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BOOK OF ABSTRACTS

XUVTRPES Workshop 2025

Extreme ultraviolet time-resolved photoelectron spectroscopy: toward the ultimate probe of molecular dynamics

January 08 to 10, 2025

University of Freiburg
Kollegiengebäude I
Platz der Universität 3
D-79098 Freiburg

universität freiburg

Imprint

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Scientific Organisation: **Lukas Bruder** and **Sebastian Hartweg**
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Welcome to Freiburg!

Freiburg im Breisgau was founded in 1120 by Konrad and Duke Berthold III of Zähringen. Because of its position at a junction of both trade routes from the Mediterranean Sea to the North Sea and the Rhine and Danube rivers, the city prospered and gained attraction from both traders and craftsmen. In ca. 1200, during the rule of the last Duke of Zähringen, construction of the Münster began, the big cathedral in the middle of the city and one of the most famous landmarks of Freiburg. The building was officially consecrated on December the 5th in 1513. While the building itself is being used by them, it does not actually belong to the catholic church. Rather it is still owned by the citizens of Freiburg, which is a rarity for churches in Europe. Roughly 45 years earlier, in 1457, after founding the first university in Austrian-Habsburg territory in Vienna, the Habsburg dynasty founded the Albert-Ludwig-University. It is the fifth-oldest university in Germany. Today, it is seen as one of the country's top universities and has gained international reputation. The city of Freiburg itself has many different unique details und secrets to find, should one go exploring. One of them is quite openly visible in some parts of the town. Framing the streets of the inner city, one of the oldest still standing parts of Freiburg, are small channels, sometimes decorated with colourful little boats. They are called "Bächle", which means "small creek" in the south-german dialect of the region allegedly, every person, who accidentally steps into one of them will marry a citizen of Freiburg, so remember... Beware of the Bächle!

General Information

Duration

Wednesday, January 08, 2025, 4:30 p.m. – Friday, January 10, 2025, 3:30 p.m.

Venue

University of Freiburg
Kollegiengebäude I – *Aula & Prometheushalle*
Platz der Universität 3
D-79098 Freiburg

Lab tours

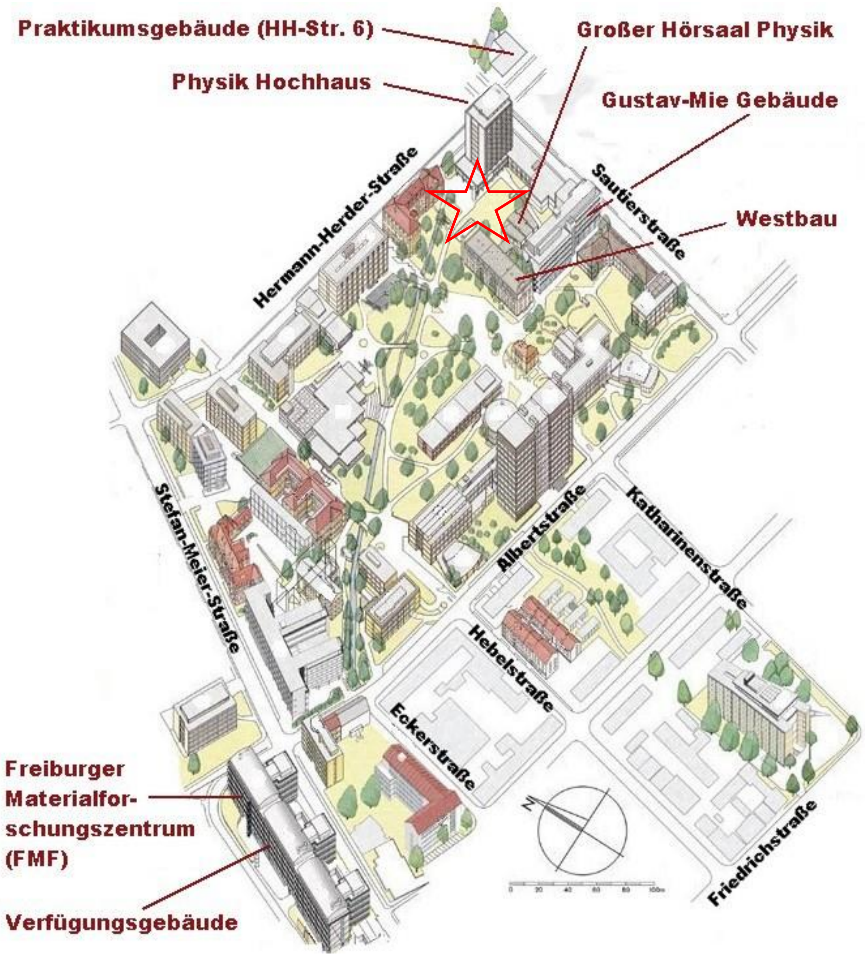
Tours are offered in the laboratories of:

Sansone (attosecond science and reaction microscopes) &
Issendorff (cluster physics and photoelectron detectors)
OR

Stienkemeier/Hartweg (TRPES) &
Bruder (coherent multidimensional spectroscopy)

The meeting point for the lab tours is *in front of the physics high rise*: Hermann-Herder-Str. 3, 79104 Freiburg.

Meeting time is 16:30 h on Wednesday 08 January.



Meals & Drinks

During the workshop a reception, lunch, coffee breaks (morning & afternoon), as well as a conference dinner will be provided.

Reception on January 8 at 6:00 pm
(During the poster session)

University of Freiburg
Kollegiengebäude I –*Prometheushalle*
Platz der Universität 3
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Lunch on January 9 & 10

Restaurant "*Haus zur Lieben Hand*"
Löwenstraße 16
D-79098 Freiburg

Thursday, January 9 at 12:20
Friday, January 10 at 12.10

Conference Dinner on January 9 at 7:00 pm

Restaurant "*Paradies*"
Mathildenstraße 26-28
D-79106 Freiburg

Program

Day 1	Wednesday, January 8
16:30-18:00	Lab tours
18:00 – 22:00	Welcome reception and poster session
Day 2	Thursday, January 9
Session 1, chair: Russell Minns	
8:45-9:00	Opening remarks
9:00-9:35	Daniel Rolles: Studying UV-induced ring reconfiguration reactions with XUV TRPES at free-electron lasers
9:35-10:10	Rocio Borrego-Varillas: Few-femtosecond UV pump – XUV probe spectroscopy of organic compounds
10:10-10:50	Coffee break
10:50-11:25	Francesca Callegari: Charge-directed reactivity
11:25-12:00	Albert Stolow: Direct Observation of Electronic Coherences in Molecules from Time-Resolved Photoelectron Angular Distributions
12:00-12:20	Hot Topic 1: Stefano Severino Probing the Non-Adiabatic Relaxation Dynamics of ortho-nitrobenzaldehyde via sub-20-fs UV-XUV tr-PES
12:20-13:50	Lunch
Session 2, chair: Rocio Borrego-Varillas	
13:50-14:25	Sonia Coriani: Theoretical approaches to (time-resolved) photoelectron spectroscopy across different frequency regimes
14:25-15:00	Thomas Wolf: Insights into ultrafast photochemical dynamics from XUV and soft X-ray spectroscopy
15:00-15:20	Hot Topic 2: Xiaojun Wang Probing electronic relaxation decay of photoexcited thymine using time-resolved XPS
15:20-15:40	Hot Topic 3: Katharina Theil Investigating Photoinduced Dynamics of a 1,4-Azaborine with Time-Resolved X-ray Spectroscopy
15:40-16:20	Coffee break
16:20-16:55	Michael Thoss: Quantum dynamical simulation of intramolecular singlet fission
16:55-17:30	Ulrich Höfer: Time-resolved photoemission orbital tomography
17:30-17:50	Hot Topic 4: Michael Heber Unleashing Functionality in Molecule–2D Material Systems

17:50-18:10	Hot Topic 5: Andrea Trabattoni Correlation-driven attosecond photoemission delay in the plasmonic excitation of C60 fullerene
19:00-22:00	Dinner
Day 3	**Friday, January 10**
Session 3, chair: Albert Stolow	
8:30-9:05	Russell Minns: From Roaming to Ring Opening: Photoelectron spectroscopy of gas phase chemical dynamics
9:05-9:40	Oleg Kornilov: Time-resolved photoelectron spectroscopy of molecules in aqueous solutions
9:40-10:00	Hot Topic 6: Xincheng Miao Ab Initio Nonadiabatic Dynamics for Photochemical Processes
10:00-10:40	Coffee break
10:40-11:15	Bernd von Issendorff: Metal cluster photoelectron spectroscopy: surprising results and new tools
11:15-11:50	Giuseppe Sansone: Attosecond metrology and spectroscopy with the RABBIT technique
11:50-12:10	Hot Topic 7: Geoffrey Carneiro Decoherence phenomena of electron dynamics in liquid water
12:10-13:40	Lunch
Session 4, chair: Bernd von Issendorff	
13:40-14:15	Philipp Demekhin: Molecular Frame Photoelectron Angular Distributions (MFPADs): A sensitive access to molecular structure and dynamics
14:15-14:50	Laurent Nahon: Recent results on PECD: from static to time-resolved approaches
14:50-15:10	Hot Topic 8: Marcel Mudrich Ultrafast relaxation processes in photoexcited helium nanodroplets probed by XUV-TRPES
15:10-15:25	Concluding remarks

Invited talks

Few-femtosecond UV pump – XUV probe spectroscopy of organic compounds

R. Borrego-Varillas[1]

[1]*Consiglio Nazionale delle Ricerche, Istituto di Fotonica e Nanotecnologie, Piazza Leonardo da Vinci 32, Milano, Italy*

Photo-induced chemical reactions are at the basis of many biologically and chemically fundamental functions. Time-resolved photoelectron spectroscopy combining ultrashort UV and XUV pulses offers the right tools to investigate non-adiabatic dynamics, which typically evolve on ultrafast timescales (10-100 fs). In this talk, I will introduce our recently developed beamlines for investigating excited-state dynamics in organic compounds with temporal resolution ranging from sub-20 fs down to few-femtosecond.

