14 – 17 September 2021

AttoChem

Attosecond Chemistry

Young Scientist Symposium 2021

Book of Abstracts

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Attosecond Chemistry

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This book of abstracts collects the contributions to the AttoChem Young Scientist Symposium 2021.

The AttoChem network will coordinate 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 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 will also act as a liaison with the relevant stakeholders to bridge the gap to industrial applications.

The AttoChem Young Scientist Symposium 2021 is organized by the AttoChem Network for fostering experimental and theoretical efforts to exploit the enormous potential of attosecond techniques in chemistry. The focus is on the recent works of emerging early career scientists related to ultrafast chemistry. This is accompanied by plenary talks and panel discussions on the state- of-the-art developments and challenges of this area and the intersection of experiment and theory by leading scientists.

The Young Scientist Symposium is organized by PhD Students and ECI within the Attochem Cost Action

- Gabriele Crippa (Politecnico di Milano, Italy)
- Hristina S. Delibašić (University of Kragujevac, Serbia)
- Torsha Moitra (Technical University of Denmark, Denmark)
- Juan José Omiste Romero (Universidad Complutense de Madrid, Spain)
- Tomislav Piteša (Ruđer Bošković Institute, Croatia)
- Vincent Wanie (CFEL, Germany)

Tuesday 14th September

9:15 – 9:30 (CET) Inauguration

Mr. Gabriele Crippa (Politecnico di Milano, IFN-CNR).

Prof. Fernando Martin (Universidad Autónoma de Madrid).

9:30 – 12:30 (CET) Ultrafast dynamics and spectroscopy of atomic and molecular systems

Prof. Henrik Stapelfeldt (Aarhus University), *Control the spatial orientation of molecules – isolated or in helium nanodroplets –by strong laser pulses.*

Dr. Sonia Marggi (Universidad Complutense de Madrid), *Probing molecular dynamics using ultrafast XUV transient spectroscopy.*

Ms. Alexie Boyer (Institut Lumière Matière), *Ultrafast dynamics induced by XUV photoionization in molecules: from electronic to vibrational relaxation.*

Mr. Lorenzo Colaizzi (DESY Hamburg), *Ultrafast molecular dynamics induced by few-femtosecond ultraviolet excitation.*

Ms. Anna Li Wang (Stanford PULSE Institute), *The role of nuclear-electronic coupling in attosecond photoionization of* H_2.

Dr. Laura Cattaneo (Max Planck for Nuclear Physics Heidelberg), *Time Resolved THz Dynamics in Thermotropic Liquid Crystals.*

14:00 – 17:00 (CET) Correlated treatment of many body dynamics

Prof. Alexander Kuleff (Universität Heidelberg), *Ultrafast charge migration in molecules initiated by ionization and excitation.*

Mr. Thierry Tran (University College London), *Simulation of coherent control of electron-nuclear dynamics with Quantum-Ehrenfest.*

Mr. Marvin Reuner (University of Hamburg), *Attosecond imaging of coupled electron-hole dynamics in fundamental compounds of organic semiconductors.*

Mr. Jasper Peschel (Lund University), *Complete characterization of multi-channel single photon ionization.*

Dr. Bruno Tenorio (Technical University of Denmark), *Multi-reference Approach to the Computation of Double-Core-Hole Spectra.*

Prof. Françoise Remacle (University of Liège), *Exploiting electronic coherences for steering selective bond formation in molecules pumped by ultrashort optical pulses.*

17:00 – 18:00 (CET) Poster session

Dr. Valeriu Scutelnic (UC Berkeley), *X-ray transient absorption reveals the 1Au (nπ*) state of pyrazine in electronic relaxation.*

Mr. Gaurav Pandey (Indian Institute of Science Education and Research), *Classical Description of Molecular Attoclock to Simulate Coupled Electron-Nuclear Dynamics of* H_2 *Molecule.*

Ms. Gaia Giovannetti (DESY Hamburg), *A table-top Soft X-ray beamline for transient absorption experiments in liquid phase.*

Mr. Thomas Rook (University College London), *Influencing Holographic Interference Patterns: Dancing Spiders and Waving Fans.*

Mr. Edvin Olofsson (Lund University), *Frustrated tunneling dynamics in ultrashort laser pulses.*

Mr. Yoshiaki Tamura (University of Toyama), *Attosecond delays in C(1s) core level photoemission of CO molecules in the framework of the multiple scattering model.*

Wednesday 15th September

9:30 – 12:30 (CET) Theoretical methods for ultrafast dynamics

Prof. Klaus B. Møller (Technical University of Denmark), *Ultrafast dynamics probed by X-ray scattering.*

Dr. Stefanos Carlström (Lund University), *Freeman resonances as the source for dynamic symmetry-breaking.*

Mr. Nicola Mayer (Max-Born-Institut), *Imprinting chirality on atoms using synthetic chiral light.*

Mr. Dino Habibovic (University of Sarajevo), *Strong-field processes driven by tailored laser fields.*

Mr. Jean-Nicolas Vigneau (Université Laval), *Strong-Field Molecular Ionization beyond the Single Active Electron approximation.*

Prof. Edit Mátyus (Eötvös Loránd University), *Relativistic and non-adiabatic developments for molecular quantum theory.*

14:00 – 16:20 (CET) Ultrafast sources, technologies and experimental techniques

Prof. François Légaré (NRS-Énergie et Matériaux), *High-energy multidimensional solitary states in hollow-core fibers.*

Dr. Vyacheslav Leshchenko (Ohio State University), *Phase-resolved transient absorption XUV spectroscopy of Ar.*

Mr. Debobrata Rajak (CELIA-Universite de Bordeaux-CNRS-CEA), *Asymmetric electron re-scattering in strong-field ionization of chiral molecules.*

Dr. David Ayuso (Imperial College London), *Ultrafast optical rotation in chiral molecules with ultrashort and tightly focused laser pulses.*

Mr. Zhaoheng Guo (SLAC National Accelerator Laboratory), *Development of Two-Color Sub-Femtosecond Pump/Probe Techniques with X-ray Free-Electron Lasers.*

16:20 – 18:00 (CET) Poster session

Dr. Marta Murillo (Universidad Complutense de Madrid), *Femtosecond XUV-IR induced photodynamics in the methyl iodide cation.*

Dr. Jakub Benda (Charles University Prague), *Molecular RABITT calculations using the time-independent multi-photon R-matrix method.*

Ms. Barbora Stachová (Comenius University Bratislava), *Electron induced fluorescence of oxygen.*

Dr. Cornelia Hofmann (University College London), *Electron Dynamics for High-order Harmonic Generation Control.*

Dr. Andrés Ordóñez (ICFO - The Institute of Photonic Sciences), *Enantio-sensitive unidirectional light bending.*

Ms. Chau Truong (Department of Physics, University of Central Florida), *Towards a low-cost short-wave infrared light field synthesizer based on rotational nonlinearity*

Thursday 16th September

9:30 – 12:30 (CET) Photoionization induced dynamics

Prof. Piero Decleva (Università degli Studi di Trieste, IOM-CNR), *Advances in the simulation of molecular ionization processes.*

Dr. Soumyajit Saha (Stockholm University), *Angular anisotropy parameters for photoionization delays.*

Dr. Felipe Zapata (Lund University), *Implementation of the relativistic time-dependent configuration interaction singles method: the case of atomic photoionization cross sections.*

Mr. Francisco Fernández (IMDEA Nanociencia), *Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules.*

Mr. Moritz Heindl (University of Vienna), *Field-induced surface hopping: validation and control.*

Dr. Solène Oberli (Ecole Polytechnique Federale de Lausanne), *Real time and local observation of ultrafast electronic and nuclear rearrangements using time-resolved X-ray spectroscopy.*

14:00 – 17:00 (CET) Ultrafast dynamics and spectroscopy of clusters and condensed matter

Prof. Matteo Lucchini (Politecnico di Milano), *Solid state spectroscopy with attosecond all-optical techniques.*

Mr. Dušan Mészáros (Comenius University Bratislava), *Low energy electron attachment to* $Co(CO)_3NO$ *clusters.*

Dr. Tadas Balciunas (ETH Zürich), *Tracing dissociation dynamics and ultrafast cooling in liquid pyridine using Time-resolved X-ray absorption spectroscopy.*

Prof. Darya Gorelova (Universität Hamburg), *Imaging kelectron currents in molecules and crystals with ultrafast resonant x-ray scattering.*

Dr. Giulio Vampa (National Research Council and University of Ottawa), *Revealing coherences during high-harmonic generation in 2-dimensional crystals.*

Dr. Mina Bionta (Massachusetts Institute of Technology), *Lightwave electronics: sampling optical fields with attosecond resolution.*

17:00 – 18:00 (CET) Poster session

Dr. Benham Nikoobakht (University of Heidelberg), *UV Absorption Spectrum and Photodissociation Dynamics of CH_2OO following Excitation to the B_1A_0 state.*

Mr. Max Waters (ETH Zurich), *Photoelectron circular dichroism as a probe for ground state dynamics.*

Ms. Anna Kristina Schnack-Petersen (Technical University of Denmark), *The structural dynamics of azobenzene.*

Mr. Gyeonghun Kim (University College London), *Coulomb distorted twisted interference patterns from elliptically polarised strong field ionisation.*

Dr. Taran Driver (Stanford PULSE Institute), *Attosecond Coherent Electron Motion in Molecules Measured with Ultrashort X-ray Pulse Pairs.*

Dr. Shota Tsuru (Ruhr-Universität Bochum), *An assessment of different electronic structure approaches for modelling time-resolved X-ray absorption spectroscopy.*

Friday 17th September

9:30 – 10:50 (CET) Poster session

Dr. Gilbert Grell (IMDEA Nanociencia), *Charge migration in aminophenol following sub-fs X-Ray pulses: Influence of nuclear effects and the XFEL shot-to-shot variation.*

Mr. Jorge Delgado (IMDEA Nanociencia), *Attosecond Spectroscopy of Small Organic Molecules: XUV pump-XUV probe Scheme in Glycine.*

Mr. Ján Blaško (Comenius University Bratislava), *Study of disociative processes by electric impact on pyridine.*

Dr. Junyang Ma (East China Normal University), *Transient valence charge localization in strong-field dissociative ionization of HCl molecules.*

Ms. Josina Hahne (CFEL Hamburg), *Design of a compact multichamber gas cell for few fs UV pulse generation.*

Mr. Rudranarayan Khatua (Indian Institute of Technology), *Air-stable and High Mobility based Electron Transport Semiconducting Material Hexachloro-hexa-azatrinaphthylene*.

Mr. Adrián Súñer (Universidad Autónoma de Madrid), *Molecular photoionization time delays.*

Mr. Mattias Bertolino (Lund University), *Multiphoton interaction phase shifts in attosecond science.*

Mr. Martin Blavier (Theoretical Physical Chemistry, University of Liège), *Electronic coherences steer the strong isotope effect in the ultrafast Jahn-Teller structural rearrangement of methane cation upon tunnel ionization.*

10:50 – 12:30 (CET) Roundtable discussion and conclusions

Dr. Vincent Wanie (DESY Hamburg)

Prof. Matteo Lucchini (Politecnico di Milano)

Prof. Piero Decleva (Università degli Studi di Trieste, IOM-CNR)

Prof. Alicia Palacios (Universidad Autónoma de Madrid)

14 September 2021

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Day 1

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Control the spatial orientation of molecules – isolated or in helium nanodroplets –by strong laser pulses

Henrik Stapelfeldt

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I will discuss how moderately intense laser pulses can be used to sharply align and orient gas phase molecules – both in the adiabatic limit where a laser pulse slowly brings molecules to strong alignment at its peak and in the impulsive limit where femtosecond pulses set molecules into coherent rotation by launching rotational wave packets. Time-resolved twisting of a chiral molecule and attosecond charge migration are used to illustrate applications of aligned molecules. Finally, I will discuss recent work where molecules or molecular oligomers are embedded inside or on the surface of nanometer-sized, 0.37 K droplets of superfluid liquid helium.

Time Resolved THz Dynamics in Thermotropic Liquid Crystals

Laura Cattaneo

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Liquid crystals (LCs) exhibit a meta-phase behavior, combining solid-like order and fluid-like flow. So far, dynamics in LCs occurring on the picosecond timescale remain largely unexplored. They show, in fact, resonant features in the THz spectral region, specifically above 3 THz, but a clear understanding of these signatures has yet to be developed. Here, we use nearly-single cycle THz pulses, generated via optical rectification, to perform both time-domain spectroscopy (TDS) and resonant, time-resolved birefringence measurements on 5CB and 8CB thermotropic LC, presenting nematic and smectic A phase, respectively.

Ultrafast charge migration in molecules initiated by ionization and excitation

Alexander I. Kuleff

Theoretische Chemie, PCI, Universität Heidelberg
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Exposing molecules to ultrashort pulses results typically in a coherent population of several and even many electronic states. This triggers ultrafast electron dynamics, which may lead to a redistribution of the charge even before the nuclei start to move and adjust – a process referred to as charge migration. The non-adiabatic coupling between the electronic and nuclear motion will eventually destroy the initial electronic coherence and trap the migrating charge. The time during which the electron coherence is maintained is an important parameter, as it can be used to modulate the charge migration process and thus predetermine the succeeding nuclear rearrangement in the molecule – the paradigm of the emerging field of attochemistry. In this talk, fully quantum simulations of ultrafast charge dynamics initiated by both ionization and excitation of polyatomic molecules will be presented and discussed.

Exploiting electronic coherences for steering selective bond formation in molecules pumped by ultrashort optical pulses

Françoise Remacle

Theoretical Physical Chemistry, Research Unit MOLSYS, University of Liège, Belgium

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Few-cycle short optical pulses allow pumping coherently several coupled electronic states towards steering nuclear motions in neutral molecules and cations. I will discuss two recent examples for which we demonstrate such a control by fully quantum dynamical computations: the selective bond formation in a 4C ring closure occurring upon excitation of norbornadiene by a few cycle, 2 fs, deep UV pulse and the strong isotope effect occurring in the ultrafast structural Jahn-Teller rearrangement in the methane cation suddenly ionized.

Probing molecular dynamics using ultrafast XUV transient spectroscopy

Sonia Marggi Poullain,[1,2] Kristina Chang,[2] Yuki Kobayashi[2,†], and Stephen R. Leone[2,3,4]

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[2]*Department of Chemistry, University of California, Berkeley, CA 94720, USA*
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[4]*Department of Physics, University of California, Berkeley, CA 94720, USA*

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Attosecond probing of core-to-valence electronic transitions is a powerful tool for real-time observation of chemical dynamics [1]. Here, ultrafast extreme ultraviolet (XUV) transient absorption spectroscopy is employed to investigate the electronic and nuclear dynamics on small polyatomic iodinated molecules. The dynamics is induced by one- or two-photon absorption using either few-femtosecond visible pulses, ranging between 500 nm and 900 nm, or 20-fs UV pulses around 260-280 nm, and is then probed by XUV attosecond isolated pulses through iodine-4d core-to-valence transitions. The motion of the wavepacket on the excited states is directly mapped, due to the strong shift of the XUV core-to-valence transitions with internuclear separation and the high sensitivity of the wave packet to the electronic configuration, allowing the method to access the full time-resolved photodynamics.

The results presented will first concern the visualization with great detail of coherent nuclear motion in the *B* excited state of molecular iodine (I_2). The wave packet spreading and later recompression, at the outer turning point and inner turning point, respectively, is clearly observed. In addition, through the imaging of this vibrational motion, direct information on the core-excited potential energy curves can be obtained. Second, the photodissociation dynamics of alkyl iodides, following one-photon absorption into the *A* band, is imaged in time from photoexcitation to photoproducts [2, 3] and in particular the wave packet bifurcation at the conical intersection is mapped in real-time.

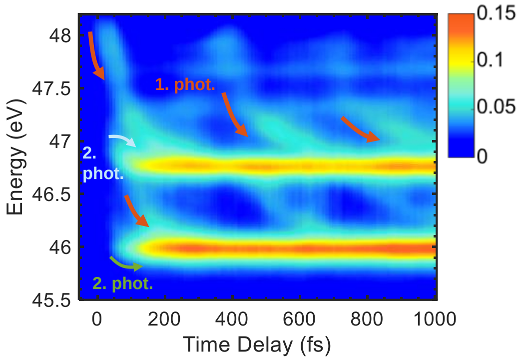

Figure 1: Transient absorption map measured for I_2 excitation by the visible pump pulse, as a function of the time delay and the XUV photon energy.

[1] Y. Kobayashi, K. F. Chang, T. Zeng, D. M. Neumark, S. R. Leone, *Science* **365** (2019) 79.

[2] K. F. Chang, M. Reduzzi, H. Wang, S. M. Poullain, Y. Kobayashi, L Barreau, D. Prendergast, D. M. Neumark, S. R. Leone, *Nature Comm.* **11** (2020) 4042

[3] K. F. Chang, H. Wang, S. M. Poullain, D. Prendergast, D. M. Neumark, S. R. Leone, *J. Chem. Phys.* **154** (2021) 234301.

