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Book of Abstracts

Editor: **Katalin Nagy-Póra**

September 9-11, 2020 │ Organized on-line

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Wednesday, September 9, 2020

(All times are in CET)

8.30	**Opening**	
	Chair: **E. Lindroth**	
9.00	**F. Martin** *Imaging electron molecular dynamics: towards attochemistry*	PT-01
9.40	**C. Vozzi** *Attosecond technologies for the study and control of electron dynamics in molecules*	PT-02
10.20	**F. Lépine** *Correlation effects in 2D molecules under XUV radiation: present and perspectives*	PT-03
11.00	**Coffee**	
	Chair: **Á. Vibók**	
11.30	**F. Calegari** *Realtime tracking of the electron dynamics in complex molecules*	PT-04
12.10	**L. Nagy** *Holograms of atoms and molecules obtained with photoelectrons induced by ultrashort laser pulses*	IT-01
12.40	**N. Dudovich** *Attosecond Interferometry*	IT-02
13.10	**M. Vacher** *How Nuclear Motion Affects Coherent Electron Dynamics in Molecules*	IT-03
13.40	**Lunch**	
	Chair: **I. Brezinova**	
15.10	**O. Smirnova** *Efficient chiral light matter interaction: challenges and opportunities*	PT-05
15.50	**T. Pfeifer** *The electronic response to attosecond excitations, and steering it with strong fields from the infrared to the extreme-ultraviolet*	PT-06
16.30	**L.B. Madsen** *Tunneling, many-electron polarization and nondipole dynamics*	IT-04
17.00	**Á. Vibók** *Few-Femtosecond Electron and Nuclear Dynamics in the Ozone: Theory and Experiment*	IT-05
17.30-19.30	**Poster Session**	

Thursday, September 10, 2020

(All times are in CET)

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9.40	**H.J. Wörner** *Attosecond Soft-X-ray spectroscopy in the gas and liquid phases*	PT-08
10.20	**J. Marangos** *Measuring chemical dynamics in the attosecond time domain*	PT-09
11.00	**Coffee**	
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11.30	**A. Brown** *The R-matrix with time (RMT) project*	IT-06
12.00	**M. Lucchini** *Few-fs Harmonic Radiation for Molecular Spectroscopy*	IT-07
12.30	**M. Ruberti** *Quantum electronic coherences emerging from molecular attosecond ionization: a B-spline RCS-ADC study.*	IT-08
13.00	**A. Bende** *Laser-Induced Molecule Excitations Using Real-Time, Time-Dependent Density Functional Theory*	IT-09
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	Chair: **L. Cattaneo**	
15.10	**F. Remacle** *Ultrafast vibronic and photoelectron dynamics in molecules photoexcited by short femtosecond pulses*	PT-10
15.50	**C. Janáky** *Ultrafast Dynamics in Semiconductors: Materials Aspects and Method Development*	IT-10
16.20	**K. Amini** *Laser-Induced Electron Diffraction Molecular Imaging*	IT-11
16.50	**J. Küpper** *Strong-field-ionization and rescattering in the molecular frame*	IT-12
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(All times are in CET)

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10.20	**N. Rohringer** *Stimulated x-ray emission and inelastic x-ray scattering at XFELs*			PT-13
11.00	**Coffee**			
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12.00	**A. Falamas** *Investigations of the Energy Transfer in the Phycobilisome Antenna of Arthrospira Plantesis Using Time Resolved Absorption and Fluorescence Spectroscopy*	WG1-02	**A. Ponzi** *Gas-phase molecules through the lens of photoelectron spectroscopy*	WG2-02
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13.00	**T. Metzger** *High-Power Ultrafast Industrial Thin-Disk Lasers*	WG1-04	**F. Marchesin** *ASAP: Atomistic Simulation Advanced Platform*	WG2-04
13.30	**Lunch**			
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15.10	**O. Kornilov** *Relaxation at complex resonances studied by wavelength-selected XUV pulses*	WG1-05	**J.E. Sienkiewicz** *Dynamics of rotational predissociation of KLi*	WG2-05
15.40	**S. Biswas** *Probing influence of molecular environment and dynamic polarization in photoemission delays*	WG1-06	**S. Coriani** *Coupled cluster methods for local and ultrafast spectroscopies*	WG2-06
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P-02 **A. Autuori**, G. Gallician, D. Platzer, M. Dalui, M. Lejman, L. Bosse, D. Bresteau, F. Lepetit, JF Hergott, O. Tcherbakoff, L. Poisson and P. Salières
Helium resonant photoemission resolved in time and space

P-03 X. Liu, K. Amini, T. Steinle, A. Sanchez, B. Belsa, J. Steinmetzer, A.T. Le, R. Moshammer, T. Pfeifer, J. Ullrich, C.D. Lin, S. Gräfe, J. Biegert
Fourier Transform Laser Induced-Electron Diffraction (FT LIED) Imaging Of An Isolated H_2O^+ Molecule

P-04 **J. Benda**, Z. Masin, J. D. Gorfinkiel
Time-dependent and time-independent calculations of multi-photon above-threshold ionization of molecules using the R-matrix method

P-05 **M. Bertolino**, D. Busto, F. Zapata, J. M. Dahlström
Propensity rules and interference effects in laser-assisted photoionization of helium and neon atoms

P-06 **J. Blaško**, J. Országh, B. Stachová, Š. Matejčík
Electron induced fluorescence of the H_2 molecule

P-07 S. Donsa, N. Douguet, J.Burgdörfer, I. Brezinova, L. Argenti
Circular Holographic Ionization-Phase (CHIP) Meter

P-08 **Sebastián Carrasco** and Ignacio R. Sola
Anti-alignment Dynamics in Strong Fields: The Whole Picture

P-09 **L. Colaizzi**, L. Ban, A. Trabattoni, V. Wanie, K. Saraswathula, E. P. Månsson, P. Rupp, Q. Liu, L. Seiffert, E. A. Herzig, A. Cartella, B. L. Yoder, F. Légaré, M. F. Kling, T. Fennel, R. Signorell and F. Calegari
Photoelectron spectroscopy of large water clusters ionized by an XUV comb

P-10 **A. Csehi**, G.J. Halász, Á. Vibók, M. Kowalewski
Quantum control with quantum light of molecular nonadiabaticity

P-11 M. Sapunar, T. Piteša, D. Davidović, N. Došlić
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P-12 **N. V. Golubev**, T. Begušić, and J. Vaníček
On-the-fly ab initio semiclassical evaluation of electronic coherences in polyatomic molecules

P-13 **C. E. M. Gonçalves**, A. Valentini, S. van den Wildenberg and F. Remacle
Ultrafast Dynamics of the CH_4 Cation Relaxation Upon Sudden Ionization

P-14 **M. Hrast**, A. Mihelič, K. Bučar and M. Žitnik
Auger decay of the 2p vacancy in chlorine

P-15 **Patryk Jasik**, Tymon Kilich, Jan Kozicki, Józef E. Sienkiewicz
Deperturbation analysis of the polar alkali diatomic molecules spectra

P-16 **Gellért Zsolt Kiss**, Sándor Borbély, Attila Tóth, Ladislau Nagy
XUV Field Induced Photoelectron Holography in Diatomic Molecules

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The impact of electron-electron correlation in ultrafast attosecond single ionization dynamics

Imaging electron molecular dynamics: towards attochemistry

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Sudden excitation or ionization of a molecule by visible, UV or XUV light is usually followed by charge redistribution on a time scale ranging from hundreds attoseconds to a few-femtoseconds, which is usually followed by fragmentation of the remaining molecular cation up to a few picoseconds. Such complex dynamics arises from the coherent superposition of electronic states covered by the broadband pulse and from rearrangements in the electronic structure of the molecular cation due to electron correlation. To investigate these ultrafast processes, attosecond pump-probe and transient absorption spectroscopies have been shown to be very valuable tools [1-9]. In this talk I will present the results of molecular pump-probe experiments and theoretical simulations in which several molecules, from the simplest H_2 one to the aminoacid tryptophan, are ionized and subsequently probed in order to obtain the complete molecular movie. The results of these pioneering works will certainly serve as a guide of future experimental efforts in more complicated molecules and may open the door to the control of charge transfer [10]. These efforts should be accompanied by the development of new theoretical methods able to accurately describe the ionization continuum of molecules [11].

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Attosecond technologies for the study and control of electron dynamics in molecules

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Attosecond science studies the motion of electrons on the atomic and molecular scale, which typically occurs on the timescale of attoseconds. Since its advent in 2001 [1,2], this field of research has captured the attention of the scientific community with its promise of deepening our understanding of fundamental processes occurring in atoms and molecules. The generation of attosecond pulses relies on the high-order harmonic generation (HHG) process. High-order harmonics are generated when an intense laser pulse is focused on a gas medium: due to the strong nonlinear interaction, very high odd harmonics of the driving pulse optical frequency can be generated [3]. This strong non-linear interaction leads to the production of a train of light bursts with attosecond duration in the XUV spectral region. Such bursts are separated by half of the period of the driving electric field. Thus, for probing electron dynamics, it is often necessary to isolate a single burst within the train that can then be synchronized with another optical pulse. This corresponds to isolating a single emission event for each driving pulse in the HHG process. Since the maximum photon energy in the harmonic spectrum - and the spectral bandwidth of the attosecond pulse - increases as the square of the driving field wavelength, longer driving wavelengths extend the HHG cutoff and allow the generation of isolated attosecond pulses up to the water window (300 - 500 eV) and beyond. State of the art isolated attosecond pulses are as short as 50 as and extends in the soft X up to the water window [4,5]. These pulses provide access to electron dynamics, the fundamental step of atomic physics and molecular chemistry.

Recently, several exciting new routes have been explored in attosecond science. For instance, the manipulation of HHG polarization and the generation of circularly polarized harmonics now allows the study of chiral molecules [6, 7]. Furthermore, attosecond pulse trains and isolated attosecond pulses enabled transient absorption and reflection measurements with extreme temporal resolution. All these advances in attosecond science would not have been possible without a number of cutting edge technological developments in the driving laser sources and the approaches for the generation and detection of HHG and isolated attosecond pulses. In this speech, I will show a general overview of these recent achievements and I will present some original results on the efficient high-order harmonic generation in hollow-core waveguides fabricated in fused-silica chips by femtosecond laser micromachining.

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Correlation effects in 2D molecules under XUV radiation: present and perspectives

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Ultrashort XUV pulses have allowed reaching ultimate precision in time-resolved experiments, down to the attosecond regime. While major progresses have been made in the study of atoms and small molecules, larger systems remain to be addressed in order to explore the connection between attosecond physics and chemistry or biology. Here we show that current ultrafast XUV technology allows to demonstrate general properties in XUV excited large systems.

We show that model 2D carbon based molecular structures can serve to decipher the role played by electron correlation and breakdown of the Born-Oppenheimer approximation. XUV-IR time-resolved VMI experiments have revealed how these interactions act on ultrafast timescale [1] and how they can be tracked down to the attosecond timescale. Reaching large sizes, XUV induced dynamics can be understood in terms of dynamics in "correlation bands", features that are intrinsic to many-electron systems [2].

We will also discuss perspectives in the case of large (bio)-molecular species at the heart of the ATTOCHEM CostAction for which new tools have to be developed.

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Realtime tracking of the electron dynamics in complex molecules

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Attosecond science is nowadays a well-established research field, which offers formidable tools for the realtime investigation of electronic processes [1]. In this context, we have recently demonstrated that attosecond pulses can initiate charge migration in aromatic amino-acids [2]. Still, there is a long path towards attochemistry and the full control of the molecule via electronic coherences.

Here, I will give a few examples on how attosecond/few-femtosecond technology can be used to observe purely electronic processes initiated in complex targets. At first, I will present a time-resolved study of the photo-fragmentation of adenine. Our most intriguing observation is that a stable dication of the parent molecule can be produced if the probing NIR pulse is briefly delayed from the XUV pulse. Our findings indicate that this time is required for a shake-up process to occur. After shake-up, a second electron can be ionized and the molecule is ultimately stabilized.

I will then show the results obtained in the C60 molecule. Here we have investigated delays in photoemission after exciting the Giant surface Plasmonic Resonance (GPR) around 20 eV. Clear signatures of the collective electron dynamics initiated by the IR pulse and the XUV pulse can be extracted from the experimental data.

Finally, I will present a novel setup combining sub-2fs UV pulses with few-fs IR and attosecond XUV pulses. We recently have combined linearly polarized UV pulses with circularly polarized IR pulses to perform time-resolved Photo Electron Circular Dichroism (PECD) in Methyl-lactate and Ethyl-lactate. Our study shows an ultrafast dynamical inversion of the PECD which we assigned to the competition between the chiral response of different electronic states excited by the broadband UV pulse.

References

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Efficient chiral light matter interaction: challenges and opportunities

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Chirality plays a key role in physics, chemistry and biology. In the molecular world, the non-superimposable mirror twins of the same chiral molecule – the left-handed and right handed enantiomers – have the same physical properties unless they interact with another chiral object. Distinguishing left- and right-handed molecular enantiomers is very challenging, especially on ultrafast time scale, with standard all-optical techniques leading to extremely weak chiral signals.

I will describe new, extremely efficient approaches to chiral discrimination, which take advantage of ultrafast electronic response [1,2] and do not require the interaction with magnetic field component of light. I will introduce the concepts of *chiral reagent*- and *chiral observer*-type measurements. The concepts help us to understand when and why chiral measurements can be done without chiral light. I will describe the new concept of synthetic chiral light [3], which can be used to trigger bright nonlinear optical response in the molecule of a desired handedness while keeping its mirror twin dark in the same frequency range. The simplicity of generating synthetic chiral light in a laboratory opens a broad field of shaping and controlling chiral matter with light.

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↑ Conference Program

The electronic response to attosecond excitations, and steering it with strong fields from the infrared to the extreme-ultraviolet

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When light interacts with atoms and molecules, electrons are the first to notice. Wiggling along with the electromagnetic fields, they are either excited (in coherent superposition with the ground state) or ionized. This electronic motional response acts back on the light field by emitting additional waves that typically interferes destructively with the incoming light, causing absorption. The electronic response thus gives rise to the characteristic absorption spectrum, the well-known fingerprint of atomic or molecular structure.

Using intensity-tunable laser fields in our labs and at free-electron lasers (FELs), we measure and modify this fundamental electronic response of atoms and molecules. We learned to understand and interpret the transformation of the spectrum of atoms in progressively intense laser fields, either acting immediately after excitation [1,2], at certain time delays [3,4,5], or even reconstructing the complete strong-field driven dynamical response function [6].

These findings on the coherent control of atoms are general and shown to apply from small atomic to complex molecular systems, ranging from isolated gas-phase particles up to and including large molecules in solution [7].

Most recently, we demonstrated resonant bound-state manipulation of matter with intense extreme ultraviolet (XUV) light at a SASE FEL (FLASH@DESY), opening a route towards site-selective quantum control [8,9].

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Angle-resolved photoionization dynamics in simple molecules: the case of H₂, CO and N₂O

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We discuss angle-resolved attosecond ionization delays for three different small molecules: H_2 [1], CO [2] and N_2O, following the benchmark results in atoms [3, 4]. We measured attosecond ionization time delays with coincidence detection in 2015 [5] and angular dependence in 2016 [3], each for the first time, and showed that a more complex continuum can strongly affect results even in atoms [4, 6, 7]. All these investigations have been carried out exploiting the XUV pump/IR probe RABBITT interferometric technique combined with coincidence detection using a COLTRIMS apparatus [8]. Molecules with lighter atoms, H_2, show that the electron and nuclear motions significantly affect each other even in the attosecond regime [1] and electron localization at the instant of birth into the CO continuum follows from experimental measurements alone [2]. In addition, we will discuss ionization dynamics from N_2O molecules with a complete time and angular resolved characterization of the shape resonance.
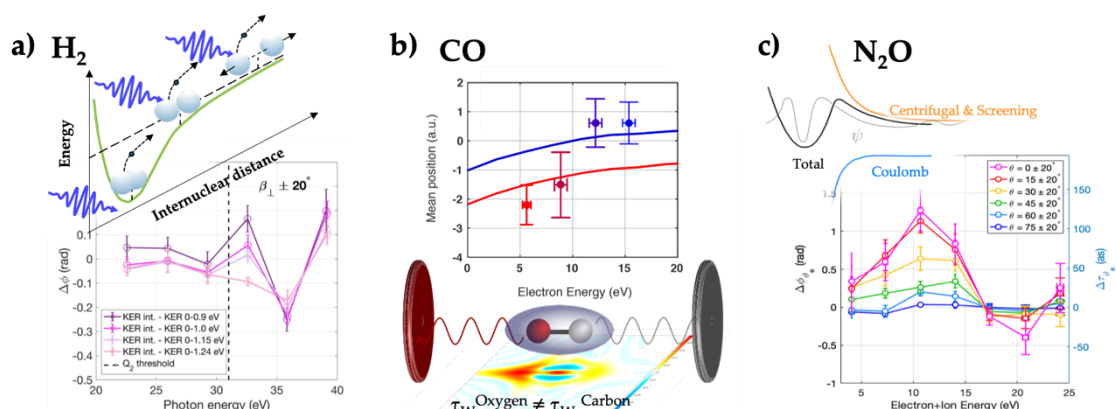
Figure 1: a) Sketch of the photodissociation process in H_2 and measured photoelectron phases as a function of photon energy; b) mean position of the electron localization at the instant of birth into the continuum of CO as a function of the electron kinetic energy; c) Angular resolved analysis of photoemitted electrons in N_2O as a function of the electron kinetic energy.

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Attosecond soft-X-ray spectroscopy
in the gas and liquid phases

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Attosecond time-resolved spectroscopy has the potential to address fundamental open questions in chemical sciences. Although the first two decades of research have led to very important advances towards this goal, the techniques of attosecond spectroscopy still need to overcome two gaps. The first gap is the complexity gap, i.e. the challenge of applying attosecond spectroscopy to complex molecules. A promising approach to overcome the complexity gap consists in exploiting the element-, site- and spin-sensitivity of X-ray spectroscopy. We have recently demonstrated the potential of table-top X-ray absorption spectroscopy with a water-window high-harmonic source, observing the temporal evolution of unoccupied molecular orbitals, as well as molecular shape resonances during chemical reactions [1]. Compressing the mid-infrared driving pulses to less than 2 optical cycles, we have demonstrated the extension of this table-top source to fully cover the oxygen K-edge with fluxes sufficient for time-resolved measurements [2]. Using the same technique, we have also demonstrated the generation of isolated attosecond pulses, which have established a new record of the shortest light pulses ever measured (43 attoseconds) [3].

The second gap is the extension from the gas to the liquid phase, which is the relevant phase to the vast majority of chemical and biophysical processes. I will discuss the first realization of time-resolved X-ray absorption spectroscopy in the liquid phase using a high-harmonic source [4]. Electronic and structural dynamics in liquid alcohols initiated by strong-field ionization have been studied by X-ray absorption spectroscopy at the carbon and oxygen K-edges. The appearance of ionization-induced absorption bands was observed to take place on a time scale significantly slower than the experimental cross correlation, revealing the occurrence of proton-transfer dynamics in the ionized alcohols. Finally, I will present the first extension of attosecond time-resolved photoelectron spectroscopy from molecules [5] to liquids [6], reporting on photoemission delays of liquid compared to gaseous water. The measured time delays range from 50-70 attoseconds and are shown to mainly originate from the solvation of water molecules, with liquid-phase electron scattering playing a minor role. These combined developments set the stage for attosecond time-resolved studies of molecular systems of chemical complexity.