In a first scheme broadband UV pump pulses are generated exploiting a scheme based on sum-frequency mixing and combined with tuneable XUV probe pulses obtained by high-order harmonic generation [1]. We are able to follow with unprecedented detail the non-adiabatic relaxation and ultrafast intersystem crossing in a prototypical aromatic molecule, acetylacetone (AcAc) (Fig. 1). The extreme temporal resolution allows us to resolve for the first time the ultrashort lifetime of the S2 state and to detect the coherent modulation of the signal characterizing the first hundreds of femtoseconds of the dynamics, unveiling an unexpected "triplet-assisted tunneling" mechanism.

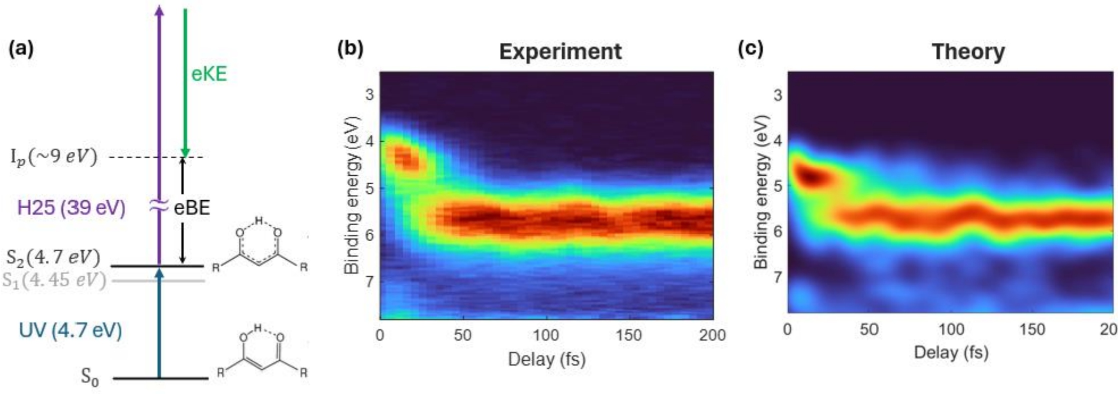

Fig. 1: a) Scheme of the experiment: the S2 state of AcAc is excited by 20-fs UV pulses, while the evolution of the wave packet is followed by 10-fs XUV probe. (b) Experimental and (c) simulated pump-probe maps.

To further extend these methods to the attosecond time scale, few-cycle UV pump pulses obtained by dispersive wave emission in hollow-core capillaries, are directly characterized for the first time with an all-in-vacuum self-diffraction FROG [2] and combined with XUV attosecond pulses. Preliminary results on pyrazine show the capability of this source for photoelectron/ion spectroscopy with unprecedented temporal resolution.

References

[1] Crego A. et al. (2024). " Sub-20-fs UV-XUV beamline for ultrafast molecular spectroscopy" Scientific Reports **14(1): 1-9.**

[2] Reduzzi M. et al. (2023) " Direct temporal characterization of sub-3-fs deep UV pulses generated by resonant dispersive wave emission" Optics Express **31**(16): 26854-26864.

Charge-directed reactivity

F. Calegari[1,2,3]

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[3]The Hamburg Centre for Ultrafast Imaging, University of Hamburg, 22761 Hamburg, Germany

The Nobel Prize in Physics awarded in 2023 underscored the transformative potential of attosecond light sources1, which now grant us unprecedented insights into the electron time scale within matter. This advancement has paved the way for the emergence of attochemistry2,3, a novel field aiming at manipulating chemical reactivity through the precise driving of electronic motion.

In this presentation, I will first give an overview of our latest developments towards compact few-femtosecond ultraviolet sources4,5 and VUV/soft-x ray attosecond sources. Additionally, I will highlight a variety of applications for these ultrashort light transients, such as the real-time observation of ultrafast charge migration and dissociative dynamics in photoexcited molecules8,9,10. A key focus will be on our novel approach to instigating well-controlled charge migration in chiral neutral molecules11, which represents a significant step toward achieving charge-directed reactivity—the ultimate objective of attochemistry.

Finally, I will present a Double-Blind Holography (DBH)-based approach12 to completely reconstruct the temporal profile of SASE FEL pulses on a single shot basis, which could be potentially used to both characterize attosecond FEL pulses and for timing with attosecond precision an FEL source with an external HHG-based attosecond source for spectroscopic applications.

References

[1] F. Calegari et al, J. Phys. B: Atom. Mol. Opt. Phys. 49, 062001 (2016)
[2] M. Nisoli, P. Decleva, F. Calegari et al, Chem. Rev. 117, 10760 (2017)
[3] F. Calegari, F. Martin, Commun Chem 6, 184 (2023)
[4] M. Galli et int., and F. Calegari, Opt. Lett. 44(6), 1308-1311 (2019)
[5] V. Wanie et int., and F. Calegari, Rev. Sci. Instrum. 95, 083004 (2024)
[8] F. Calegari et al, Science 346, 336 (2014)
[9] E. P Månsson et int., and F. Calegari, Communications Chemistry 4 (1), 1-7 (2021)
[10] L. Colaizzi et int, and F. Calegari, Nature Communications 15 (1), 9196 (2024)
[13] V. Wanie et int., and F. Calegari, Nature 630, 109–115 (2024)
[12] O. Pedatzur, et al. "Double-blind holography of attosecond pulses". Nature Photon 13, 91–95 (2019)

Theoretical approaches to (time-resolved) photoelectron spectroscopy across different frequency regimes

S. Coriani[1]

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Understanding at the molecular level which excited states are initially populated by light irradiation and through which ultrafast electron relaxation pathways they evolve is a fundamental enabling step to decode molecular functionalities and to be able to exploit such processes for technological applications. The last two decades have witnessed a proliferation of experimental techniques to investigate excited-state dynamics in real time, and hereby shed light on fundamental photochemical processes like, e.g., ultrafast internal conversion and intersystem crossing in RNA/DNA-bases, singlet fission, metal-to-ligand and metal-to-metal charge transfer in transition metal complexes, ring opening, H-bonding networks in solvated species. X-ray free electron lasers, for instance, have opened an extraordinary window for imaging individual events in chemical reactions with (sub-)femtosecond time resolution via techniques like time-resolved X-ray absorption (XAS) and photoelectron (XPS) spectroscopy. However, experiments alone are not sufficient: theory and computational simulations are indispensable for unravelling the information encoded in the spectra.

I will present some of our work on the development and application of rigorous quantum chemical methods to simulate (time-resolved) photoelectron spectroscopy across different frequency regimes, in particular soft x-ray, and their application to the interpretation of cutting-edge experimental studies that investigate electronic structure and relaxation mechanism following electronic excitation and/or ionization of functional molecules [1-4].

References

[1] Vidal, M.L.; Krylov, A.I., Coriani, S., (2020) "Dyson orbitals within the fc-CVS-EOM-CCSD framework: theory and application to X-ray photoelectron spectroscopy of ground and excited states". Phys. Chem. Chem. Phys. 22, 2693; ibidem 3744-3747.

[2] Moitra, T., Paul, A.C., Decleva, P., Koch, H., Coriani, S., (2022) "Multi-electron excitation contributions towards the primary and satellite states in the photoelectron spectrum". Phys. Chem. Chem. Phys. 24, 8329.

[3] Tenorio, B. N. C., Møller, K.B., Decleva, P., Coriani, S. (2022) "Disentangling the resonant Auger spectra of ozone: overlapping core-hole states and core-excited state dynamics". Phys. Chem. Chem. Phys. 24 28150-28163

[4] Bonanomi, M.; Tenorio, B.N.C., Ovcharenko, Y., Usenko, S., Avaldi, L., Bolognesi, P., Callegari, C., Coreno, M., Coriani, S., Decleva, P., Devetta, M., Došlić, N., Faccialà, D., De Fanis, A., Di Fraia, M., Lever, F., Mazza, T., Mullins, T., Pal, N., Piancastelli, M.N., Richter, R., Rivas, D. E., Senfftleben, B., Sapunar, M., Vozzi, C., Gühr, M., Meyer, M., Prince, Kevin C., and Plekan, O., (2024) "Unraveling the relaxation dynamics of Uracil: insights from time-resolved X-ray photoelectron spectroscopy", submitted.

Molecular Frame Photoelectron Angular Distributions (MFPADs): A sensitive access to molecular structure and dynamics

P. V. Demekhin[1]

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The body-fixed frame angular emission distributions of electrons emitted upon photoionization and decay processes (the so-called molecular frame photoelectron angular distributions, MFPADs) are known to be very sensitive probes for molecular structures and dynamics. When escaping from the ion, the emitted electrons accumulate detailed information on the target and on the dynamics of a process itself, illuminating the molecular potential from within. MFPADs provide the most complete information, which is not accessible otherwise. Over the past 25 years, our group has been developing and permanently improving a method for the theoretical description of electron continuum spectrum in molecules, which is known as a single center method. It allows for an accurate theoretical interpretation of the angle-, time -, and spin-resolved ionization and decay processes in molecules [1-4]. During this talk, I will discuss resent applications of the method to: diffraction imaging of molecular structure and dynamics by high-energy photoelectrons [5,6] and a fascinating chiroptical phenomenon of photoelectron circular dichroism (PECD) [7-9], which is prominent at low electron kinetic energies. Finally, I will elaborate towards a time-resolved emitter-site-selective PECD of chiral molecules in the gas phase [10] and speculate on perspectives of ultrafast determination of their structure and dissociation dynamics at high-repetition XFELs with the light polarization control [11].

References

[1] Demekhin, Ph. V., Ehresmann, A. and Sukhorukov V. L. (2011) “Single center method: A computational tool for ionization and electronic excitation studies of molecules.” J. Chem. Phys. 134: 024113.

[2] Galitskiy, S. A., Artemyev, A. N., Jänkälä, K., Lagutin, B. M. and Demekhin, Ph. V. (2015) “Hartree-Fock calculation of the differential photoionization cross sections of small Li clusters.” J. Chem. Phys. 142: 034306.

[3] Artemyev, A. N., Müller, A. D., Hochstuhl, D. and Demekhin, Ph. V. (2015) “Photoelectron circular dichroism in the multiphoton ionization by short laser pulses. I. Propagation of single-active-electron wave packets in chiral pseudo-potentials.” J. Chem. Phys. 142: 244105.

[4] Artemyev, A. N., Kutscher, E., Lagutin, B. M. and Demekhin, Ph. V. (2023) “Theoretical study of spin polarization in multiphoton ionization of Xe.” J. Chem. Phys. 158: 154115.