Ultrafast dynamics induced by XUV photoionization in molecules: from electronic to vibrational relaxation

A. Boyer[1], M. Hervé[1], V. Despré[2], P. Castellanos Nash[3], V. Loriot[1], A. Marciniak[1],
A. Scognamiglio[1], G. Karras[1], R. Brédy[1], E. Constant[1], A. G. G. M. Tielens[3],
A. I. Kuleff[2] and F Lépine[1]

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Unraveling ultrafast dynamics induced by energetic radiation in molecules is essential to understand their chemical evolution under extreme conditions. Until now, these dynamics remained barely explored due to the lack of experimental tools. In this context, the development of attosecond technology has brought new perspectives to study in real time electron and nuclear dynamics induced by energetic radiations. Several experiments have investigated ultrafast XUV induced processes in atoms and small molecules. It is only recently that these studies were extended to larger systems [1, 2].

Here, we study the relaxation of highly excited Polycyclic Aromatic Hydrocarbons (PAHs) using XUV-IR time-resolved experiments. In the experiment, the neutral molecules are ionized by XUV pulses of few tens of eV. The resulting cations are left in a large number of electronic states and features named correlation bands (CBs) appear due to electron correlation. By measuring the two color dication signal (Fig. 1.a), we show that we can access the electronic relaxation of the CBs [3]. We also show that the time-dependent signal of the fragment yield (Fig. 1.b) gives access to the subsequent vibrational energy redistribution [4]. Our results show a non-linear increase of the electronic relaxation timescales of the CBs with the size of the PAH (blue curve in Fig. 1.c). This trend is explained by a model that we developed based on an analogy with solid-state physics. In our model, the electronic relaxation is associated to electron-phonon scattering. The timescale of the vibrational dynamics shows an opposite trend and decreases with the size of the PAH (green curve in Fig. 1.c), providing an onset for coherent wavepacket manipulation. Similar results have been obtained in diamondoids.

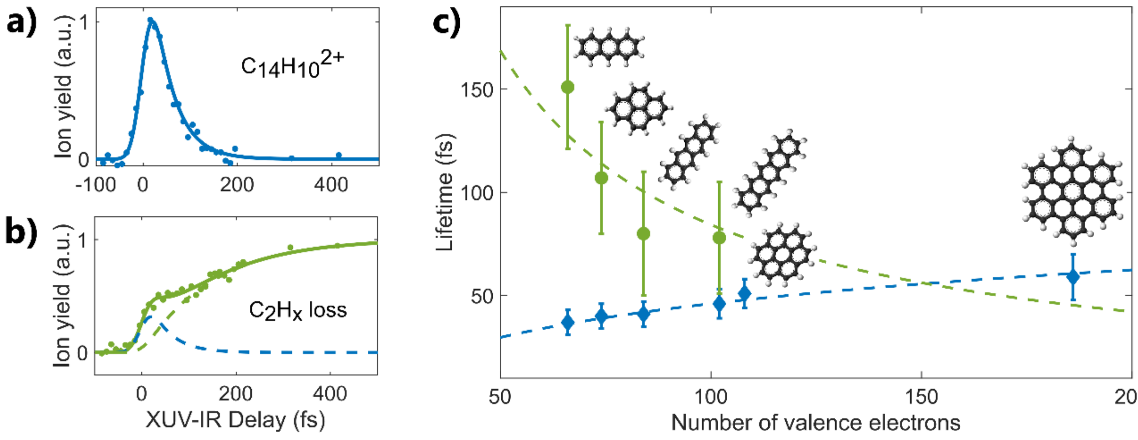

Figure 1: a) Two color time-dependent signal of the doubly charged anthracene. b) Two color time-dependent signal of the loss of C_2H_x in anthracene. c) Timescales of the electronic relaxation of the CBs (blue diamonds) and the vibrational dynamics (green dots) as a function of the size of the PAHs.

[1] F. Calegari et al., *Science* **346** (2014) 336–339.

[2] A. Marciniak et al., *Nat. Commun.* **10** (2019) 337.

[3] M. Hervé et al., *Nat. Phys.* **17** (2021) 327–331.

[4] A. Boyer et al., *accepted in Phys. Rev. X.*

Ultrafast molecular dynamics induced by few-femtosecond ultraviolet excitation

L.Colaizzi[1,2], K. Saraswathula[2], S. Riabchuk[1,3], E. P. Månsson[2], V. Wanie[2], A. Trabattoni[2] and F. Calegari [1,2,3]

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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].

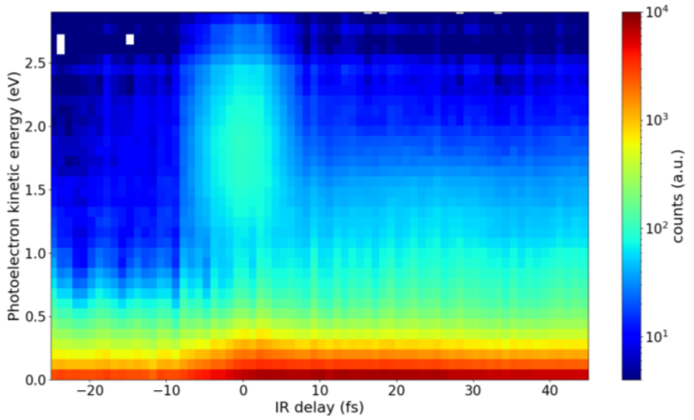

Figure 1: Angularly integrated photoelectron kinetic energy as a function of the IR delay obtained in acetone. Positive delay means NIR pulses come later. 75% of the first delay spectrum has been subtracted as background to enhance visualization.

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.

[1] R.P. Sinha, D.P. Häder, *Photochem. Photobiol. Sci.* **1** (2002) 225–36.

[2] R.W. Schoenlein, L.A. Peteanu, R.A. Mathies, C.V. Shank *Science* **254**.5030 (1991) 412-415.

[3] M. Galli, V. Wanie, D.P. Lopes, et al. *Optics letters* **44.6** (2019): 1308-1311.

[4] E.P. Månsson, V. Wanie, M. Galli, et al. *EPJ Web of Conferences* **205** (2018) 03007

The role of nuclear-electronic coupling in attosecond photoionization of H_2

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The separation of electronic and nuclear dynamics due to differing timescales is a useful concept for understanding ground-state molecular systems. However, coupling between these degrees of freedom is critical to understanding the evolution of most excited state systems. To access nuclear-electronic coupling, we study photoionization of H_2. In this context, light, vibrationally excited nuclei and low energy photoelectrons allow for some matching of timescales and energy coupling. The effect of nuclear motion on photoemission delays has previously been studied in dissociating photoionization of H_2, demonstrating the possibility of energy exchange between nuclei and electrons on attoscond timescales [1]. The effect of bond separation on photoemission delay has been considered for N_2 [2] and H_2 [3], where both studies use vibrational states for their distribution of bond lengths. Our study presents evidence for a related phenomenon: nuclear-electronic channel coupling between continuum vibrational states. We measure two-photon ionization delays of H_2 and compare to calculations of the same measurement in a frozen-nuclei approximation. We find discrepancies between the vibrationally resolved measurement and bond length dependent theory, suggesting that nuclear motion affects H_2 photoionization on attosecond timescales.

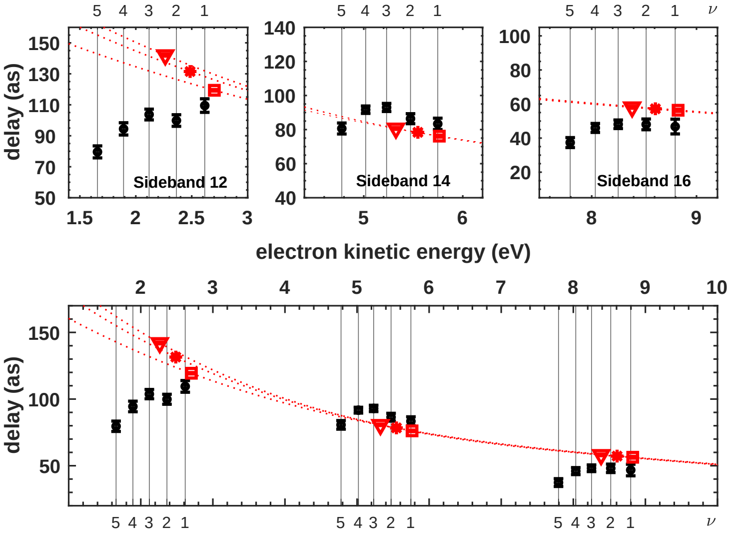

Figure 1: Two-photon ionization delays for H_2. The measured two-photon ionization delay (black circles) is compared to fixed-nuclei TDSE simulation for three different nuclear separations $R = 1.4, 1.45, 1.5$ a.u. (red triangle, red asterix, red square, respectively). Each R simulation is connected by interpolation (red, dashed line). The top panels show a closer view of the bottom panel for each sideband of the RABBITT measurement.

[1] L. Cattaneo, J. Vos, R. Y. Bello, A. Palacios, S. Heuser, L. Pedrelli, M. Lucchini, C. Cirelli, F. Martín, and U. Keller., *Nature Physics* **14** (2018) 733-738.

[2] S. Nandi, E. Plésiat, S. Zhong, A. Palacios, D. Busto, M. Isinger, L. Neoričić, C. L. Arnold, R. J. Squibb, R. Feifel, P. Decleva, A. L'Huillier, F. Martín, and M. Gisselbrecht., *Science Advances* **6** (2020).

[3] T. Nishi, E. Lötstedt, and K. Yamanouchi., *Phys. Rev. A* **102** (2020).

Simulation of coherent control of electron-nuclear dynamics with Quantum-Ehrenfest

T. Tran[1,2], G. A. Worth[1], M. A. Robb[2]

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The field of attosecond spectroscopy allows the monitoring of ultrafast phenomena occurring at the timescale of electronic motion using ultrashort pulses in the extreme ultraviolet energy range. The photoionization will excite the molecule onto multiple cationic states at the same time. Thus, the resulting dynamics involves a coherent superposition of states with heavily coupled electron and nuclear dynamics. Subsequent control of the dynamics can be achieved with a short IR pulse.

To unravel the mechanism behind the coherent superposition of electronic states and the effect of the pulse on the electron and nuclear dynamics, the Quantum-Ehrenfest method[1] was employed to simulate the time evolution of the molecular wavefunction within a full quantum approach for system such as allene,[2] PSB,[3] benzene,[4] and ethylene. The effect of the pulse is included in the simulation by implementing it directly within the electronic structure method.[2]

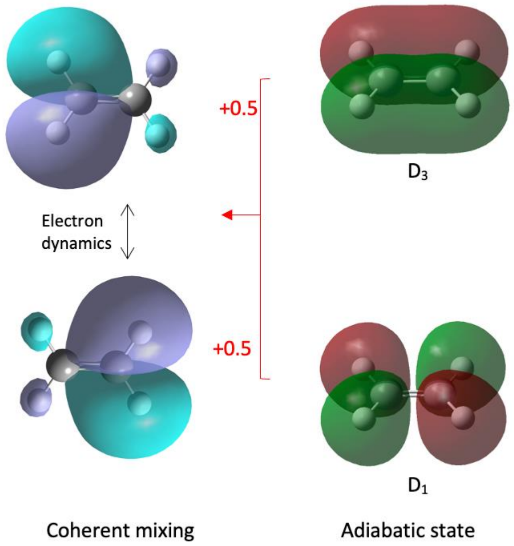

Figure 1: Schematic of link between adiabatic states, the coherent superposition of states and the resulting electron dynamics.

[1] A., Jenkins, E. K., Spinlove, M., Vacher, G. A., Worth and M. A. Robb, *J. Chem. Phys.* **149** (2018) 094108.

[2] T., Tran, A., Jenkins, G. A., Worth and M.A., Robb, *J. Chem. Phys.* **153** (2020) 031102.

[3] M., Olivucci, T., Tran, G. A., Worth and M. A., Robb, *J. Phys. Chem. Lett.* **12** (2021) 5639–5643.

[4] T., Tran, G. A., Worth and M. A., Robb, *Commun. Chem.* **4** (2021) 48.

Attosecond imaging of coupled electron-hole dynamics in fundamental compounds of organic semiconductors

Marvin Reuner[1], Daria Popova-Gorelova[1]

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We theoretically study how to reveal coupled electron-hole dynamics in molecules by means of time- and angle-resolved photoelectron spectroscopy (tr-ARPES). We consider experiments in which a pump pulse creates a coherent superposition of singlet states of molecules that are fundamental compounds of organic semiconductors. An attosecond soft x-ray pulse probes the dynamics by ionizing a molecule. We calculate photoelectron momentum distributions taking into account all transitions that a broadband probe pulse can induce. We demonstrate that simulated excited state properties of the isolated molecule map onto unique features of momentum maps. This approach provides a powerful method of following excited state dynamics on few-femtosecond time scales with atomic resolution.

Complete characterization of multi-channel single photon ionization

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Ionization of atoms and molecules by absorption of a light pulse results in electron wave packets carrying information on the dynamics of the ionization process. These wave packets can be described as a coherent sum of partial waves of given angular momentum, each characterized by an amplitude and a phase. The determination of amplitude and phase of all angular momentum channels is experimentally challenging, as it requires the energy- and angle-resolved analysis of the interference between partial waves.

We completely characterize one-photon ionization from the $2p^6$-ground state of neon, obtaining the amplitude and relative phase of the transition matrix elements towards s- and d-continuum states. The channel-resolved one-photon ionization phases are obtained using the reconstruction of attosecond beating by interference of two-photon transition (RABBIT) technique [1] with angle-resolved photoelectron detection. The determination of the one-photon phases is based on the universality of continuum-continuum transitions, which are used in the RABBIT technique. The channel-resolved one-photon amplitudes are extracted from static measurements with only the XUV field. The obtained values for the channel-resolved amplitudes and phases are in excellent agreement with calculations using angular-channel-resolved many-body perturbation theory [3], as shown in figure 1. The measurement of the phases of the different angular momentum channels, allows us to unravel the interplay between short-range, correlation and centrifugal effects.

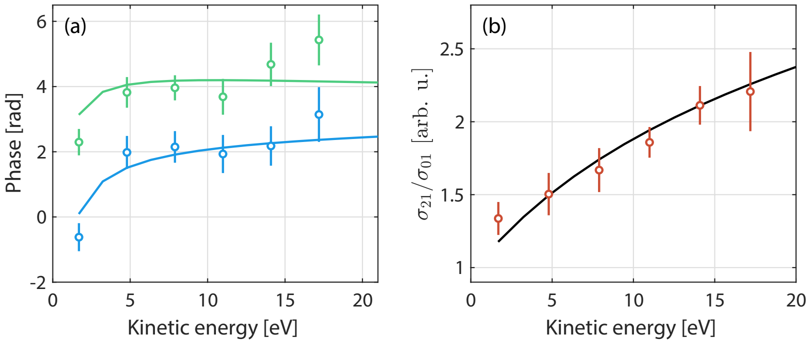

Figure 1: Extracted one-photon amplitudes and phases as a function of the kinetic energy. (a) Scattering phases for s- (green) and d-waves (blue) for experimental (dots) and simulated data (solid lines). (b) Ratio between amplitudes for s- and d- waves (σ_{01} and σ_{21} respectively) extracted from XUV only data (dots). The black line shows the result of angular-channel-resolved many-body perturbation simulation.

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Multi-reference Approach to the Computation of Double-Core-Hole Spectra

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We present a new methodology to compute same-site double core hole (ssDCH) spectra [1-4], that exploits multi-state restricted active space perturbation theory of second order to generate the relevant initial and final states, and a state-interaction approach to obtain the spectral intensities from biorthonormal sets of molecular orbitals. This ensures an unbiased representation of the initial and final states and an appropriate description of the relaxation and correlation effects associated with the shake-up satellites of a ssDCH spectrum. DCH spectroscopy is gaining popularity as experimental technique, thanks to new-generation free-electron laser facilities. This calls for accurate computational methods to interpret the DCH spectral signatures, but the number of such methods is still extremely limited. Our approach is alternative to, and arguably computationally more efficient than, the NOTA+CIPSI approach of Ferté et al. [4], based on non-orthogonal truncated CI expansions.

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X-ray transient absorption reveals the ^1A_u (nπ*) state of pyrazine in electronic relaxation

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X-rays promote electrons from the core levels to vacant valence orbitals, thus endowing them with a unique element specificity. Moreover, the core level transitions can easily sense the shifts in the electron density in the proximity of the probed element. We produce soft X-rays at the carbon K-edge driving high harmonics in a helium gas target with 1470 nm pulses. This table-top broad band X-ray source allows us to investigate the ultrafast dynamics in photoexcited pyrazine ($C_4H_4N_2$) with a new view of the electronic states involved. In addition to the previously characterized $^1B_{2u}$ (ππ*) (S_2) and $^1B_{3u}$ (nπ*) (S_1) states, the participation of the optically dark ^1A_u (nπ*) state is assigned by a combination of experimental X-ray core-to-valence spectroscopy, electronic structure calculations and nonadiabatic dynamics simulations. The ^1A_u (nπ*) state is populated about 200 femtoseconds after electronic excitation and plays a key role in the relaxation of pyrazine to the ground state.