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Measuring chemical dynamics in the attosecond time-domain

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In this presentation we will overview recent advances in the measurement of attosecond processes. This will cover the developments arising from HHG sources, especially the generation isolated sub-femtosecond pulses into the soft X-ray ranges [1]. These sources are opening up attosecond timescale X-ray spectroscopy of photoexcitation driven processes in the condensed phase as well as the gas. We will also discuss the recently demonstrated X-ray FEL based attosecond capability for producing high brightness single and two-colour attosecond pulses [2]. The exceptional brightness of these new sources (see figure) is opening up the possibility not only for a new generation of incisive attosecond pump-probe measurements but also for the development of non-linear X-ray spectroscopies. These new methods could allow the electronic couplings between locations in a material to be uncovered with unprecedented sensitivity and time resolution.
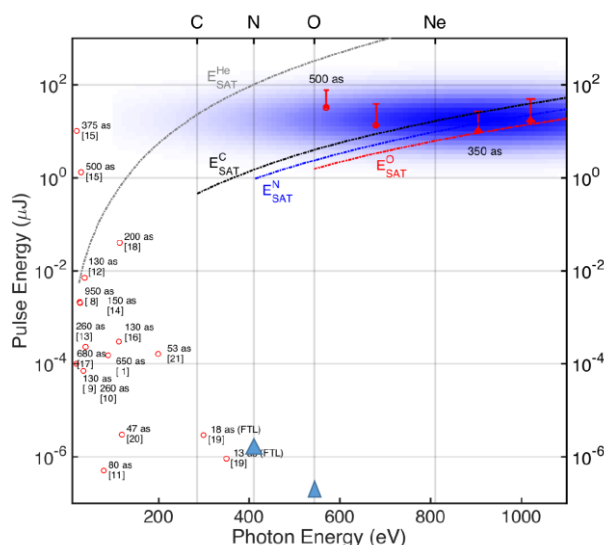
Figure. Recent results (Duris et al) showing eSASE can produce attosecond pulses of $> 10^8$ times higher brightness than HHG sources in the soft X-ray range

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↑ Conference Program

Ultrafast vibronic and photoelectron dynamics in molecules photoexcited by short femtosecond pulses

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Few-cycle short IR or UV pulses allow excitation of coherently coupled electronic states towards steering nuclear motions in molecules. The progress of the non stationary vibronic density towards the products can be monitored using a second pulse, by transient absorption spectroscopy or photoionization. The Hamiltonian used includes the pump and probe pulses which provides a quantum mechanical description of both multiphoton excitation and ionization. For pumping the LiH molecule, the dynamics is driven by a few cycle IR pulse with a controlled phase between its envelope and carrier wave. The interplay between photoexcitation and photoionization in shaping the ensuing coupled electronic-nuclear dynamics in both the neutral excited electronic states and the cationic states is followed by solving the time-dependent Schrodinger equation at nuclear grid points using the partitioning technique. We show that the coherent dynamics in the neutral subspace is strongly affected by the amplitude exchanges with the ionization continua during the pulse, as well as by the onset of nuclear motion which drives non adiabatic interactions in the Franck-Condon region and on the way to the reaction products. If time permits, I will then discuss how short UV pulses can be used to steer the photoisomerization of the norbornadiene molecule to quadricyclane.

Opto-Optical Modulation
of Extreme Ultraviolet Light Pulses

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There is a profound, almost symbiotic, relation between electrons and photons. When light, i.e., photons, interacts with matter the electrons in the material will start to move and oscillate. When a charged particle, such as an electron, oscillates it will act as a dipole and emit light. We propose to utilize this symbiotic relation and extend the control of light and matter to the extreme ultraviolet (XUV) region using the newly developed XUV opto-optical modulator.

To control light with short wavelengths is challenging since the tools available for visible light do not work. We present a technique to control the phase of light that works also in the XUV wavelength region. We do it using the recently demonstrated opto-optical modulator, a method for controlling the direction, duration and timing of XUV pulses using infrared (IR) control pulses [1-3]. Coherent XUV light is used to promote an ensemble of atoms to a superposition of the ground state and a series of excited states and the IR pulse is used to control the phase of the light emitted by the excited atoms. The technique can be used to steer or split XUV pulses, but it can also be used to probe both the phase and amplitude of excited states in atoms or molecules.
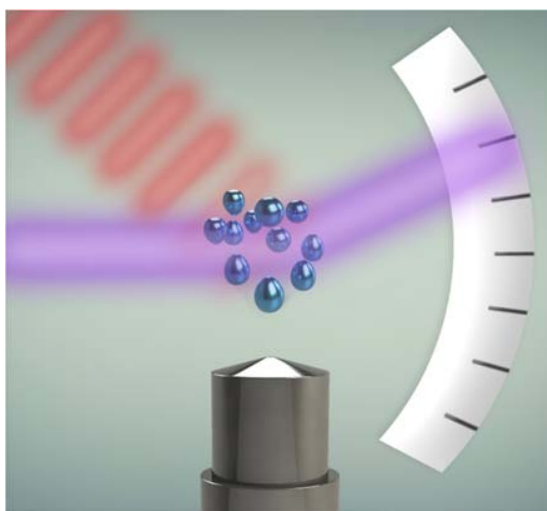
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Attosecond metrology at Free Electron Lasers

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Recently the generation of trains [1] and isolated[2] attosecond pulses was demonstrated at Free Electron Lasers (FELs) operating in the extreme ultraviolet (XUV) and soft X-ray spectral range. FEL-driven attosecond sources present important advantages with respect to table-top attosecond sources based on high-order harmonic generation, including high-energies per pulse (typically in the microjoule range), tunability of the photon energy and shaping capability (in the case of train of attosecond pulses). On the other hand, these sources present significant drawbacks such as temporal jitter between the XUV waveform and the optical/infrared laser and low-repetition rates. In this talk we will review the techniques recently used for the temporal characterization of attosecond pulses at LCLS [3] and FERMI [4]. In particular, we will show how the control of the relative phase between the harmonics achieved at FERMI [5] gives access to its characterization, by implementing a correlation-based analysis of the photoelectron spectra generated by the combination of the attosecond and infrared pulses. We will also present a novel approach based on correlation-analysis for extending attosecond metrology to FELs-based attosecond sources.

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Stimulated x-ray emission and inelastic x-ray scattering at XFELs

Nina Rohringer

With the invention of x-ray free-electron lasers (XFELs), studies of light-induced chemical reaction dynamics by time-resolved x-ray spectroscopy reach a new era. Despite the high brilliance of XFELs, it remains challenging to capture high-resolution x-ray emission spectra under exposure of a single XFEL pulse, which however is advantageous for comprehensive pump-probe studies with these highly fluctuating sources. In the soft x-ray range, coherent amplification of spontaneous x-ray emission [1] and stimulated resonant inelastic x-ray scattering (SRIXS) [2] have been demonstrated in atomic gases, with amplification levels of up to eight orders of magnitude. A next crucial step for advancing time resolved spectroscopy is the transfer of stimulated emission and SRIXS to the hard x-ray domain that would allow single-shot spectroscopy in chemically and biologically relevant samples in the liquid phase. Recently, amplified spontaneous K-α emission was demonstrated in solid copper [3]. Here, we present results of amplified spontaneous K-α emission in Manganese salts in aqueous solutions [4] with highly focused XFEL beams. Coherent amplification of the Mn K-α emission by four orders of magnitude and saturation of the signal has been demonstrated in $MnCl_2$ one-molar solution. More excitingly, the chemical shifts of $MnCl_2$ and $KMnO_4$ aqueous solution is maintained in the strongly spectrally sharpened stimulated K-α emission spectra and coherent amplification has been shown at lower concentration. A more comprehensive technique for the study of chemical structure is SRIXS. Although demonstrated in Neon [2], the realisation of SRIXS in molecular targets is more difficult to achieve, even in the soft x-ray range [5-7], due to a smaller stimulated gain-cross section, that is distributed over many electronic, vibrational and rotational channels. We present two experimental studies, based on different two-colour XFEL schemes, that were specifically developed to achieve vibrationally resolved SRIXS in CO. In a first attempt [5], the XFEL was operated in a two-colour self-amplified spontaneous emission (SASE) scheme, with one frequency band tuned to the Oxygen π^* resonance, and the other band overlapping with the Stokes-shifted emission frequencies. According to our theory [6], this setting should result in high-resolution SRIXS spectra by covariance analysis. Experimentally, the spectra are, however, contaminated by strong absorption features of molecular ions generated in competing processes. In a second experiment [7], the SASE pump pulse was replaced with a self-seeded, narrow-band pulse at considerably lower pulse energy that resulted in a significant decrease of the background. A comparison with theory shows that the experimental conditions were at the onset of an observable SRIXS signal, but so far, no statistical evidence is seen, to confidently report the demonstration of SXRIS in a molecular target. We however developed an experimental protocol that allows for the detection of relatively small SRIXS signals with highly fluctuating XFEL spectra. The challenges and the necessary experimental parameters to ultimately reach the conditions for stimulated x-ray emission spectroscopy in chemically relevant targets will be critically assessed.

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↑ Conference Program

Holograms of atoms and molecules obtained with photoelectrons induced by ultrashort laser pulses

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If a laser pulse ionizes an atom or molecule, the ejected electron may be rescattered by the target, and this signal electron wave in combination with the direct wave results in a hologram observable in momentum space [1]. We have studied theoretically the formation of this hologram for the hydrogen atom [2] and noble gases [3] solving the one-electron time-dependent Schrödinger equation numerically. The ionization energy and the shape of the potential created by the residual ion determine the pattern of the hologram (Figure 1). Now we have extended our studies by investigating the formation of the hologram for the H_2^+ target. The obtained hologram is strongly influenced by the scattering potential of the molecular target, but the characteristics of a two-center interference are barely observable.
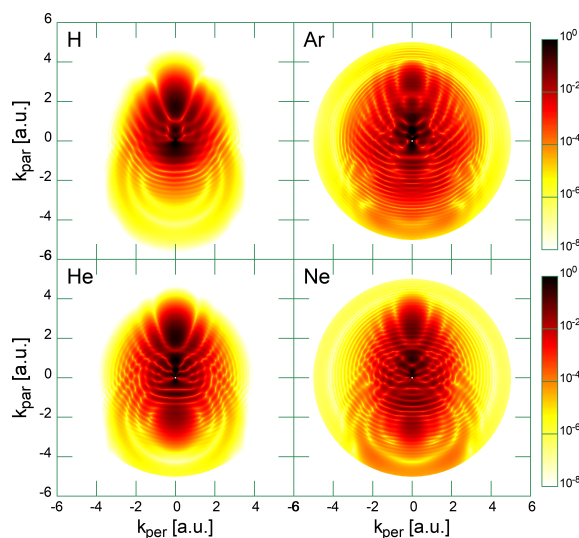
Figure 1: Ionization probability density as a function of electron momentum components parallel and perpendicular to the laser polarization axis for H, He, Ne, and Ar targets. The atoms are ionized by a two-cycle laser pulse with $\omega = 0.4445$ a.u., $E_0 = 1$ a.u. and $\tau = 28.26$ a.u.

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↑ Conference Program

Attosecond Interferometry

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One of the most important aspect of attosecond spectroscopy lies in its coherent nature. Resolving the internal coherence is a primary challenge in this field, serving as a key step in our ability to reconstruct the internal dynamics. As in many other branches in physics, coherence is resolved via interferometry. In my talk, I will describe advanced schemes for attosecond interferometry. The application of these schemes provides direct insights into a range of fundamental phenomena in nature, from tunneling and photoionization in atomic systems to ultrafast currents in solid state systems.

How Nuclear Motion Affects Coherent Electron Dynamics in Molecules

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Excitation or ionisation of a molecule with attosecond pulses leads to the coherent population of several electronic states, called an *electronic wavepacket*. The interference between electronic states in such a superposition, alternating between constructive and destructive, leads to oscillating motion of the electron cloud. This purely quantum process relies on the coherence of the electronic wavepacket. A fundamental challenge has been to understand to what extent the electronic wavepacket retains its coherence, i.e., how long the oscillations in the electron cloud survive, in the presence of interactions with the nuclei of the molecule. To address this question, we have developed semi-classical and quantum mechanical methods to simulate the dynamics upon ionisation of polyatomic molecules. The presentation contains an overview of the theoretical methods [1, 2] we have used and some applications [3, 4, 5] illustrating new important physical insights about the predicted decoherence process.

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↑ Conference Program

Tunneling, many-electron polarization and nondipole dynamics

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Strong-field and attosecond physics and chemistry has witnessed tremendous progress the last couple of decades. There are, however, a number of fundamental theoretical and computational challenges that remain. To name a few, the exponential scaling of the size of the computational problem with number of electrons and orbitals, often referred to as the curse of dimensionality, impedes the direct numerical solution of the time-dependent Schrödinger equation. Likewise, high-intensity and high- and low-frequency regimes, which are now accessible experimentally, implies entering dynamical regimes, where the application of the electric dipole approximation and possibly also the use of non-relativistic quantum mechanics can be questioned.

In this talk, I will discuss recent progress addressing certain aspects of the challenges mentioned above related to many-electron dynamics and nondipole effects. First, I will briefly outline a formulation and numerical implementation of tunneling theory for large molecules. Next, I will discuss how multielectron polarization effects simplify the response of a many-electron system facilitating the formulation of effective single-active-electron models. Finally, I will discuss an approximate nondipole approach, which accounts for nondipole effects in an accurate and effective manner.

Few-Femtosecond Electron and Nuclear Dynamics in the Ozone: Theory and Experiment

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In the last few years we reported a series of numerical simulations proving that it is possible to create an electronic wave packet and subsequent electronic motion in a neutral molecule photoexcited by a UV pump pulse within a few femtoseconds [1, 2, 3, 4, 5]. The ozone molecule has been served as sample system. By using extreme ultraviolet probe pulse the splitting of the excited B state nuclear wavepacket were followed into a path leading to molecular fragmentation and an oscillating path, revolving around the Franck-Condon point with 22-fs wave packet revival time [2]. Recent experiment was strongly corroborated with our full quantum-mechanical ab initio simulations [6].

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↑ Conference Program

The R-matrix with time (RMT) project

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In the last several years experimental techniques have become sufficiently advanced to probe the strong-field-driven dynamics of correlated electrons in atomic and molecular systems. Theoretical approaches to describe these processes can fall short when the quantum effects under inspection defy the classical, three-step paradigm, and this presents a uniquely challenging prospect for computational modelling. It has long been held that a solution of the Time-Dependent Schrödinger Equation (TDSE) is impossible for all but the simplest target systems, and thus massively simplified approaches– invoking a single-active electron model, for instance– have dominated.

However by making use of the R-matrix approach, and building capability hierarchically on more than half-a-century-worth of atomic, molecular and optical physics software, we have developed the R-matrix with time-dependence (RMT) code explicitly for the solution of the TDSE for general multielectron atomic and molecular systems driven by strong fields [1].

In this talk I will report on the new scientific insights that RMT provides. To demonstrate new capability to describe arbitrarily polarised laser pulses, I will show results of research into electron vortices and the attoclock scheme [2]. Furthermore, by expanding the methodology to account explicitly for spin[3], we can show new schemes to address spin-polarised electrons and polarisation in high-harmonic generation. Finally, RMT can now desribe electronic dynamics in molecular systems. I will discuss some initial applications of RMT to molecular photoionisation, outline the boundaries of our current capability and our vision for future developments.
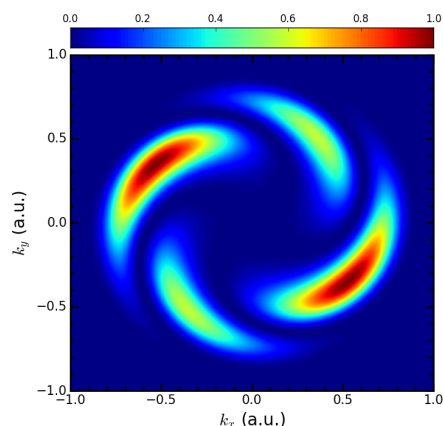
Figure 1: Photoelectron momentum distribution in the polarization plane, following ionization of He by time-delayed, counter-rotating circularly polarized, 15 eV laser pulses.

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↑ Conference Program

Few-fs Harmonic Radiation for Molecular Spectroscopy

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High-order harmonic generation is primarily used as a source of attosecond pulses by exploiting the whole radiation spectrum. A single harmonic (SH) is instead a source of few-femtosecond tunable pulses in the extreme-ultraviolet (XUV) spectral region, hence relevant for many applications where a proper degree of energy resolution is preferred over an extreme temporal resolution [1]. In molecular spectroscopy, for example, several electronic states can be simultaneously excited by a broadband attosecond pulse, thus rendering the interpretation of the experimental results a formidable task. SHs can therefore be used to study few-femtosecond relaxation dynamics with relatively high spectral selectivity, complementing standard attosecond techniques.
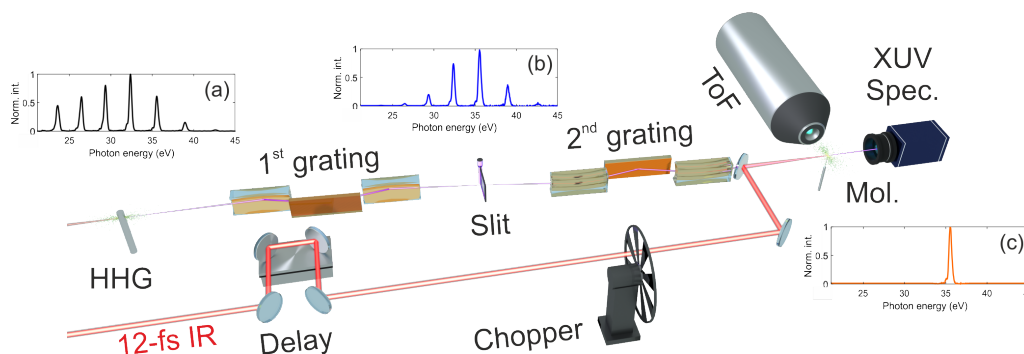
Figure 1: Schematic of the TDCM used for the selection of HHs. **(a)**-**(c)**, harmonic spectrum after generation, after the first grating (open slit) and the second grating (closed slit), respectively.

Here we report on the generation and full characterization of sub-10-fs XUV pulses, obtained with a time-delay compensated monochromator [2] (TDCM, Fig. 1). Furthermore, we demonstrate the potential of SH radiation in combination with few-fs infrared pulses for photoion and photoelectron time-resolved spectroscopy. The former has been used to investigate ultrafast relaxation processes in ethylene cation. The latter was employed to study ultrafast vibrational and nuclear dynamics in carbon dioxide super-excited states.

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Quantum electronic coherences emerging from molecular attosecond ionization: a B-spline RCS-ADC study.