[5] Kastirke, G., et al. (2020) “Photoelectron Diffraction Imaging of a Molecular Breakup Using an X-Ray Free-Electron Laser.” Phys. Rev. X 10: 021052.

[6] Vela-Perez, I. et al. (2023) “High-energy molecular-frame photoelectron angular distributions: a molecular bond-length ruler.” Phys. Chem. Chem. Phys. 25: 13784.

[7] Tia, M., et al. (2017) “Observation of Enhanced Chiral Asymmetries in the Inner-Shell Photoionization of Uniaxially Oriented Methyloxirane Enantiomers.” J. Phys. Chem. Lett. 8: 2780.

[8] Fehre, K., et al. (2021) “Fourfold Differential Photoelectron Circular Dichroism.” Phys. Rev. Lett. 127: 103201.

[9] Fehre, K., et al. (2022) “A new route for enantio-sensitive structurebdetermination by photoelectron scattering onbmolecules in the gas phase.” Phys. Chem. Chem. Phys. 24: 26458.

[10] Ilchen, M., et al. (2021) “Site-specific interrogation of an ionic chiral fragment during photolysis using an X-ray free-electron laser.” Communication Chemistry 4:119.

[11] Ilchen, M., et al. (2024) “Opportunities for Gas-Phase Science at Short-Wavelength Free-Electron Lasers with Undulator-Based Polarization Control.” arXiv:2311.11519v1

Time-resolved photoemission orbital tomography

U. Höfer[1,2]

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[2]Regensburg Center for Ultrafast Nanoscopy (RUN), Universitätsstrasse 31, 93053 Regensburg, Germany

Photoemission orbital tomography (POT) is a powerful technique, by which the electron distribution in orbitals of well-ordered molecules at solid surfaces can be imaged in momentum space [1]. Combined with laser-pump probe techniques, the method cannot only be used to investigate the dynamics of charge transfer processes at molecular interfaces. Time-resolved photoemission orbital tomography (tr-POT) also has unique potential to take slow motion videos of bond formation processes at surfaces.

In this talk, I will first review the basic principles of POT and then discuss first results obtained by tr-POT [2,3]. For the model system PTCDA/Cu(100)-2O, we have revealed two distinct excitation pathways with visible light. While the parallel component of the electric field makes a direct HOMO-LUMO transition in PTCDA, the perpendicular component transfers a substrate electron into the molecular LUMO (Figure 1). For CuPc on the same surface, coherent two-photon photoemission out of the HOMO, simultaneous to one-photon photoemission from the incoherently populated LUMO gives rise to a momentum distribution of the photoelectrons that changes as function of delay time [3]. A promising strategy to time-resolve surface bond formation with tr-POT is to drive the molecular frame by the strong electric field of THz pulses and to perform photoelectron spectroscopy with subcycle time resolution [4].

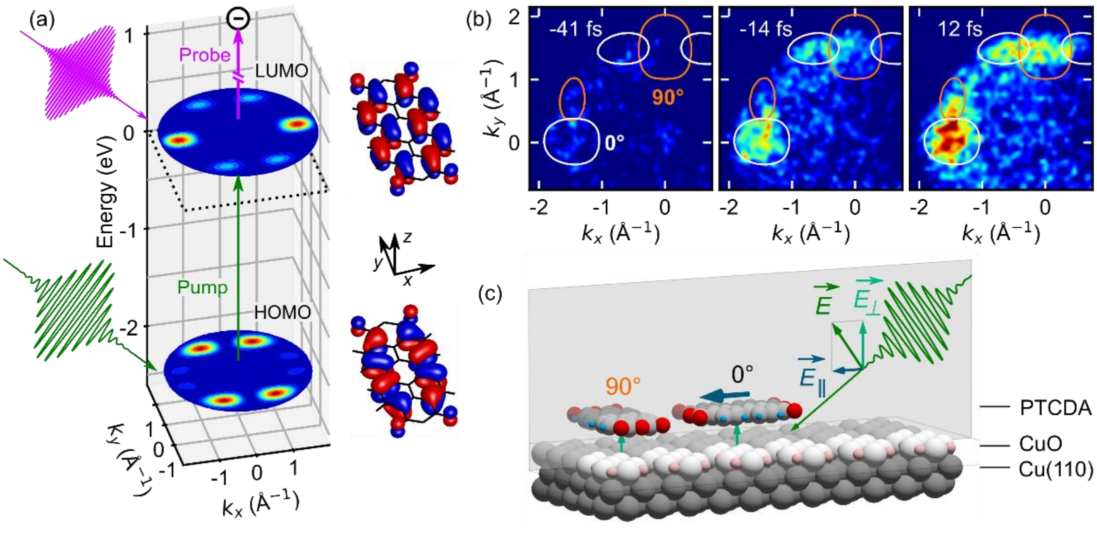

Figure 1: (a) Excitation scheme for time-resolved photoemission orbital tomography. (b) Measured LUMO momentum maps of PTCDA/Cu(100)-2O for three selected delay times between pump and probe pulses. (c) Scheme of intramolecular and substrate-to-molecule excitation pathways. The LUMO pattern of the 0° molecule in (b) is seen to light up faster due to resonant HOMO-LUMO excitation than that of the 90° populated across the CuO interface [2].

References

[1] Puschnig, P., et al. (2009). "Reconstruction of molecular orbital densities from photoemission data" Science 326(5953): 702.
[2] Wallauer, R., et al. (2021). "Tracing orbital images on ultrafast time scales" Science 371(6533): 1056.
[3] Adamkiewicz, A., et al. (2023). "Coherent and incoherent excitation pathways in time-resolved photoemission orbital tomography of CuPc/Cu(001)-2O" J. Phys. Chem. C 127(41): 20411.
[4] Ito, S., et al. (2023). "Build-up and dephasing of Floquet–Bloch bands on subcycle timescales" Nature 616: 696.

Metal cluster photoelectron spectroscopy: surprising results and new tools

B. v. Issendorff[1]

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Simple metal clusters are close to ideal few to many particle quantum systems; they can be seen as a well-defined number of electrons trapped in the harmonic potential produced by the almost homogeneously charged spherical ion background.

This leads to the well know electron shell structure discovered almost 50 years ago [1], a highly discretized density of states consisting of angular momentum eigenstates. But it also has direct consequences for dynamics like photoemission; as we could recently demonstrate, the angular distribution of photoelectrons exhibits a universal behaviour in accordance with a very simple model [2]. Nevertheless, the almost free electrons in simple metal clusters do interact with the structured ion background, which perturbs and mixes the electronic states. Characterizing this perturbation by measuring the electronic density of states via photoelectron spectroscopy can therefore yield information about the cluster geometric structure. In fact, this has been one of the main tools in cluster physics for cluster geometry determination; it, however, only works if measured spectra are sufficiently well resolved to distinguish between different isomers and if good calculations of the electronic density of states are available.

On both the experimental and the theoretical part a significant progress has been made over recent years, permitting a much more detailed insight into the electronic structure of metal clusters and its interplay with the geometric structure. I will discuss examples of simple metal cluster systems of increasing complexity, from sodium over copper and silver to gold. Here a number of unexpected geometric structures can be identified, as well as exotic electronic states.

Additionally I will discuss recent technical developments in cluster spectroscopy, with the aim to make use of new light sources like high harmonic sources, FELs and synchrotrons.

References

[1] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Electronic Shell Structure and Abundances of Sodium Clusters, Phys. Rev. Lett. 52, 2141 (1984)
[2] A. Piechaczek, C. Bartels, C. Hock, J.-M. Rost, and B. von Issendorff, Decoherence-Induced Universality in Simple Metal Cluster Photoelectron Angular Distributions, Phys. Rev. Lett. 126, 233201 (2021)

Time-resolved photoelectron spectroscopy of molecules in aqueous solutions

O. Kornilov[1]

[1]*Max-Born-Institut, Berlin, Germany*

We report on the state-of-the-art time-resolved photoelectron spectroscopy (LJ-TRPES) of molecular chromophores solvated in aqueous environment using wavelength-selected XUV pulses from high-order harmonic generation and micro-liquid jet (LJ) technology. LJ-TRPES is one of the most direct analytic methods to follow transient electronic structures of complex photoexcited molecules. It allows observation of dynamics via conical intersections in contrast to all-optical measurements, which are often blind to these regions of potential energy surfaces. Relaxation dynamics of azobenzene-based (N=N) and C=C based isomerization in molecules will be discussed, including theoretical considerations for molecules in solution and comparison with all-optical transient absorption spectroscopy measurements.

From Roaming to Ring Opening: Photoelectron spectroscopy of gas phase chemical dynamics

R. Minns[1]

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Extreme ultraviolet probes in photoelectron spectroscopy measurements allow detection of critical structures, from the initial electronic ground-state, through to the photochemical reaction products. In this presentation I will discuss recent gas phase measurements with a particular focus on the dynamics of halothiophenes (2-Bromothiophene and 2-Iodothiophene). The measurements highlight competing internal conversion processes that lead to either dissociation of the carbon-halogen bond, or ground state recovery followed by ring opening on the electronic ground state. The relative contribution of each is shown to be dependent on the identity of the halogen and excitation wavelength.

Recent results on PECD : from static to time-resolved approaches

L. Nahon[1]

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Chirality is ubiquitous in nature, especially in the biosphere, and the so-called chiral recognition process is fundamental for metabolism and drug action. Within a bottom/up approach of molecular complexity, the study of isolated, substrate- and solvent-free chiral species is crucial, but classical chiroptical probes such as Circular Dichroism (CD) in absorption are poorly-adapted to dilute matter because of their very weak associated asymmetries.

At the opposite, two decades ago was introduced a new chiroptical effect called Photoelectron Circular Dichroism (PECD), allowed in the electric dipole approximation, leading to very intense (up to 40 %) forward/backward asymmetries, with respect to the photon axis, in the angular distribution of photoelectrons produced by circularly-polarized light ionization of gas phase pure enantiomers. PECD happens to be a universal, orbital-specific, photon energy dependent chiroptical effect and is a subtle probe of the molecular potential being very sensitive to static molecular structures such as conformers, isomers, clusters, as well as to vibrational motion, much more so than other observables in photoionization such as the cross section (Photoelectron Spectrum-PES) or the usual (achiral) b asymmetry parameter (for a review see [1]). Therefore, PECD studies have both a fundamental and an analytical interest.