Classical Description of Molecular Attoclock to Simulate Coupled Electron-Nuclear Dynamics of H_2 Molecule

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Molecular dissociation and ionization are the most fundamental processes to understand the electronic and nuclear dynamics in their natural time scale. Shining ultrashort highly intense laser pulses can trigger these processes in the molecules. Because of the high intensity of the laser pulse, the strong coupling between nuclear and electronic motion arises; thereby, the Born-Oppenheimer approximation is no longer valid. The complete quantum treatment of multi-electron coupled dynamics is computationally prohibitive and only be achieved for one electron molecule.

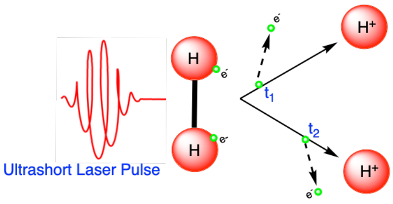

Figure 1: Sequential double ionization of H_2

We present a quasi-classical treatment of such coupled dynamics of H_2 molecule to simulate dissociation and ionization simultaneously with attosecond temporal resolution. We have studied the sequential double ionization of H_2 molecule exposed to 750 nm, 4.5 fs elliptically polarized laser pulse. Through theoretical exploitation of molecular attoclock technique, the evolution of the vibrational wave packet of H_2^+ formed by over-the-barrier ionization of H_2 is tracked between the first and second ionization events with the temporal resolution of 140 attoseconds. The results have been compared with the experiment and found to be in excellent quantitative agreement. Our results show that the quasi-classical model accurately describes and predicts light-induced multi-electron processes in small molecules and can be applied to large molecules.

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Influencing Holographic Interference Patterns: Dancing Spiders and Waving Fans

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We investigate ultrafast photoelectron holography in linearly polarized bichromatic fields, with emphasis on existing symmetries and their dependence on the driving-field parameters, such as the frequency and amplitude ratio between both driving waves and their relative phase. We show that the temporal symmetries satisfied by a bichromatic field can be controlled by varying the phase of the second colour and the frequency ratio. These symmetries are retained in the solutions to the saddle point equations within the Strong-Field Approximation (SFA). Using the Coulomb-quantum orbit strong-field approximation (CQSFA) [1], we perform a detailed analysis of what symmetries are broken or retained in a Coulomb-distorted continum. The prominece, the contrast and the shapes of holographic patterns [2] such as the fan, spider and spiral can be controlled by varying the phase in association with the symmetries of the field. The features encountered can be traced back to the quantum interference of Coulomb-distorted orbits.

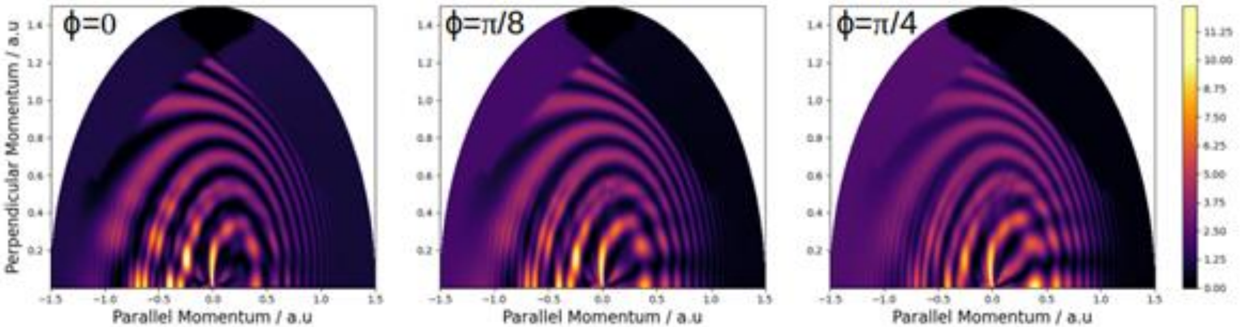

Figure 1: Photoelectron momentum distributions computed for hydrogen in a bichromatic ω – 2ω driving field of fundamental frequency ω=0.057 a.u and intensities 0.02 a.u and 0.02/100 a.u using the CQSFA.

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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, a 2 fs 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 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 $n \geq 4$. 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 either removed entirely from the state space, or damped during propagation, and find that the continuum states must be included in order to get the correct Rydberg state population.

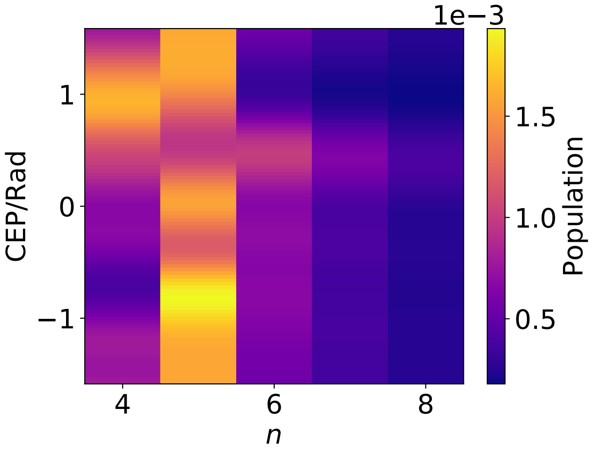

Figure 1: CEP dependence of the Rydberg population with principal quantum number n, calculated with the TDSE.

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Attosecond delays in C(1s) core level photoemission of CO molecules in the framework of the multiple scattering model

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We derived analytical expression of photoemission time delay (TD) for the 1s core photoionization process of heteronuclear diatomic molecules as a function of photoelectron emission angle and momentum in the molecular frame using Muffin-tin and single scattering approximations.

Using Fermi's golden rule and the electric dipole approximation, in the single electron and single-channel model, the photoemission TD, τ, is defined as the energy derivative of the phase of the transition amplitude in atomic units [1]:

$$\tau(\boldsymbol{k},\hat{\boldsymbol{\epsilon}}) \equiv \frac{d}{dE}\arg\{\langle\psi^{-}(\boldsymbol{k})|\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{r}|\phi^{\mathrm{c}}_{L_\mathrm{c}}\rangle\}, \tag{1}$$

where $\hat{\boldsymbol{\epsilon}}$ is the linear polarization vector, $\psi^{-}(\boldsymbol{k})$ is the wave function of a photoelectron with momentum vector $\boldsymbol{k}$ with the incoming boundary condition, and $\phi^{\mathrm{c}}_{L_\mathrm{c}}$ is the wave function of a core-electron with angular momentum quantum number $L_\mathrm{c} = (l,m)$. Combining multiple scattering theory, which expands the scattering state by multiple atoms to a multi-center expansion, and the Muffin-tin approximation, which spherically averages the scattering potential of each atom, to describe $\psi^{-}(\boldsymbol{k})$, the τ of core-level (1s) photoemission can be divided into three terms,

$$\tau = \tau_{\mathrm{abs}} + \tau_{\mathrm{path}} + \tau_{\mathrm{sc}}. \tag{2}$$

Where τ_{abs} is the TD that occurs during the process that a photoelectron escaped from the absorbing atom right after the photoelectron is excited at the absorbing atom. Where τ_{path} and τ_{sc} are the TDs due to the photoelectron propagation between atoms and scattering at each atom, respectively. These terms reflect the molecular shape.

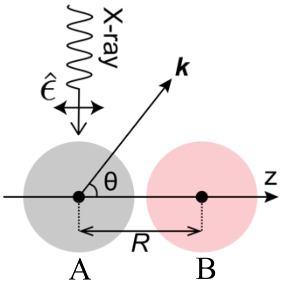

Figure 1: Coordinates for AB molecule used in Eqs. (3a-c) .

In this study, as shown in Fig. 1, $\hat{\boldsymbol{\epsilon}}$ is taken parallel to the molecular axis, the bond length is R, and the angle between the molecular axis and k to be θ, so that $\tau(\boldsymbol{k},\hat{\boldsymbol{\epsilon}}) = \tau(k,\theta)$. The $\tau_{\mathrm{path}}(k,\theta)$ in the forward ($\theta = 0$), vertical ($\pi/2$), and backward (π) scattered waves can be expressed as following equations under the single scattering and plane wave approximations, respectively,

$$\tau_{\mathrm{path}}(k,0) = 0, \tag{3a}$$

$$\tau_{\mathrm{path}}(k,\pi/2) = R/k, \tag{3b}$$

$$\tau_{\mathrm{path}}(k,\pi) = \frac{R}{k}\left(1 - \frac{1-|f^{\mathrm{B}}(k,\pi)|^2R^{-2}}{J(k,\pi)}\right). \tag{3c}$$

Where $f^{\mathrm{B}}(k,\pi)$ is the scattering amplitude by atom B in backscattering, and $J(k,\theta)$ is a function representing the molecular frame photoelectron angular distribution, which oscillates with period $2kR$,

$$J(k,\theta) = 1 - \frac{2}{R}|f^{\mathrm{B}}(k,\theta)|\cos[2kR + \arg\{f^{\mathrm{B}}(k,\theta)\}] + \frac{1}{R^2}|f^{\mathrm{B}}(k,\theta)|^2. \tag{4}$$

In the presentation, we will discuss the analytical expression of τ_{path} together with the results of numerical multiple scattering calculations of τ for C (1s) photoemission delay of the CO molecule.

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15 September 2021

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Day 2

Ultrafast dynamics probed by X-ray scattering

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The fundamental understanding of ultrafast events in atoms and molecules has undergone significant advancements thanks to time-resolved studies. Modern ultrafast X-ray techniques are particularly suited for such investigations. Yet, the analysis and interpretation of the experimental outcomes need support from detailed atomistic simulations. I will highlight key elements in our contribution to the theory of ultrafast X-ray scattering [1,2] and provide examples of applications to atoms and molecules in the atto- to femtosecond regime [1-5].

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Relativistic and non-adiabatic developments for molecular quantum theory

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High and ultra-high resolution spectroscopy experiments of small molecular systems make it possible to test and further develop the fundamental theory of molecular matter. I will speak about complementary, perturbative and variational approaches to the non-adiabatic and relativistic problems of molecular quantum theory [1–5]. I will sketch theoretical, algorithmic, and computational challenges that were recently met and that are still open for an increasingly complete and accurate description of small atomic and molecular systems.

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High-energy multidimensional solitary states in hollow-core fibers

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Using sub-picosecond pulses, we report the first time observation of the formation of highly-stable multidimensional solitary states (MDSS) in molecular-filled hollow-core fibers. The MDSS have broadband red-shifted spectra with an uncommon negative quadratic spectral phase at output, originating from strong intermodal interactions. This approach paves the route to compress sub-picosecond Ytterbium laser systems to few-cycle pulse duration using a compact setup.

Freeman resonances as the source for dynamic symmetry-breaking

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We study the coherence between ion cores of the spin–orbit split xenon ion, in the region where the ionizing photon energy is similar to the energy splitting; the defining ratio is $\eta \equiv \omega/\Delta E_{\text{s–o}}$. Since the parity of the two ion cores, $5\text{p}_{3/2}^{-1}$ and $5\text{p}_{1/2}^{-1}$, have the same parity, we intuitively expect any coherence between the ion cores to vanish in this energy region, since the photoelectrons have opposite parity (see figure) [1]. However, we observe a non-zero coherence with a rich structure dependent on η, which we attribute to Freeman resonances [2] which aid in transitions between the ion cores using the "atomic antenna" mechanism [3].

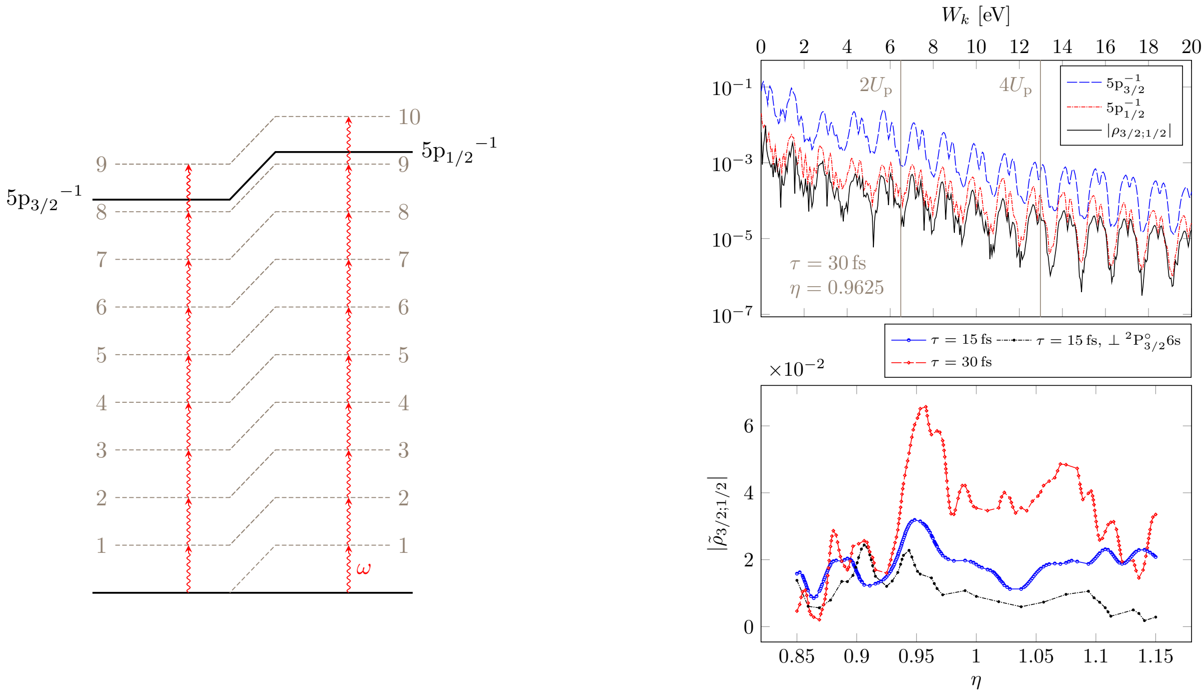

Figure 1: ATI from xenon. Left panel shows a sketch of the energy diagram when ionizing xenon using a laser field with photon energy ω equalling the spin–orbit splitting $\Delta E_{\text{s–o}}$ of the xenon ion, i.e. $\eta = 1$; slanted lines indicate same final kinetic energy of the photoelectron. In this case, photoelectrons correlated with the ion cores $5\text{p}_{3/2}^{-1}$ and $5\text{p}_{1/2}^{-1}$ will overlap energetically, but will have absorbed a number of photons differing by unity, implying opposite parity of the continuum wavepacket, which should destroy any coherence between the ion cores. Top right panel shows a typical ATI spectrum resolved on the different ion cores, as well as the (non-zero) energy-resolved coherence between them (black line). Bottom right panel shows the degree of coherence between the ion cores, as a function of η, for two different pulse durations. By preventing one state from interacting with the field, we partially destroy the atomic antenna, and the degree of coherence decreases (black dash-dotted line)

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Imprinting chirality on atoms using synthetic chiral light

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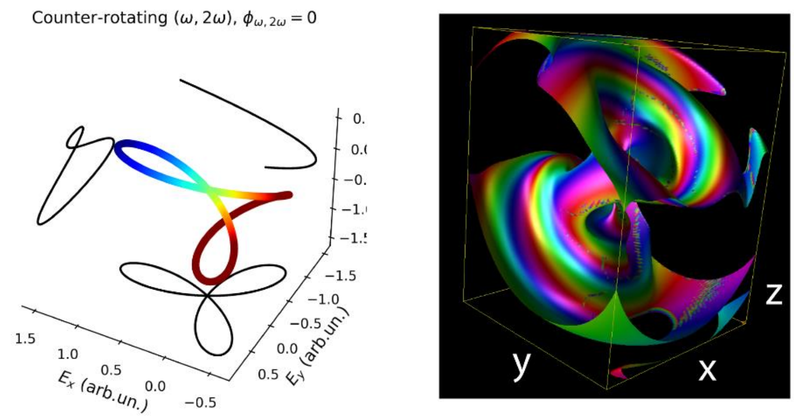
Chiral light fields in the dipole approximation can be synthetized by crossing two beams with different frequency and suitable polarization properties. The interaction of this particular type of lightwave with a chiral sample leads to giant enantio-sensitive responses [1]. While atoms are usually thought 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].