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Here I present a new *ab initio* method for many-electron dynamics in polyatomic molecules, time-dependent B-spline Restricted Correlation Space-Algebraic Diagrammatic Construction (RCS-ADC) [1,2]. RCS-ADC describes molecular ionization from first principles by combining the accurate description of electron correlation of quantum chemistry with the full account of the continuum dynamics of the photoelectron. This method is based on the separation of the orbital space into correlation and ionization spaces and naturally bridges between the multi-configurational *ab initio* techniques and closed-coupling schemes based on the limited number of essential ionic states, combining the key advantages of both.

In this work, I present a study of the correlated many-electron dynamics upon attosecond ionization of pyrazine (Fig.1). In particular, I characterize the atto-ionized many-electron state
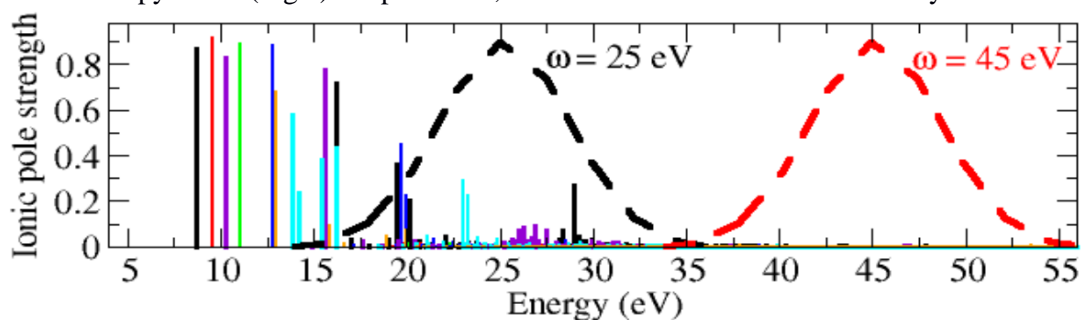
Figure 1: Electronic spectrum of ionized Pyrazine

by calculating the ionic reduced density matrix (R-IDM) of the bipartite ion-photoelectron system with full inclusion of the correlated shakeup states, its Schmidt decomposition and the von Neumann entropy of the prepared entangled state and investigating the effect of the ion–photoelectron interaction on the onset of the quantum electronic coherences during the laser-induced dynamics. Finally, I present an *ab initio* time-resolved study of X-ray attosecond transient absorption spectroscopy (ATAS) in pyrazine and discuss the possibility to retrieve, within a UV/X-ray pump-probe setup, the many-electron quantum ionic coherences which arise in attosecond photoionization and pre-determine the subsequent charge-directed photo-chemical reactivity. The simulation of the X-ray attosecond transient absorption measurement is performed by solving the von Neumann equations for a series of characterized R-IDM interacting with the X-ray probe field, and allows one to unveil the mapping of the measurement results onto the non-zero R-IDM matrix elements.

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Laser-Induced Molecule Excitations Using Real-Time, Time-Dependent Density Functional Theory

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The fully propagated real time-dependent density functional theory (RT-TDDFT) method for describing the laser-induced electron excitation and charge fluctuation is presented. The briefly presentation of the theoretical background together with different numerical solutions used for the efficient propagation of the electron density in real time is followed by a discussion of several real-case applications, including the computation of the full electronic absorption spectrum, resonant and charge-transfer-type excitations, as well as the dynamics of different orbital populations in real time [1,2]. In the next step, the implementation of the RT-TDDFT method in different quantum chemistry codes is discussed. The roles of the different laser field parameters as: direction, strength, wavelength, or pulse shape needed in order to get efficient and selective excitation behaviors for a specific molecular system are also presented. Finally, some remarks about the advantage and disadvantage of RT-TDDFT as well as about the possible further developments are given.

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↑ Conference Program

Ultrafast Dynamics in Semiconductors: Materials Aspects and Method Development

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Various photoinduced processes in semiconductors occur at distinctly different timescales. Ultrafast laser spectroscopy has been long the tool for examining mechanistic aspects of light induced processes in semiconductors as well as at semiconductor interfaces. Most of these studies, however, monitored the charge carrier dynamics under ex situ conditions. Since charging effects occur in both photovoltaic and photoelectrochemical devices, these ex situ tests have limited relevance to practical applications.

In the first part of my talk, I will present a method to study charge dynamics under conditions where charging effects can be simulated. I will show how pump-probe experiments under in situ electrochemical control can provide better understanding of the factors which influence efficiency of such materials in solar energy applications.[1,2]

In the second part of my talk, I will show how we have succeeded in probing the influence of electrochemical bias on the charge carrier recombination process in $CsPbBr_3$ films deposited on a mesoscopic TiO_2 film. The transient absorption spectroscopy experiments conducted at different applied potentials indicate a decrease in the charge carrier lifetimes of $CsPbBr_3$ as we increase the potential from -0.6 V to + 0.6 V vs. Ag/AgCl. The charge carrier lifetime increased upon reversing the applied bias, thus indicating the reversibility of the photoresponse to charging effects. The ultrafast spectroelectrochemical experiments described here offer a convenient approach to probe the electron injection process from the excited perovskite film to the ETL and thus allow a convenient evaluation tool for different perovskite/ETL pairs.[3]

As an outlook I will discuss that most of the work so far has focused on relatively long timescales, where charge trapping and recombination occur. Much less is known about the photo-excitation process itself, carrier cooling and the fate of hot carriers, which can be studied at shorter timescales. Our efforts in this direction will be presented.

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Laser-Induced Electron Diffraction Molecular Imaging

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Chemical reactivity is governed by the location and interaction of electrons and nuclei within atoms and molecules. Pinpointing the location of atoms that typically have an atomic radius of ~0.5 Ångstrom (Å; 1 Å = 10^{-10} m) is crucial in determining bond lengths in molecules which typically span 1-3 Å. Moreover, tracking chemical reactions in real-time requires snapshots to be recorded on the nuclear (*i.e.* femtosecond, fs; 1 fs = 10^{-15} s) timescale. Mid-infrared laser-induced electron diffraction (MIR-LIED) [1,2,3,4,5] fulfills and goes beyond these requirements through its capability in directly retrieving static and transient molecular structures with sub-atomic picometre (pm; 1 pm = 10^{-12} m) and attosecond (as; 1 as = 10^{-18} s) spatio-temporal resolution by utilizing the molecule's own emitted electron following strong-field ionization [6], as illustrated in Figure 1. In this contribution, we demonstrate MIR-LIED's sub-atomic sensitivity in the deprotonation reaction of $[C_2H_2]^{2+}$ [3] and the field-induced Renner-Teller dynamics in CS_2 [4]. An outlook will be given of the MIR-LIED field including the generation of a full attosecond resolved "molecular movie" of a chemical reaction by two-pulse pump-probe measurements [1].
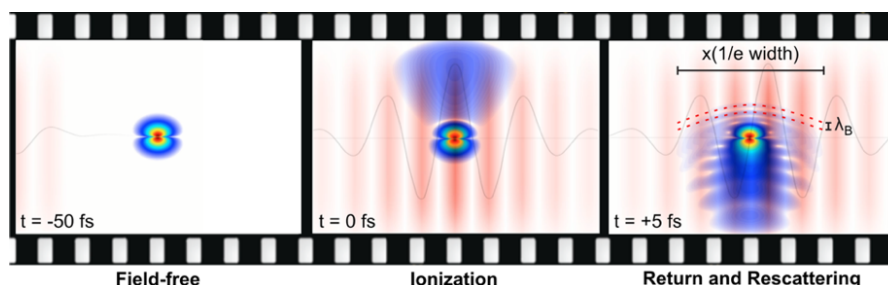
Figure 1: Quantum mechanical illustration of the laser-driven recollision process leading to MIR-LIED. An electron wave packet (EWP) from an argon *p* atomic orbital is emitted at the peak of a laser pulse (t = 0 fs) before returning and recolliding (t = +5 fs) with an EWP extent and de Broglie wavelength of *x* and λ_B, respectively.

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↑ Conference Program

Strong-field-ionization and rescattering in the molecular frame

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The interaction of strong laser fields with matter intrinsically provides powerful tools to image transient dynamics with an extremely high spatiotemporal resolution. We studied the strong-field ionization of laser-aligned OCS molecules [1] and show a full real-time picture of the photoelectron dynamics in the combined action of the laser field and the molecular interaction [2]. We demonstrate that the molecule has a dramatic impact on the overall strong-field dynamics: it sets the clock for the emission of electrons with a given rescattering kinetic energy. This result benchmarks the seminal statements of molecular-frame strong-field physics and has strong impact on the interpretation of atomic-resolution self-diffraction experiments [3, 4]. Furthermore, the resulting encoding of the time-energy relation in molecular-frame photoelectron momentum distributions shows the way of probing the molecular potential in real-time and accessing a deeper understanding of electron transport during strong-field interactions.

Furthermore, utilizing our strong control over complex molecules [5] and experimentally resolving intensity-averaging effects [6], we acquired photoelectron momentum distributions in the molecular frame for a well-defined, narrow range of incident intensities for the prototypical biomolecule indole (C_8H_7N) and its water cluster ($C_8H_7N–H_2O$). We disentangled these photoelectron momentum images with a novel, highly efficient semiclassical simulation setup based on the adiabatic tunneling theory and employing a quantum-chemically exact description of the cation during the subsequent continuum dynamics [7].

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↑ Conference Program

Methods to perform gas-phase X-ray spectroscopy of isolated complex systems: large (hydrated) biomolecules, clusters and functionalized nanoparticles

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The gas-phase spectroscopy of an isolated target offers several important advantages: 1) the incoming projectile (photon/electron/ion) is well defined (energy, direction, flux, charge); 2) the target is well-defined (chemical formula, structure, quantum state, temperature, charge); 3) the interaction products are well defined (photoelectrons, ionic fragments, scattered electrons, emitted photons etc.) and we can characterize them (by kinetic energies, mass over charge, frequency etc.) 4) the interaction conditions are well-defined. Therefore, we may learn about fundamental properties of both the target system itself (e.g. its physicochemical properties) and the interaction between the projectile and the target system. Also, we can more accurately compare with theory. However, it is not trivial to bring large complex systems in the gas phase and produce a target beam of a sufficient density in the interaction region to perform a spectrometric study. Some of these methods have been developed only recently.

In this talk we will present state-of-the-art experimental systems and methods that allow for performing a gas-phase X-ray spectroscopy of isolated complex systems. The later include large biomolecules such as peptides, proteins and DNA subunits, as well as such biomolecules hydrated well-defined water clusters [1,2], large biomolecular clusters [3] and nanoparticles [4]. Each of these systems possesses its specific properties that will be described in more details. Also, example results will be presented. Finally we will discuss some present limitations and perspectives for improvements.

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↑ Conference Program

Investigations of the Energy Transfer in the Phycobilisome Antenna of Arthrospira Plantesis Using Time Resolved Absorption and Fluorescence Spectroscopy

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The energy conversion efficiency of organic solar cells could be improved by the use of biomimetic devices inspired from light harvesting systems found in cyanobacteria [1]. Phycobilisomes (PBSs) may be such systems, which have adapted for a long time to collecting solar radiation and transferring it to the photosynthesis apparatus. We aim to understand the ultrafast excitation energy transfer in the PBS extracted from *A. plantesis* and its components and further use this insight for building biomimetic hybrid systems based on phycobiliproteins and nanoparticles optimized for solar energy collection and photo-current amplification. We present here the ultrafast dynamics [3] in a hemidiscoidal PBS containing phycocyanin (PC) and allophycocyanin (APC) phycobiliproteins. The samples were excited with ultrafast laser pulses of 170 fs duration and 80 kHz repetition frequency obtained using an optical parametric amplifier from the 1030 nm pulse emitted by an Yb:KGW laser (Pharos, Light Conversion).

Following the ultrafast laser excitation, the transient absorption signal showed the bleaching of the ground state and positive absorption changes at the wings of the bleaching band (Fig. 1). The equilibration of the excitation energy occurred with time constants of around 1 ps, 20 ps, 130 ps, and 1 ns. The result was confirmed by the time-correlated single photon counting experiments, which reflected the fluorescence emission of APC with a lifetime of 1.6-1.8 ns, as well as the energy transfer within the PBS complex which took place in 300 -600 ps.
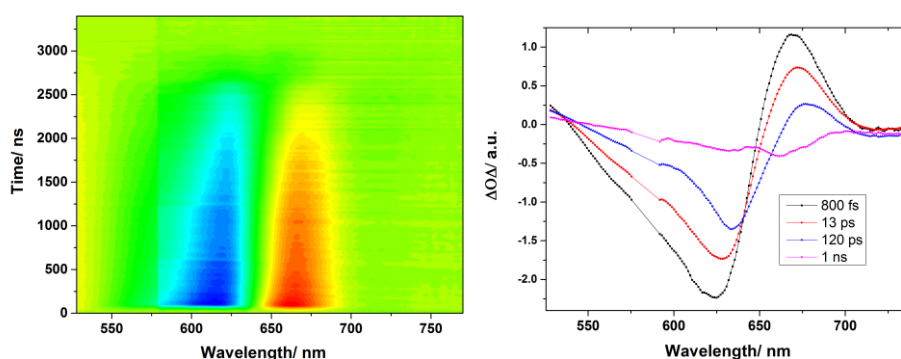
Figure 1: Transient absorption three-dimensional carpet characteristic to the PBS obtained following ultrafast excitation at 580 nm (left) and the obtained kinetic components (right)

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Probing Electronic Processes in Large Molecules

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Attosecond science is nowadays a well-established research field, which offers formidable tools for the real-time investigation of electronic processes. In this context, we have recently demonstrated that attosecond pulses can initiate charge migration in aromatic amino-acids [1,2]. This talk will give an overview of our ongoing investigation of electron dynamics in large molecules.

The first part of the presentation covers a combined experimental and theoretical study of molecular stabilization in the nucleobase adenine. Singly or doubly photoionized by an isolated XUV attosecond pulse (20–35 eV), adenine is most likely to break apart. We find that stable adenine^{2+} can be produced by sending a NIR pulse within a narrow time window, starting 2–3 fs after the XUV pulse and ending with a 24 fs exponential lifetime. We simulate the electronic dynamics (Green's function method, confirmed by a rate equation model) and identify the stabilization mechanism. The required delay of the NIR pulse can be assigned as the time taken to populate a particular molecular orbital (LUMO+6) through a shake-up–like transition.

Additionally, we will present our ongoing work on related topics: A beamline to generate few-femtosecond pulses in the UV (~5 eV) offers the ability to excite dynamics in neutral molecules, of greater relevance to chemical applications. A VMI & high-mass spectrometer with the option of electron–ion covariance analysis increases the amount of information that can be extracted from the photoreaction. The spectrometer was recently commissioned and employed for pump–probe experiments, from which preliminary results will be shown.

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↑ Conference Program

High-Power Ultrafast Industrial Thin-Disk Lasers

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The thin-disk laser technology was originally perfectioned by TRUMPF for high power industrial applications such as laser cutting and laser welding. More than 14 kW of average power can be obtained from a single thin-disk. Today thin-disk based ultrafast amplifiers are also commercially available. Using the same thin-disk technology, TRUMPF Scientific Lasers offers tailored robust ultrafast lasers. Sub-ps pulse durations, multi-mJ pulse energies at multi-kHz repetition rates and average powers beyond 1 kW can be achieved with near-diffraction-limited output beams [1-2].

With our regenerative CPA, consisting of two thin-disk laser heads, we achieved a maximum compressed pulse energy of >200 mJ at 5 kHz and close to 2 kW at 20 kHz. Applying spectral seed shaping led to compressed output pulse durations of <500 fs at 5 kHz. New developments with compact thin-disk based multipass amplifier cells demonstrated multikilowatt average output powers with good temporal and spatial properties [3]. Lately, TRUMPF Scientific Lasers has been developing a Joule-class thin-disk based multipass amplifier at 1 kHz [4].

A promising nonlinear compression concept at pulse energies of hundreds of millijoules is gas-filled Herriott cells [5]. Recently, researchers have demonstrated a >30-fold pulse compression from 1.3 ps to 41 fs with an output pulse energy of 18 mJ at 5 kHz [6]. TRUMPF Scientific Lasers has started the development of a nonlinear compression scheme based on a gas-filled Herriott cell, targeting sub-40 fs pulse durations with pulse energies beyond 150 mJ at 5 kHz. In parallel, first compression experiments based on multiplates were undertaken with a micromachining laser TruMicro 2000. The initial 100-μJ pulses were shortened from 300 fs to <50 fs with an optical efficiency of >85%.

Our first measures for scaling up the energy will be presented, uncovering new perspectives of applications such as pumping optical parametric amplifiers for attosecond spectroscopy, Laser lightning rod, X-ray lasers, inverse Compton scattering and laser wakefield acceleration.

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↑ Conference Program

Relaxation at complex resonances studied by wavelength-selected XUV pulses

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In the last three decades the development of the ultrafast pulsed lasers and high-order harmonic generation opened access to time-dependent studies in XUV photon energy range. Excited electronic states accessible in this energy region often have a complex character combining several coupled electronic states, such as multi-state Fano resonances, and undergo ultrafast relaxation dynamics such as autoionization, dissociation or relaxation via conical intersections on nanosecond to attosecond timescales. In this contribution we investigate dynamics at complex resonances using time-resolved photoelectron spectroscopy with wavelength-selected XUV pulses. In one set of experiments, the XUV pulses prepare i) highly excited neutral molecules or cations and the quantum-mechanically delayed relaxation is followed by ionization with moderately strong NIR pulses. Related time-domain effects are predicted for dynamics at conical intersections in a molecule coupled to environment. To address this problem the method is extended to solvated molecules opening route to study relaxation at conical intersections perturbed by the environment.

Probing influence of molecular environment and dynamic polarization in photoemission delays

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The advancement of attosecond chronoscopy has made it possible to reveal ultrashort time dynamics of photoionization [1]. Ionization delay measurements in atomic targets provide a wealth of information about the timing of the photoelectric effect [2], resonances, electron correlations and transport. The extension of this approach to molecules, however, presents great challenges. In addition to the difficulty of identifying correct ionization channels, it is hard to disentangle the role of the anisotropic molecular landscape from the delays inherent to the excitation process itself. Other than that the feature of dynamic polarizability in case of molecules, especially the larger ones, makes the problem even harder, however presents a rich play ground to see collective electron dynamics. Here, we first present the measurements of ionization delays from ethyl iodide around the 4d giant dipole resonance of iodine, which could disentangle the contribution of electron propagation effect within the molecular (ethyl group in this case) environment exclusively to the ionization delay. In the second case to illustrate the effect of molecular dynamic polarization effect on ionization delay, we used ionization of C_{60} molecule around its well know giant dipole resonance at 20 eV. In both the cases, we employed attosecond streaking spectroscopy where an attosecond extreme ultraviolet (XUV) pulse ionizes the molecule around the energy of the respective giant resonances and the released electron is exposed to the ponderomotive force of a synchronized near-infrared (NIR) field, which yields a streaking spectrogram. Comparative phase analysis of the spectrograms corresponding to iodine 4d or C_{60} valance electrons with neon 2p emission permits extracting overall photoemission delays in both cases. In the ethyl iodide case the experimental results are compared to classical Wigner propagation [3] and quantum scattering [4] calculations. Here the outgoing electron, produced via inner shell ionization of the iodine atom in ethyl iodide, and thereby hardly influenced by the molecular potential during the birth process, acquires the necessary information about the influence of the functional ethyl group during its propagation. We find significant delay contributions that can distinguish between different functional groups, providing a sensitive probe of the local molecular environment [5]. This would stimulate to perform further angle resolved measurements in molecules to probe the potential landscape in three dimension. In case of C_{60}, the measurements are compared with simulations involving classical and quantum mechanical descriptions of fullerene under the effect of near infrared short laser pulses and subsequent propagation effect. This indicates a clear signature of dynamic polarizability of the target and also some contribution of Eisenbud-Wigner-Smith type of delay.