Several recent results regarding static one VUV-photon valence-shell PECD will be presented, including the specific sensitivity of PECD to conformations [2], completed by a recent two-photon REMPI demonstration of conformer-selective PECD [3], as well as a first evidence of induced-PECD onto an achiral chromophore within a molecular complex [4].

We will then move towards Time-Resolved PECD (TR-PECD), performed with the FERMI FEL enabling the chemical-specific, site-specific, and enantio-sensitive observation of the electronic structure of a transiently photoexcited chiral molecule via core-shell TR-PECD [5].

References

[1] R. Hadidi, D. Bozanic, G. Garcia, L. Nahon, Electron asymmetries in the photoionization of chiral molecules: possible astrophysical implications, Advances in Physics: X, 3 (2018) 1477530.

[2] J. Dupont, V. Lepere, A. Zehnacker, S. Hartweg, G.A. Garcia, L. Nahon, Photoelectron Circular Dichroism as a Signature of Subtle Conformational Changes: The Case of Ring Inversion in 1-Indanol, J Phys Chem Lett, 13 (2022) 2313-2320.

[3] E. Rouquet, J. Dupont, V. Lepere, G.A. Garcia, L. Nahon, A. Zehnacker, Conformer-Selective Photoelectron Circular Dichroism, Angew. Chem. Int. Ed. Engl., (2024) e202401423.

[4] E. Rouquet, M. Roy Chowdhury, G.A. Garcia, L. Nahon, J. Dupont, V. Lepère, K. Le Barbu-Debus, A. Zehnacker, Induced photoelectron circular dichroism onto an achiral chromophore, Nat. Commun., 14 (2023) 6290.

[5] D. Faccialà et al., Time-Resolved Chiral X-Ray Photoelectron Spectroscopy with Transiently Enhanced Atomic Site Selectivity: A Free-Electron Laser Investigation of Electronically Excited Fenchone Enantiomers, Phys. Rev. X, 13 (2023) 011044.

Studying UV-induced ring reconfiguration reactions with XUV TRPES at free-electron lasers

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TRPES is a powerful tool to study electronic de-excitation and chemical changes during photochemical reactions. However, when using visible or ultraviolet (UV) pulses as probe, the observation window is often limited to low-binding-energy excited states near the Franck-Condon region. This limitation can be overcome when probing the reaction with extreme ultraviolet (XUV) pulses produced, e.g., from a free-electron laser (FEL) or a high harmonic generation (HHG) source. This allows for the entire reaction pathway to be probed, including any structural rearrangement or dissociation occurring on the electronic ground state. I will present two examples of XUV TRPES experiments performed at the FERMI FEL that take advantage of these capabilities: an investigation of the UV-(266-nm)-induced ring-opening reaction of the prototypical heterocyclic molecule thiophenone (C4H4OS), and a study of the UV-(200-nm)-induced ring-reconfiguration of the quadricyclane-norbornadiene (C7H8) photo switch. I will also compare the findings to results obtained for the same molecules with other ultrafast techniques to highlight the strengths and weaknesses of each method and the power of a multi-modal probing approach. Finally, if time permits, I will present first results from a new 100-kHz, HHG-based TRPES setup at Kansas State University optimized for coincident detection of photoelectrons and ions.

RABBIT for attosecond metrology and molecular spectroscopy

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The reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) technique is at the heart of attosecond metrology [1] and has been widely used in attosecond spectroscopy of molecules [2].

Typically, RABBIT reconstructs the relative phase between odd harmonics of a fundamental infrared (IR) field by measuring the photoelectron spectra generated in the photoionisation process by an extreme ultraviolet comb assisted by an IR pulse. To achieve this goal, the intensity of the IR field is limited to allow ionisation pathways characterised by the exchange of only one infrared (IR) photon.

In this presentation, I will show that the same underlying principle, based on the interference of different photoionisation pathways, can be used to determine the relative phase of harmonics separated by up to six IR photons, where each pathway may require the exchange of up to five IR photons[3,4].

I will also present experimental data showing how the RABBIT technique can be used to infer information about the molecular potential [5] and the molecular dynamics [6] triggered by the photoionisation event induced by the absorption of an extreme ultraviolet photon in small molecules.

References

[1] Paul, P. M. et al. Observation of a Train of Attosecond Pulses from High Harmonic Generation. Science **292**, 1689–1692 (2001)

[2] Calegari, F. et al Advances in attosecond science J. Phys. B: At. Mol. Opt. Phys. **49** 062001 (2016)

[3] Maroju, P. K. et al. Attosecond pulse shaping using a seeded free-electron laser. Nature **578**,
477 386–391 (2020)

[4] Maroju, P. K. et al. Attosecond temporal structure of non-consecutive harmonic combs revealed by multiple near-infrared photon transitions in two-color photoionisation (submitted)

[5] Ahmadi, H. et al. Attosecond photoionisation time delays reveal the anisotropy of the molecular potential in the recoil frame. Nature Communications **13**, 1242 (2022).

[6] Ertel, D. et al. Influence of nuclear dynamics on molecular attosecond photoelectron interferometry. Science Advances **9**, eadh7747 (2023).

Direct Observation of Electronic Coherences in Molecules from Time-Resolved Photoelectron Angular Distributions

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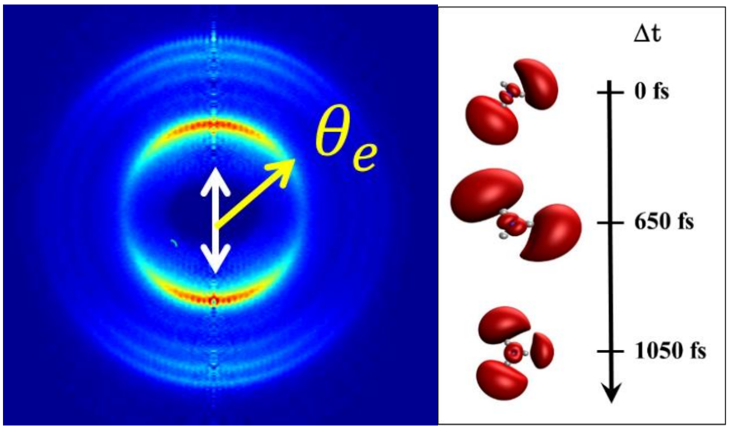
Electronic coherences in molecules are ultrafast charge oscillations on the Molecular Frame (MF). Their direct observation and separation from electronic population dynamics is a long-standing goal. We discuss a valence shell Lab Frame (LF) scattering method for probing electronic coherences in isolated targets. MF electronic coherences lead to LF electronic anisotropies directly observable by an ultrafast angle-resolved scattering technique. The scattering probe may be based on ultrafast electron or X-ray scattering, or angle-resolved photoelectron spectroscopy, as shown here. Moment analysis of the measured LF anisotropy completely separates electronic coherences from population dynamics. Our proof-of-concept demonstration is based on the technique of ultrafast Time-Resolved Photoelectron Angular Distributions (TRPADs). We emphasize that this general time-angle resolved scattering anisotropy approach applies equally to attosecond/femtosecond electronic coherences in isolated systems.



Direct observation of electronic coherences in isolated molecules

References

[1] "Ultrafast Molecular Frame Quantum Tomography", Phys.Rev.Lett. 131, 193001 (2023)
[2] "Formation of electronic coherences in conical intersection-mediated dynamics", J.Phys.B 55, 044004 (2022)
[3] "Ultrafast molecular frame electronic coherences from lab frame scattering anisotropies", J.Phys.B. 53 114001 (2020)

Quantum dynamical simulation of intramolecular singlet fission

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Singlet fission (SF) is a multiple exciton generation process in which two triplet excitons are generated from a singlet exciton [1]. It has received significant attention recently as a potential way to overcome the Shockley-Queisser limit of conventional solar cells. In this contribution, we study the dynamics of intramolecular SF in a series of pentacene dimers covalently bonded through different spacer groups [2,3]. The study employs a combination of multireference perturbation theory and quantum dynamical multiconfiguration methods [4,5]. The results provide insight into the key roles that the molecular and electronic structure of the spacer, the electronic states involved in the process, and the coupling to molecular vibrations play in intramolecular SF. In particular, it is shown that the population of the multiexcitonic state, corresponding to the first step of the intramolecular SF process, occurs mainly through a superexchange-like mechanism involving charge transfer states and is facilitated by vibronic coupling. Furthermore, the influence of spin-dipolar coupling on the singlet fission process is discussed [6].

References

[1] M. B. Smith, J. Michl, Chem. Rev. 110, 6891 (2010).
[2] J. Zirzlmeier, D. Lehnherr, P. B. Coto, E. T. Chernick, R. Casillas, B. Basel, M. Thoss, R. R. Tykwinski, D. M. Guldi, Proc. Natl. Acad. Sci. (USA), 112, 5325 (2015).
[3] B. Basel, J. Zirzlmeier, C. Hetzer, B. Phelan, M. Krzyaniak, R. Reddy, P.B. Coto, N. Horwitz, R. Young, F. White, F. Hampel, T. Clark, M. Thoss, R.R. Tykwinski, M. Wasielewski, and D.M. Guldi, Nat. Comm. 8, 15171 (2017).
[4] S. R. Reddy, P. B. Coto, M. Thoss, J. Phys. Chem. Lett. 9, 5959 (2018).
[5] S. R. Reddy, P. B. Coto, M. Thoss, J. Chem. Phys. 160, 194306 (2024).
[6] R. K. Kathir, P. B. Coto, M. Thoss, J. Phys. Chem. Lett. 15, 11517 (2024).

Insights into ultrafast photochemical dynamics from XUV and soft X-ray spectroscopy

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Many important photoinduced processes in chemistry and biology take place on ultrafast timescales. They involve nonadiabatic dynamics through conical intersections, which still challenge both experiment and theory in their description and understanding. Gas phase charged particle spectroscopic methods have been highly successful in increasing the mechanistic understanding of nonadiabatic dynamics in general by investigating comparably small model systems.
The nucleobase thymine, for instance, exhibits surprisingly low photochemical reactivity given its significant absorption cross-sections in the UV. This photostability is attributed to a rapid, femtosecond-scale depopulation mechanism of the photoexcited state. However, the details of this mechanism are the subject of a long-standing discussion among both experimentalists and theorists.