Counter-rotating $(\omega, 2\omega)$, $\phi_{\omega,2\omega} = 0$

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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Strong-field processes driven by tailored laser fields

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Exposing atomic or molecular targets to a strong laser field it is possible to observe many nonlinear processes among which the most significant are high-order above-threshold ionization (HATI) and high-order harmonic generation (HHG) [1]. In both processes, after the ionization, the liberated electron propagates in the laser field and can be returned in the vicinity of the parent ion. Then the electron can be rescattered off the parent ion and driven towards a detector (HATI) or recombined with the parent ion releasing the excess energy in the form of an emitted high-energy photon (HHG). After ionization, the electron dynamics is mostly determined by the laser field so that the influence of the parent ion can be neglected until the eventual rescattering or recombination. This assumption is usually called strong-field approximation (SFA).

The electron's dynamics is mostly determined by the laser field which induces the process. Therefore, it is desirable that this field depends on many parameters which can be used for control of the laser-induced processes. For a linearly polarized laser field control parameters are its intensity and wavelength. On the other hand, when a so-called tailored laser field is employed to induce the process, many other parameters, the example of which is the relative phase between the field components, are available. The most prominent examples of tailored laser fields are bicircular and orthogonally polarized two-color (OTC) fields. A bicircular (OTC) field consists of two circularly (linearly) polarized components with commensurable frequencies. The relative phase which does not affect the spectra generated by the bicircular field [2] has an enormous effect on the spectra obtained using the OTC field [3,4]. For example, the intensity and polarization of the emitted harmonics, as well as the differential ionization rate for the electrons with a given final momentum strongly depend on this parameter. In addition, for the molecular targets the orientation of the molecule in the laser field also plays an important role and affects the HATI and HHG spectra [5,6].

In this work we explore the possibilities of control of various processes on atomic and molecular targets with the help of the laser-field parameters. In particular, we investigate how the HATI and HHG spectra depend on the intensities and frequencies of the bicircular and OTC laser-field components. For the case of the OTC field we also explore the influence of the relative phase. We show that a subtle control of the process can be achieved using various parameters of the applied tailored laser field.

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Strong-Field Molecular Ionization beyond the Single Active Electron approximation

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The present work explores quantitative limits to the Single-Active Electron (SAE) [1] approximation, currently in use to deal with strong-field ionization and subsequent attosecond dynamics.

Using a time-dependent multiconfiguration approach, specifically a Time-Dependent Configuration Interaction (TD-CI) [2] method, we solve the time-dependent Schrödinger's equation (TDSE) for the two-electron dihydrogen molecule, with the possibility of tuning at will the electron-electron interaction by an adiabatic branching/debranching function. We focus on signals of the single ionization of H_2 under a strong NIR ($\lambda = 790, 750, 700\ nm$) two-cycle, linearly-polarized laser pulse of varying intensity (up to $I = 2.25 \times 10^{14}, 3 \times 10^{15}, 9 \times 10^{16} W/cm^2$). To assess the dynamical importance of the electron repulsion, V_{ee}, we consider three values of the internuclear distance R taken as a parameter, the nuclei being frozen in each geometry in the spirit of the Born-Oppenheimer approximation: $R = R_{eq} = 1.4\ au$, the equilibrium geometry of the molecule, represents a field-free situation of weak electronic correlation, while $R = 5.0\ au$ and $R = 10.2\ au$, denoting respectively an elongated and a dissociating molecule, are situations of increasing field-free correlation.

As expected, in the equilibrium geometry $R = R_{eq}$, tuning off the electron repulsion have no impacts on the channel-resolved and total ionization probabilities exhibited as functions of the field-intensity. The profile is typical of a tunnel ionization, except for the highest range of I, for which a sudden increase in the total ionization probability is observed and interpreted as due to the onset of an above-the-barrier ionization. At the elongated geometry, $R = 5.0\ au$, the ionization probability does not exhibit such a sudden increase as one approaches the high-intensity end, i.e. no above-the-barrier enhancement of the ionization is observed. The strong electronic correlation prevailing at this geometry now induces considerable modifications to the dynamics, (they are no longer observed when the the electron repulsion was tuned-off), and the ionization probability varies non-monotonously with I, passing through a dip, denoting a quenching of the ionization, at some moderate intensity I_{min}, the value of which depends on the field frequency (or on λ). A possible explanation is that the ionization is a mixture of a tunnel one (TI) [3] from the (correlated) ground-state and multiphoton ionizations (MPI) [4] from excited states, accessible from the ground state also by multiphoton excitations. The dynamics thus proceeds through a Resonance-Enhanced-Multiphoton Ionization (REMPI) [5] with interfering overlapping resonances resulting from excited electronic states. This non-monotonous behaviour is not observed in the dissociative limit, $R = 10.0\ au$, the strongest field-free correlation situation, and only subtle differences are observed between correlated and uncorrelated dynamics. This stunning observation is explained by the fact that no multiphoton transition to the excited states are possible from the correlated ground state, as these transitions between these states become dipole-forbidden in this geometry.

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Phase-resolved transient absorption XUV spectroscopy of Ar

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Attosecond and femtosecond transient absorption spectroscopy in the extreme ultraviolet (XUV) and x-ray regimes is a powerful tool to follow electronic and structural dynamics associated with chemical reactions. Thus far, it has been limited to detection of absorbance corresponding to the imaginary part of the pump-induced dipole, which is only half of the full signal, since the real part of the dipole is missing. We present an approach that enables detection of both imaginary and real parts of the dipole and provides more comprehensive information on mechanisms guiding ultra-fast electron dynamics.

The detection of the real part of the XUV induced dipole response is enabled by the measurement of the interference between two nearly identical XUV beams generated by a double-foci infrared (IR) driving pulse, which is realized by inserting a binary 0–π phase grating [1] (see the experimental setup in Fig. 1(a)), with only one of them being dressed with an IR pulse.

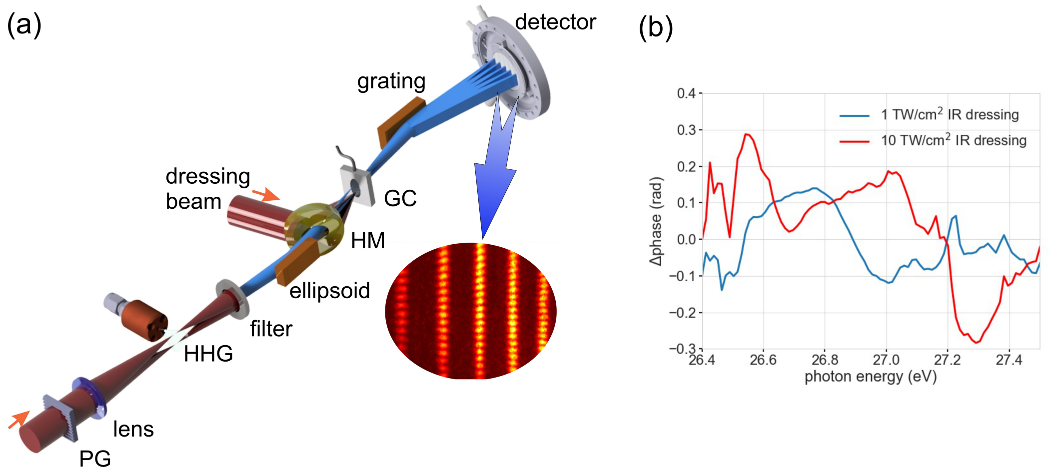

Figure 1: **a**. Scheme of the experimental setup. PG: phase grating; HM: holey mirror; GC: gas cell; HHG: high harmonic generation. **b**. Dependence of the phase response measured in Ar around the 4p Fano resonance on the dressing intensity at the temporal overlap between the pulses.

Using argon as a proof-of-principle target we show that the technique provides new nontrivial information even for a well studied sample. In particular, the measured phase has a nontrivial dependence on the IR dressing intensity and at $\gtrsim 1\,TW/cm^2$ could not be reconstructed from the absorption spectrum using the Kramers-Kronig relation.

The proposed technique can be applied to a broad range of XUV/X-ray spectroscopy applications with almost any sample in both transmission and reflection. Virtually, any absorption/reflection spectroscopy can be extended to a phase-resolved version. The only requirement is a 2D detector in the spectrometer, which enables detection of spatial profile in the dimension orthogonal to the diffraction plane. Thus, we expect this technique to facilitate and advance many studies.

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Asymmetric electron re-scattering in strong-field ionization of chiral molecules

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Strong-field ionization provides us with an ubiquitous tool for investigating the structure and dynamics of molecules. In the strong-field ionization regime, the molecule is impinged with an electromagnetic radiation, an electron is born into the continuum by tunneling out of the resultant potential barrier formed by the incident electromagnetic field and the molecular potential. These tunneled out electrons are accelerated in the incident electromagnetic field and their trajectories are dictated by the time at which they are released from the molecular potential. These electrons may be driven partly back towards the ionic core and then accelerated to the detector (indirect electrons) by the electromagnetic field or they may propagate directly towards the detector (direct electrons)[1,2]. The Photo-electron Angular Distribution (PAD) recorded, is a coherent superposition of these trajectories, thus encoding information about the molecular potential through photo-electron holography or laser-induced electron diffraction (LIED). In polyatomic molecules, the complexity of the molecular potential and random alignment of the molecules makes it challenging to retrieve the structural information of the molecule from PAD. In this work we propose a novel approach based on a symmetry property which survives the random alignment: Photo-Electron Circular Dichroism (PECD).

When chiral molecules are ionized with circularly polarized light, there is an asymmetric emission of electrons along the forward-backward (FB) direction relative to the propagation axis of the laser which depends on the handedness of the molecule. This chiroptical process which emerges from the scattering of electrons off the chiral potential is called PECD [3,4]. In strong-field regime the influence of molecular potential on the outgoing electron is expected to vanish, but the re-collision of indirect electrons onto the ionic core could make them very sensitive to the chiral molecular potential. PECD measurements are usually conducted using circularly polarized radiation, which suppresses the re-collision of electrons. As a compromise we use elliptically polarized light. The 3-D PAD is recorded using a velocity map imaging spectrometer with tomographic reconstruction. In circular polarization, the PAD has a topology of doughnut (Fig.1a), with clear FB asymmetry. In elliptical polarization, we observe a clear signature of the electron re-collision in PAD (Fig.1b), leading to energies between $2U_p$ and $10U_p$. These electrons show a strong FB asymmetry, which is highly sensitive to the molecular structure. These results demonstrate the possibility to observe chiral re-collision and opens the way to chiral holographic imaging

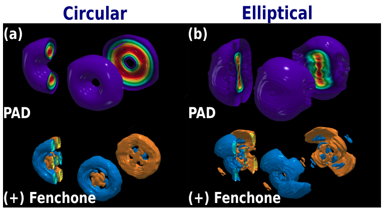

Figure 1: Cuts of the 3D PAD (up) and its forward-backward asymmetric component (down) is obtained by ionizing (+) fenchone molecules with a circularly (a) and a fixed ellipticaly (b) polarized laser field.

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Ultrafast optical rotation in chiral molecules with ultrashort and tightly focused laser pulses

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Chiral molecules exist in pairs non-superimposable "mirror twins" called enantiomers. They have identical properties, unless interacting with another chiral "object". Light is a unique tool for probing the chirality of matter. However, circularly polarized light, the standard chiro-optical tool, is not efficient: the weakness of non-electric-dipole effects makes its interaction with opposite enantiomers virtually identical and chiral recognition challenging, especially on ultrafast time scales. We have recently introduced *synthetic* chiral light [1], which enables huge enantio-sensitivity within the electric-dipole approximation, surpassing the accepted standards by several orders of magnitude [1].

However, light's chirality is not needed to detect the chirality of matter. Even linearly polarized light leads to optical activity: its polarization rotates in opposite directions in chiral media of opposite handedness. While this effect relies on weak magnetic interactions, it can produce large rotation angles in optically dense media. Still, detecting the chirality of diluted samples is challenging.

Intense few-cycle laser pulses bring new opportunities for ultrafast spectroscopy. When the laser's electric field amplitude $E(t)=E_0a(t)\cos(\omega t+\varphi_{CEP})$ is strongly modulated by its rapidly varying envelope a(t), the carrier-envelope phase φ_{CEP} determines the temporal structure of the wave, and thus the nonlinear optical response of matter. Here we show how tailoring the temporal structure of such ultrashort waveforms allows us to image and even control the ultrafast electronic response of chiral matter, with extremely high enantio-sensitivity [2].

Figs. 1a,b show the polarization of the nonlinear response of randomly oriented propylene oxide to an ultrashort and tightly laser focused pulse. Tight focusing creates transverse spin, which is key to record the medium's handedness in the sign on ellipticity and sense of rotation of the polarization ellipses of the emitted harmonic light. The giant enantio-sensitivity at response wavelengths 195, 130 and 97.5 nm (harmonic numbers 2, 4 and 6) is remarkable. It can be turned into highly enantio-sensitive intensity with a standard polarizer, to reach the ultimate efficiency: CD=200%, see Fig. 1c.

This ultrafast optical activity enables highly efficient imaging of chiral matter and ultrafast chiral dynamics at the level of electrons. Furthermore, the polarization of the emitted harmonic light can be fully controlled with the driver's CEP in a molecule-specific manner, opening the way to identifying highly enantio-sensitive molecular markers of attosecond chiral dynamics.

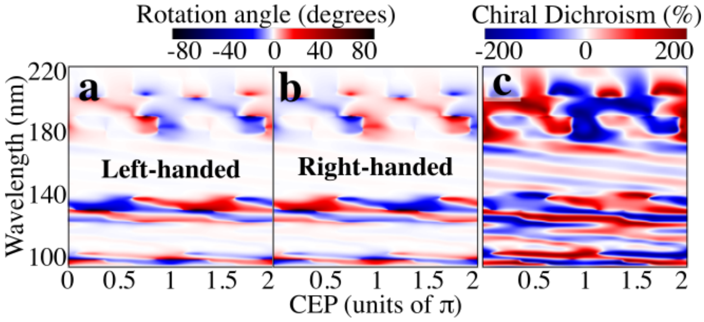

Figure 1. a,b, Rotation of the polarization ellipse of the harmonic light emitted by left- and right-handed propylene oxide as a function of the CEP of the driving field and the nonlinear response wavelength. **c**, Chiral dichroism, $CD=2(I_L-I_R)/(I_L+I_R)$, in the harmonic intensity $I_{L/R}$ using a polarizer at 85° relative to input polarization. TDDFT calculations; pulse duration 7fsec, intensity $6\cdot10^{13}$W/cm^2, λ=780nm, focal diameter 5μm.

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Development of Two-Color Sub-Femtosecond Pump/Probe Techniques with X-ray Free-Electron Lasers

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Probing dynamics on timescales extending below one femtosecond requires the generation of attosecond pulse pairs with variable delay and synchronization down to the sub-femtosecond level. X-ray pulses address core-to-valence transitions in molecular systems, allowing to measure or excite valence electron density with elemental localization. We report the experimental demonstration of two-color attosecond pulses with GW-level power produced by an X-ray free-electron laser (XFEL) at the Linac Coherent Light Source (LCLS). Sub-femtosecond, 380 eV pump pulses are generated via the Enhanced Self-Amplified Spontaneous Emission (ESASE) method [1, 2]. After a magnetic chicane, attosecond 760 eV probe pulses are produced by re-amplifying the electron beam microbunching created by the pump pulses, as shown in Fig. 1. As a result of the harmonic amplification, the minimal delay between the pulses (limited by slippage between the light field and the electron bunch) can be shorter than 0.5 femtoseconds. We verify the temporal delay and temporal jitter between the pulses using the angular streaking technique. We find the minimum achievable delay to be 200~300 attoseconds, with a corresponding delay jitter that is shorter than the duration of the pulse. These results are used to benchmark start-to-end XFEL simulations that provide greater confidence in the robustness of the two-color generation technique. Looking toward future experiments, our sub-femtosecond pump/probe technique can be applied to observe electronic charge dynamics in molecular systems.

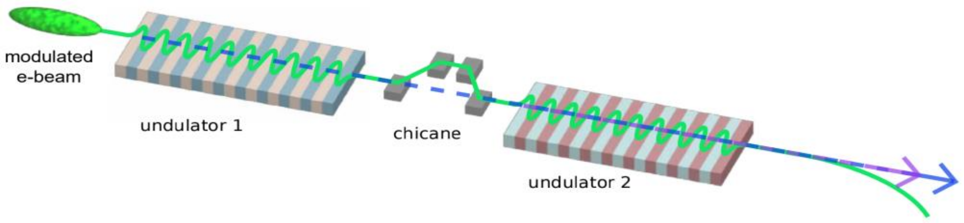

Fig. 1: **Schematic representation of the two-pulse technique.** The split undulator technique creates pairs of attosecond pulses from a single ESASE current spike.

