponds to a particular Rydberg state. Since we are dealing with short laser pulses, the carrier-envelope phase (CEP) becomes important. The solutions to the modified SFA equations show an intricate dependence on CEP and angular momentum l. As the CEP is varied in our TDSE simulations, we see a modulation in the total population of states with different principal quantum numbers n, see Fig. 1, that the SFA theory can qualitatively reproduce for n greater than 4. However for n=2, 3 we do not see agreement between the TDSE and SFA results. Additionally, when we resolve the CEP variations in l, we do not find agreement between TDSE and SFA for any n.

In conclusion, we have showed that population transfer to Rydberg states in ultrashort, intense pulses can be interpreted by frustrated tunneling. To support this conclusion, we have also performed TDSE simulations where the continuum states are damped during propagation and find that continuum dynamics are important for the Rydberg state population.

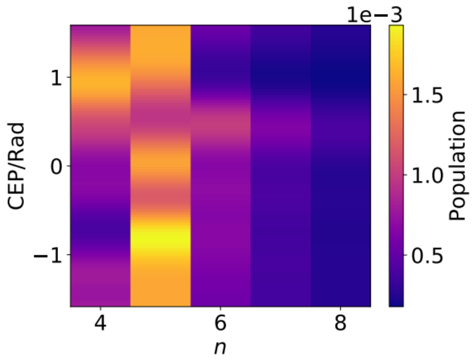

Figure 1: CEP dependence of the Rydberg population with principal quantum number n, calculated with the TDSE.

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Photoelectron circular dichroism as a probe for ground state dynamics

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Lochfrass is a mechanism by which one can create a vibrational wavepacket in the electronic ground state of a molecule [1]. It requires an intense pump pulse, typically in the strong-field or multiphoton regime, but it provides a pathway by which one can initiate ground state dynamics. By combining this with high-energy, circularly polarised pulses, generated from a high-harmonic source, we demonstrate how coherent vibrational dynamics can be followed in time in the ground electronic state of methyl *p*-tolyl sulfoxide (MTSO).

Using a circularly polarised femtosecond probe, and a velocity map imaging spectrometer, we extract information that shows the dynamic evolution of molecular chirality in the electronic ground state of MTSO. This signature of chirality we observe is photoelectron circular dichroism (PECD), and encoded in the intensity difference of the photoelectron emission seen in the forwards and backwards hemispheres of the Newton sphere, with respect to the direction of laser propagation [2]. This intensity difference arises from the outgoing photoelectron scattering off the effective chiral potential of the molecule. Because of this nature, PECD is quite sensitive to molecular structure, and can be used as a dynamic probe.

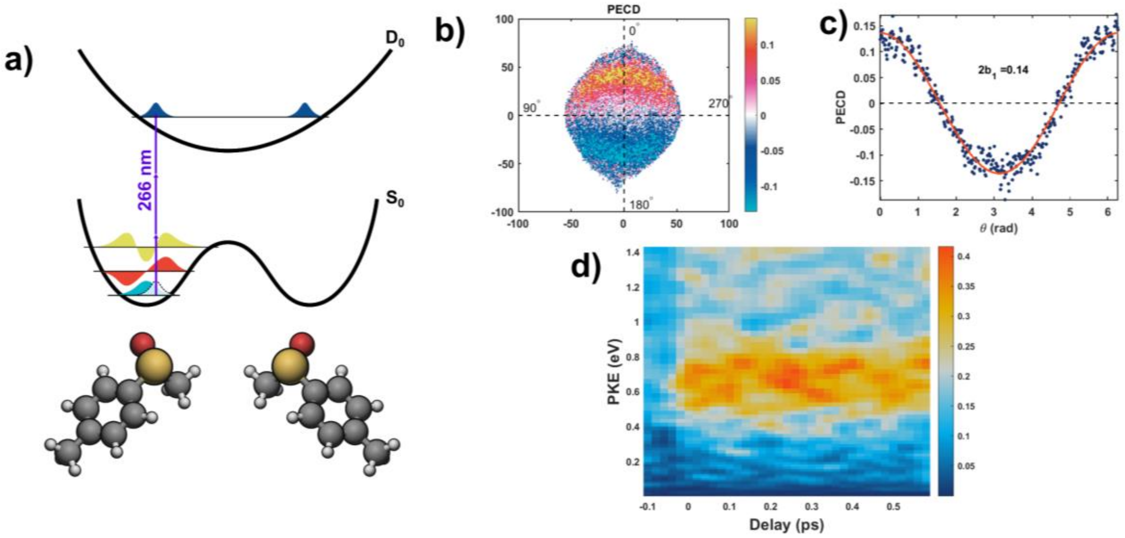

Figure 1: Panel a) shows a scheme for Lochfrass excitation, where a portion of an electronic ground state vibrational wavefunction is depleted through ionisation. The chemical structure of MTSO is shown above. Panel b) shows the static PECD of MTSO by ionisation of a 133 nm photon. Panel c) is the fit of the forward/backward asymmetry, in order to obtain the chiral asymmetry parameter b_1. The timeresolved photoelectron spectrum is shown in panel (d).