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Sub-femtosecond snapshots of molecular wavepackets and molecular ionization

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Recently, an experimental method was demonstrated where the two intrinsic timescales of a molecule, the slow nuclear motion and the fast electronic motion, are simultaneously measured in a photoelectron photoion coincidence experiment [1]. Using coincidence imaging, the nuclear wave packet of a stretch motion on the state $1s\sigma_g$ of H_2^+ was directly observed with attosecond temporal and picometer spatial resolution. The demonstrated method should enable insight into the first few femtoseconds of the vibronic dynamics of ionization-induced unimolecular reactions of larger molecules.

Alongside, it was shown that the near-circular few-cycle polarized laser field forces the electron emission from the molecule into the sub-cycle bursts [2]. Using pulses with known carrier-envelope phase it was possible to disentangle contributions of first and second emitted electrons in the measured electron spectra. This will allow the investigation of charge-state specific Coulomb-distortions on emitted electrons in polyatomic molecules.
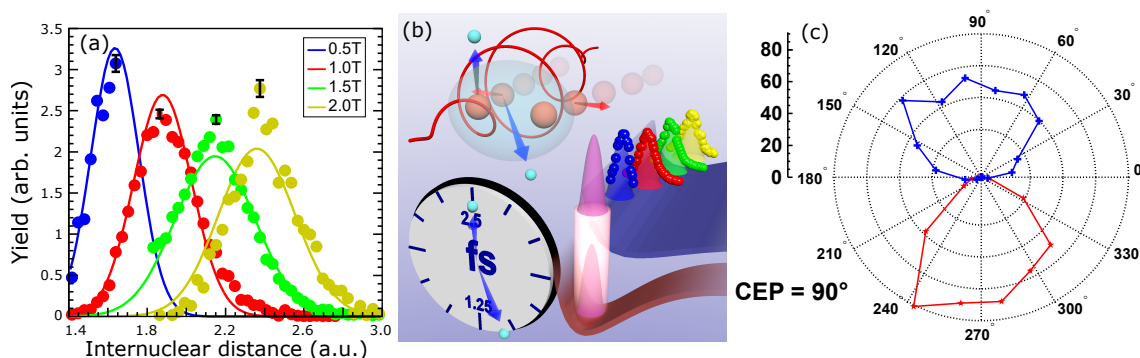
Figure 1: (a) Snapshots of H_2^+ vibrational wavepacket in time from 1.25 to 5 fs after the ionization from the neutral hydrogen. Snapshots taken with 70 as exposure time and repetition rate of half of the laser cycle (T). (b) The representation of the presented method of attosecond snapshots. (c) Halfcycle snapshot of the angular distribution of the electrons from the molecular ionization with experimentally separated contributions of first (red) and second (blue) emitted electron.

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↑ Conference Program

Ehrenfest Molecular Dynamics with Time-Dependent Density-Functional Theory: In and out of equilibrium.

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Ehrenfest Molecular Dynamics (EMD) is the most basic of all mixed quantum-classical non-adiabatic models. It is theoretically well founded as a Hamiltonian system, just as purely classical or quantum systems are. The fact that the force acting on the classical particles (typically the nuclei) is an explicit functional of the density of the quantum particles (typically the electrons) makes EMD ideal to be combined with time-dependent density-functional theory (TDDFT). It has some severe shortcomings, however. For example, the study of an ensemble of Ehrenfest systems at finite temperature must be taken with care, as its canonical equilibrium distribution is not the one that should correspond with the one of hybrid quantum-classical system. I discuss this issue, and possible ways to use EMD, nonetheless, to obtain correct hybrid canonical ensemble averages. However, EMD has been mostly used in non-equilibrium circumstances, to discuss ultra-fast phenomena: I present calculations on ion-atom collisions, molecular isomerization, and on the coupling of EMD-TDDFT with optimal control theory.

Gas-phase molecules through the lens of photoelectron spectroscopy

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This talk will focus on the dynamics of photoemission processes for molecules in the gas phase. In particular, the investigation of highly correlated systems through photoelectron spectroscopy will be discussed, as fundamental issues concerning satellite transitions, multiple electron ejections and ionization of excited states are still open and controversial topics.

Some key points will be discussed, such as:

* Differentiating different excited states through the molecular-frame photoelectron angular distribution profiles that are highly characteristic signatures of the final ionic states.

* The appearance of multi-slit interference in inner-valence photoionization which can be used to extract quantitative information on the geometric structure of the target systems [1].

* The implications of molecular chirality in investigating photoelectron dynamics.

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Molecular R-matrix method as a detailed probe of electronic dynamics in external fields and scattering

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In this contribution I describe the results of our recent R-matrix calculations for RABBITT in H_2 and strong field ionization of water using a coupled-channel model and illustrate how our models are able to provide detailed insights into the electronic dynamics of isolated molecules in external fields. The time-dependent calculations were performed with RMT [1] which is a recent extension of the UKRmol+ [2] stationary molecular R-matrix codes.

We show that inclusion of channel coupling and multi-electron effects in strong field ionization are crucial to obtain correct quantitative and qualitative picture of the process. Specifically, we show that the polarization-dependent channel-resolved ionization yields, shown in Fig.1, change their relative importance and shape significantly as a function of the laser field intensity.
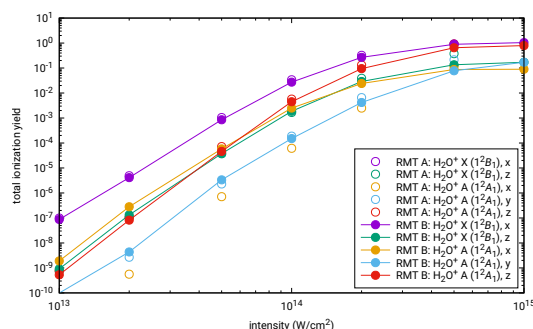
Figure 1: Polarization dependenent channel-resolved ionization yields for water. Full circles: coupled-channel model results, empty circles: uncoupled model results.

The RABBITT delays of H_2 computed using RMT are analyzed with the help of the stationary (Wigner) delays obtained from the UKRmol+ suite. We demonstrate that the unique merge of the time-dependent and stationary R-matrix approaches allows us to unambiguously interpret the origin of the various features in the time-delays. A progress in development of R-matrix methodology for stationary computation of multi-photon matrix elements is described.

Finally, we describe the recently developed method that allows to localize and manipulate all resonances and virtual states (Siegert states) appearing in R-matrix calculations thereby opening the door to a detailed interpretation of scattering and photoionization observables in terms of resonances and their interferences.

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ASAP: Atomistic Simulation Advanced Platform

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SIMUNE is a company expert in computational simulations of materials and the development of scientific software tools related. SIMUNE was launched in 2014 as a spin-off from the CIC Nanogune,[1] and part of its shareholders are the original and current developers of the SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms).[2] In this talk, I will present SIMUNE's main activities and our in-house developed software ASAP (Atomistic Simulation Advanced Platform). ASAP is composed of a set of tools developed around different powerful open-source software, including SIESTA, to facilitate their use for academical and industrial users. ASAP also incorporates specific modules designed to automate the workflow involved when addressing common problems in industry by computational simulations.

Figure 1: Schematic representation of ASAP workflow.

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↑ Conference Program

Dynamics of rotational predissociation of KLi

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Adiabatic potential energy curves of KLi were calculated by means of pseudopotential method. Very good agreement between the calculated and the experimental curves allowed for a reliable description of the dissociation process through potential energy barriers. The barrier supports several rovibrational quasi-bound states and explicit time evolution of these states via the time-dependent nuclear Schrödinger equation showed that the state populations decay exponentially in time. We were able to precisely describe the time-dependent dissociation process of several rovibrational levels and found that our calculated spectrum match very well with the assigned experimental spectrum[1,2,3] (e.g. Fig.1). Moreover, our approach is able to predict the positions of previously unassigned lines, particularly in the case of their low intensity.
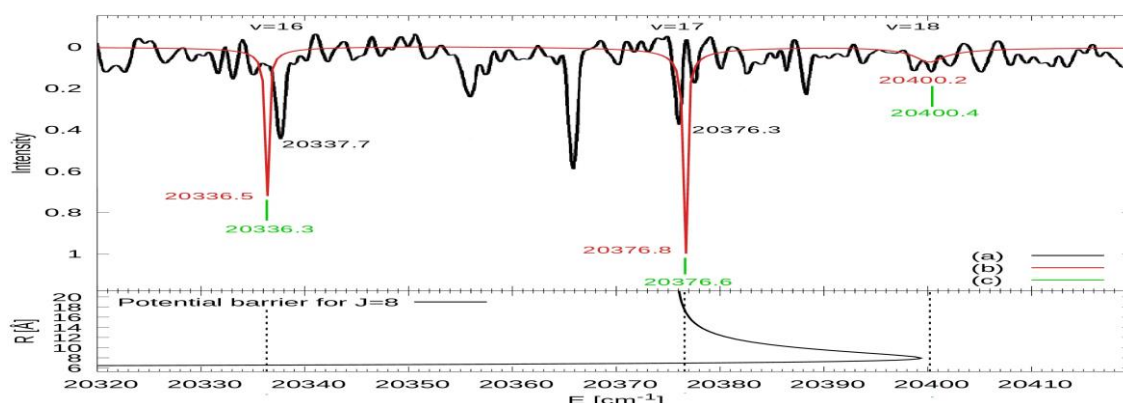
Figure 1: The black color gives to the experimental spectrum of KLi observed with a linearly polarized pump laser beam. The assigned progression corresponds to transitions from the ground state levels $v'' = 3$, $J'' = 8$ to the levels $v' = 16$, 17, and 18, for $J' = 8$ of 2^1P. The red color gives our spectrum calculated using our potential curve of 2^1P. The green color is the spectrum calculated from the program LEVEL

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Coupled cluster methods for local and ultrafast spectroscopies

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The massive investments in light source facilities working in the x-ray frequency range has increased the popularity of X-ray-based spectroscopic techniques to probe molecular systems. At the same time, it has stimulated the development of quantum-chemical theory and computational tools to simulate such spectra. Theory and simulation tools are essential components to unambiguously relate experimental measurements to both structural and dynamical properties of the probed system.

The accurate description of core excited states presents some additional challenges, compared to the one of valence excited states, that have for a long time prevented the application of electronic structure methods, like the coupled cluster ones, generally considered among the most reliable and accurate to describe excited states.

During the last decade, we have tried to rectify this situation, developing approaches, rooted on the coupled cluster ansatz, to address X-ray spectroscopic techniques like X-ray absorption (XAS) [1-10], emission (XES) [11-13], circular dichroism (XCD) [12], resonant inelastic x-ray scattering (RIXS) [11-13], photoelectron (XPS) [14], that are applied to probe both the electronic ground state and electronic excited states in a pump-probe [5,8,10,14] set up. An overview of their performance and capabilities will be presented.

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Exploring electron dynamics using attosecond pulses: from atoms to amino acids

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This talks introduces the current theoretical challenges for the description of the ultrafast electron dynamics triggered by coherent laser pulses. We will discuss the relevance of nuclear motion, non-adiabatic couplings, pulse-shape dependencies and electron correlation effects in molecular ionization induced by attosecond pulses. We review the available methodologies to describe a large range of targets, from atoms to amino acids.

In our most recent studies, we investigate the ultrafast electron dynamics in ionized glycine using an attosecond XUV-pump/XUV-probe scheme. The existence of ultrafast charge migration in organic molecules was initially discussed in the nineties [1], but the first experimental evidence was only obtained recently using an attosecond UV-pump/IR-probe scheme [2]. The large bandwidth of the attosecond pulse generated a superposition of one-hole states leading to a highly delocalized hole density that fluctuates in the attosecond time scale. It was then shown that a realistic description of ultrafast charge migration requires an accurate evaluation of the ionization amplitudes, only achieved by a few theoretical approaches [2, 3]. Most existing studies of charge migration in biomolecules to date assume the nuclei to be frozen, which is a valid approach for the first few femtoseconds [4], but unable to predict the subsequent molecular fragmentation. More importantly, the role of the probe pulse is usually ignored but for very scarce works [5]. Here, we will present our progress to describe a complete XUV-pump/XUV-probe experiment in glycine. Ionization amplitudes are accurately evaluated using the static-exchange DFT approach within the time-dependent perturbation theory formalism [4], while the coupled electron-nuclear motion leading to different fragmentation paths is then described using a Surface Hopping approach [6]. The final photoelectrum spectrum is retrieved for different pump-probe schemes.

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Angular streaking in F$^-$

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The *R*-matrix with time dependence (RMT) suite of codes [1] has recently been extended to treat multielectron dynamics in arbitrarily-polarized light fields. The code has been applied to range of problems using circularly-polarized laser pulses, and its accuracy has been demonstrated through comparisons with alternative numerical and analytical methods [2, 3].

We use RMT to study attosecond angular streaking of F$^-$. This negative-ion system is free of long-range Coulomb interactions, and can elucidate the role of short-range electron correlation effects in an attoclock scheme [4]. We solve the multielectron time-dependent Schrödinger equation, and capture the response of both an ejected electron and residual ion to the laser field. Fig.1a shows the photoelectron momentum distribution for F$^-$ in an 800-nm, 2-cycle circularly-polarized pulse. We observe significant negative offset angles in the distribution, despite the short-range nature of the binding potential. In Fig.1b, we show that the offset angle is sensitive to the atomic structure description of the residual F atom. We also investigate the response of co- and counter-rotating electrons, and observe an angular separation in their emission.
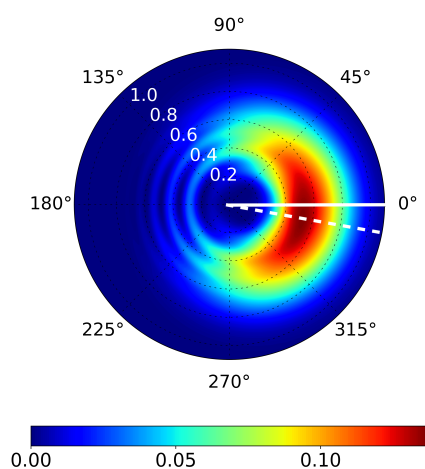
(a) Momentum distribution for a two-cycle, 800-nm, 5×10^{13} W/cm^2 circularly-polarized pulse.
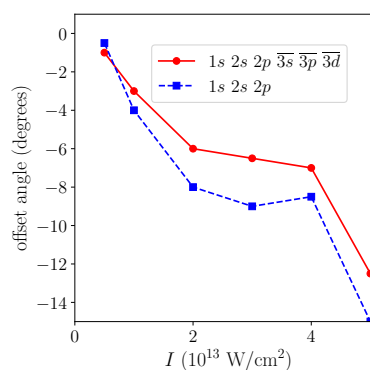
(b) Intensity dependence of offset angles calculated with different atomic structure models.

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Helium resonant photoemission resolved in time and space

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Photoionization processes unfold on the attosecond time scale. To access such short times, interferometric methods, such as the RABBIT [1,2] technique, have been developed to measure both spectral amplitude and phase of the electron wave packet. They have been used to investigate resonant photoionization for various types of resonances in the continuum, but can also be applied to below-threshold bound states [3], in particular the 1s3p state of helium [4]. To access the ionization dynamics both spatially and temporally, we used a Velocity Map Imaging Spectrometer (VMIS) on the SE1 beamline at ATTOLab, an XUV attosecond source pumped by a 1-kHz Ti:Sapphire infrared (IR) laser at 800 nm.

We looked into two-photon resonant ionization dynamics where the harmonic 15 of the laser excites the 1s3p resonance and one IR photon enables the ionization. This transition interferes in the sideband (SB) 16 with another two-photon transition, the absorption of harmonic 17 and reemission of one IR photon which is used as a reference (Fig. 1a). This allows measuring the spectral amplitude and phase of the resonant wave packet with an excellent angular and spectral resolution in the VMIS (Fig. 1b). The extracted phase (Fig. 1c) exhibits a π phase jump induced by the intermediate 1s3p resonance which is relatively homogeneous up to 45°. We thus have access to the whole angular dynamics of the resonant ionization at the attosecond time scale [5].
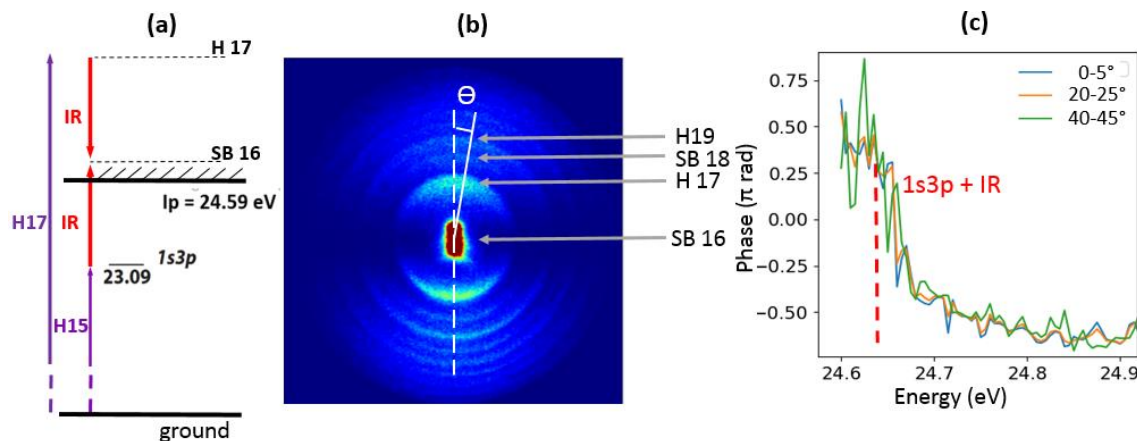
Figure 1: (a) Energy diagram of He and two-photon ionization channels. (b) VMIS image showing the angular and energy distribution of the photoelectrons. Dotted line: laser polarization axis. (c) Spectral phase of the resonant wave packet H15+IR for different emission angles Ө.

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Fourier Transform Laser Induced-Electron Diffraction (FT-LIED) Imaging Of An Isolated H_2O^+ Molecule

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Viewing molecular structure transformations in real-time requires spatio-temporal resolutions on the Ångstrom and femtosecond scales. Laser-induced electron diffraction (LIED) is the first table-top technique that can image ultrafast structural changes of gas-phase molecules with such resolutions [1,2]. In the present work, we image the geometric structure of isolated H_2O^+ molecules using LIED by Fourier Transform (FT-LIED) [3,4], without the need for employing retrieval algorithms or *ab initio* calculations. Water plays a fundamental role in numerous physical, chemical and biological processes. For instance, altering the structure of water may affect the folding dynamics of proteins enclosed by water solvation shells. Moreover, it has been previously described that each water molecule experiences a local electric field of 2 V/Å from nearby water monomers in the absence of an external field. Here, we explore the geometrical changes that a single H_2O^+ molecule experiences in an intense 3.2 µm linearly polarized laser pulse. We observe that when increasing the laser field strength from 2.5 to 3.8 V/Å the molecule is stretched and slightly bent [4]. Consequently, this leads to an increase in its dipole moment and, in turn, a stronger dipole interaction between the nuclear framework of the molecule and the intense laser field. Our results provide meaningful insights into the coupling of the nuclear framework to a laser field as the molecular structure of H_2O^+ is modified in the presence of an external field.