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Femtosecond XUV-IR induced photodynamics in the methyl iodide cation

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Ultrashort extreme ultraviolet (XUV) pulses obtained from high harmonic generation (HHG) allow for studies of molecular cations dynamics with excellent time-resolution making feasible to observe processes such such as charge migration [1], evolution of electronic and vibrational wavepackets [2], and fast decays through conical intersections [3]. However, using the full bandwidth of HHG sources leads to a manifold of signals from different states which are mixed and so difficult to interpret. A time-delay-compensating XUV monochromator [4] can be employed to define the photon energy preserving the temporal resolution, allowing the study of state by state dynamics and also to distinguish processes in cations from those in highly excited neutrals, because the former are present with all harmonics of sufficient energy and the latter are resonant and thus only present for a certain XUV photon energy.

In here, we investigate the time-resolved dissociation of the methyl iodide cation (CH_3I^+) prepared in electronically excited states, and, in particular, the role of a time-delayed moderately strong IR probe pulse on the electronic and vibrational dynamics. The ground $\widetilde{X}\,^2E_{1/2,1/2}$ and excited $\widetilde{A}\,^2A_1$ states of CH_3I^+ are populated using the 9th harmonic of 800 nm (13.95 eV), the latter leading to CH_3^+ and I^+ fragments through different dissociation pathways, which are modified by the additional presence IR probe pulses.

Velocity map imaging is employed to detect selected fragment ions – in particular CH_3^+ and I^+ – as well as photoelectrons. The experimental results are complemented by high level *ab initio* calculations of the potential energy curves, in combination with full dimension on-the-fly trajectory calculations on the $\widetilde{A}\,^2A_1$ state in the absence and presence of the IR pulse. The results provide a detailed picture of the CH_3I^+ cation dissociation and the action mechanisms of the probe IR pulse.

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Molecular RABITT calculations using the time-independent multi-photon R-matrix method

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The theoretical analysis of RABITT interference experiments has been so far most often performed either using time-dependent codes of high computational complexity [1], or using approximate asymptotic approaches that separate the observed sideband delay into the molecular (one-photon) delay and a correcting contribution [2], which break down at low energies above the threshold.

In this work we apply the recently developed time-independent multi-photon molecular R-matrix method [3] to calculate accurate above-threshold two-photon ionization amplitudes and obtain the RABITT delays directly with no asymptotic approximation, yet with modest computational cost. The presented approach is implemented into the time-independent molecular scattering package UKRmol+ [4] and directly benefits from its flexibility in quantum-chemical description of the molecular target.

We calculate RABITT delays for several molecules, namely N_2, N_2O, H_2O and CO_2, and compare our results to recent available experiments. For some of these systems we obtain very good agreement (see Fig. 1), while we get striking disagreement for others. Effects of the electron correlation in resonant and non-resonant regions and more generally of the complexity of the molecular model are discussed, together with possible reasons for disagreement between theory and experiments in the particular cases.

Finally, we briefly discuss inconsistencies in theoretical approaches for molecular time delays employing the asymptotic methods of Baykusheva and Wörner [2] and of Kamalov *et al.* [5] and provide a consistent theory for the multi-channel molecular problem.

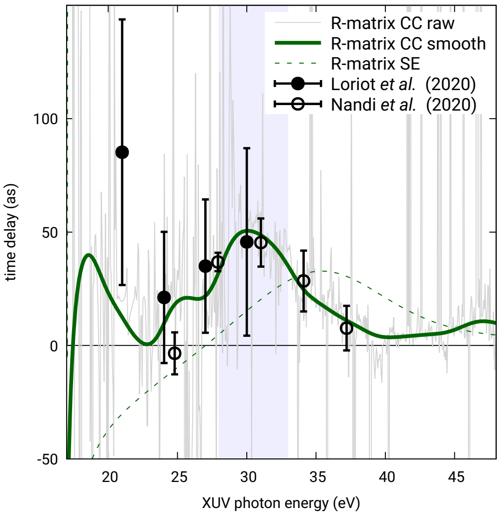

Figure 1: Calculated relative RABITT delays in unoriented N_2, compared to experiments.

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Electron induced fluorescence of oxygen

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Electron impact induced fluorescence of oxygen was studied using optical emission spectroscopy. Oxygen is the third most abundant element in the universe, it is present in the atmospheres of Earth, Europa, Ganymede [1] or cometary comas. This study is a part of spectroscopic data analysis of the comet 67P/Churyumov–Gerasimenko coma acquired by Rosetta's Optical, Spectroscopic, and Infrared Remote Imaging System (OSIRIS) [2].

The experimental apparatus is based on the crossed electron and molecular beams method and is further described elsewhere [3]. The emission spectrum was measured at 50 eV electron energy within the wavelengths of 200-650 nm, corrected for the apparatus sensitivity and calibrated to absolute values of intensity. The spectrum is shown in Figure 1. The emission band in the wavelength range from 200 to 450 nm corresponds to the second negative system of O_2^+ ($A^2\Pi_u$ - $X^2\Pi_g$). Individual vibrational transitions of the system were identified as well. Several bands of the first negative system of O_2^+ ($b^4\Sigma_g^-$ - $a^4\Pi_u$) were detected within 490 – 650 nm. The emission lines of atomic oxygen O I and O II were also identified in the spectrum. All the emission lines and bands were identified according to the previous research [4,5]. The emission cross sections Q_{em} at 50 eV of all identified transitions were determined, making a major contribution to the database of previously published experimental results. The aim of this experiment was to extend the collection of the emission cross sections to be sufficient for the study of extra-terrestrial bodies.

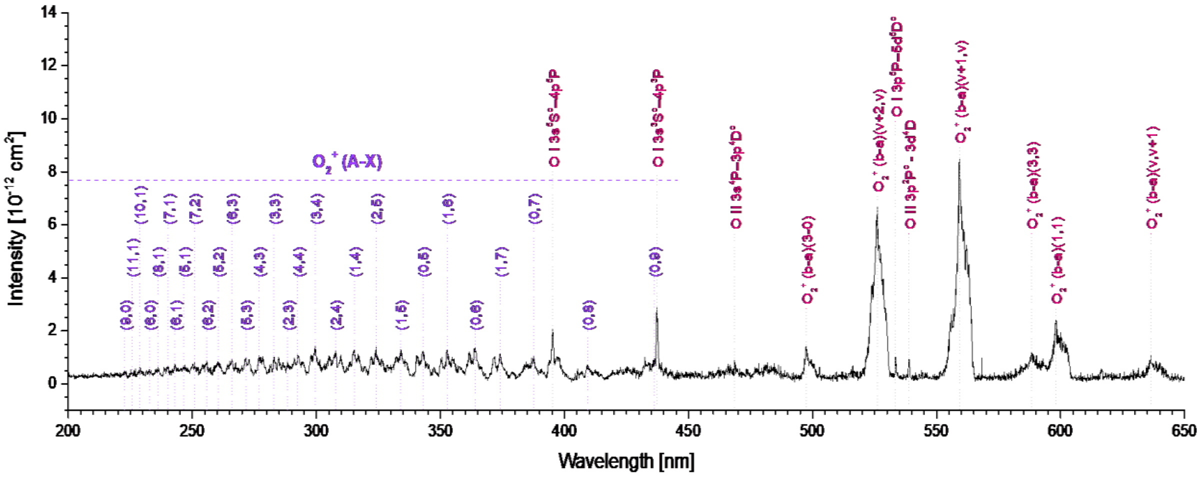

Figure 1: The emission spectrum of O_2 measured at 50 eV. The transitions correspond to the systems O_2^+ ($A^2\Pi_u$ - $X^2\Pi_g$) (purple) and O_2^+ ($b^4\Sigma_g^-$ - $a^4\Pi_u$), O I and O II lines (pink).

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Electron Dynamics for High-order Harmonic Generation Control

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Control over the polarization of attosecond pulses is necessary to probe chiral-sensitive light-matter interactions [1] at ultrafast time scales. This challenge goes beyond generating individual harmonics of particular polarization [2], since filtering harmonics loses the sub-femtosecond temporal resolution.

In our work, we combine a bichromatic counter-rotating circularly polarized (BiCRCP) driving field with a spatial inhomogeneity. We show that the direction and strength of the plasmonic-enhanced field provides a knob to shape the polarization of attosecond pulses from High Harmonic Generation (HHG) [3]. We solved the two-dimensional time-dependent Schrödinger equation (TDSE) [5] and ran classical trajectory Monte Carlo (CTMC) simulations [6] for a neon p-orbital model potential ionised by the total plasmonic-enhanced laser electric field. We applied a linear approximation for the spatial dependence characterized by β_i, leading to a validity region of $\approx 1/\beta_i$ [7].

Figure 1 shows recombining trajectories, (a) for the homogeneous case and (b)-(d) under the influence of a plasmonic field. The interplay between the plasmonic enhancement direction and the recombination directions determines the polarisation of each attosecond pulse, allowing rich but still predictable control from nearly circularly through elliptically to linearly polarized pulses [3].

Furthermore, investigations into the phase beyond the Strong Field Approximation, from different electron trajectories until recombination, lead to insights into optimised quasi phase matching conditions.

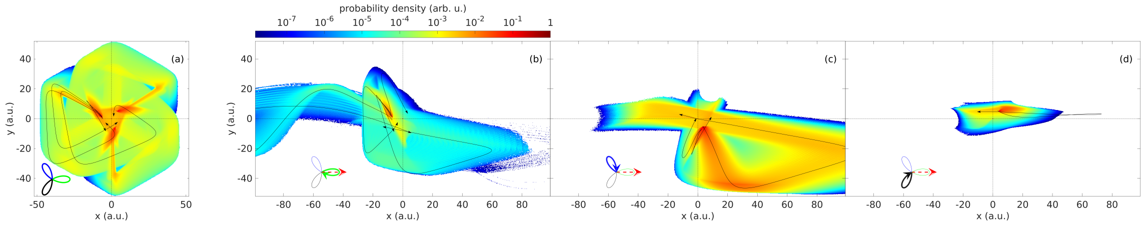

Figure 1: Recombining CTMC trajectories. **(a)** Trajectories from one optical cycle with a trefoil symmetry in the homogeneous case. **(b)-(d)** Trajectories ionized during different lobes (see insets) of the electric field. Plasmonic enhancement along x direction with $\beta_x = 0.01$ a.u. and shown as a red dashed arrow. Some exemplary trajectories are highlighted by black arrows.

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Enantio-sensitive unidirectional light bending

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Structured light, which exhibits nontrivial intensity, phase, and polarization patterns in space, has key applications ranging from imaging and 3D micromanipulation to classical and quantum communication [1]. However, to date, its application to molecular chirality [2] has been limited by the weakness of magnetic interactions. Here we show how to lift this limitation by structuring light's local chirality – a new type of chirality effective within the electric-dipole approximation [3]. We introduce structured light that when interacting with chiral molecules leads to unidirectional bending of the emitted light, in opposite directions in media of opposite handedness. This effect constites a chiral and highly non-linear extension of the classical double slit experiment. Our work introduces the concepts of polarization of chirality and chirality-polarized light, exposes the immense potential of sculpting light's local chirality, and offers novel opportunities for efficient chiral discrimination, enantio-sensitive optical molecular fingerprinting and imaging on ultrafast time scales [4].

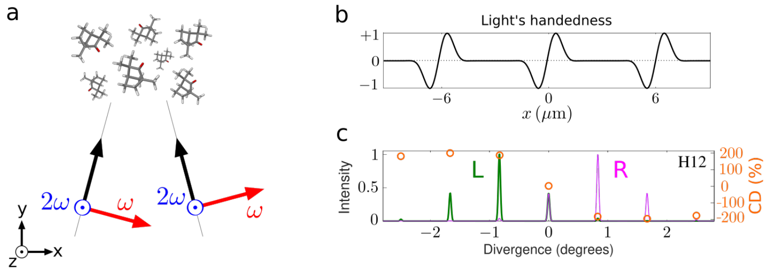

Figure 1: **a** We consider high harmonic generation in an isotropic chiral medium driven by two non-collinear beams carrying linearly polarized ω and 2ω fields orthogonal to each other. **b** By controlling the two-color relative phase in both beams we achieve light with a *structured local handedness* $h(x)$ that resembles the charge density in a polarized dielectric. That is, we achieve light with *polarization of chirality*. Note that in average, the chirality of this field vanishes. Its interaction with randomly oriented gas phase chiral molecules induces an x-dependent non-linear polarization $P_z = P^{(\text{chiral})} + P^{(\text{achiral})}$ composed of enantio-sensitive ($P^{(\text{chiral})}$) and non-enantiosensitive parts ($P^{(\text{achiral})}$). **c** These two parts interfere in the far field and yield shifted diffraction pattern, whose shift is enantio-sensitive. Here we show the calculated intensity as a function of the emission angle along with the chiral dichroism $CD = 2(I_L - I_R)/(I_L + I_R)$ for the 12th harmonic of Fenchone for $\omega = 0.044$ a.u., $F_\omega = 0.0146$ a.u., $F_{2\omega}/F_\omega = \sin\alpha$, and an angle between the beams $2\alpha = 10°$.

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Towards a low-cost short-wave infrared light field synthesizer based on rotational nonlinearity

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Spectral broadening in gas-filled hollow-core fibers (HCF) and subsequent compression with chirped mirrors is commonly used to reach few-cycle pulses for attosecond science. By splitting, compressing and recombining different spectral regions of the self-phase modulated spectrum, field synthesis of sub-cycle pulses has also been demonstrated. We have previously shown that rotational nonlinearity of molecular gases can be exploited to expand the spectrum of Yb-doped lasers, yielding red-shifted multi-octave bandwidth which could be compressed with chirped mirrors to <6 fs [1]. In this work, we show that compressed pulse durations below 20fs, centered at 1200nm and 1600nm, can be achieved from the long wavelength side of the broadened spectrum without chirped mirrors, by using bulk materials [2]. By combining these two channels in a low-cost field synthesizer, we demonstrate the generation of sub-two-cycle pulses in the short-wave infrared.

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Advances in the simulation of molecular ionization processes

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Complex processes due to interaction of a molecule with electromagnetic radiation are currently investigated in a vast domain of photon ranges, field intensities and time domain. Most processes involve photoionization and in fact electron detection is one of the most common and powerful probe.

Analysis of the results is not easy and often sophisticated models are developed and prove essential for interpretation, at various levels of accuracy. In principle it is always possible to resort to a full Quantum mechanics calculation, which could include the full complexity of the phenomenon, although for larger systems unavoidable approximations have to be introduced, which must be carefully considered. A full simulation may also be the only way to extract vital information from the experiment. A case is the determination of absolute configuration of chiral molecules from spectroscopic signatures, like circular dichroism, optical rotation or more recently photoelectron circular dichroism.

In the presentation I shall broadly review the main problems and tools available for electronic structure calculations in molecules, and go into more detail about the description of continuum states, and the use of B-spline bases. Examples of molecular photoionization will be presented to illustrate current capabilities and open problems.

Real time and local observation of ultrafast electronic and nuclear rearrangements using time-resolved X-ray spectroscopy

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The possibility to generate ultrashort (femtosecond down to attosecond) and intense pulses in the X-ray domain at the new X-ray Free Electron Laser (XFEL) facilities open the door to the investigation of the coupled electron and nuclear dynamics in molecules, which marks the fate of chemical and biological processes. In addition to this extremely high temporal resolution X-ray pulses offer atomic spatial resolution, which allows us to trigger and probe ultrafast dynamics at a particular site in the molecule, and to create localized electronic wavepacket and coherent dynamics via nonlinear X-ray excitation [1]. In this talk, we will present recent joint theoretical and experimental studies, in which we demonstrate the potential of time-resolved X-ray spectroscopy to sensitively probe the rich X-ray induced dynamics in molecules. With such a tool, we are able to follow in real time and site-selectively ultrafast changes in electron density [2], the rapid decay of transient states driven by electron correlations, as well as the formation and breaking of chemical bonds [3]. This work offers ample perspectives to resolve ultrafast evolution of excited states of complex systems in space and time.

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Solid state spectroscopy with attosecond all-optical techniques

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The possibility to manipulate the electrical properties of matter with very short optical pulses is a fascinating field of research with expected far reaching implications for many relevant technological fields. In the last decade, attosecond all-optical techniques have been established as powerful tools to investigate the primary physical processes at the basis of light matter interaction in atoms, molecules and condensed targets, moving the first step towards optical control. In my talk I will introduce attosecond transient absorption and reflection spectroscopies, reviewing the most important experiments performed with these techniques and discussing non-equilibrium ultrafast electron and exciton dynamics in dielectrics driven by few-cycle PHz pulses.

Lightwave electronics: sampling optical fields with attosecond resolution

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Time-domain sampling of arbitrary electric fields with sub-cycle resolution enables complementary time-frequency analyses of a system's electromagnetic response. However, scaling such techniques to the visible and near-IR spectral regimes has remained challenging, and seemingly demand high-energy optical sources and complicated optical apparatuses. We have developed and demonstrated an all-on-chip, optoelectronic device capable of sampling arbitrary, low-energy, near-infrared waveforms under ambient conditions with sub-optical-cycle resolution. Our detector uses field-driven photoemission from resonant nanoantennas to create attosecond electron bursts that probe the electric field of sampled waveforms. Additionally, our measurements directly reveal the localized plasmonic dynamics of the emitting nanoantennas *in situ*.