We have investigated the ultrafast dynamics of thymine using several charged particle spectroscopy methods including time-resolved photoelectron spectroscopy, time-resolved near-edge X-ray absorption spectroscopy, and time-resolved resonant Auger-Meitner spectroscopy with probe wavelengths from the XUV to the soft X-ray regime. In combination, these diverse observables provide new insight into the relaxation mechanism of thymine and helped to stimulate developments in the quantum chemical description of photochemical dynamics. Additionally, they offer an interesting perspective into the nature and sensitivity of the specific observable.

Hot topic contributions

Decoherence phenomena of electron dynamics in liquid water

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The dynamics of electron scattering in liquid samples is of prime importance due to its fundamental implication in a wide range of fields, including radiobiology as well as ultrafast chemistry and physics. It presents stringent experimental challenges as it occurs starting from the attosecond timescale [1] and the effective mean free path of electrons in water is limited to 8 Å [2]. In order to look into the dephasing dynamics of photoelectrons we performed Reconstruction of Attosecond Beating By Interference of two-photon Transitions (RABBIT) experiments [3] in gas and liquid phase water over the photon range from 37 to 74 eV.

The RABBIT technique is based on an interferometric principle and the oscillation contrast can be used as an observable of the decoherence phenomena occurring during liquid water experiments [4]. The experimental setup used for this work combines a liquid micro jet device [5] with a two-foci geometry and two magnetic bottle electron spectrometers (one for gas phase whereas the second one is designed for liquid phase measurements) enabling us to have a simultaneous atomic reference in the measurement [6]. In our experiment, decoherence can originate from measurements biases (e.g. temporal jitter, focusing aberrations) but also spectral overlap in complex systems. The influence of the experimental decoherence is evaluated by measurement of the oscillation contrast in an atomic gas, here neon. Instead, the effect of spectral overlap is gauged by measuring the contrast in gaseous water, which shows a monotonic decrease of contrast from 0.7 to 0.6, similarly to the atomic reference. On the other hand, the contrast in liquid water increases from 0.2 to 0.3 in the same energy range. This difference in behaviour hints that RABBIT could be used to assess decoherence in liquid jets. Further analysis is ongoing to evaluate the influence of geometrical effects [7] and to quantify decoherence over the large kinetic energy range, which is expected to shed light on electron's scattering dynamics in liquid water [8].

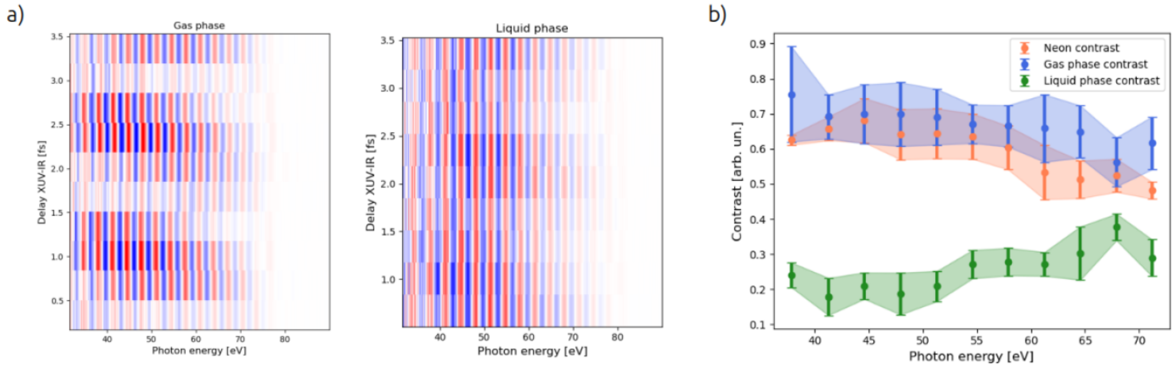

Figure 1. a) RABBIT traces of gas and liquid phase water, sidebands are in red and harmonics in blue. b) Evolution of the contrast extracted from sidebands oscillations in the atomic reference (in orange), gas phase water (in blue) and liquid phase water (in green).

References

[1] Jordan *et al.*, Science **369**, 974 – 979 **(2020)**
[2] Mondal *et al.*, Nat. Phys. **19**, 1813 – 1820 **(2023)**
[3] Borrego–Varillas *et al.*, Rep. Prog. Phys. **85**, 066401 **(2022)**
[4] Bourassin–Bouchet *et al.*, Phys. Rev. X **10**, 031048 **(2020)**
[5] Faubel *et al.*, J. Chem. Phys. **106**, 9013 – 9031 **(1997)**
[6] Locher *et al.*, Rev. Sci. Instrum. **85**, 013113 **(2014)**
[7] Lucchini *et al.*, Opt. Express **23**, 8867 – 8879 **(2015)**
[8] Signorell *et al.*, Phys. Chem. Chem. Phys. **24**, 13438 – 13460 **(2022)**

Unleashing Functionality in Molecule–2D Material Systems

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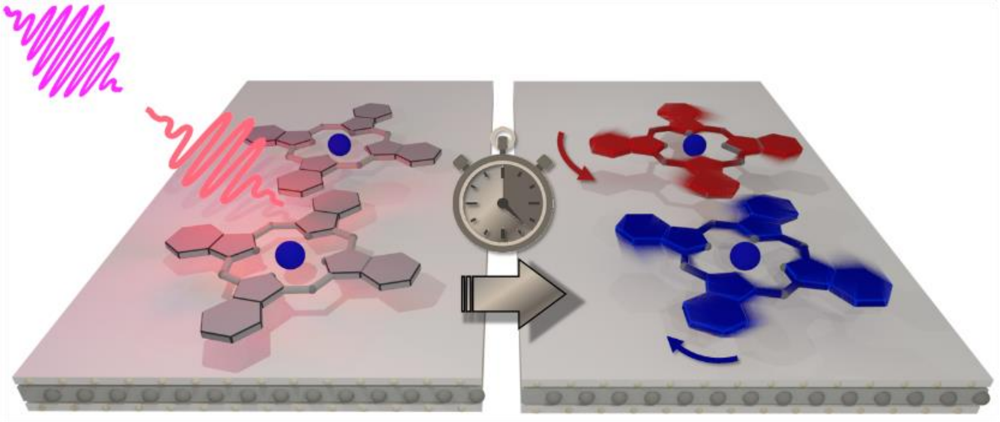
Engineering atomic interfaces between functional molecular systems and 2D materials enables innovative device functionalities. Non-equilibrium dynamics further expands these possibilities by sustaining systems in energy-driven states through inputs such as light, electric fields, or chemical fuels. These energy inputs allow molecular assemblies to reconfigure in real time and exhibit reversible behaviors, mirroring the adaptability of transient natural systems. For instance, in a non-equilibrium system, long-range molecular order can be periodically adjusted or fully dismantled in response to external triggers, enabling controlled rearrangement and functional switching. Using a "full molecular movie" approach, we simultaneously capture molecular positions, orbital wavefunctions, and substrate electronic states with femtosecond, sub-Ångström precision. Therefore, several variations of photoelectron spectroscopy were utilized employing a momentum microscope paired with a HHG source and the free-electron laser FLASH. This multimodal technique unveils the mechanisms driving surface-adsorbed molecular rotation, presenting a new framework for adaptive functionalities in electronic engineering and dynamic molecular devices.



References

[1] Baumgärtner, K., et al. (2022). "Ultrafast orbital tomography of a pentacene film using time-resolved momentum microscopy at a FEL" Nat Commun **13**, 2741.
[2] Baumgärtner, K., et al. (2023). "Multiplex movie of concerted rotation of molecules on a 2D material" https://arxiv.org/abs/2305.07773.

Ab Initio Nonadiabatic Dynamics for Photochemical Processes

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The investigation of photochemical dynamics requires quantum chemical methods that can accurately describe both ground state and electronically excited states, as well as a framework to enable radiative and nonradiative transitions between them. In our work, we employed the complete active space self-consistent field (CASSCF) method together with second-order perturbation theory (CASPT2) or spin-orbit multireference configuration interaction (CASSCF/SO-MRCI), combined with trajectory surface hopping for the inclusion of nonadiabatic effects to accurately simulate photoisomerisation of cis-stilbene[1] and photochemical dissociation of cyclobutanone[2]. Based on the simulated trajectories, time-resolved observables such as time-resolved photoelectron spectrum (TRPES) or gas-phase ultrafast electron diffraction (GUED) patterns can be predicted.

The cis-stilbene molecule was studied using the state-averaged extended multistate CASPT2 method. Our simulation reproduces the experimental TRPES (cf. Fig. 1 a–b) and identifies an ultrafast ring closure reaction of cis-stilbene, apart from the well-known cis–trans isomerisation. For the cyclobutanone molecule, which has been studied in the frame of the “Prediction Challenge: Cyclobutanone Photochemistry”, the state-averaged CASSCF/MRCI method was employed. By including spin-orbit coupling and modifying the surface hopping equation to allow intersystem crossing, we demonstrate, a minimal impact of triplet states on the photodynamics of cyclobutanone excited to its 3s Rydberg state. To enable a direct comparison to future experiments, we simulate the GUED patterns (cf. Fig. 2 c–d). Because the photodissociation products of cyclobutanone have different ionisation energies, it would also be interesting to study this reaction using time-resolved photoelectron spectroscopy.

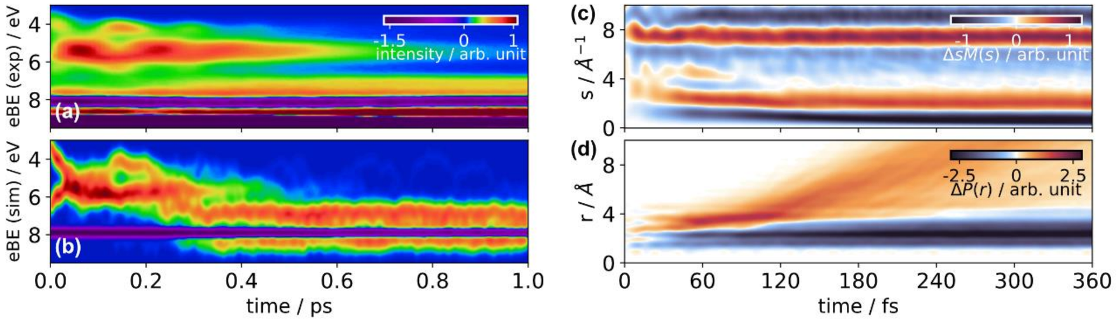

Figure 1: (a) Experimental and (b) simulated time-resolved photoelectron spectrum of cis-stilbene[1], (c) Ultrafast electron diffraction pattern and (d) difference pair distribution function of cyclobutanone[2].