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Time-dependent and time-independent calculations of multi-photon above-threshold ionization of molecules using the R-matrix method

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We formulate a time-independent method for calculation of multi-photon transition matrix elements based on the ab initio molecular R-matrix method, implemented within the molecular R-matrix suite UKRmol+ [1].

With this method we study the above-threshold ionization of atoms and small molecules, focusing—among other topics—on the absorption of a photon in the continuum during the RABBITT process and the analysis of the continuum-continuum contribution to the RABBITT time delays. We compare our results with the time-dependent results of the molecular "R-marix with time" (RMT) approach [2], which has been validated for similar systems [3] earlier.
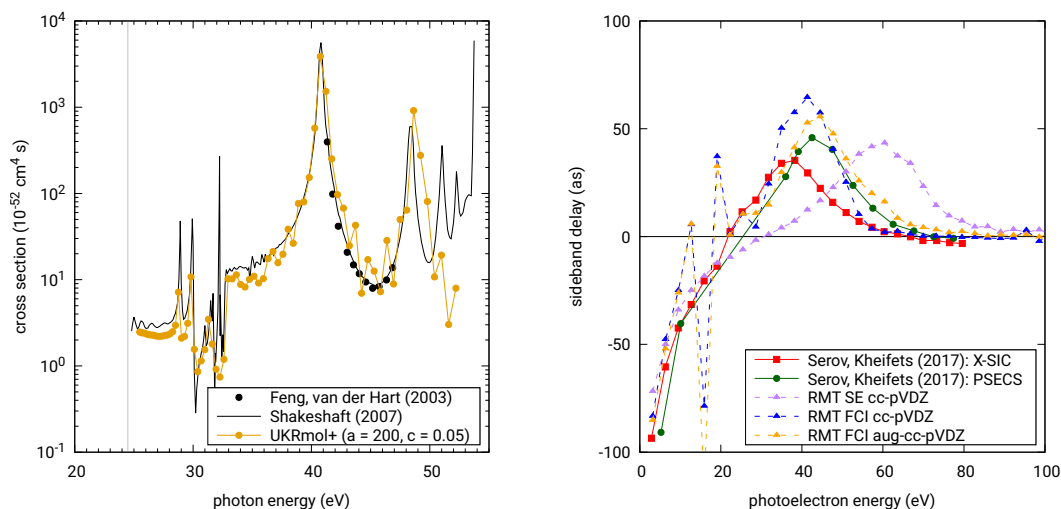
Figure 1: (Left) Generalized stationary cross section for above-threshold two-photon ionization of He; preliminary benchmark results. (Right) Time delays for photoionization of H_2 obtained from a time-dependent simulation of RABBITT.

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Propensity rules and interference effects in laser-assisted photoionization of helium and neon atoms

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We investigate the angle-resolved photoelectron spectra from laser-assisted photoionization of helium and neon atoms, where the atoms are photoionized by an XUV-field under influence of an IR-field,

$$A + \gamma_{XUV} \pm q\gamma_{IR} \rightarrow A^+ + e^-,$$

using *ab initio* calculations based on time-dependent surface flux [1] and configuration interaction singles [2]. In Fig. 1, the angle-resolved photoelectron spectrum of Ne2p with the $m = \pm 1$ channel resolved from Ref. [3] is presented. We find an interplay between a radial propensity rule and an angular partial wave interference effect in the angular probability distribution (PAD) of the photoelectron. A different number of minima occurs for sidebands due to absorption and emission of IR-photons in the continuum. In alignment with Busto et al. [4], the difference is clearest in the low-energy limit, where the propensity rule is the strongest. In the high-energy limit, the PAD is mostly explained by the interference effects, as expected from the soft-photon approximation.
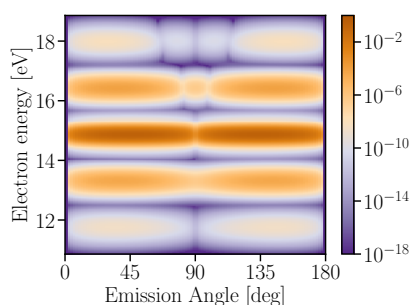
Figure 1: Angle-resolved photoelectron spectrum in Ne2p with the $m = \pm 1$ channel resolved using an XUV-photon energy of 38 eV. Figure from Ref. [3].

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Electron induced fluorescence of the H_2 molecule

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We report results of an experimental study focused on the fluorescence of H_2 initiated by electron impact. Emission spectra and excitation cross sections of hydrogen are the main results of the study. The experiment was described in detail in publication [1]. It utilizes a crossed beams configuration. The sources of electron and molecular beams are located in vacuum and resistively heated filament is source of electrons. The electron beam is formed by a trochoidal electron monochromator. Molecular beam is formed by effusive capillary. The fluorescence radiation signal is analyzed by Czerny–Turner optical monochromator and photomultiplier working in photon counting regime resulting in very high sensitivity and low noise of the system The emission spectra of H_2 at electron energies of 25 eV, 50 eV and 100 eV have been measured in the spectral range of 320–670 nm. The emission spectrum is dominated by Balmer emission lines, Fulcher α, β, γ and δ bands and different singlet transitions of H_2. In addition to the atomic lines and molecular bands, the presence of H_2 ($a^3[\sum]_g^+ \rightarrow b^3[\sum]_u^+$) continuum radiation is present in the whole studied range. We have determined the emission cross sections for particular processes leading to the emission of the Balmer ($n = 3, 4, 5, 6, 7, 8 \rightarrow 2$) lines and for selected bands of the Fulcher α system of H_2 ($d^3\prod_u \rightarrow a^3\sum_g^+$)) as a function of electron energy in the range 5–100 eV. Emission cross sections for the Balmer lines ($n = 6, 7, 8 \rightarrow 2$) and Fulcher α (1, 0), (1, 1), (2, 2), (3, 3) bands were measured for the first time.
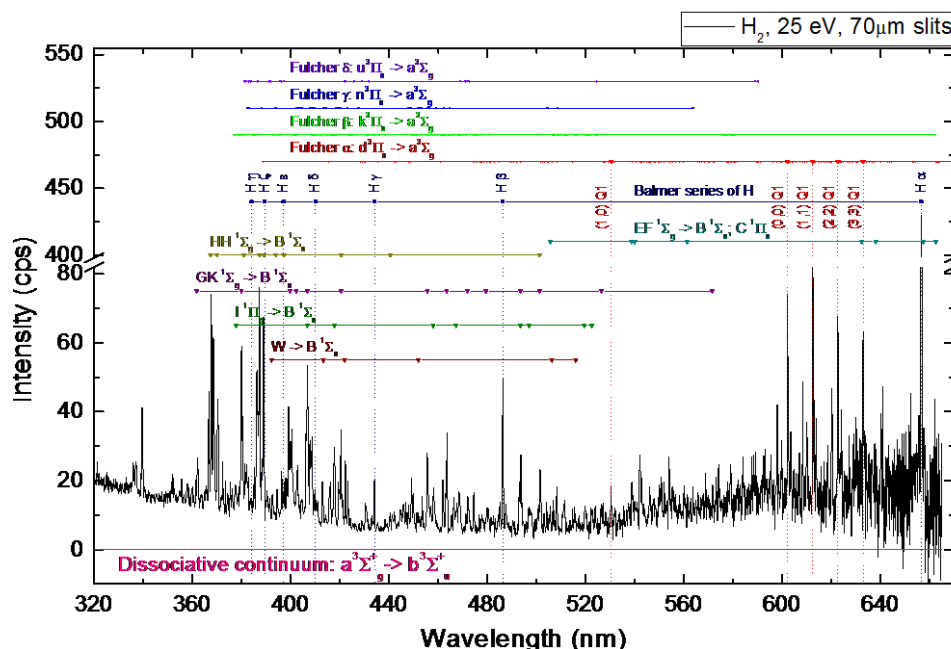
Figure 1: Fluorescence spectrum of the H_2. Rovibronic transitions of some molecular systems are marked along with the Balmer series of atomic hydrogen.

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Circular Holographic Ionization-Phase (CHIP) Meter

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We propose an attosecond extreme ultraviolet pump IR-probe photoionization protocol that employs pairs of counter-rotating consecutive harmonics as experimentally realized in [1] and provides a direct measurement of ionization phases. The ionization phase is imprinted onto the angularly resolved photoelectron momentum distribution through the interference of a one- and a two-photon transition. Ionization phases can thus be measured without the need of time-delay scans provided that the phase variations in the reference path can be neglected as a function of energy in the respective region.
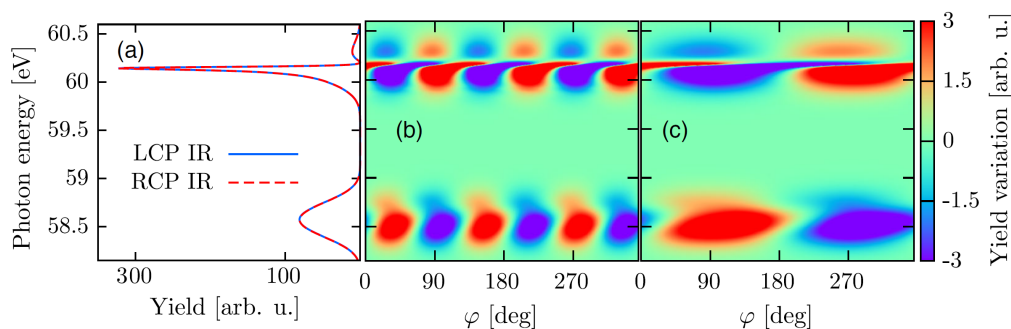
Figure 1: Single ionization spectrum of atomic helium ionized by a bicircular APT and a co- or counterrotating IR pulse. (a) Spectrum at fixed azimuthal angle $\phi = 0$ in the polarization plane $\theta = \pi/2$. Angular resolved photoemission spectrum with IR pulse (b) corotating with the lower harmonic and (c) counterrotating with the lower harmonic. .

As an example for the application of CHIP, we directly reconstruct the Fano phase variation caused by the optically allowed $(2s2p)^1P^o$ resonance in atomic helium. Considering the experimental difficulties in obtaining the full angular distribution at high energy we demonstrate that the method works already if only 4 directions of the ionized electrons are measured and investigate the influence of finite energy resolution of the electron detector on the retrieved phase [2].

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Anti-alignment Dynamics in Strong Fields:
The Whole Picture

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We study the dynamics of the excited state of H_2^+ and HD^+ molecules under a strong field through two approaches. In the first one, we combine the Ehrenfest approach for nuclear motion with the well established prolate spheroidal treatment for an electron in a two-center molecule [1]. In the last one, we solve the three coordinates of the electronic motion using the same treatment but combining it with the second-order split-operator method, to solve the nuclear motion over a square grid. One of the major advantages of these models is that is that they take into account the full electron dynamics and the exact Coulomb interactions, allowing to study accurately molecular orientation effects. One can therefore assess whether or not novel predicted phenomena such as anti-alignment [2], are artifacts of approximations such as dimensionality reductions or soft-core Coulomb potentials.

In Figure 1, we observe the dynamics of the excited state of both molecules under a strong field, starting from an aligned nuclear wave packet (or a distribution of nuclear arrangements with a certain standard deviation in the Ehrenfest approach). For the H_2^+ molecule, we observe that the standard deviation grows due to the anti-alignment in concordance with the results from Chang *et al* [2]. Unexpectedly, we find that the HD^+ molecule also experiments anti-alignment. Here the transition dipole goes to zero for large internuclear distances, but the effect is driven by the permanent dipole moment. In both cases, the molecule ultimately dissociates as it passes through the anti-aligned geometry. As one can observe, the deviation of the Ehrenfest model from the exact results grows in time, but still provides a qualitatively correct description of the process.

(a) H_2^+ case.

(b) HD^+ case.
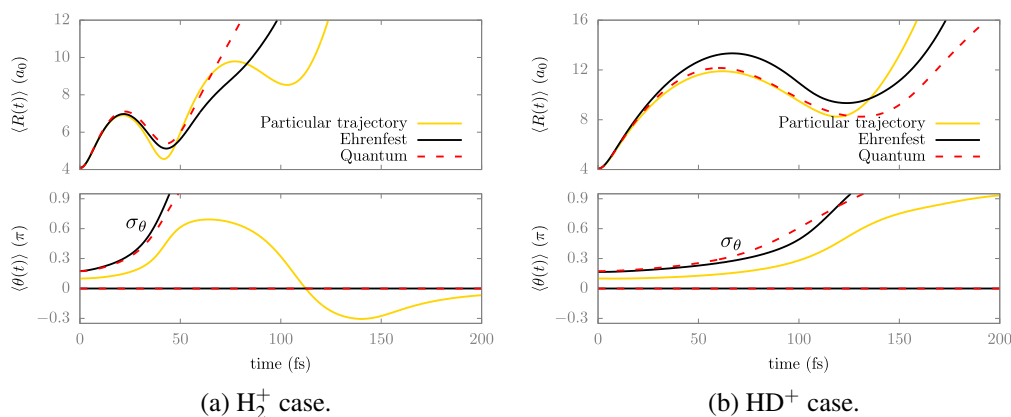
Figure 1: Quantum dynamics of the excited state of the (a) H_2^+ and (b) HD^+ molecules under a strong field starting from an aligned nuclear wave packet or distribution with a certain standard deviation. In red, the Split-operator results. In black, the Ehrenfest results, which are averaged from an ensemble of trajectories. In yellow, a particular trajectory from the ensemble.

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Photoelectron spectroscopy of large water clusters ionized by an XUV comb

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Detailed knowledge about photo-induced electron dynamics in water is key to the understanding of several biological and chemical mechanisms, in particular for those resulting from ionizing radiation [1]. We report a method to obtain photoelectron spectra from neutral water clusters following ionization by an extreme-ultraviolet (XUV) harmonic comb. Typically, a large background signal in the experiment arises from water monomers and carrier gas used in the cluster source. We report a protocol to quantify this background in order to eliminate it from the experimental spectra. We disentangle the accumulated XUV photoionization into contributions from the species under study and the photoelectron spectra from the clusters. This study demonstrates feasibility of background free photoelectron spectra of large water clusters illuminated with XUV combs and paves the way for the detailed time-resolved analysis of the underlying dynamics.

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Quantum control with quantum light of molecular nonadiabaticity

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Coherent control experiments in molecules are often done with shaped laser fields. The electric field is described classically and control over the time evolution of the system is achieved by shaping the laser pulses in the time or frequency domain. Moving on from a classical to a quantum description of the light field allows one to engineer the quantum state of light to steer chemical processes. The quantum field description of the photon mode allows one to manipulate the light-matter interaction directly in phase space.

In this work we demonstrate the basic principle of coherent control with quantum light on the avoided crossing in lithium fluoride [1]. Using a quantum description of light together with the nonadiabatic couplings and vibronic degrees of freedoms opens up alternative perspective on quantum control. We show the deviations from control with purely classical light field and how back-action of the light field becomes important in a few-photon regime.
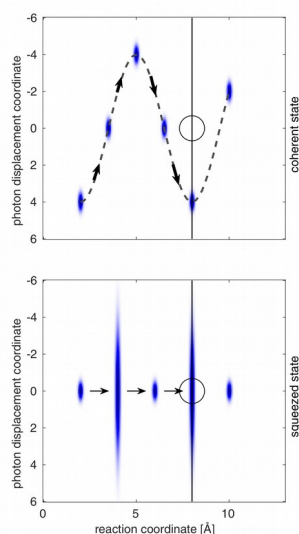
Figure 1. Illustration of the interaction of a molecule with a coherent state (upper panel) and a squeezed vacuum state (lower panel) in a wave packet picture. The nuclear wave packet follows the gradient on the potential energy curve from the Franck-Condon point towards the avoided crossing (empty circle).

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Analysis of excited electronic states

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Trajectory surface hopping calculations are performed in the adiabatic basis, where the excited states are given as solutions to the Schrödinger equation at fixed nuclear geometries and are ordered by their energies at each geometry. The analysis, however, is best performed in the diabatic basis in which the properties of electronic states change smoothly with the nuclear geometry.

We present two algorithms for calculating overlaps between CIS (or TDDFT) type excited state wave functions and show how overlaps between many-electron wave functions offer an intuitive and straightforward way to track the electronic character through different nuclear geometries without the need for complex diabatization procedures.[1] The contribution focusses on examples from UV spectroscopy and shows how an assignment algorithm is used to track excited electronic states.[2]

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On-the-fly *ab initio* semiclassical evaluation of electronic coherences in polyatomic molecules

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Irradiation of a molecular system by an intense laser field can trigger dynamics of both electronic and nuclear subsystems. Being much lighter than the nuclei, the electrons usually move on much faster time scale that is reflected in the attosecond dynamics of the electron density along a molecular chain. Due to a strong correlation between electronic and nuclear motion, the slow nuclear rearrangement damps ultrafast electronic oscillations, leading to the decoherence of the electronic dynamics on the time scale of a few femtoseconds. A crucial question in the emerging field of attochemistry is whether pure electronic coherences last long enough to allow for their efficient observation and eventual manipulation by ultrashort laser pulses.

In order to explore the interplay between nuclear rearrangement and the ultrafast electronic motion, a concerted description of the electron-nuclear dynamics is required. Although full-dimensional quantum calculations [1, 2, 3] performed using MCTDH-based approaches allows the accurate evaluation of electronic coherence time, it is still very case specific and also hides the underlying physics behind the general effects of nuclear motion. In contrast to numerical quantum methods, semiclassical approaches reveal the physical mechanism of decoherence, making it possible to describe the electronic coherence quantitatively with just two semiclassical parameters—the phase space distance and signed area between the trajectories moving on two electronic surfaces.

Here we present an application of a simple single-trajectory semiclassical scheme [4] for computing the electronic coherence time in polyatomic molecules. This technique employs direct on-the-fly evaluation of the electronic structure, avoiding thus the "curse of dimensionality" appearing in large systems. We argue that the proposed scheme can be used for fast preselection of molecules to be studied experimentally. An excellent agreement of the presented approach with the full-dimensional quantum calculations is demonstrated [5].

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Ultrafast Dynamics of the CH4 Cation Relaxation Upon Sudden Ionization

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Recent developments in the engineering of attosecond and few fs optical pulses made possible to experimentally follow the dynamics of nuclear reorganization with sub-femto second resolution using a variety pump-probe schemes[1]. One can for example use the photoionization process as a pump to build a coherent superposition of the electronic states of the cation and induce coupled electron-nuclei dynamics in the cation. Upon time evolution, these optically accessed cationic electronic states can reach conical intersection and it becomes important to take into account the dynamical effects driven by the non adiabatic couplings[2, 3, 4]. In the case of the CH4 ionization, the non stationary superposition of optically accessed states will lead to an ultra fast nuclear relaxation due to the Jahn-Teller (JT) effect, which can be probed by High Harmonic Spectroscopy[2].