Angular anisotropy parameters for photoionization delays

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The photoelectron angular distribution is conveniently described with angular anisotropy parameters [1]. For linearly polarized light and within the dipole approximation:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{int}}{4\pi}\left(1+\sum_{n=1}^{N}\beta_{2n}P_{2n}\left(\cos\theta\right)\right) \tag{1}$$

where, P are Legendre polynomials and θ is the detection angle relative to the polarization axis. N is the number of exchanged photons and σ_{int} is the cross section integrated over all angles.

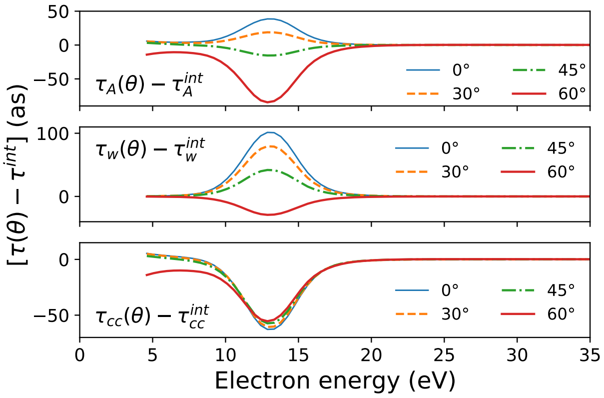

Figure 1: Ionization from Xe(5*s*). The upper panel shows $\tau(\theta) - \tau^{int}$ for the measurable *atomic delay*. The middle panel displays it for the underlying one-photon *Wigner delay*. Here the angular dependence is of purely relativistic origin, and significant only around the so-called Cooper minimum. The bottom figure shows the *difference* between the *atomic delay* and the *Wigner delay* (labelled *cc-delay*). It is clear that for low electron energies the angular dependence is mainly a two-photon effect.

Here, we define anisotropy parameters, describing the angular dependence of the measurable two-photon *atomic delay*, τ_A. The parametrization is similar to that in Eq. (1):

$$\tau_A\left(\theta\right) = \tau_A^{int} + \frac{1}{2\omega}\arg\left(1+\sum_{n=1}^{2}\tilde{\beta}_{2n}P_{2n}\left(\cos\theta\right)\right)$$

where, τ_A^{int} is the angular integrated atomic delay and ω is the laser frequency. The new $\tilde{\beta}$-parameters, are closely related to the ordinary parameters in Eq. (1), but they are complex. Also the the underlying one-photon *Wigner delay*, τ_W, can be similarly parametrized.

Angular dependent delays [2, 3] for ionization from the outermost *s*-shell in rare gases will be presented. The *s*-shell Wigner delay is isotropic in a non-relativistic framework, but the presence of two channels, $s \rightarrow p_{1/2}, p_{3/2}$, relativistically allow for an angular dependence. The atomic delay, being due to a two-photon process will, on the other hand, always allow for an angular dependence. Results for xenon are shown in Figure 1.

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Implementation of the relativistic time-dependent configuration interaction singles method: the case of atomic photoionization cross sections

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Attosecond chemistry aims to unravel the electron motion and coherence in atoms and molecules. A major contribution to this field was the real-time observation of the motion of valance-shell electrons in krypton ions made by Goulielmakis *et al.* in 2010 [1]. Since then, ATAS has been widely used in different scenarios [2]. Despite the great success of ATAS, all studies so far are based on non-relativistic ATAS theory [3], although the importance of spin-orbit coupling was demonstrated already by the first ATAS experiment [1]. Regarding the lack of a relativistic theory, our aim is to develop a general relativistic attosecond transient absorption spectroscopy method for studying heavy elements far beyond the perturbative regime [4]. In order to achive our goal, the N-electron time-dependent Dirac equation (TDDE) must be solved. As a compromise between computational cost and accuracy, the relativistic time-dependent configuration interaction singles (RTDCIS) method is proposed as an efficient option to solve this complicated task. In oder to validate RTDCIS, different observables has been computed for krypton and xenon, such as the photoionization cross sections. RTDCIS results have been compared with other relativistic calculations and experimental data, *see* Figure 1. As expected, RTDCIS results are similar to RRPA within the Tamm-Dancoff approximation (RRPA(TD)). This novel method opens the possibility to describe the electron spin dynamics by means of spin-resolved ATAS experiments far beyond the perturbative regime [5].

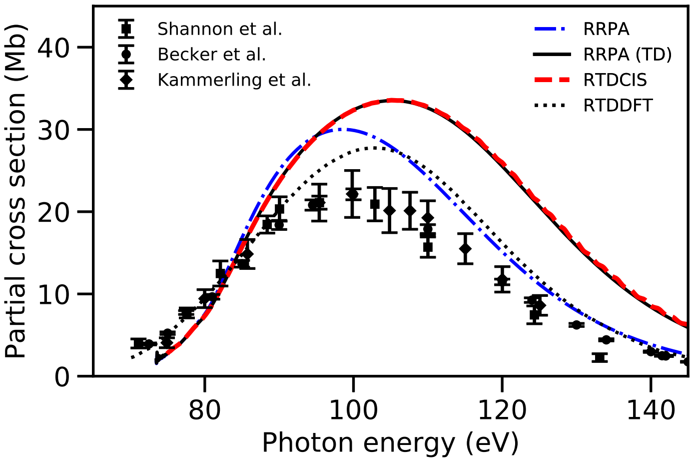

Figure 1: Xenon partial 4d photoionization cross section computed with different relativistic methods and experimental data.

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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.

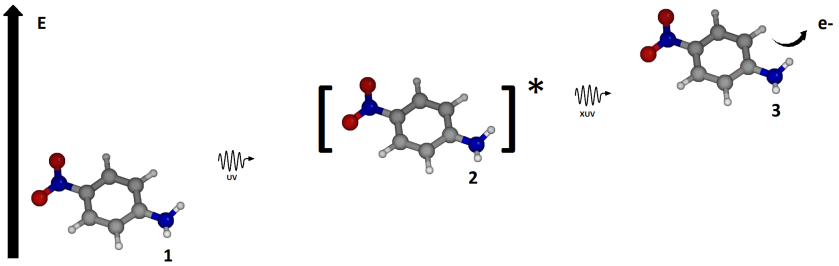

Figure 1: Diagram of the pump-probe scheme.

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Field-induced surface hopping: validation and control

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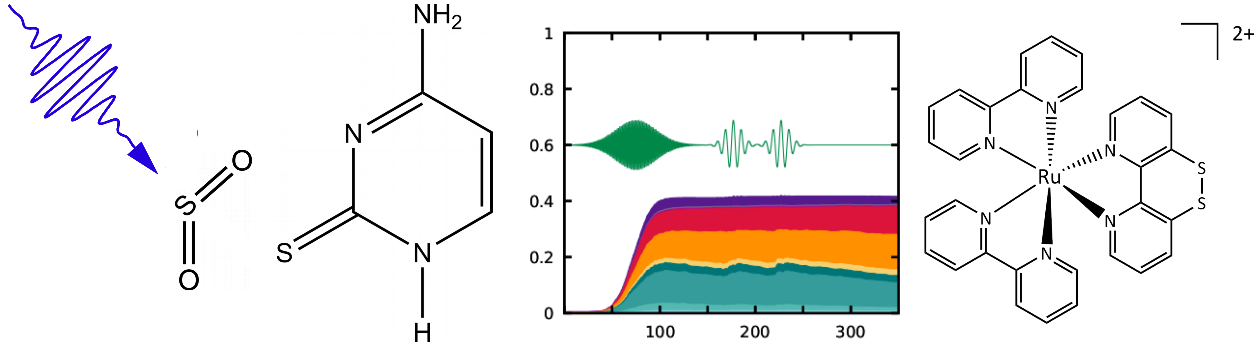
External electromagnetic fields in the IR and UV range play a major role in unravelling the mysteries of ultrafast processes involving coupled electronic and nuclear motion. While being the tool of choice and the starting point of any excited state investigation in a experimental setup, the explicit inclusion of laser pulses in theoretical simulations is still far from being standard procedure. The popular semi-classical surface hopping methodology (SH) to simulate dynamics has been extended in the past to include external fields [1,2] but has been shown to be sometimes unreliable in 1-dimensional test cases. [3,4]

To bridge the gap between theoretical and experimental protocol and to assess the validity of SH, we investigate the strengths and shortcomings of SH to simulate explicit laser pulses on two test systems: SO_2 and a 10-dimensional model of 2-thiocytosine.[5] Reference multi-configurational time-dependent Hartree (MCTDH) calculations for both systems are used to benchmark the accuracy of different surface hopping protocols, focusing on the treatment of overcoherence, the basis of states to propagate in and various approaches to conserve the total energy along a trajectory. For both systems, qualitative agreement of most simulated SH setups with the MCTDH reference is observed, with the use of an appropriate decoherence correction being the most influential variation.

Furthermore, an explicit excitation pulse has been used to simulate the dynamics of a ruthenium complex. Subsequently, modification of the excited state dynamics of this complex is accomplished, showing that the non-radiative relaxation towards the lowest energy triplet state can be slowed or even completely halted using a set of simple control pulses.



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Low energy electron attachment to $Co(CO)_3NO$ clusters

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Low energy electron attachment (EA) and dissociative attachment (DEA) to $Co(CO)_3NO$ clusters will be presented. $Co(CO)_3NO$ is used as a precursor gas for deposition of Co in Focused Electron Beam Induced Deposition (FEBID) and following Electron Beam Induced Surface Activation (EBISA) [1]. Ion yields from our cluster measurements (created by co-expansion with Ar gas) will be compared to previous EA and DEA gas phase $Co(CO)_3NO$ studies [2] and He nanodroplet cluster studies [3]. The gas phase DEA products from Ar clusters agree well with previous works [2,3], comparison with existing gas phase data [2] is shown in Figure 1 (left). However, formation of cluster products in He nanodroplets [3] and our co-expansion with Ar reveal some differences mostly the shape of the ion yield curves due to the higher energy resolution of the electron beam used in our experiment. The exclusive formation of the molecular ion of $Co(CO)_3NO$ in clusters was confirmed in our measurements but we have detected the ~0 eV resonance for this ion contrary to previous work [3], similarly to other cluster fragments shown in Figure 1 (right).

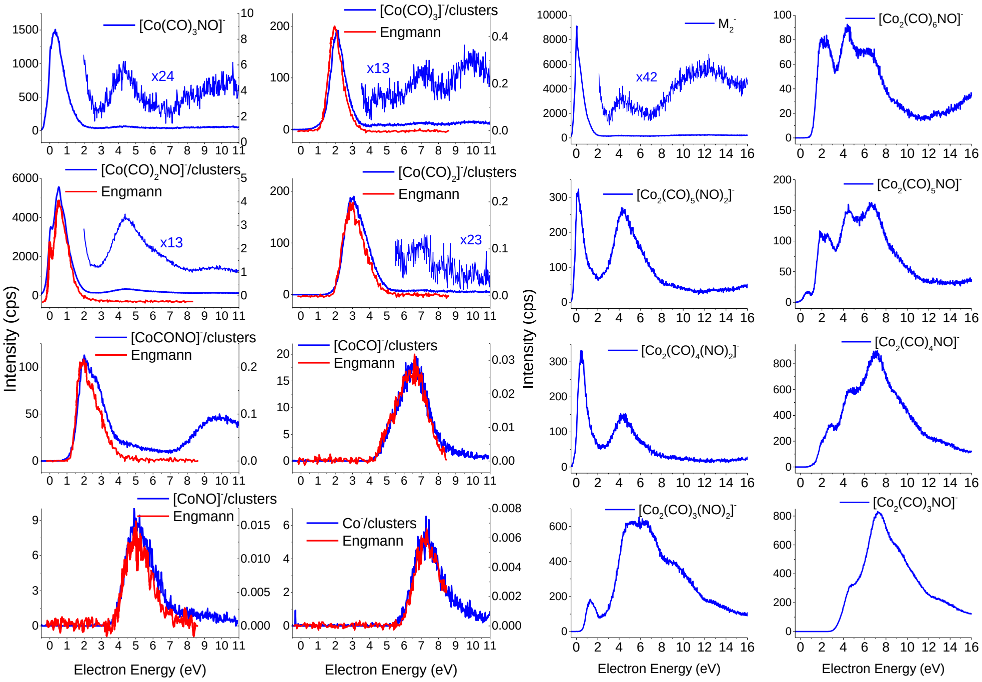

Figure 1: (left) Comparison of gas phase products from our Ar cluster measurements (blue) with pure gas phase products (red) [2]; (right) Selected cluster fragments from our Ar cluster measurements

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Tracing dissociation dynamics and ultrafast cooling in liquid pyridine using Time-resolved X-ray absorption spectroscopy

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In this work, by utilizing time-resolved soft X-ray transient absorption spectroscopy of liquid and gaseous pyridine at the carbon and nitrogen K-edges, we reveal the different reaction pathway dynamics initiated by multiphoton ionization. We show that photolytic cage effect and excited cationic state cooling via environment-coupled vibrational relaxation leads to long-lived cationic, ring-open and hydrogen-transfer isomerised state in the liquid phase, while in the gas phase the excess energy leads to fragmentation.

Photoinduced transformations exist at the heart of many chemical processes, such as the synthesis of natural products, and ultrafast pump-probe investigations facilitate the direct probing of the preliminary steps occurring after excitation, pushing the frontiers of our understanding of these core processes. Complexity arises from the highly non-equilibrium state created by the initial photoexcitation, which often leads to a number of dissipation channels, including radiative decay and non-radiative processes such as internal conversion (IC) and intramolecular vibrational redistribution (IVR).

Here we report the use of TR-XAS in a liquid (pyridine, C_5H_5N) for demonstrating the key role played by intermolecular interactions in selecting the reactive pathways after strong field ionization. While the pyridine cation is stabilized in an isomerized structure via ring-opening and hydrogen transfer in the liquid phase, it dissociates into fragments involving ring-open intermediates in the gas phase. The broadband soft X-ray probe pulse covers the carbon and nitrogen absorption edges as outlined in Fig. (a-c). The experimental setup allows directly comparing the dynamics in liquid and gas phase samples thus enabling the direct comparison of dynamics in the two phases. The transient absorption signal in liquid and gas samples (Fig. 1 (c-d)) exhibit features on different time scales in the 1 ps time range and were attributed to the differences of photoionized pyridine dissociation and isomerization in the gas phase and rapid cooling of excited cationic states in the liquid phase.

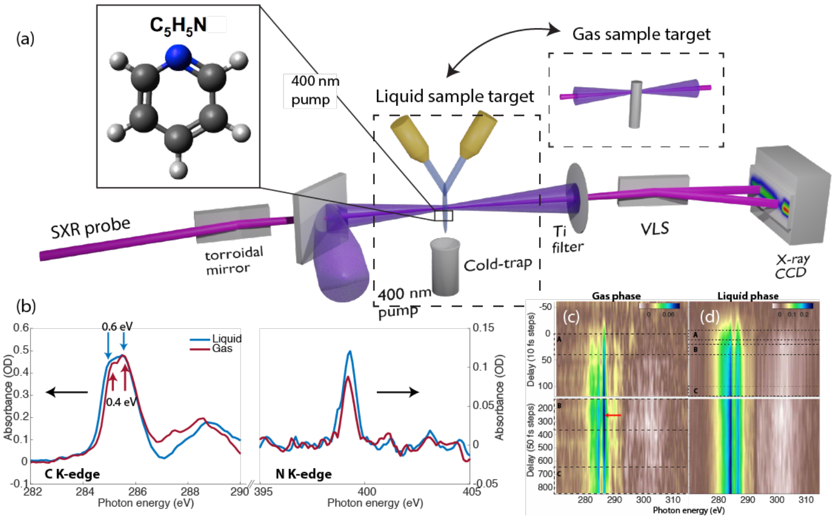

Figure 1: (a) experimental scheme; (b) measured transmission spectra of liquid ethanol and methanol at C-K and O-K absorption edges; (c, d) time-resolved X-ray differential absorption spectra of pyridine in gas and liquid phases.

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Imaging electron currents in molecules and crystals with ultrafast resonant x-ray scattering

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We study how ultrashort x-ray pulses can be employed to image dynamical properties of nonstationary electron systems with (sub-)femtosecond temporal and sub-nanometer spatial resolutions. Using a rigorous theoretical analysis based on a framework of quantum electrodynamics, we accurately describe time-resolved signals taking into account all transitions that a broadband probe pulse can induce in a nonstationary electron system. Although individual spectral lines cannot be resolved in this case, it turns out that signals still encode valuable time- and space-resolved information about electron dynamics. Comparing various imaging techniques, namely, ultrafast resonant x-ray scattering[1,2], nonresonant x-ray scattering (Compton scattering) [3] and time- angle-resolved photoelectron spectroscopy (trARPES)[4], we could identify a common procedure to reveal charge and electron current distributions from the time- and momentum-resolved signals [5].