In this contribution, we show both the remarkably strong PECD from MTSO (Fig. 1), and demonstrate a general scheme for preparing and following molecular dynamics in their electronic ground state. The implementation in this work reveals a vibrational coherence within a subset of vibrational modes of the molecule, which changes the PECD in time.

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Non-adiabatic dynamics of solvated cyclopropanone and cyclopropanone hydrate with efficient ΔSCF

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The photodissociation of cyclopropanone was modelled using non-adiabatic molecular dynamics in combination with the Kohn-Sham ΔSCF (delta self-consistent field) electronic structure method. [1-3] Previous studies using multi-reference methods found two photodecomposition pathways with symmetric and asymmetric geometries at the conical intersection. [4–6] These results were successfully reproduced with the faster ΔSCF technique. Moreover, a reduced photodissociation and significantly increased lifetime were observed in aqueous solution using a periodic simulation box with 25 solvent molecules in order to model the liquid state in a sophisticated way. In water, cyclopropanone is in equilibrium with the 1,1-dihydroxycyclopropane adduct. The non-adiabatic dynamics of cyclopropanone hydrate, an enzyme inhibitor [7], excited to the first singlet state revealed a different decay mechanism and no ethylene formation. In addition, a new approach to calculate the absorption spectrum [8] with ΔSCF was shown to well reproduce the experimental spectrum for cyclopropanone.

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High-order harmonic generation in Zinc Telluride

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High-order harmonic generation (HHG) from solids is an emerging technique that is becoming increasingly popular, both for the possibility to use it as a novel kind of compact coherent XUV source [1], and for probing the ultrafast dynamic of electrons in solids [2] as well as structural features of systems in the condensed matter phase.
Several theoretical models have been developed for describing HHG in solids [3][4], highlighting the uniqueness of this process. The simplest model is known as the three-step model. A strong laser field promotes an electron in the conduction band, leaving a hole in the valence band. Subsequently, the laser field accelerates the electron and hole in their respective bands and finally, they recombine emitting the high harmonic field. Even with a so simple model, it is clear that the harmonics emission strongly depends on the laser field polarization direction, which selects a region of the band structure crossed by electrons and holes.
In this work, we study the angular dependence of the HHG emission as a function of the laser field polarization direction. The source is an optical parametric amplifier, able to produce few cycles, linearly polarized Mid-IR pulses at 3.2µm wavelength. The sample under investigation is a 500µm-thick Zinc Telluride (ZnTe) crystal cut along the <110> plane.

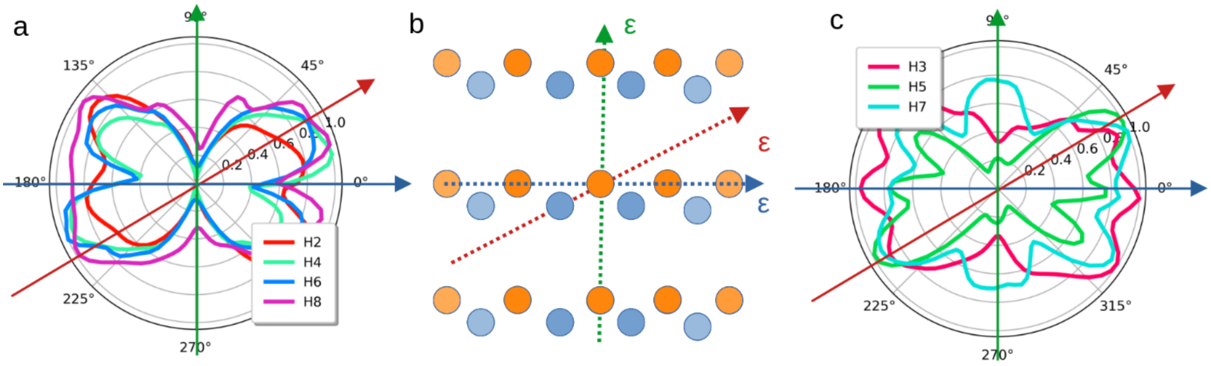

Figure 1: Angular dependence of the emitted even (a) and odd (c) harmonics. (b) 2D cut of ZnTe along the <110>plane.