References

[1] Karashima, S., Miao, X., Kanayama, A., Yamamoto, Y.I., Nishitani, J., Kavka, N., Mitrić, R., Suzuki, T. (2023). "Ultrafast ring closure reaction of gaseous cis-stilbene from S1(ππ*)" J. Am. Chem. Soc. 145(6): 3283–3288.

[2] Miao, X., Diemer, K., Mitrić, R. (2024). "A CASSCF/MRCI trajectory surface hopping simulation of the photochemical dynamics and the gas phase ultrafast electron diffraction patterns of cyclobutanone" J. Chem. Phys. 160(12): 124309.

Ultrafast relaxation processes in photoexcited helium nanodroplets probed by XUV-TRPES

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Helium nanodroplets are unique quantum fluid clusters that feature extraordinary properties such as ultralow temperature and superfluidity. They have mostly been used as inert cryo-matrices for spectroscopy of embedded molecules and clusters. However, resonant excitation or ionization of helium nanodroplets by XUV radiation initiates rich relaxation dynamics such as nano-bubble formation, electron scattering and recombination, as well as charge-transfer processes and interatomic Coulombic decay (ICD) [1-6].

In this contribution I'll present experiments probing the ultrafast dynamics of photoexcited pure and doped helium nanodroplets using synchrotron radiation, free-electron lasers and high-harmonic generation of XUV pulses by intense lasers. Recent XUV pump-probe experiments were performed at the ELI-Beamlines Laser Center using a tunable HHG source [7]. Greatly enhanced above-threshold ionization (ATI) was observed when irradiating excited or doped helium nanodroplets by intense infrared or visible pulses due to laser-assisted electron scattering (LAES) [8,9]. This process in turn induces ICD in large helium droplets through electron-helium impact excitation [5]. The dynamics of XUV-induced ICD is found to proceed on two timescales reflecting two distinct relaxation mechanisms. Fast dynamics (~1 ps) is due to the merging of adjacent nano-bubbles [10] whereas slow dynamics (~1 ns) is attributed to the roaming motion of helium excitations about the droplet surface. Fig. 1. shows time-resolved photoelectron spectra measured by resonantly exciting large helium droplets (50 nm radius) by HHG-XUV pulses tuned to a photon energy of 21.8 eV. The intense 1.6 eV-probe pulses induce ATI (increasing with pump-probe delay) and LAES (decreasing) as well as depletion and replenishment of ICD (depletion at short delay, increasing).

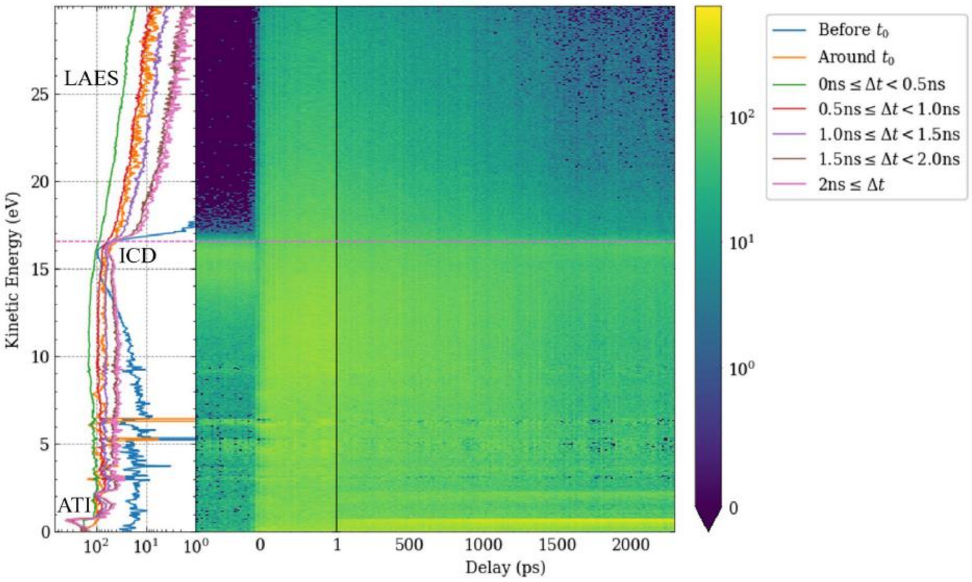

Figure 1: XUV-pump and NIR-probe photoelectron spectra of large helium nanodroplets

References

[1] Mudrich, M. et al. (2020). "Ultrafast relaxation of photoexcited superfluid He nanodroplets " Nat. Commun. **11:** 112

[2] LaForge, A. C. et al. (2022). "Relaxation dynamics in excited helium nanodroplets probed with high resolution, time-resolved photoelectron spectroscopy" PCCP **24**: 28844

[3] Asmussen, J. D. et al. (2022). "Time-Resolved Ultrafast Interatomic Coulombic Decay in Superexcited Sodium-Doped Helium Nanodroplets" J. Phys. Chem. Lett. **13**: 4470–4478

[4] Medina, C. et al. (2023). "Long-lasting XUV activation of helium nanodroplets for avalanche ionization" New J. Phys. **25**: 053030

[5] Ltaief, L. B. et al. (2023). "Efficient Indirect Interatomic Coulombic Decay Induced by Photoelectron Impact Excitation in Large He Nanodroplets" Phys. Rev. Lett **131**: 023001

[6] Bastian, B. et al. (2024). "Observation of interatomic Coulombic decay induced by double excitation of helium in nanodroplets", Phys. Rev. Lett **132**: 233001

[7] Jurkovičová, L. et al. (2024). "Bright continuously-tunable VUV source for ultrafast spectroscopy", Commun. Phys. **7**: 26

[8] Treiber, L. et al. (2021). "Observation of laser-assisted electron scattering in superfluid helium." Nat. Commun. **12**: 4204.

[9] Michiels, R. et al. (2021). "Enhancement of Above Threshold Ionization in Resonantly Excited Helium Nanodroplets" Phys. Rev. Lett **127**: 093201

[10] LaForge, A. C. et al. (2021). "Ultrafast

Probing the Non-Adiabatic Relaxation Dynamics of ortho-nitrobenzaldehyde via sub-20-fs UV-XUV tr-PES

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The photochemistry of nitro-aromatic compounds is pivotal in various chemical applications, including their use as photoactivated acids or as photolabile protecting group [1,2]. Understanding the details of such light-induced relaxation dynamics on their ultrafast timescale is therefore crucial. In this study, we use sub-20-fs XUV time-resolved photoelectron spectroscopy (tr-PES) to investigate the non-adiabatic relaxation dynamics following photoexcitation of ortho-nitrobenzaldehyde (oNBA), a prototypical nitro-aromatic compound. The photochemical reaction initiated by the UV pump pulse (4.8 eV) is probed by few-femtosecond XUV pulses, generated through high-order harmonic generation and spectrally selected by a time-delay compensated monochromator [3] (see Fig.1 (a)). The resulting trace shown in Fig1 (b) reveals the details of the ultrafast relaxation dynamics of oNBA. The excellent comparison with high-level theoretical predictions, described in detail in [4] and summarized in Fig.1 (c), allows us to assign the time constant of 50 fs to the ultrafast transition from the S_4 to S_3 state, followed by the relaxation to the S_1 minimum in 140 fs. Moreover, we observe coherent vibrational oscillations with a period of 25 fs, which align closely with theoretical predictions and are consistent with coherent ring breathing and contraction of the C−N and $C{-}C_{\mathrm{aldehyde}}$ nuclear distances. These findings provide significant insights into the ultrafast processes governing the photochemistry of oNBA and highlight the potential of tr-PES in unraveling the intricate dynamics of photochemical systems.

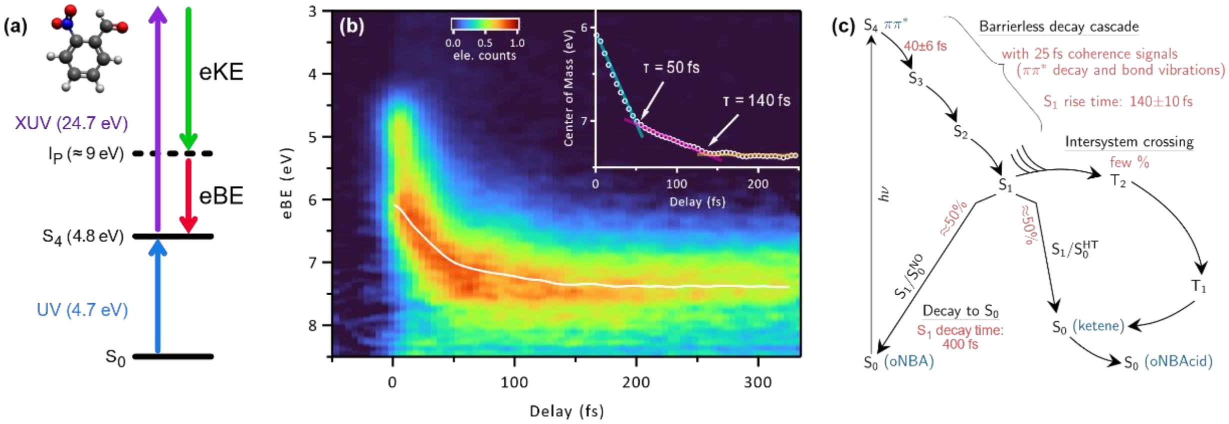

Figure 2. (a): Diagram of the experiment: the UV pump excites the system in the S_4 level and the XUV probe ionizes, tracking the dynamics from the resulting electron Binding Energy (eBE) (or the electron Kinetic Energy (eKE)). (b) Experimental tr-PES trace. In white, superimposed to the traces, the evolution of the center of mass (highlighted in the inset the crucial delays at which there is a change in the slope). (c) Overview scheme of the oNBZA relaxation dynamics adapted from [4].