In my presentation, I will focus on the ultrafast resonant x-ray scattering technique for imaging coherent electron dynamics in molecules [1] and crystals [2], and show our method to reconstruct interatomic electron currents based on our finding above.

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Revealing coherences during high-harmonic generation in 2-dimensional crystals.

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Shine intense laser pulses on a crystal and, most likely, high-order harmonics will be generated. Nowadays, high harmonics have been measured from a wide variety of crystals, ranging from semiconductors [1], to dielectrics [2,3], to metals [4], and even in 2-dimensional van der Waals solids , such as the "wonder material" graphene [5] and various transition-metal dichalchogenides (e.g, MoS_2 [6]). 2D materials offers a unique opportunity to explore exotic phenomena like topological and correlated states and their potential applications for electronics [7]. They are also a very versatile and adaptive platform due to the possibility to design heterostructures. For the same reasons, van der Waals materials will allow control of high-field nonlinearities with unprecedented precision.

The solid state introduces significant complexity to the inner workings of high-harmonic generation, such as scattering [8] and the excitation of multiple quantum paths (e.g, excitation of multiple energy bands [9]). Often times these signatures are difficult to disentangle. I will show how the polarization of high-order harmonics reveals interference between multiple quantum paths responsible for harmonic emission from the 2-dimensional van der Waals crystals MoS_2 and ReS_2. Our results reveal the microscopic high-field physics inside these materials with exquisite detail and suggest a simple path towards controlling their high-field response.

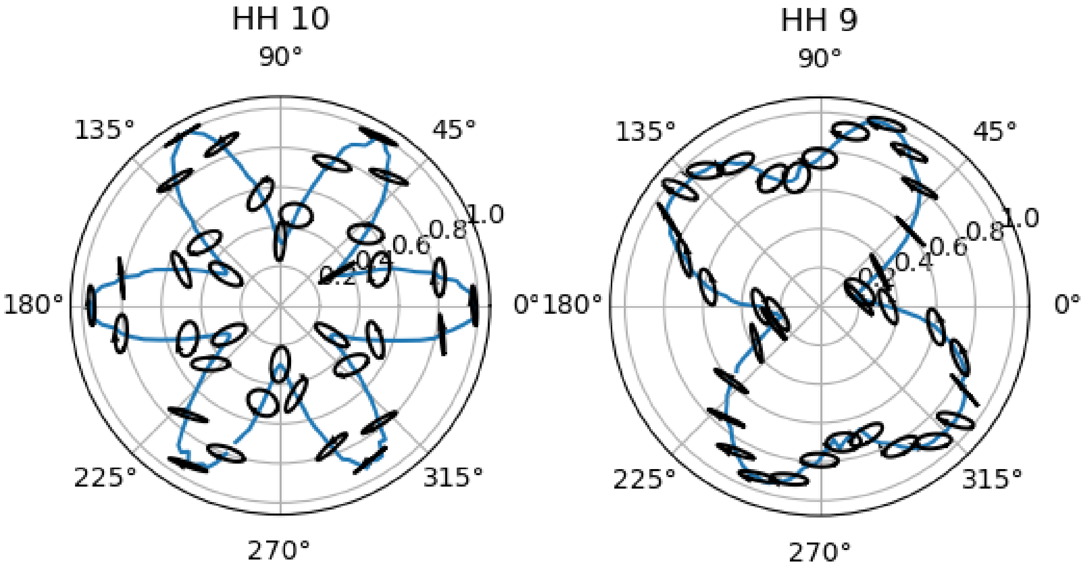

Figure 1: Orientation dependence (colored line) and polarization state (black lines) of high-order harmonics emitted from MoS_2 (left, HH10) and ReS_2 crystals (right, HH9). Simple symmetry arguments indicate that high harmonics should be linearly polarized, contrary to experimental findings. Interference between multiple quantum paths can yield to elliptical-polarized harmonics.

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UV Absorption Spectrum and Photodissociation Dynamics of CH_2OO following Excitation to the $B^1\mathrm{A}'$ state

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The spectroscopy and dynamics of the smallest Criegee intermediate CH_2OO following UV excitation to the B state is studied theoretically, based on multireference electronic wave functions and a quantum dynamical approach for the nuclear motion. Two interacting electronic states and three nuclear degrees of freedom are considered in the dynamical treatment. The UV absorption spectrum is found to agree very well with available experimental recordings when accounting for broadening effects due to vibrational and rotational congestion and lifetime effects. Upon higher resolution two different energetic regimes can be approximately distinguished, a higher-energy regime where the spectral envelope is broad and structureless, and dissociation is prompt, and a lower-energy regime featuring narrow resonances which are supported by the shallow well occurring at intermediate O−O distances, and decay by tunneling to the repulsive outer part of the potential energy surface. The importance of nonadiabatic coupling effects is pointed out and future steps for an improved theoretical treatment are outlined.

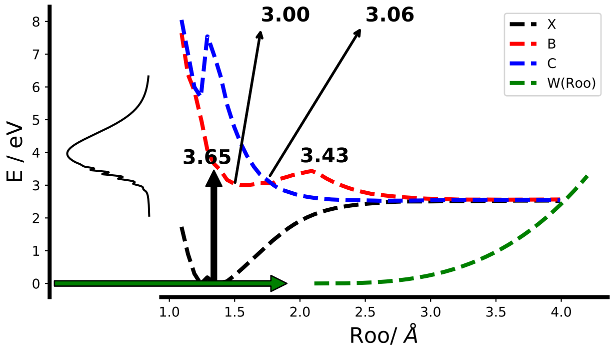

Figure 1: The simulated $B^1\mathrm{A}' - \mathrm{X}^1\mathrm{A}'$ excitation spectrum and the potentail enenrgy curves for the $X^1\mathrm{A}'$, $B^1\mathrm{A}'$ of CH_2OO and $C^1\mathrm{A}'$ states and the imaginary part $W(R_{OO})$ of the complex absorbing potentials(CAPs)[1].

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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.

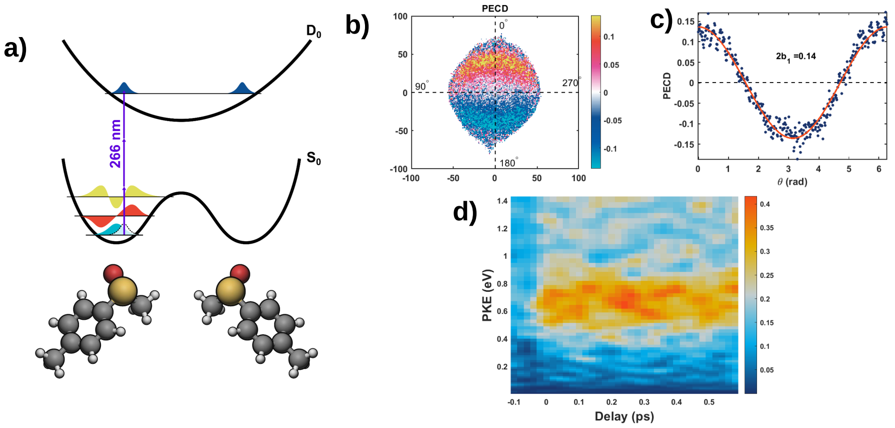

Figure 1: Panel a) shows a scheme for Lochfrass excitation, where a portion of an electronic ground state vibrational wavefunction is depleted through ionisation. The chemical structure of MTSO is shown above. Panel b) shows the static PECD of MTSO by ionisation of a 133 nm photon. Panel c) is the fit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

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Azobenzene and its derivatives have been studied widely [1-4] ever since the discovery of the photo-induced isomerization process of azobenzene in 1937 [5]. Even so, both theoretical [2, 3] and experimental [6] studies continue to be published as the isomerization process is not yet fully understood and azobenzene and its derivatives appear promising for many possible applications in e.g. optical data storage and as good photoswitches etc. [7].

Here, the photoisomerization reaction of azobenzene in both directions have been investigated using the surface hopping procedure[8,9] with forced jumps at the BHandHLYP/cc-pVDZ level of theory. Both simulations gave quantum yields and lagtimes in reasonably good agreement with experiment[1] and previous theoretical studies[2-4]. The cis to trans isomerization was found to appear as a stepwise reaction if only considering movement along a single degree of freedom, which is usually how the reaction is considered, while the trans to cis isomerization was observed to be one smooth step along this degree of freedom. The further investigations of the cis to trans isomerization revealed that, while the CNNC angle is an important degree of freedom for describing the reaction, it is insufficient for describing all of the dynamics and at least one other degree of freedom must be included. The trans to cis isomerization on the other hand was found to be well described by a single degree of freedom, and its slowness could be ascribed to the slow oscillations of this degree of freedom rather than an energy barrier.

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Coulomb distorted twisted interference patterns from elliptically polarised strong field ionisation

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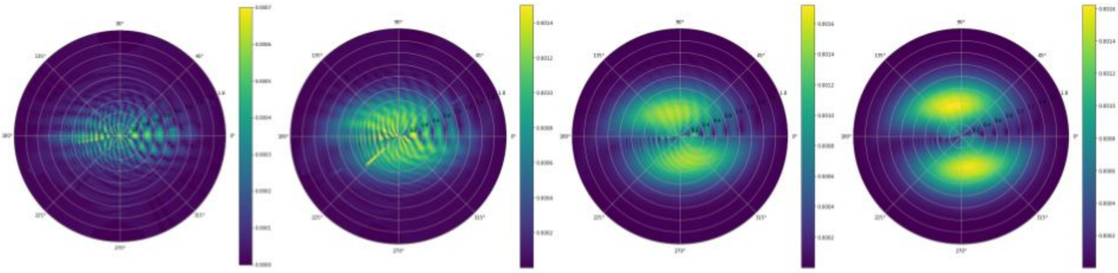
Tailored fields are powerful tools for probing and ultimately controlling laser-matter interaction at the subfemtosecond scale. They can be used, for instance, for exploring chiral-sensitive processes [1] or investigating the electron angular momentum electron in strong-field ionisation [2]. In particular, elliptically polarised fields have been widely used in the investigation of tunnel ionisation dynamics [3]. Nonetheless, the influence of the residual binding potential and its interplay with tailored fields remains largely unexplored.

In the present work, we investigate the interplay of the residual Coulomb potential and the external laser field in ultrafast photoelectron holography for elliptically polarised driving fields, with focus on quantum interference and small ellipticity. Using the Coulomb quantum-orbit strong-field approximation (CQSFA) [4], we show that the Coulomb distortion leads to twisted interference patterns. This twisting effect is absent for the standard, Coulomb-free strong-field approximation. We investigate how the interplay of the field and the potential alters well-known holographic patterns such as the fan and the spider, in comparison to their counterparts for linearly polarised fields [5], by performing a detailed assessment of the interference between specific orbit pairs. Our results also exhibit Coulomb focusing and the offset phase caused by the residual potential. These twisted patterns are illustrated in Fig. 1.



e = 0.05 e = 0.2 e = 0.3 e = 0.4

Figure 1: Photoelectron momentum distributions computed with the CQSFA for helium in an elliptically polarised field of intensity 1×10^{14} $\mathrm{W/cm^2}$, wavelength $\lambda = 800$ nm and small ellipticities ε.

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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 sudden valence ionization [3], which is performed in our experiments by a 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. This measurement is 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 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.

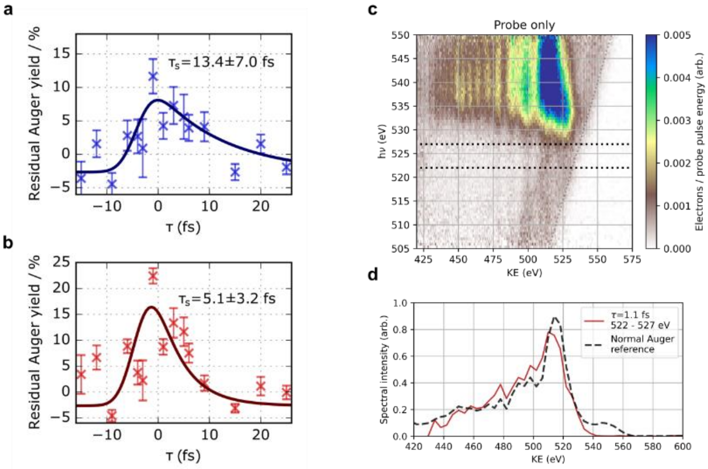

Figure 1. **a** & **b** time-resolved electron hole dynamics in isopropanol following ionization from the 7*a* (**a**) and 6*a* (**b**) orbitals. **c**) resonant Auger-Meitner (AM) absorption of para-aminophenol measured with attosecond X-ray pulses. At the photon energy indicated by the horizontal dashed 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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An assessment of different electronic structure approaches for modelling time-resolved X-ray absorption spectroscopy

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X-ray absorption spectroscopy (XAS), one of the oldest methods for structural analysis, is developing in the pump–probe scheme and has success in observing elusive intermediates of photoexcited molecules on femtosecond timescales [1–3]. For future application of time-resolved (TR) XAS to tracking more photoinduced or chemical reaction dynamics, performance of the electronic structure theories for the spectral simulation, on which interpretation of TR-XAS relies, needs to be asssessed.

Since experimental TR-XAS spectra are still relatively scarse, we set out assessing the performance of four selected single-reference methods from the perspective of the three requirements: They should be able to accurately describe the core and valence excitations from the ground state, to give the transition strengths between the core-excited and valence-excited states, and yield the XAS spectra of the valence-excited states over the entire pre-edge region, i.e., describe the spectral features due to the transitions of higher excitation character. More specifically, we extend the use of the maximum overlap method (MOM) [4] approach to the CCSD framework and evaluate its accuracy relative to standard fc-CVS-EOM-EE-CCSD [5]. We have finally confirmed that only the CCSD and TDDFT schemes with the MOM approach can reproduce the entire pre-bleaching region of the excited-state XAS spectra of Refs. 1 and 2, despite spin contamination of the singlet excited states [6].

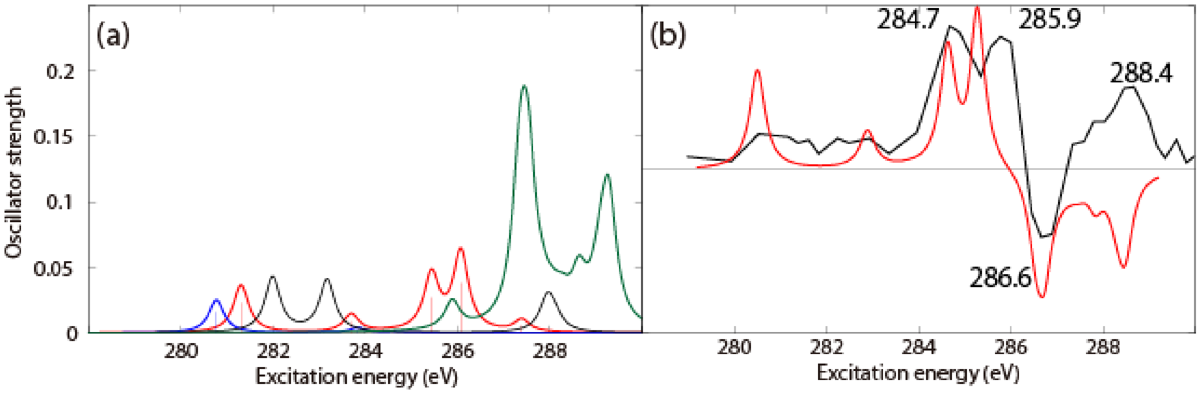

Figure 1. (a) Carbon K-edge NEXAFS spectra for acetylacetone in the $S_2(\pi\pi^*)$ state calculated at the fc-CVS-EOM-CCSD/6-311++G** level at the geometry optimized for the $S_1(n\pi^*)$ state: (red) using the MOM-UHF (excited state) Slater determinant as reference; (blue) from transitions between EOM valence and core-excited states; and (black) using a high-spin open-shell reference for the ground state. The green curve is the NEXAFS spectrum of ground state at the Franck-Condon geometry. (b) (black) Experimental transient absorption spectrum in 120-200 fs [1], and (red) spectrum calculated from the red and the green curves of panel (a), shifted by 0.8 eV.