The angular dependence of the harmonics emission is reported in figure 1. We can see that a four-leaf pattern appears for the even harmonics, while for the odd ones, additional lobes appear along the bisectors. The harmonics emission is enhanced when the laser field polarization is aligned to a direction connecting two nearest neighbors. The presence of the additional peak for the odd harmonics can be explained by the presence of inversion symmetry when the laser field is polarized parallel to the direction connecting atoms of the same species, allowing odd harmonics generation, while the even harmonics are suppressed. This suggests that the harmonics emission is strongly dependent on the orientation of the sample under investigation and the capability to probe different band structure regions through angular scans.

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Tracing the vibrational motion of diatomics via the spectrum of emitted photofragments

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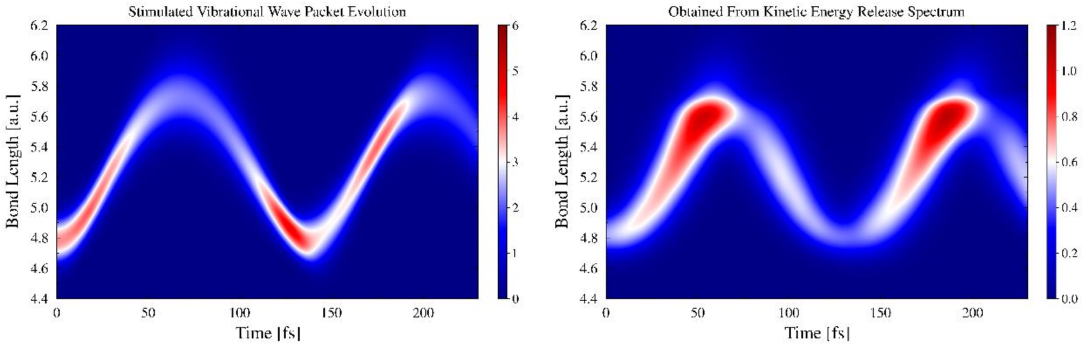
We present a method for tracing the nuclear vibrational motion of diatomic molecules in the kinetic energy release (KER) spectra of the dissociating photofragments.

To exemplify our procedure, we consider the widely studied sodium iodine (NaI) molecule, which features an ionic-covalent avoided crossing between its ground and first excited electronic states [1]. Applying an IR control pulse, a nuclear wave packet of NaI is created in the ground electronic state as a coherent superposition of the vibrational eigen states. This nuclear motion is then probed by a series of few-femtosecond UV pump pulses that promote the system to the excited electronic state where it dissociates through the nonadiabatic avoided crossing on an ultrafast time scale [2].

The central frequency of the probe pulses are chosen such that the electronic states are coupled resonantly in the whole region of the nuclear motion, so a direct mapping of the nuclear wave packet into the continuum is achieved (see Fig.1). The presented procedure works the best for short multi-cycle probe pulses. Upon increasing the probe pulse duration, nuclear wave packet interference effects start to dominate the KER spectra which prevent the procedure to be applied for tracing purposes. The appearance of these interferences is also discussed [3]. The time-propagation of the nuclear wave packets has been carried out with the multi-configuration time-dependent Hartree (MCTDH) method.



Stimulated Vibrational Wave Packet Evolution

Obtained From Kinetic Energy Release Spectrum

Figure 1: Simulated nuclear vibrational wave packet evolution of NaI (left panel), compared with that reconstructed from the KER spectra (right panel). Besides the amplitude, the phase of the wave packet is also well described by the applied tracing procedure. The probe pulse duration is 18 fs and the intensity is 3x10^11 W/cm^2.

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Imaging electron currents in molecules and crystals

with ultrafast resonant x-ray scattering

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The ability to image electronic motion on its natural time and length scale will provide new insights into chemical and phase transfromations in atomic, molecular and condense matter systems. This task can be achieved by (sub-)femtosecond x-ray pulses employing different techniques.

In my research group, we theoretically predict, how attosecond x-ray pulses can be applied for characterization of electronic motion on atomic length scale. In my poster, I will present several proposals for attosecond x-ray experiments based on three different techniques, time-resolved resonant [1,2] and nonresonant x-ray scattering [3,4], and time- and angle-resolved photoelectron spectroscopy [5].

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