References

[1] Barltrop J. A., et al. (1996) "Photosensitive protective groups" Chem. Commun. 822-823.
[2] Causgrove T. P. and Dyer R. B. (2006) "Nonequilibrium protein folding dynamics: laser-induced pH-jump studies of the helix–coil transition" Chem. Phys. **323**(1) 2−10
[3] Crego A. et al. (2024) "Sub-20-fs UV-XUV Beamline for Ultrafast Molecular Spectroscopy" Sci. Rep. **14**(26016)
[4] Vörös D. and Mai S., " Role of Ultrafast Internal Conversion and Intersystem Crossing in the Nonadiabatic Relaxation Dynamics of ortho-Nitrobenzaldehyde" J. Phys. Chem. A, **127**(28) 5872−5886

Investigating Photoinduced Dynamics of a 1,4-Azaborine with Time-Resolved X-ray Spectroscopy

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Azaborines are molecules containing boron and nitrogen, offering unique electronic properties by replacing carbon bonds in organic compounds. This makes them promising for energy and electronic applications, such as optoelectronics and singlet fission materials.[1]

In this study, the ultrafast dynamics of the non-commercial 1,4-di-tert-butylazaborine were studied using time-resolved X-ray photoelectron spectroscopy. Experiments at FLASH2 at DESY used a pump-probe setup to investigate boron-specific electronic changes after UV excitation.[2] Key processes, including fast relaxation via a conical intersection and slower long-term dynamics, were observed.

Supported by static theoretical calculations and quantum dynamic simulations, the study provided insights into excitation energies, long-lived reaction products, and detailed relaxation pathways. These findings highlight the potential of 1,4-azaborines as versatile building blocks for optoelectronic materials, where understanding ultrafast dynamics is key to optimizing performance.

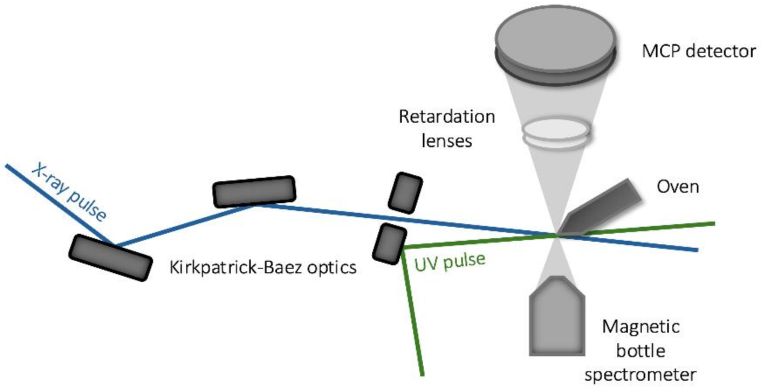

Figure 3: Schematic of the pump-probe XPES experiment, showing the experimental setup for investigating photoinduced dynamics of the 1,4-azaborine using time-resolved X-ray spectroscopy. Adapted from [2].

References

[1] Giustra, Z. X., and Liu, S.-Y. (2018). "The State of the Art in Azaborine Chemistry: New Synthetic Methods and Applications." J. Am. Chem. Soc. **140**(4): 1184–1194.
[2] Metje, J., et al. (2020). "URSA-PQ: A mobile and flexible pump-probe instrument for gas phase samples at the FLASH free electron laser." Applied Sciences **10**(21): 7882.

Correlation-driven attosecond photoemission delay in the plasmonic excitation of C_{60} fullerene

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Plasmonics offers a way to achieve extreme light confinement and control surpassing the constraint of the diffraction limit. It harnesses the ability to confine light within the nanoscale size by hybrid ‘quasiparticle states involving light and collective electron excitation. In this context, the studies of surface plasmons and the even more peculiar giant plasmon resonances (GPRs) have already enabled transformational applications including solar energy harvesting, ultrafine sensor technology, and controlled photocatalysis [1-3].

The plasmonic response for particles with diameter larger than ~10 nm can be well characterized by classical Mie-type models involving electromagnetic theory and Drude-like dielectric response. For smaller particles, i.e., approaching the nm or sub-nm, the above-mentioned classical interpretation breaks down, and the plasmonic response in this case is poorly understood. Among the family of subnm plasmonic particles, fullerenes represent and extreme case. The ultrafast study of the plasmonic response of these systems, still mostly unexplored, represents an excellent platform to understand the fundamental physical mechanisms of collective electron motion in sub-nm particles.

In our work, we employed attosecond photoemission chronoscopy to directly access the fundamental mechanisms of the plasmonic response in the fullerene C60. We found that the delay accumulated by the electron in the plasmonic potential is dominated by quantum mechanical correlations. We measured it to range between 300 as to 50 as in the kinetic energy range between 8 eV and 24 eV [4].

Given the importance of plasmonics in many fields of science, our study contributes to understand the fundamental mechanisms of plasmons in the extreme conditions of sub-nm systems. This knowledge can be particularly important for the future development of novel technology involving quantum plasmonics.

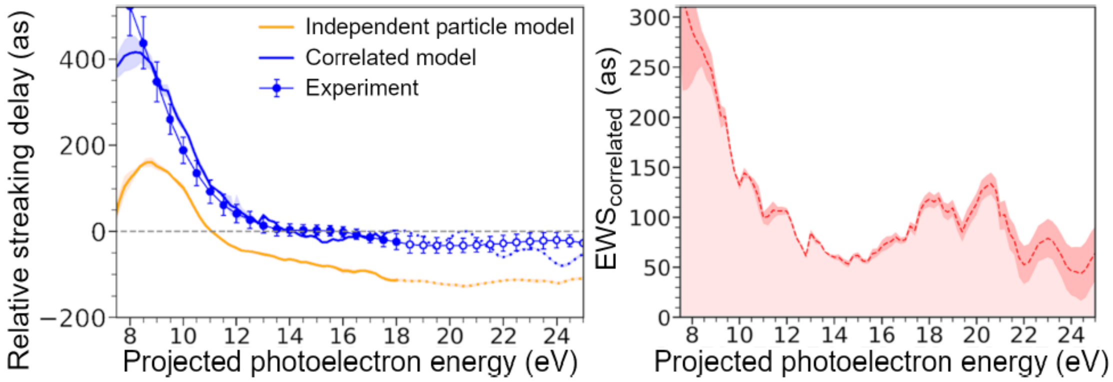

Figure 1: (left) Experimental and theoretical streaking delay in C60, relative to a neon reference sample. (right) The correlated excitation´s Eisenbud-Wigner-Smith delay (EWS) is the difference between correlated and independent particle models.

References

[1] Koenderink, A. F., Alu, A. & Polman, A. Nanophotonics: Shrinking light-based technology. *Science* **348**, 516-521 (2015).

[2] Stockman, M. I. *et al.* Roadmap on plasmonics. *J Optics-Uk* **20**, 043001 (2018).

[3] Chapkin, K. D. *et al.* Lifetime dynamics of plasmons in the few-atom limit. *P Natl Acad Sci USA* **115**, 9134-9139, doi:10.1073/pnas.1805357115 (2018).

[4] Biswas, S., *et al.* (under review) "Correlation-driven attosecond photoemission delay in the plasmonic excitation of C60 fullerene" Science Advances.

Probing electronic relaxation decay of photoexcited thymine using time-resolved XPS

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The photoprotection mechanism of thymine involves complex relaxation dynamics, where energy from photoexcitation is converted into vibrational energy through radiationless transitions. Previous studies have indicated that isolated thymine molecules undergo $^1\pi\pi^*$-$^1n\pi^*$ internal conversion within 100 femtoseconds (fs) [1], followed by the intersystem crossing from $^1n\pi^*$ to $^3\pi\pi^*$ within 10 picoseconds (ps) [2]. However, no relaxation pathway from the $^3\pi\pi^*$ back to ground state has been identified. To explore the electronic relaxation, we employed the time-resolved x-ray photoelectron spectroscopy (XPS), which is sensitive to local charge and thus the electronic state. Isolated thymine molecules were excited with a fs UV laser pulse at a wavelength of 263 nm, and their relaxation dynamics were tracked using an fs X-ray pulse at 337 eV. Photoelectron spectra (Figure 1) of the carbon 1s electrons of thymine were collected over delay times up to 600 picoseconds. The lifetimes of different electronic states and state-associated spectra were extracted from the time-resolved difference spectra using a global/target analysis method [3]. Our findings confirm the ultrafast electronic decay sequence $^1\pi\pi^*$-$^1n\pi^*$-$^3\pi\pi^*$ and indicate the presence of an additional intermediate state before relaxation to the ground state.

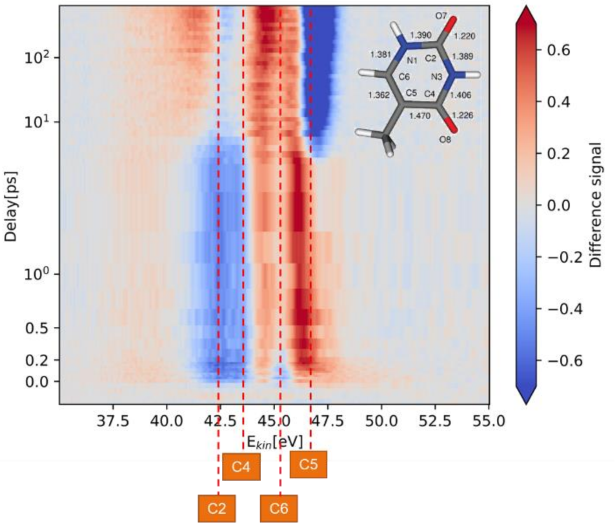

Figure 4: Experimental time-resolved XPS spectra of thymine, false-color plot of time-resolved difference XPS with red indicating UV-induced increase of the photoelectron spectrum and blue a UV-induced decrease.

References

[1] Wolf, T. J. A., et al. Nature communications 8.1 (2017): 29.
[2] Wolf, T. J. A., et al. The Journal of Physical Chemistry A 123.32 (2019): 6897-6903.
[3] Fernández-Terán, Ricardo J., et al. Journal of Chemical Education 99.6 (2022): 2327-2337.

Poster contributions

Pump-control scheme for imaging and modification of excited neutral molecules

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Imaging and control of chemical reactions in small and large systems – a key goal in modern physics – is into reach across a variety of recently developed diffraction and spectroscopic techniques for studies of laser-induced coherent control on the natural ultrafast timescale.