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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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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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STUDY OF DISOCIATIVE PROCESSES BY ELECTRON IMPACT ON PYRIDINE

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The pyridine is found, for example, in nicotine or in B vitamins and it is used as a solvent or precursor for agrochemicals in fertilizers [1,2]. Pyridine in B vitamins has also been found on the surface of meteorites [3]. The aim of this work is the experimental study of electron-induced processes such as ionization and dissociative ionization, dissociative excitation, and ionization excitation of pyridine. Using two experiments, both crossed beams one utilizing quadrupole mass spectrometry and other optical emission spectrometry, we are able to provide more complex study of electron-induced processes. In the emission spectrum the Douglas - Herzberg system of CH^+, CH^+ (B-A), C^+, the hydrogen Balmer series, Deslanders - d´Azambuja system of C_2, Swann system of C_2 and CH (A-X), CH (B-X), CH (C-X), CN (B-X), NH (A-X) transitions are observed. In the mass spectrum the sequential dissociation of C, H and CH from parent of pyridine is observed.

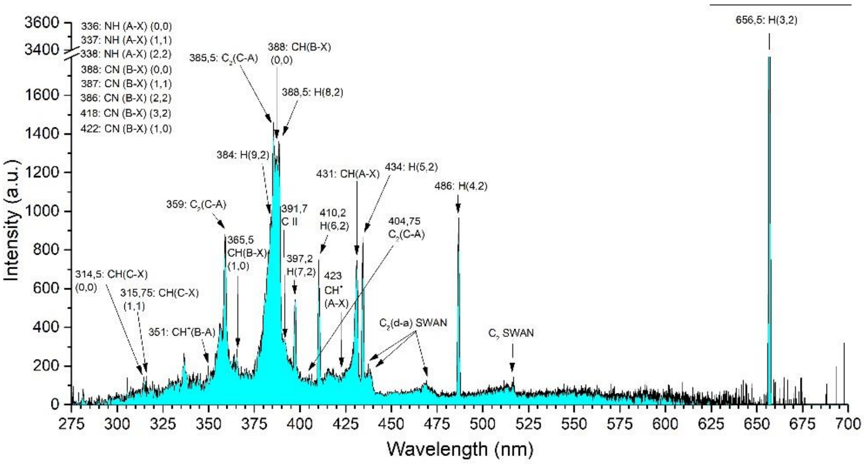

Figure 1: Fluorescence spectrum of pyridine

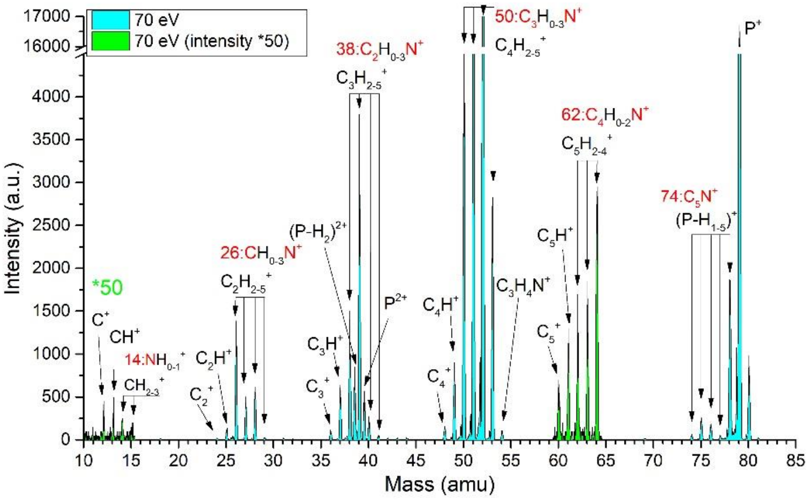

Figure 2: Mass spectrum of pyridine

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Transient valence charge localization in strong-field dissociative ionization of HCl molecules

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We show that the ultrafast electron tunneling ionization by an intense femtosecond laser pulse could induce an asymmetric transient charge localization in the valence shell of the HCl molecule during the dissociative ionization process. The transient charge localization is encoded in the laser impulse acquired by the outgoing ionic fragments $\boldsymbol{p}_{\text{ion}} = \int Z_{\text{ion}}(t)\boldsymbol{E}(t)dt$, where the transient ionic charge $Z_{\text{ion}}(t)$ naturally sets in, with its effect enlarged by the coupling to the laser electric field $\boldsymbol{E}(t)$ and manifested in the asymptotic ionic momentum $\boldsymbol{p}_{\text{ion}}$. The transient valence charge localization is thereby revealed by examining the electron tunneling-site distinguished momentum angular distribution of the ejected H^+ fragments, as displayed in Fig. 1. The asymmetric rotation angle in the figure reveals different evolution of the transient charge localization when the electron is released from different molecular sites. A two-level quantum dynamics simulation and a classical dynamics simulation incorporating a transient charge localization support our experimental observations. Our work proposes a way to visualize the transient valence charge motion and will stimulate further investigations of the tunneling-site-sensitive ultrafast dynamics of molecules in strong laser fields.

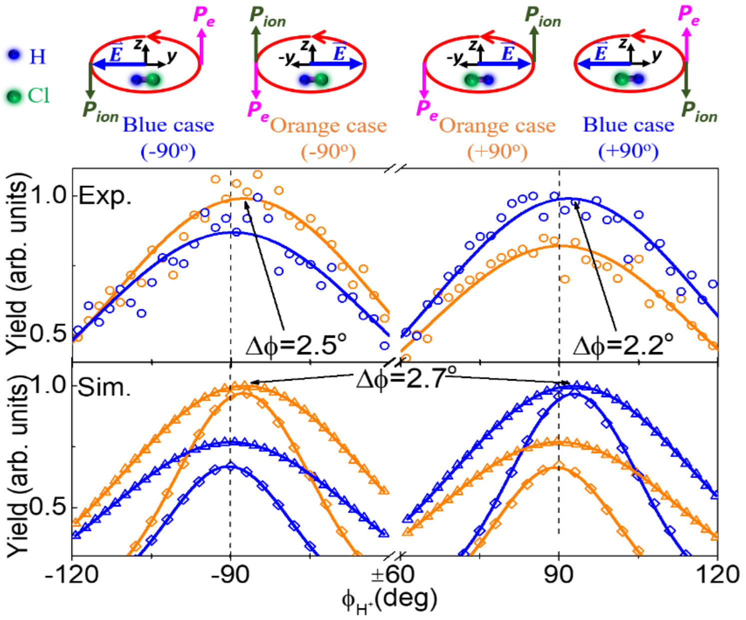

Figure 1: The measured and simulated angular distributions of the H^+ fragments of the HCl(1, 0) channel when the electron is released from two different sites driven by the elliptically polarized laser field as illustrated in the sketches. Δϕ is the offset angle of the peak position of the fitted curves with respect to the y axis ($\pm 90°$).

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Design of a compact multichamber gas cell for few fs UV pulse generation

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Ultraviolet (UV) radiation triggers many biochemical reactions. For instance, it can play a dominant role for DNA damage or the production of vitamin D. Ultrafast UV laser pulses can be used in pump-probe experiments to investigate the electronic motions leading up to conformational change, charge migration or ionization in molecules.

The nonlinear process dominating the UV generation in gas cells with an infrared fundamental pulse is third harmonic generation (THG). This process is density dependent and demands several bars of gas pressure for the optimal UV conversion efficiency [2]. At the same time, to avoid absorption and phase mismatch effects a gas scarcity before and after the UV generation region is required. Therefore, an extremely sharp pressure profile of the gas medium is needed. Recently, a gas cell has been designed to minimize the outflowing gas and placed inside a differential pumping system to reduce the gas pressure in the surrounding high vacuum. This setup has been shown to generate sub-2-fs UV pulses using frequency upconversion of 5-fs near-infrared pulses in argon [1].

In this work, the cell design was improved employing the FLICE (Femtosecond Laser mIcromachining followed by Chemical Etching) technique [3, 4]. A 49 x 6 mm multichamber fused silica chip was created, incorporating the differential pumping system (Fig. 1). Simulations of the gas density distribution along the optical axis have been performed and show the decrease of the gas profile by almost 5 orders of magnitude in the pumping chambers. This new design presents all the advantages of integrated devices such as compactness, replicability, easy integration in different setups and, when paired with a tiltable and movable stage, high flexibility.

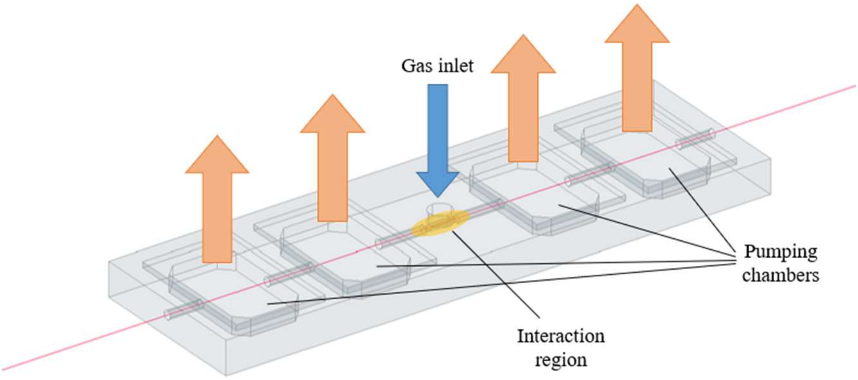

Figure 1: Multichamber chip design. The central gas-laser interaction region is supplied with gas from the top. The four chambers on both sides are connected to vacuum pumps.

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Air-stable and High Mobility based Electron Transport Semiconducting Material Hexachloro-hexa-azatrinaphthylene

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Since last few years, organic semiconductors (OSCs) have attracted a considerable amount of attention due to their wide potential applications in various electronic devices such as organic field-effect transistors (OFETs), organic photovoltaic devices (OPVs), organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) [1-2]. Unlike their inorganic counterparts, organic semiconducting materials are cost-effective, lightweight and fairly flexible and also provide the versatility of chemical synthesis. However, one of the major challenges for the development and fabrications of organic semiconductors for industrial applications are their air-instabilities. From the theoretical point of view, the air-stability of the organic semiconducting material depends upon its low-lying frontier molecular orbitals and the energy gap in between them [3-5]. A new n-type organic semiconductor-based on haxachloro-hexaaza-trinaphthylene compound is reported. The electronic structure and charge transport properties of the compound is calculated in the framework of density functional theory (DFT). The electron-withdrawing group (-Cl) on the end position of the compound could help to lower the LUMO energy level and improve the air-stability and charge carrier mobility. The large electron affinity (2.60 eV) and low LUMO energy (-3.63 eV) suggests that the compounds were to be air-stable and N-type organic semiconductor. Moreover, lower values of electron-injection barrier as compared to those of hole-injection barrier implied that the investigated compounds were basically N-type semiconductors [6]. The computed electronic coupling of LUMO of the compound was found to be comparatively larger in the transverse-channel (86.6 meV) than other channels. The computed large electron and hole mobility was found to be 3.54 $cm^2V^{-1}s^{-1}$ and 0.014 $cm^2V^{-1}s^{-1}$. Further, Hirshfeld analysis depicting the distribution of surface charge in between the molecular layers of the crystals revealed that the principal interactions were mostly due to the Cl…H/H…Cl and Cl…Cl contacts of the compounds.

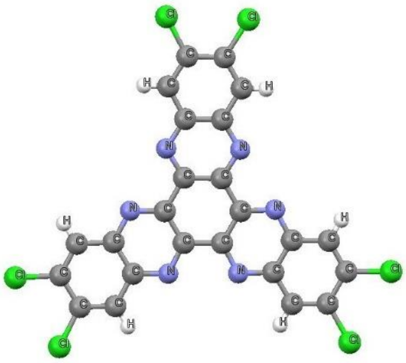

Figure 1: Molecular structure of Hexachloro-hexa-azatrinaphthylene

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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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Multiphoton interaction phase shifts in attosecond science

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In Ref. [1] we study three recent attosecond and free-electron laser experiments from Ref. [2-4], using an ab initio method based on the time-dependent configuration interaction singles [5] (TDCIS). We find that the dependence on the carrier-envelope phase can partly be understood based on accumulation of interaction phase in multiphoton processes. We derive the following rule of thumb, valid in the limit of a small ponderomotive energy, which expresses the nth laser-assisted photoionization process as

$$c_{\mathbf{k}}^{(n)} \approx (-i)^{|n|} J_{|n|} \exp(in\varphi) f_{\mathbf{k}}^{(\mathrm{pump})},$$

where $f_{\mathbf{k}}^{(\mathrm{pump})}$ is the elementary photoionization amplitude, φ the CEP difference between pump and probe fields, $J_{|n|}$ a Bessel function and $(-i)^{|n|}$ an interaction phase which accumulates for each included interaction.

This rule of thumb is used to provide an explanation to why laser-assisted photoionization experiments with mixed parity express no RABBIT modulation, see Fig. 1, and why interferometric above-threshold ionization experiments are shifted relative to RABBIT experiments.

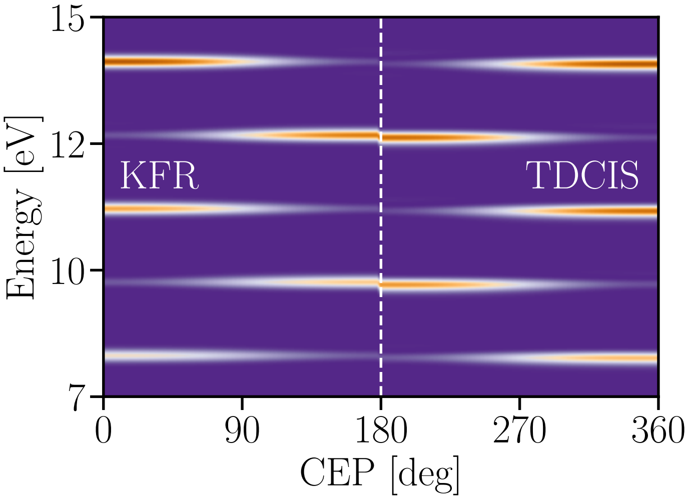

Figure 1: Photoelectron spectrum in neon from odd and even high-order harmonics 20–24 as in Ref. [2] using (left) Keldysh–Faisal–Reiss theory and (right) TDCIS.

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Electronic coherences steer the strong isotope effect in the ultrafast Jahn-Teller structural rearrangement of methane cation upon tunnel ionization

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We report on fully quantum electronic-nuclear dynamics following sudden ionization from the neutral in the three lowest electronic states of the CH4+ and CD4+ cations [1]. There is a strong Jahn-Teller effect in the Franck-Condon region and we employ two nuclear degrees of freedom that span the internal coordinates involved in the Jahn-Teller coupling. The initial state results from tunnel ionization by a strong IR pulse which coherently pumps the three lowest states of the cation, D0, D1 and D2. Tunnel ionization is described using a MO-ADK model [2]. The quantum dynamics is computed by solving the time-dependent Schrödinger equation for the three coupled electronic states of the cation on a grid of the two nuclear coordinates. The quantum dynamics is averaged over 8000 random orientations of the molecules with respect to the polarization of the IR pulse.

The quantum dynamical simulations show that a strong isotope effect occurs when the ionization accesses significantly the D2 state of the cation in the Franck-Condon region. The computed isotope effect is larger than expected on the basis of the effective mass ratio. The strong effect is due to fast oscillations of the electronic coherences between the D2 and the D1 and D0 electronic states and their modulation by the non adiabatic couplings before a significant onset of nuclear motion. The magnitude of the effect is similar to the one that we previously reported for a sudden photoionization process [3]. The magnitude of the isotope effect is in agreement with the experimental value reported using high harmonic spectroscopy [4,5].

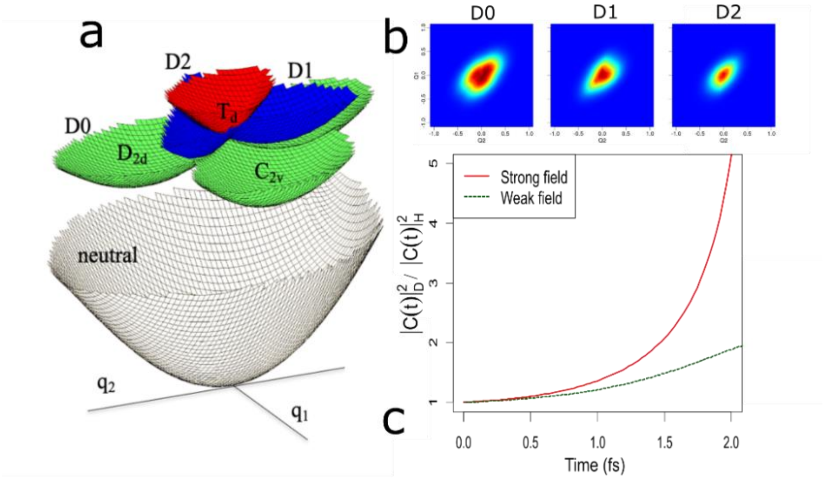

Figure 1: a) The potential energy surfaces of the neutral ground state and of the three lowest states of the cation. b) Computed heatmaps of the localization of the initial state in the two nuclear coordinates for the three electronic states of the cation using a strong field strength that allows accessing the D2 state. c) The computed ratio of the autocorrelation functions for a low and a high field strength of the IR field.

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