We report on quantum dynamical simulations of the coupled electron-nuclei dynamics in the JT region of CH_4^+ following the sudden ionization of the neutral molecule. In the T_d geometry, the CH_4^+ is triply degenerate, and quickly undergoes JT distortion to either a C_{2v} or a D_{2d} symmetry of the nuclei. In this work we computed a nuclear grid in two reduced dimensions that includes these two most stable geometries. The electronic structure of CH_4^+ was computed using the MOLPRO package, with a SA-CASSCF/6-31G++(2D,2P) electronic wave function with 3 electronic states and 8 active orbitals. The photoionization amplitudes resulting from the sudden ionization of the neutral ground electronic state with a XUV pulse were computed for a distribution of random molecular orientations using the methodology of ref.(5) or each grid point in the JT region. We investigate the importance of the molecular orientation to the shape of the initial wave packet in the cationic states. Our simulations allows following in time the wave packet localization in the region of the C_{2v} and D_{2d} geometries for an average over the orientations of the CH4 neutral molecule at the time of ionization.

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↑ List of Posters

Auger decay of the $2p$ vacancy in chlorine

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We present the calculated spectra of electrons emitted upon Auger decay of the $2p$ vacancy in chlorine. The vacant atomic and ionic states are populated by a single photon absorption from the ground state of the chlorine atom and are tested by comparing the calculated photoabsorption spectrum with the existing theoretical and experimental photoionization data [2, 3, 4]. The agreement is reasonably good, although the calculated Auger decay rates and oscillator strengths of the low-lying states are overestimated due to neglect of the core polarization effects. In the absence of any published experimental result, the nonresonant L-M_{23}^2 Auger spectrum of Cl at 220 eV photon energy is compared to the Cl L-V^2 Auger spectrum of HCl, measured at 235 eV photon energy. The calculated spectator and participator resonant Auger spectra of some strongly photoexcited Cl $2p^{-1}$ states are presented for future reference.

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Deperturbation analysis of the polar alkali diatomic molecules spectra

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Studies of polar alkali dimers provide valuable insight into several basic phenomena, such as perturbations in excited states, potential curve crossings and avoided crossings, photodissociation, photoassociation, and new quantum matter, namely the Bose-Einstein condensate and ultracold two-fermionic species [1]. The development of spectroscopic methods allows for very accurate measurements, providing valuable data for the ground and excited states of these molecules. From the theoretical point of view heteronuclear alkali metal dimers are very attractive objects due to their simple electronic structure and the possibility of treating them as effective two-electron systems with separated atomic cores. Pseudopotential methods with longtail core polarization model potentials are well suited to treat such systems [2, 3].

In this work, we consider three excited states ($2^3\Sigma^+$, $3^1\Sigma^+$ and $1^1\Pi$) of the KCs molecule. Such states are promising candidates for establishing the new path of creation the ultracold KCs molecule in the deeply bound ground state. We present the new deperturbation approach based on the 3-channel model, in which the $3^1\Sigma^+$ and $1^1\Pi$ states are connected by L-uncoupling term as well as the $2^3\Sigma^+$ and $1^1\Pi$ states are connected by SO coupling term. Using our theoretical potential energy curves, calculated couplings and the experimentally recorded spectra of $2^3\Sigma^+$ (642 lines), $3^1\Sigma^+$ (390 lines) [4] and $1^1\Pi$ (2475 lines) [5, 6] excited states, we are able to determine high accuracy potentials allowing for the investigation of formation dynamics of the ultracold KCs molecules. All calculations are performed by means of the sPYtroscopy program package [7].
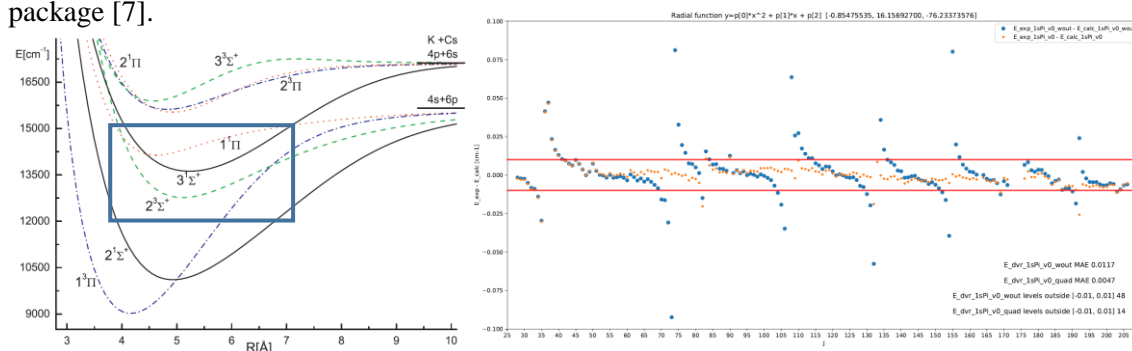
Figure 1: (left panel) The potential energy curves of the KCs molecule [4].
(right panel) Distribution of the residuals in line positions of the $3^1\Sigma^+\sim1^1\Pi$ system for ν=0 in KCs before (blue dots) and after (orange dots) the coupled channels fit.

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XUV Field Induced Photoelectron Holography in Diatomic Molecules

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In this work the photoelectron spectrum of the H_2^+ molecule irradiated with few-cycle XUV laser pulses have been studied using first principle calculations, based on the numerical solution of the electronic time-dependent Schrödinger equation within the fixed nuclei approximation [1].

By performing calculations for different field amplitudes and internuclear distances, we have investigated how the intensity of the laser pulse and the structure of the target system is influencing the spatial interference pattern occurring in the molecule's photoelectron spectrum [2-4]. This interference pattern is the result of the coherent superposition of electronic wave packets emitted at the same temporal part of the radiation field, which afterwards are driven by this along different spatial paths in the continuum[5].

We found that by increasing the intensity of the light the density of the interference pattern in the molecule also increases. On the other hand, we observed that the location of the interference minima in the spectra is dominantly determined by the target's ionization potential. However, by comparing the H_2^+ results with model calculations implying spherically symmetric potentials (having the same ionization energy as the molecule), clear differences were observed for the molecular target's potential relative to the central potentials, which proves that the spatial profile of the target system also influences the formation of interferences fringes in the spectra.

Next to the main feature (spatial interference) we have also identified the traces of the two-center interference in the photoelectron spectra, however, these were mainly washed out due to the complex electronic wave packet dynamics that occurs during the interaction with the employed laser field.

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Investigation of Photoelectron Dynamics Induced by IR Fields on Plasmonic Nanosurfaces

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In this work, we investigate how the photoelectron emission from the surfaces of different metal nanostructures is influenced by the temporal and spatial profile of an incident IR pulse. In order to have a deeper insight into the physical processes taking place at the nanoscopic scale, and to interpret the characteristics of the measured photoelectron spectra acquired for different type of plasmonic - nanotips, nanorods, and nanotriangles - targets, we employed a theoretical method based on the numerical solution of the time-dependent Schrödinger equation, which describes the motion of an active (laser-driven) electron initially located on the Fermi level inside the metal.

Within this approach the Hamiltonian and the wave function of the active electron was discretized on a finite difference grid, and the split-operator method alongside the Crank-Nicolson scheme was employed to represent the evolution operator [1]. Using this approach, we aim to study the effects of the spatial inhomogeneity of the optical near-field, the field-enhancement effects at the edges of plasmonic nanoparticles [2-3], and to identify the moment of the electron recollisions onto the metal surface, i.e., those recollision events that are responsible for the creation of the plateau regions at the upper (high energy) part of the measured photoelectron spectra.

By this, our goal was to bring new knowledge into the understanding of the underlying processes that lead to the formation of these features appearing in the high energy region of the obtained spectra.

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Observation of dissociation dynamics of methyl iodide by two-color time-resolved photoelectron spectroscopy

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We present a direct detection of the transient population and dissociation dynamics of the methyl iodide (CH_3I) excited to the photo-dissociating A-state by a pump pulse centered at 267 nm. Efficient, sensitive and background-free measurement was realized by properly adjusting the intensity of a probe pulse at 800 nm and by measuring the time-resolved photoelectron spectra (TR-PES). The dependence of the first photoelectron peak produced by above-threshold ionization (ATI) as a function of the pump-probe delay is shown in Fig. 1. It can be decomposed into two components: a non-resonant cross-correlation term that is identical to that obtained in the xenon reference gas, and a resonant term directly proportional to the evolution of the population of photo-excited molecules. The latter exhibits a clear shift of maximum due to the competition between the population by the 267 nm pulse and the dissociation with time constant of 90 fs. Other parameters of the ATI spectra like the peak positions and the widths are correlated with the evolution in Fig. 1 and give an additional insight into the very beginning of the fundamental process of molecular dissociation.
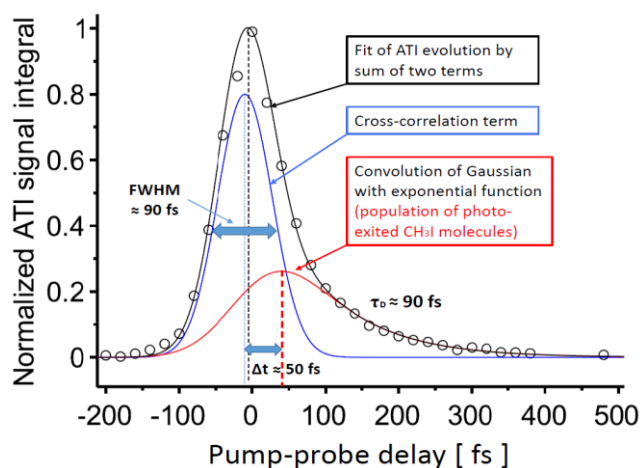
Figure 1: Evolution of the photoelectron yield from photo-excited CH_3I molecules (circles). The fit (black solid line) is decomposed in two components (blue and red) detailed in the figure.

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Attosecond ionization delays around molecular shape resonance by stereo-photoionization interferometry

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Ionization time delay around a shape resonance in N_2 has been investigated [1]. Nitrogen molecule has two main electronic states in its valence band (*X* and *A*-state) that are separated by about 1.4 eV. It is known that the *X*-state presents a shape resonance around 30 eV [2]. The *A*-state that does not present any structure at such photon energy is hence used as a reference.
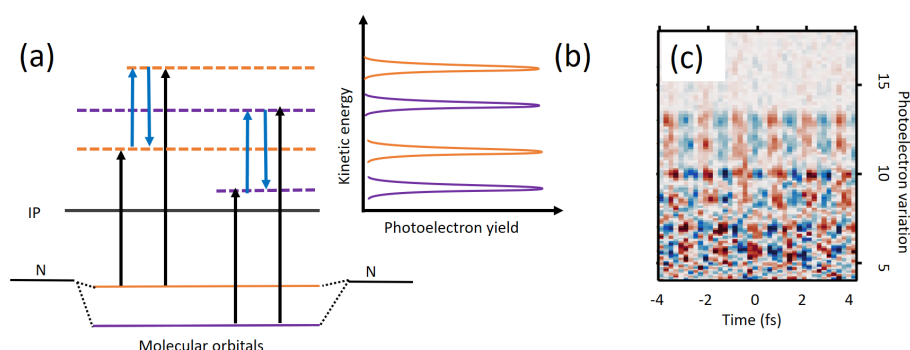
Figure 1: (a) Ionization pathways using HHG(black arrows)-$2\omega_0$(blue arrows) scheme. (b) Corresponding photoelectron spectrum. (c) HHG-$2\omega_0$ interferometric scan photoelectron upper-side.

We use an attosecond pulse train produced by high harmonic generation (HHG) dressed with the second harmonic $2\omega_0$ of the fundamental frequency ($\omega_0 \approx 1.55$ eV) to resolve the dynamic at the attosecond time scale. The measurement of the two states are energetically separated (Fig. a-b) allowing the measurement of the attosecond dynamics using the electron emission anisotropy in the laboratory frame (Fig. c).

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ASAP: Atomistic Simulation Advanced Platform

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SIMUNE is a company expert in computational simulations of materials and the development of scientific software tools related. SIMUNE was launched in 2014 as a spin-off from the CIC Nanogune,[1] and part of its shareholders are the original and current developers of the SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms).[2] We are presenting SIMUNE's main activities and our in-house developed software ASAP (Atomistic Simulation Advanced Platform). ASAP is composed of a set of tools developed around different powerful open-source software, including SIESTA, to facilitate their use for academical and industrial users. ASAP also incorporates specific modules designed to automate the workflow involved when addressing common problems in industry by computational simulations.

Figure 1: Schematic representation of ASAP workflow

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Module Photoion: Streamlining the study of molecular photoionization processes in time domain

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Materials modelling and simulation are becoming an integral part of product life cycle management in industry. Nowadays, both open-source and commercial software are used to design new materials and to predict specific material properties of interest in a wide range of fields. However, the complexity associated with open-source simulation codes often hampers its use in industry. They are usually too customized or specific and challenging to learn and to use. We present the joint efforts of SIMUNE and Autonomous University of Madrid (UAM) to make *Xchem* package[1] ready for industry. *Xchem* has been proved to provide reliable predictions[2] and opens the way to new applications in emerging scientific disciplines, as attochemistry, single-molecule imaging, coherent attosecond control of chemical reactions, etc.[3]

Figure 1: Illustration of the XChem basis architecture in benzene. Cyan: B-splines, mangenta: Gaussians at the center of mass of the molecule, blue and black: Gaussians at the atomic sites not overlapping with B-splines. Figure taken from www.xchem.uam.es

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Electron Collisions with H_2 from the Ground and Electronically Excited States using the R-matrix Method

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Electron collisions with molecular hydrogen occur in industrial plasmas, planetary atmospheres and interstellar medium. Quantifying how these collisions take place is of practical importance to the plasma modelling community. To date, there are very few electron impact electron excitation cross section data available from theory or experiment. Furthermore, most of the calculations or measurements for H_2 are carried out for transitions from the molecular ground state, however, under more realistic conditions the molecule may exist in its excited electronic states [1], particularly the metastable $c\,^3\Pi_u$ and quasimetastable $a\,^3\Sigma_g^+$ state.

In a recent publication (ref. [2]) we benchmarked two accurate close-coupling methods, namely, R-matrix and Molecular Convergent Close-Coupling (MCCC), for electron collisions with H_2. The R-matrix calculations were shown to provide good agreement for the integrated cross section (ICS) data when compared with recent experiments, recommended data and theoretical MCCC data (Fig. 1). Using this as a foundation, we have extended our calculation to obtain ICS for electronic (de-)excitation from initially excited states. In this presentation we will discuss our latest R-matrix results for transitions from the ground and initially excited states.
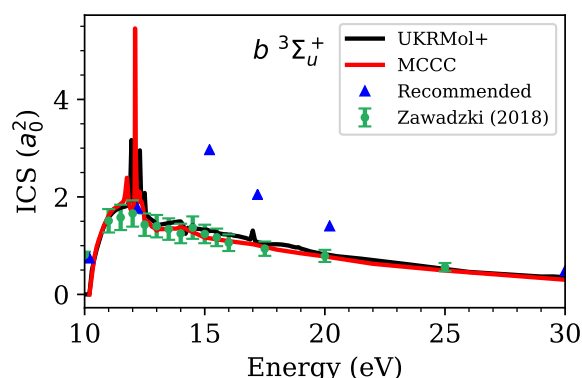
Figure 1: ICS for the $X\,^1\Sigma_g^+ \to b\,^3\Sigma_u^+$ transition obtained from UKRMol+ R-matrix calculations (black), MCCC calculations (red), recommended data (blue triangles) and recent experimental data (green circles) (see Ref. [2] for more details).

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Low Energy Electron Attachment to Octafluorocyclobutane Molecules and Clusters

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We present low energy electron interaction studies of a precursor c-C_4F_8 used in plasma technologies. The electron attachment (EA) and dissociative electron attachment (DEA) will be compared in the gas phase [1] and in the molecular clusters (first data ever with the recent CLUSTER-ILN experiment [2]). The energy profiles of gas phase DEA products, the electron affinities of the neutral c-C_4F_8 and most of its fragments were already known [1]. We have revealed some differences in our gas phase and cluster measurements of molecular ion c-$C_4F_8^-$ and its main cluster products c-$C_4F_7^-$ and F^- (Fig. 1). As the common feature, the formation of molecular ion and its dimer or trimer clusters is dominantly a low energy process with a strong resonance ~0 eV. This resonance for the gas phase c-C_4F_8 is well known, but in the clusters the higher energy resonances (4.4 eV, 8.6 eV, 11.9 eV or 15.5 eV) typical for gas phase DEA products were found to be accessible for c-C_4F_8 as well (via molecular ion excitation $e + c$-$C_4F_8 \rightarrow c$-$C_4F_8^{\#-}$, or electron self-scavenging $e + c$-$C_4F_8 \rightarrow e + C_4F_8$). Other important aspects have to be taken into account as well, the formation of fragments F^- and c-$C_4F_7^-$ is a competitive process, its efficiency should depend on the electron affinities of the corresponding fragment products F (>3eV) *vs* c-C_4F_7 (unknown).
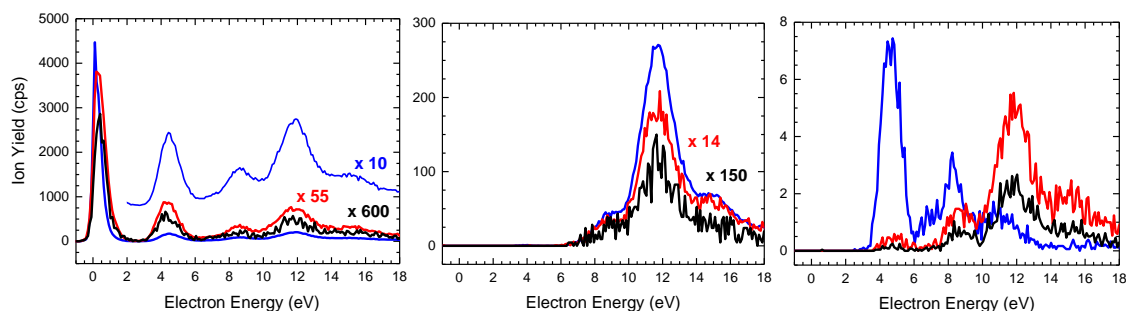
Figure 1: Energy dependence spectra of EA/DEA to c-C_4F_8 forming the ions: a) c-$C_4F_8^-$, b) c-$C_4F_7^-$ and c) F^-, isolated (blue), with one (red) and two (black) c-C_4F_8 molecules in a cluster.

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↑ List of Posters

Theoretical modelling of photoionization dynamical parameters

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The last two decades have witnessed a remarkable increase in the study of sophisticated light-matter interactions, due to enormous advancements in synchrotron and laser sources. This is dictating high demands for reliable theoretical and computational methodologies [1]. The aim of my work is to present an overview of our development of theoretical models for calculation of dynamical parameters for photoionization. This requires an accurate description of both initial and final states of the system, as well as of the outgoing electron. Our studies show that using a linear combination of atomic orbitals (LCAO) B-spline density functional (DFT) method to describe the outgoing electron, in combination with correlated equation-of-motion coupled cluster singles and double (EOM-CCSD) Dyson orbitals, gives good agreement with experiment and outperforms other simpler approaches, like plane wave (PW) and Coulomb waves (CW), used to describe the photoelectron [2, 3].
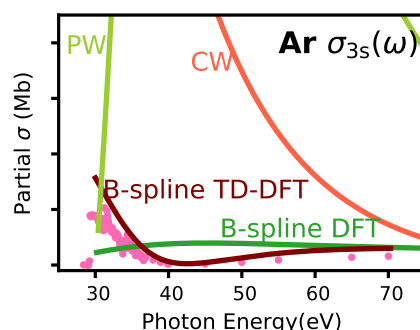
Figure 1: Partial cross-section for photoionization from 3s orbital of Argon. EOM-CCSD Dyson orbitals are used to describe the bound state.

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Observation of a periodic many-body system: probing electron motion at ELI

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We report the experimental observation of a very striking periodicity in a many-body system--an ultra-cold plasma. A long life-time (>0.3 ms) *quantum degenerate* molecular Rydberg plasma is generated in the high-density region of a pulsed supersonic jet expansion by two-color resonant excitation of nitric oxide (10%) in neon (5bar) into the high-n Rydberg threshold region close to the ionization limit. For plasma densities of $> 10^{16}$ cm^{-3} reached in our experiments the electrons should become quantum degenerate, *i.e.* the electron *de Broglie* wavelength becomes larger than the Wigner-Seitz radius a relevant to describe the mean distance between the particles.

The time-of-flight (ToF) mass spectrometer used is depicted in the *r.h.s.* figure. Experimentally, two synchronous UV laser pulses produce the plasma a few mm away from the jet nozzle. After 170μs, when the plasma cloud is still *ca.* 130mm in front of aperture plate 1 (ap.1), two successive high-voltage (HV) pulses of 3.6 kV with a 0.2μs gap are applied to ap.1. The first HV pulse (P1,1; length 5.5μs) is followed by a gap of 0.2μs and a second pulse: P1,2. The observed ToF spectrum *w.r.t.* the falling slope of P1,1 is shown in the *l.h.s.* figure (positive particle detection on MCP). The observed sharp peaks ("*slices*") in the ToF spectrum follow a fully reproducible progression of (m/z) mass to charge ratios from 35 to 92.5 (blue: *w.r.t.* m(NO$^+$) = 30u). From the m/z one obtains the corresponding ion to electron ratios of the 12 slices (bottom of figure), from 7/1 to 37/25.
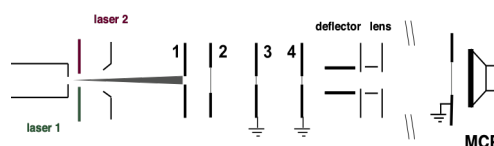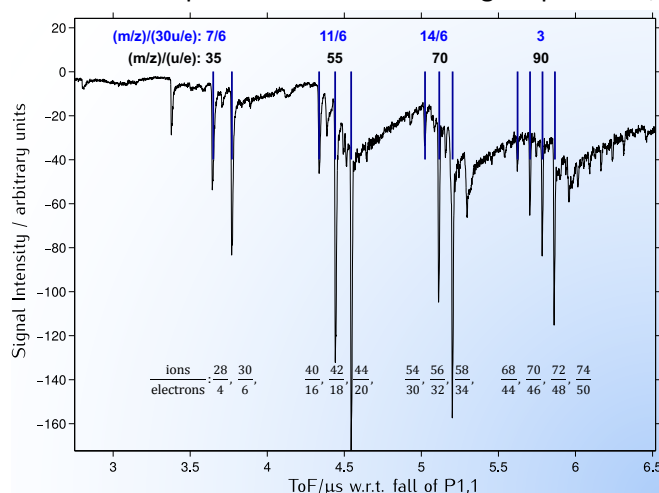
In conclusion, we observe a many-body system consisting of a series of objects that contain a magic number of ions and electrons for which the ion/electron ratio follows a periodicity. These objects are manipulated by fields in a ToF spectrometer without being destroyed, which shows that they behave as objects with a center of mass. The bizarre ion to electron ratios could be explained by the *Fractional Quantum Hall Effect,* by which a number I of ions is bound by a number e of electrons that are distributed as fractional elementary charges e/I. From experimental considerations we know that the number of ions in one object is of the order of a few ten thousands so, for example, the first object of I/e=28/4=7/1 could consist of 28000 ions bound by 4000 electrons and each electron is distributed as 7 fractional charges 1/7. The second last object of I/e=72/48=3/2 would then contain 72000 ions bound by 48000 electrons with each electron pair being distributed as 3 fractional charges of 2/3. As a further interpretation, the production of the object could be understood by a two step process: first a *Wigner-Abrikosov ion crystal* is formed in the plasma which is then „shaken" by the applied electric field and planar objects are ejected from the lattice planes of the ion crystal.

This discovery could lead to some new insight into the behavior of ultra-cold many-body systems, for instance, are the electrons really at 0K (10^{-42}K)? We plan to probe fractional charge and the electron motion in these strange objects by using the ELI Szeged Facility.

Non-Linear Spatial Control of Ultrafast Pulses in the Extreme Ultraviolet

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Spatial control of extreme ultra-violet (XUV) pulses by opto-optical modulation utilizes the Stark shift from a non-resonant infrared (IR) pulse to temporarily shift the energy levels of gas atoms that absorb and then re-emit the XUV. Without the Stark shift (i.e no applied IR pulse), the phase shift due to the absorption and re-emission is global and cause no change in the propagation direction. With an applied IR pulse causing a Stark shift of the energy levels, there can be a net phase shift over the interaction region that results in a tilted wavefront and spatial redirection of the re-emitted XUV [1]. Conversely, it has been shown that studying the redirection can give insight on the properties of the Stark shift of an energy level [2].

By simulating the interaction between the atoms and the XUV- and IR-pulses, we show that the appearance of the XUV pulse in the detector plane is dependent on the IR pulse shape in the focus (near-field) where the interaction takes place. A Gaussian intensity profile, similar to the experimental case, gives rise to an interference pattern if the XUV-IR offset is within certain intervals (see Fig. 1). The interference pattern for a Gaussian IR pulse intensity has been reproduced experimentally, see Fig. 2.
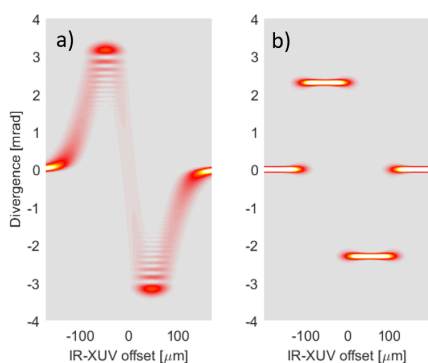
Figure 1: Simulated effect of the IR intensity profile used to modulate the XUV pulse: a) Gaussian, b) Triangular (note the beam-splitting around x=0).
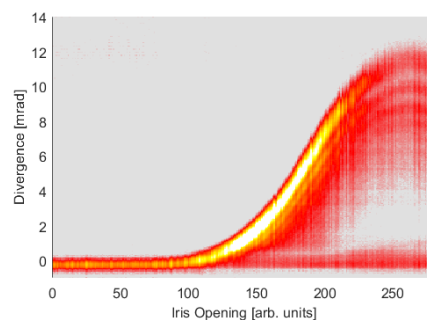
Figure 2: Experimental result using an XUV pump - IR probe setup (details in [1]) and varying the IR pulse intensity by adjusting an iris.

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↑ List of Posters

Attosecond XUV pump-probe spectroscopy of glycine

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We investigate the ultrafast electron dynamics in ionized glycine using an attosecond XUV-pump/XUV-probe scheme. The existence of ultrafast charge migration in organic molecules was initially discussed in the nineties [1], but the first experimental evidence was only obtained recently using an attosecond UV-pump/IR-probe scheme [2]. The large bandwidth of the attosecond pulse generated a superposition of one-hole states leading to a highly delocalized hole density that fluctuates in the attosecond time scale. It was then shown that a realistic description of ultrafast charge migration requires an accurate evaluation of the ionization amplitudes, only achieved by a few theoretical approaches [2, 3]. Most existing studies of charge migration in biomolecules to date assume the nuclei to be frozen, which is a valid approach for the first few femtoseconds [4], but unable to predict the subsequent molecular fragmentation. More importantly, the role of the probe pulse is usually ignored but for very scarce works [5]. Here, we will present our progress to describe a complete XUV-pump/XUV-probe experiment in glycine. Ionization amplitudes are accurately evaluated using the static-exchange DFT approach within the time-dependent perturbation theory formalism [4], while the coupled electron-nuclear motion leading to different fragmentation paths is then described using a Surface Hopping approach [6]. The final photoelectrum spectrum is retrieved for different probe pulses.
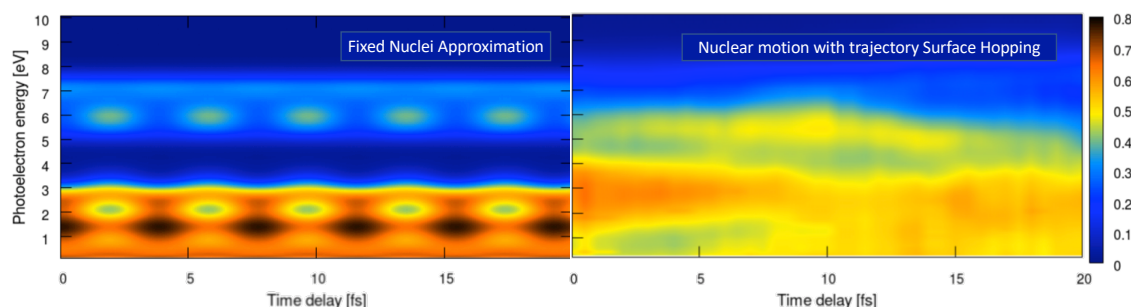
Figure 1: XUV-pump/XUV-probe time-resolved photoelectron spectra for glycine.

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Off-resonance-enhanced polarization control in two-photon ionization

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We investigate a polarization control scheme in two-color two-photon atomic ionization. Experiments employing free-electron laser or high-order harmonic generation sources have shown light polarization dependencies in above threshold ionization of atoms assisted with an IR field. These were mostly performed at relatively high photoelectron energies where the soft-photon approximation remains valid [1]. We use here a perturbation theoryapproach to show the larger degree of control that can be attained when the short wavelength photon energy is below the ionization threshold. This largely unexplored energy region offers unique possibilities to achieve polarization control of the reaction [2].

We have further investigated angularly resolved one-color two-photon single ionization yields that reveal the underlying dominant mechanism in different energy regions [3]. We specifically explore the contributions of radial and angular electron correlation terms. A single active electron picture is a qualitatively valid approach for the lowest photon energies, even in the above-threshold ionization region. Nonetheless, angular correlation plays a detectable role in the low-energy region and a major role at higher energies when autoionizing states are populated. As the photon energy increases, sequential ionization-excitation dominates; therefore, the resulting probability distributions are explained as the result of two active uncorrelated electrons. This uncorrelated picture fails again for photon energies above ionization potential of the ion.

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Tunneling Ionization Study Of Linear Molecules In Strong-Field Laser Pulses

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In the past decade substantial progress has been made in the understanding of the dynamics of molecules in intense-laser fields ($10^{13} - 10^{18}$ Wcm^2) [1,2]. As a result, experimental, theoretical and computational investigation of this phenomena have demonstrated fundamental processes such as bond softening and hardening, laser induced alignment, and enhanced ionization at critical internuclear distances. Most of these phenomena are based on tunnel ionization of neutral atoms and molecules as the first step of the physical processes [3]. There is a wealth of theoretical approaches to the atomic ionization dynamics in a strong field that have entertained theoretical physicists since Keldysh [4] early work. One has been developed from extensions to Keldysh theory into the so-called Strong Field Approximation (SFA) [5]. Following the Keldysh formalism of the tunneling ionization rate in a strong electromagnetic field Perelomov, Popov and Terent'ev developed another tunneling model (PPT) [6] that was further extended by Ammosov, Delone and Krainov and is now known as ADK-theory [7]. During the last years, the scope of strong field physics has been extended to the systems more complex than atoms, including molecules, fullerenes and clusters where all abovementioned theories are also being suitably adapted (molecular orbital SFA (MO-SFA) [8], molecular orbital PPT (MO-PPT) [9], and molecular orbital ADK (MO-ADK) [10]). Up to now, we have carefully examined the MO-SFA, MO-PPT and MO-ADK models by comparing ionization rates and ionization probabilities of several linear molecules (N_2, O_2, NO and Cl_2) with recently performed experimental and numerical findings. To better understand and control the tunneling ionization dynamics of photoelectrons from more complex molecules in intense ultrashort laser pulses, in our further work, we would like to create a Monte Carlo simulation. In this way, we would gain an insight into the mechanism of this process and its potential application in specific fields.

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Attosecond transient absorption in graphene

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The revolution of producing pulses as short as several attoseconds (10^{-18} s) enables observing the fast motion of electron in complex systems. In particular, the ultrafast technique coined as attosecond transient absorption (ATA) results from such technology. ATA has been successfully applied in studies of electron dynamics in extended systems. Some previous experimental works demonstrated the possibility to track the tunneling excitation induced by intense laser pulses [1], the sub-femtosecond dynamics of both holes and electrons in semiconductors [2], to name just a few. However, ATA has not been investigated for graphene, a very interesting 2D material that has no band gap.

Here we theoretically investigate a ATA pump-probe setup, see Fig. 1, by solving a modified Bloch equations [3] for a tight-binding graphene. Our simulations show the possibility to track in real-time the carrier injection through the Dirac points by a mid-IR laser pulse.
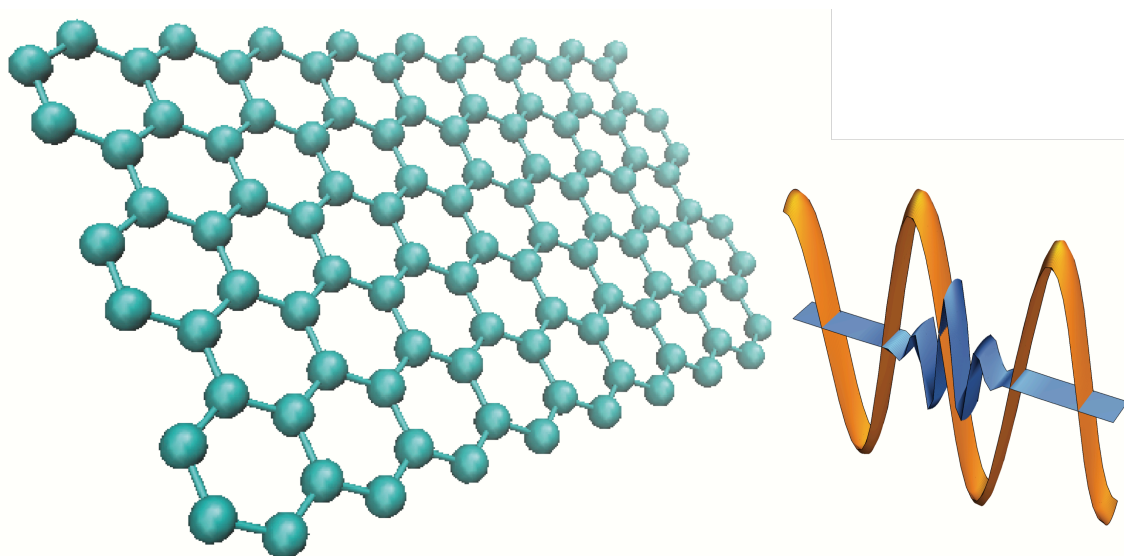
Figure 1: Schematic figure of ATA spectroscopy in graphene.

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Mapping initial transverse momenta of tunnel-ionized electrons to rescattering double ionization in nondipole regimes

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We investigate the double ionization of a model Neon atom in strong middle infrared laser pulses by simulating the classical trajectories of the electron ensemble. After one electron tunnels out from the laser-dressed Coulomb barrier, it might undergo different returning trajectories depending on its initial transverse momentum, which in this wavelength may propagate along or deviate from the polarization direction. This initial transverse momentum determines the rescattering time, and thus some trajectories can have returning time longer than one optical cycle. These late-returning trajectories determine the correlated electron-electron momentum distribution for double ionization and allow us to disentangle each double ionization event from the final momentum distribution. The description of these trajectories allow us also to understand how the nondipole effects modify the correlated electron-electron momentum distribution in double ionization.
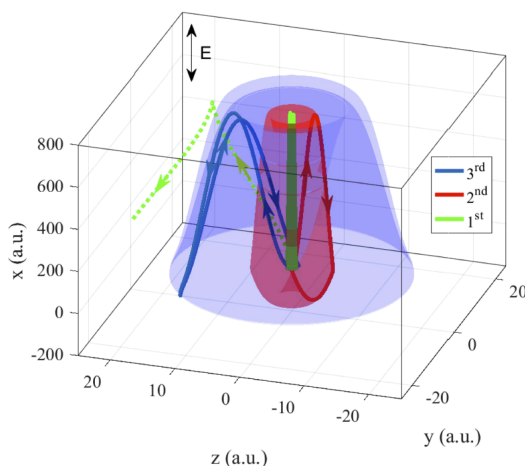
Fig. The typical trajectories for the first (green), second (red) and third (blue) rescattering without considering the magnetic field. The laser wavelength is 3000 nm, and the intensity is 3×10^{14} W/cm^2 . Surfaces are formed by rotating each trajectories with respect to the x-axis. The dashed curve is the trajectory starting with the identical displacement and momentum of the first rescattering trajectory but including the magnetic effect.

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High Resolution Mass Spectrometry and Velocity Map Imaging for Ultrafast Electron Dynamics in Biomolecules

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Pump-probe experiments with few-fs or sub-fs temporal resolution are excellent tools to investigate ultrafast dynamics in large molecules, such as amino acids [1] and DNA bases, or nanosize systems such as C_{60} and dielectric nanoparticles. We recently studied single nucleosides in a XUV-pump NIR-probe experiment, by resolving the dissociated ionic fragments according to their masses [2]. For larger molecules, a high mass resolution is required for distinguishing between different isotopes or protonated species.

We present experimental results using a new design and characterization of a velocity-map-imaging electron spectrometer combined with a reflectron mass spectrometer [3]. Simulations show that masses up to 1500 u can be resolved at room temperature and 150 u for 2-eV dissociation fragments, with simultaneous VMI of electrons up to 30 eV. We will present preliminary results of photoelectron and mass spectroscopy experiments performed with this double-sided spectrometer.

Attosecond and femtosecond pump-probe methods together with this double-sided spectrometer will enable us to make electron-ion covariance measurements, allowing us to reach a deeper understanding of non-adiabatic ultrafast dynamics occurring in complex bio-relevant molecules.

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A Parametric Waveform Synthesizer for Tunable Isolated Attosecond Pulse Generation without gating

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Isolated attosecond pulses obtained via high harmonic generation (HHG) enable the observation of sub-femtosecond dynamics underlying ultrafast chemical processes [1]. The bottleneck of these sources is a low flux, especially for high energy ((0.25-1) keV) photons. Multicolor fields have been demonstrated to improve on the yield and cut off energy of the harmonics [2].
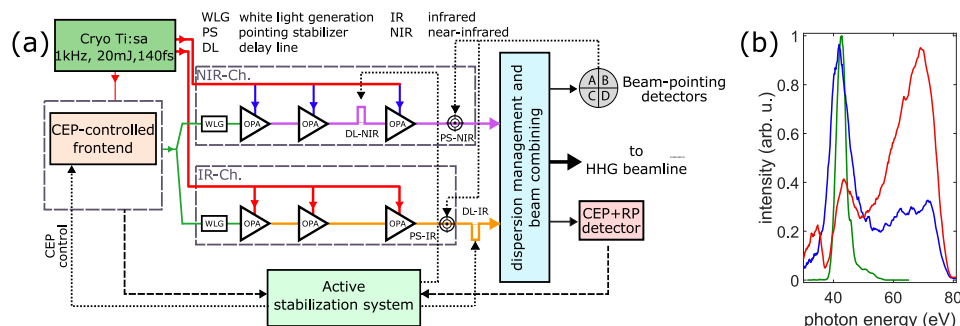
Figure 1: (a) Schematic of the parametric waveform synthesizer pumped by a Ti:S laser, including the frontend to generate carrier-envelope phase (CEP) stable seed pulses, optical parametric amplification (OPA) stages for both spectral channels and the feedback and stabilization units. (b) Maximum of HH continua tunable by varying the relative phase (RP) and/or the CEP.

We present a multi-octave, fully phase stable, sub-cycle parametric waveform synthesizer as shown in Fig. 1a, comprising a near infrared channel (0.65-0.95) μm and an infrared channel (1.2-2.2) μm with three amplifying stages each, resulting in an output pulse with 0.5 mJ energy and $\sim$3 fs FWHM duration at a central wavelength of 1.4 μm. For HHG in argon we have shown the generation and control of the XUV continua as shown in Fig. 1b. Streaking measurements have confirmed isolated attosecond pulse generation and an excellent long term stability of the waveform. We are currently exploring HHG in the water window spectral region with sub-cycle, non-sinusoidal driving fields. The predicted improvement in harmonic yield [2] should enable attosecond pump - attosecond probe experiments.

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Partial-wave analysis of multiphoton ionization of sodium by short laser pulses in over-the-barrier regime

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Multiphoton ionization of sodium by laser pulses of 800 nm wavelength and 57 fs duration is studied in the range of laser peak intensities belonging to over-the-barrier ionization regime. Photoelectron momentum distributions (PMD, see Figure 1) and energy spectra are determined numerically by solving the time dependent Schrödinger equation [1]. The calculated spectra agree well with the spectra obtained experimentally by Hart et al. [2]. The contributions of photoelectrons with different values of the orbital quantum number in the PMD are determined by expanding the photoelectron wave function in terms of partial waves. Partial wave analysis of the spectral peaks related to Freeman resonances has shown that each peak has photoelectron contributions from different ionization channels which are characterized by different photoelectron energies and different symmetries of released electron wave-packets.
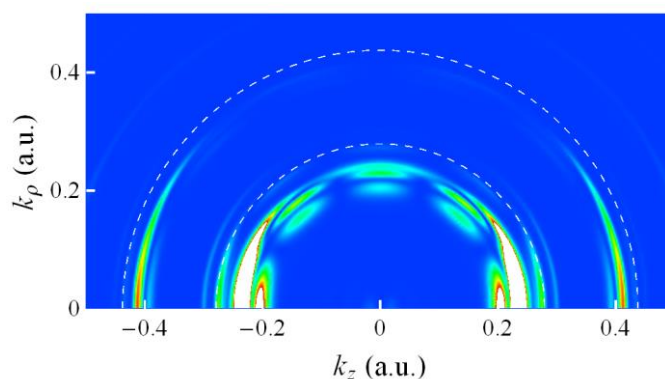
Figure 1: Calculated momentum distribution of photoelectrons produced in the ionization of sodium by the laser pulse of 800 nm wavelength, 57 fs FWHM and 4.9 TW/cm^2 peak intensity.

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Impact of Photoinduced Charge Migration on Photochemistry of Radicals and Switches

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Pre-excitation of certain vibrational modes of photoswitches as well as alteration of the photoinduced charge migration on sub-femtosecond timescale can influence the efficiency of the photoisomerization and ionization and can alter their photochemical reactivity.

Indolylfulgide (Figure 1) is a molecular photoswitch with high thermal stability and excellent switching properties. We have recently introduced this compound as a universal chemical actinometer for UV-NIR range suitable for measurement of the photon flux in various applications from material science to medicine.[1] It has been found that its photoisomerization is temperature- and wavelength-dependent. This unusual aspect has been attributed to its ultrafast (picosecond to sub-picosecond) ring-opening and ring closure that can be individually addressed by pre-excitation of photochemically active modes of photoreaction.[2]

Pre-excitation of the Z-form of the fulgide by UV light leads to the ring closure reaction. This fast ring closure generates a non-equilibrium state which is more likely to be opened by another light pulse. The quantum yield of the ring-opening reaction thus depends on the time-delay between the first pre-excitation UV pulse and the second visible light pulse with a peak at very short delay times (~2 ps).

This behavior offers a great possibility for investigation of the system by means of attosecond chemistry where a modulation of charge migration can dramatically influence the photochemical output of the reaction. Addressing the correct vibrational modes, one could expect severe increase of the reaction efficiency, turning off the reaction, or complete change of the reactivity leading to unprecedented results.
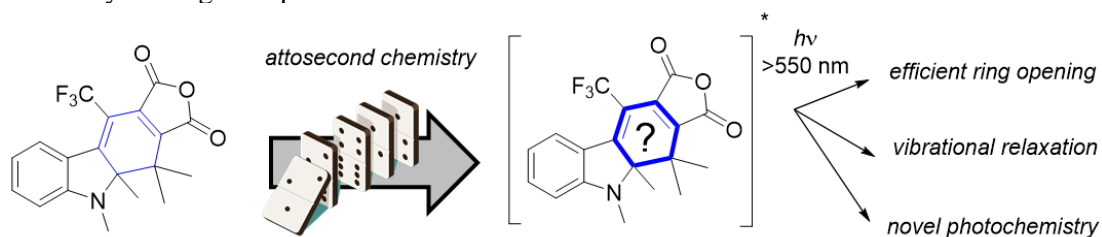
Figure 1: Attosecond-controlled photochemistry of fulgide-based molecular switches.

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Strong-field Fourier-transform spectra of H_2O^+ and D_2O^+

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Introduction. After molecules interact with external fields they are usually left in a superposition of field-free eigenstates, leading to the time-dependence of certain physical quantities, such as the ionization probability. This fact is exploited in the pump-probe method of strong-field Fourier-transform spectroscopy [1], whereby the pump pulse generates the cations to be measured (in a superposition state), while the probe pulse induces Coulomb explosion. The resulting ion-yield signal is an oscillating function of the time-delay between the two pulses. The Fourier transform (FT) of the signal provides transition frequencies of the cations generated by the pump pulse. In this study, we use theoretical methods to reproduce and interpret the experimental strong-field FT infrared spectra of H_2O^+ and D_2O^+.

Theory and results. We determine the vibrational states of H_2O and H_2O^+ with considerable accuracy, employing a dedicated software [2] and high-quality potential energy surfaces (PES) [3]. Then, assuming instantaneous ionization, the vibrational ground state of neutral H_2O is projected onto the H_2O^+ PES and time propagation is carried out, during which the expectation values of structural parameters, strongly related to the ionization probability, are evaluated. By taking the FT of these time-dependent expectation values, the peaks in the experimental spectrum can be reproduced and assigned to vibrational transition frequencies of H_2O^+ (see Fig. 1). Experimentally unresolved fine structures are also predicted by our accurate computations. However, certain experimental features could not be obtained with this simple approach; therefore, the possible role of enhanced ionization and rotational alignment was also investigated using basic models [4,5]. All the above steps were repeated for D_2O^+, as well.
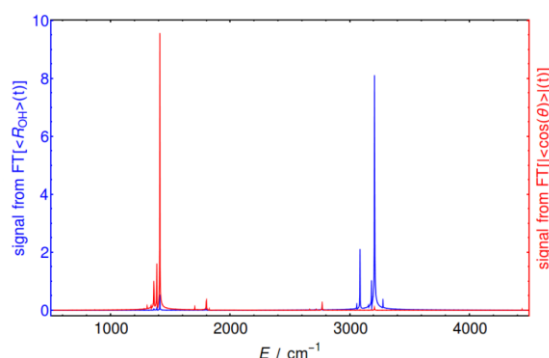
Figure 1. Simulated vibrational spectrum of H_2O^+ in its electronic ground state, obtained by taking the Fourier transform of time-dependent expectation values of structural parameters.

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Inner-shell photoabsorption and photoionization cross sections of valence excited states from asymmetric-Lanczos equation-of-motion coupled cluster singles and doubles theory

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The asymmetric-Lanczos-based equation-of-motion coupled cluster formalism to compute photoabsorption and photoionization cross sections of valence excited states [1] has been modified to enable the calculation of photoabsorption and photoionization spectral signatures from inner-shell electrons. The total photoionization curves were generated for the first two electronically excited states of water, ammonia, ethylene, carbon dioxide and uracil in both the ground state and the excited state optimized geometries by two different methodologies: an analytic continuation procedure based on the Padé approximants and by Stieltjes imaging.

Excited state property is dependent on both the electronic character of the molecular wavefunction and the nuclear dynamics. To take into account the later effect, we computed the spectra using both the optimized excited state geometry and FC geometry. Within the set of molecules under study, we see that electronic dynamics plays a significant role both in the pre and the post edge regions.

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Photodissociation of the LiF Molecule Controlled by THz Radiation

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Due to the intrinsic avoided crossing between their lowest lying Σ electronic states, alkali-halides became popular testing grounds for non-adiabatic effects. Recently, we started to investigate the lithium fluoride from this family of molecules, and showed the importance of the usually overlooked lowest lying Π state and rotational motion [1], which are both necessary for the accurate description of the system.

In the present work we investigate how a single-cycle laser pulse in the terahertz regime influences the photodissociation process. The laser molecule interaction follows the instantaneous electric field through the permanent dipoles and manifests in the Stark deformation of the potential surfaces. This entails the dynamical shifting of the crossings between these light induced potentials. These fluctuations lead to modulations of both the excitation probability and the branching ration between the two dissociation channels [2].

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Quantemol Electron Collisions: user-friendly software for electron scattering calculations

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Electron collisions with molecules are important in various applications such as molecular plasma physics and chemistry, electron-beam spectroscopy, photoelectron spectroscopy, astrophysics, and more. R-matrix theory[1] was developed to compute parameters of scattering taking into account quantum chemical effects. The underlying idea of the method is treating the incoming electron in the same manner is the molecular electrons in the vicinity of the molecule. Quantemol-Electron Collisions is a new generation highly automated software to calculate electron-molecule scattering cross sections based on R-matrix theory. The underlying calculations are carried out with the use of UKRmol+ codes [2] and Molpro package for electron structure calculations [3]. Quantemol-EC has attractive user-friendly interface and can be easily run by a researcher with limited experience in quantum chemical calculations. We are presenting examples of cross-section calculations for several molecules in cases where no experiment is available.
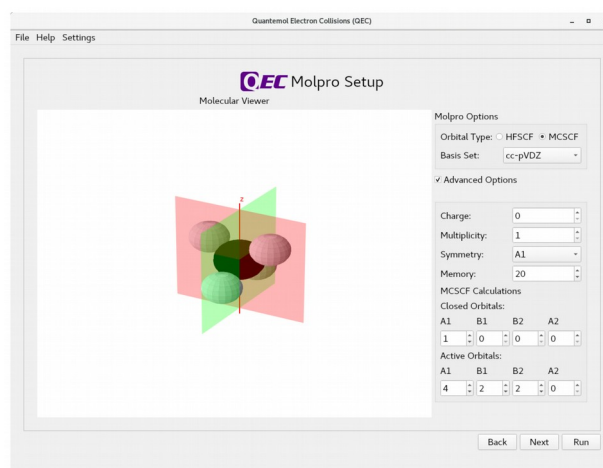
Figure 1. Screenshot of Quantemol-EC interface

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Two- vs. three-body fragmentation in photo-double-ionization of the six-membered heterocyclic molecules containing oxygen

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The heterocyclic rings containing oxygen or nitrogen atoms are incorporated into a wide variety of structures that play a significant role in many different fields of chemistry, medicine, and biology. Due to a specific atomic composition and bond arrangement, many of these molecules possess unique electronic properties, which may be probed by diverse spectroscopic techniques, including those utilizing synchrotron radiation. In particular, the photoelectron-photoion coincidence (PEPICO) technique provides detailed information about the presence of specific bonds, the reactivity of these molecules, as well as their electronic structure and decomposition mechanisms.

Therefore in the present communication, we present results on the photo-double-ionization and fragmentation of the six-membered heterocyclic molecules containing oxygen, namely 3,4-dihydro-2*H*-pyran (DHP, C_5H_8O) and tetrahydro-2*H*-pyran (THP, $C_5H_{10}O$). The experiments were carried out at the Gas Phase Photoemission beamline at the Elettra-Sincrotrone radiation facility exploiting the VUV excitation and the ion time-of-flight spectrometry combined with the PEPICO technique. The dissociative processes where only one electron is emitted are quite well known. However, double ionization is a more complex mechanism producing the doubly charged parent ion after the emission of two correlated electrons. These doubly charged ions are usually very reactive, short-living entities that can dissociate into the ionic fragments through a few many-body fragmentation pathways. The present experimental study aims at elucidating the mechanisms of these dissociation channels in DHP and THP. In particular, we show how the character of the bond arrangement in DHP and THP impacts the generation of two- and three-body charge separation reactions occurring at the lowest energies. C_5H_8O has a non-aromatic ring with five carbon atoms and one oxygen atom. It contains one double bond. By removing the double bond by two more hydrogen atoms, we get a saturated six-membered ring of tetrahydro-2*H*-pyran. The analysis reveals that this small change in the bond rearrangement may provide a pronounced stabilization of the DHP ring compared to the THP structure, featuring the activation of a two-body fragmentation pathway with competition to a three-body breakup.

Acknowledgments

Electron-transfer in the collisions of pyridyne with a low energy cations

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Electron-transfer (ET) reactions occur in the numerous biological processes involving oxygen binding, photosynthesis, or cellular respiration. Inner and outer sphere electron transfers in coordination complexes are also a topic of current research efforts in the bioinorganic and bioorganometallic chemistry. However, the most intense studies have been recently performed to understand the role of the ET ionization and fragmentation mechanisms in ionic collisions with molecules (see, e.g. [1, 2]). In particular, these processes are responsible for the generation and evolution of numerous gas-phase compounds in the interstellar medium and the atmospheres of planets [3]. The ion irradiation is assumed as one of the factors required in the conversion of non-organic molecules into the prebiotic building blocks of life in these environments. Indeed, carbon-rich meteorites contain many biologically relevant organic molecules. The most recent observations indeed show evidence of extraterrestrial amino acids [4], nucleobases [5], and ribose [6] in those primitive rocks. It is thus believed that meteorites could have been carriers of biological material needed to create life on the early Earth. However, the questions arise: How were these molecules formed? How could they have survived the bombardment of the solar wind consisting of photons, electrons, protons, and a few percent of heavier nuclei? Can we identify the processes leading to their creation or destruction? The laboratory investigations of collisions of the DNA, amino acids, and vitamins building blocks or their analogs with a different kind of radiation may shed some light on these issues.

Therefore, in the present communication, we present results of collisions of low energy cations with the pyridine molecules, the heteroaromatic building blocks of vitamins, pharmaceuticals, and agrochemicals. We have utilized the collision-induced emission spectroscopy to explore the collisional excitation products and the spectral signatures of collisional mechanisms occurring in the $H^+/H_2^+/He^+$ + pyridine impact systems. Particular attention will be paid to the electron capture from the target molecules to the projectiles.

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Relativistic attosecond transient absorption

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Attosecond transient absorption spectroscopy (ATAS) has been developed in the last decade with the aim of studying the electron dynamics on its natural time scale [1]. In this context, relativistic effects may play an important role. For example, when investigating heavy noble gases, Pauli's spin-orbit coupling interaction has to be included in the calculations to properly describe the theoretical spectra [2]. However, despite the success of this kind of approximations, they are not fully relativistic and present a limited range of application. For this reason, we have decided to elaborate a general relativistic attosecond transient absorption theory. As in the non-relativistic formulation, a generalized photoabsorption cross section can be derived from the definition of energy ganied by the atom when interacting with the electromagnetic field. Nevertheless, the electron dynamics is not controlled by the time-dependent Schrödinger equation (TDSE) any more, but by the time-dependent Dirac equation (TDDE). Then, the relativistic instantaneous power delivered to the atom can be obtained in the length and in the velocity forms. In order to validate our relativistic formulation of ATAS, and inspired by previous theoretical works [3, 4, 5], we have reproduced different ATAS scenarios by solving numerically the TDSE and the TDDE.

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The impact of electron-electron correlation in ultrafast attosecond single ionization dynamics

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The attosecond ultrafast ionization dynamics of correlated two- or many-electron systems have, so far, been mainly addressed investigating atomic systems. In the case of single ionization, it is well known that electron-electron correlation modifies the ionization dynamics and observables beyond the single active electron picture, resulting in effects such as the Auger effect or shake-up/down and knock-up/down processes. Here, we extend these works by investigating the attosecond ionization of a molecular system involving correlated two-electron dynamics, as well as non-adiabatic nuclear dynamics. Employing a charge-transfer molecular model system with two differently bound electrons, a strongly and a weakly bound electron, we distinguish different pathways leading to ionization, be it direct ionization or ionization involving elastic and inelastic electron scattering processes. We find that different pathways result in a difference in the electronic population of the parent molecular ion, which, in turn, involves different subsequent (non-adiabatic) postionization dynamics on different time scales.
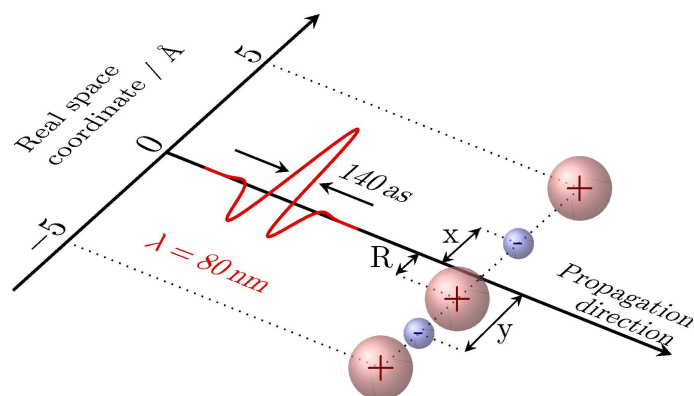
Figure: Configuration of the extended Shin-Metiu system: An attosecond XUV pulse is used to ionize a linear molecule aligned with the pulse's polarization axis. The molecule consists of two fixed nuclei at ± 5 Å, two mobile electrons at x and y, and a movable central nucleus at R.

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