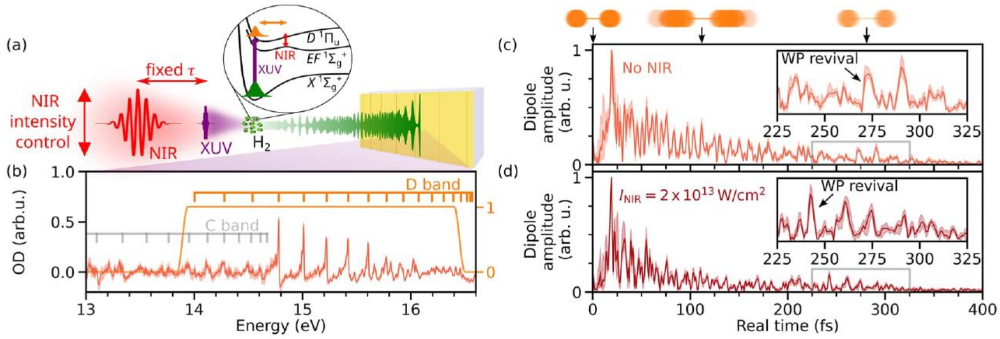

Figure 1: (a) Schematic of the experimental setup for XUV time-domain absorption spectroscopy in H2. (b) Optical density (OD) spectrum showing the detected vibronic resonances in neutral H2. (c) and (d) Reconstructed time-dependent dipole amplitude of the D-state vibrational wave packet in an XUV-only configuration and for an NIR control field with INIR ≈ 2×1013W/cm2, respectively. The insets show the wave-packet revival region.

In a newly introduced pump-control scheme, we focus on the time-domain interpretation of absorption spectra in correlated molecular systems [1]. Our novel experimental approach for imaging vibrational wave packets in the electronically excited states of neutral molecules allows access to the fastest nuclear motion down to the 10-fs-timescale in the lightest H2 molecule. Here, the molecular ground state reveals the system's dynamics through the molecular dipole emission, thus acting as a self-probe. Experimentally, measured single absorption spectra with high spectral resolution allow for the reconstruction of this time-dependent dipole response through a Fourier-based technique, previously developed for isolated atomic states [2]. The revealed ultrafast vibrational dynamics of an excited vibrational wave packet in the neutral H2 molecule reaches up to the first wave-packet revival at around 270 fs. An experimental study of the intensity dependence of the wave-packet revival and a supporting multi-level simulation solving the time-dependent Schrödinger equation show: the higher the NIR intensity, the earlier the revival time. We further extract the state-specific NIR-induced phaseshifts, which are a key contributor to the observed time shifts. In this general approach for vibronic (electron+nuclear) wave-packet modification, transferable also to complex molecules, only two laser pulses in a pump-control configuration are required for both the time-dependent reconstruction and the control of the molecular vibrational wave-packet. Different control knobs of the control field – intensity, polarization, wavelength control or shaping through the introduction of chirps - can induce almost any set of couplings and, with this, possibilities for coherent control of the studied molecular system.

References

[1] Borisova et al., Phys. Rev. Res. 6 (2024) 033326.
[2] Stooß et al., Phys. Rev. Lett. 121 (2018) 173005.

The study of photoelectron circular dichroism in the ionization of (R) - (-) - Fenchone by femtosecond laser

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Photoelectron circular dichroism (PECD) is an intense chiroptical effect when chiral molecules are ionized by circularly-polarized light (CPL). It would show a forwards/backward asymmetry in photoelectron angular distribution with respect to the CPL propagation direction and be several orders of magnitude more intense than traditional circular dichroism (CD) methods [1]. As it's high sensitivity, PECD could be a fine tool for chirality identification [2]. And combining PECD research with pump-probe technique, ultrafast relaxation dynamics of chiral molecules [3], the pathways of stereoselectivity in biochemistry and chirality changes during chemical reactions [4] can also be studied.

Here we aim to study the time-resolved PECD effect of (R)-(-)-Fenchone in helium droplets. In the beginning, we used CPL 400nm laser to ionized the Fenchone which is seeded in helium beam and detected the photoelectron by velocity map imaging method. We detected a significant PECD effect after subtracting the signals ionized by CPL lasers at different helicity. Then we will apply linear-polarized 200nm pump laser and circularly-polarized 266nm probe laser together with helium droplets method to study the time-resolved PECD effect in (R)-(-)-Fenchone. This will help us to figure out how the helium-droplets environment influences the ultrafast relaxation dynamics in chiral systems.

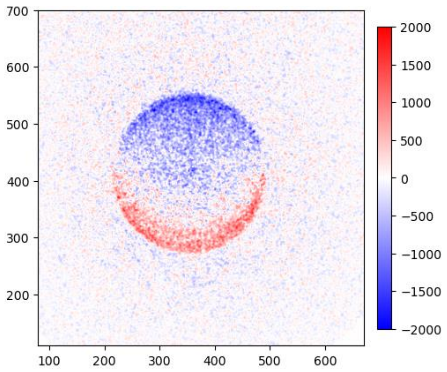

Figure 5: PECD signal for (R)-(-)-Fenchone with 400nm circularly-polarized laser

References

[1] Lux, C., et al. (2012). "Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone from Multiphoton Ionization with Femtosecond Laser Pulses" Angew. Chem. Int. Ed., 51: 5001.

[2] Janssen, M. H. M., Powis, I. (2014). "Detecting chirality in molecules by imaging photoelectron circular dichroism" Phys. Chem. Chem. Phys., 16: 856.

[3] Comby, A., et al. (2012). "Relaxation Dynamics in Photoexcited Chiral Molecules Studied by Time-Resolved Photoelectron Circular Dichroism: Toward Chiral Femtochemistry" J. Phys. Chem. Lett., 7: 4514.

[4] Svoboda, V., et al. (2022). "Femtosecond photoelectron circular dichroismof chemical reactions" Sci. Adv., 8: eabq2811.

Decoding The Ring Currents In Organic Molecules Using tr-ARPES

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Recent experimental and theoretical advancements in attosecond science have enabled us to revisit and verify the chemical properties of materials with unprecedented precision. In this study, we employ advanced quantum chemistry calculations to investigate ring currents in organic molecules1,2. Utilizing the NIR pump--XUV probe technique, we initiate and observe these dynamics, generating time- and angle-resolved Photoelectron spectroscopy (tr-ARPES). The calculated angle resolved photoelectron distribution allow us to identify the direction of ring currents in the organic molecule after photoexcitation.

References

[1] M. Reuner et al., (2023), Physical Review A, 107, 023101
[2] D. Popova-Gorelova, et al., (2016), Physical Review A, 94, 013412

Calculating excitonic interactions using transition currents with application to PTCDA

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Many systems in physics, chemistry, biology, and nanotechnology consist of assemblies of particles, such as atoms, molecules, quantum dots, and metal nanoparticles, that are so far apart that their electronic wavefunctions do not overlap [1]. However, long-range interactions can lead to significant changes in the optical and transport properties of these assemblies.

When the particles are sufficiently distant from one another, the interaction can often be approximated as the interaction between the transition dipoles of the respective particles. Nonetheless, in many cases, this approximation may not be accurate enough. In such situations, the interaction matrix element is typically evaluated using the Coulomb interaction between the transition charge densities of the two molecules.

In this study, we demonstrate that it is feasible to evaluate interactions using transition current density instead of transition charge density. To compute the interaction matrix elements—whether for transition charge density or transition current density—we utilise discretisation schemes. These schemes approximate continuous densities using a finite number of elements. We present our numerical results using perylene tetracarboxylic dianhydride (PTCDA) as a case study. Additionally, we analyse the interaction of a PTCDA dimer with a typical monolayer arrangement in free space, offering a more precise assessment that surpasses the dipole-dipole approximation. Our future work will focus on modifying this interaction through the use of layered surfaces encoded in the Green function.

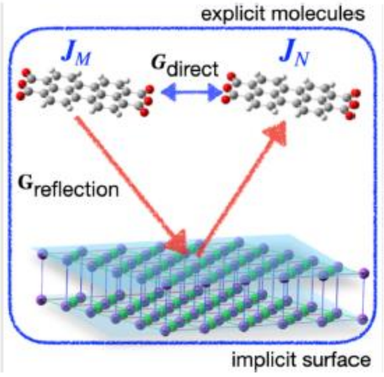

Figure 1: Interaction between a PTCDA dimer is described by transition current density and Green function.

References

[1] A, Eisfeld et al, "Superradiance from two dimensional brick-wall aggregates of dye molecules: The role of size and shape for the temperature dependence." Phys. Rev. Lett., 119:097402, Aug 2017

Attosecond photoionization dynamics of liquid and gas phase water

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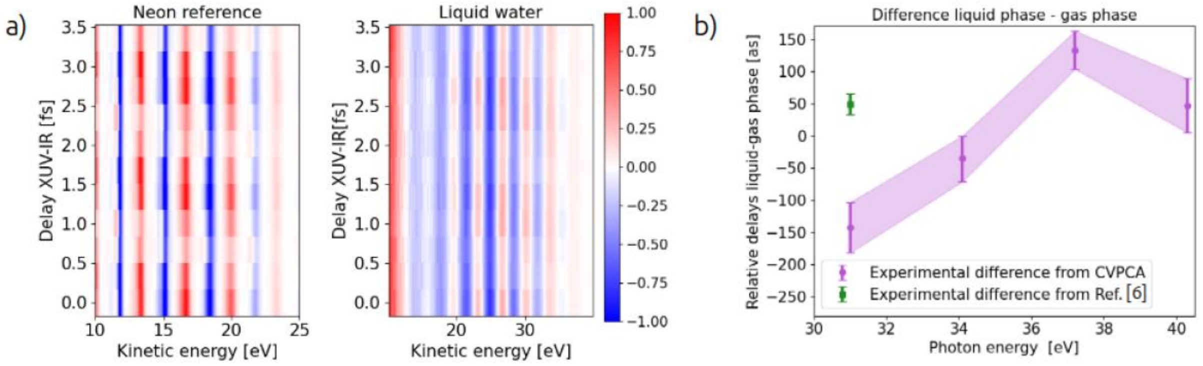
Reconstruction of Attosecond Beating By Interference of two-photon Transitions (RABBIT) is an established technique to study attosecond photoionization dynamics of atoms molecules and solids [1]. Extension of this observable to the liquid phase aims at probing the electron transport and scattering on this uncharted timescale. In the photoelectron kinetic energy range accessible with typical harmonics sources, these processes are important both for fundamental and applied research [2].

In this work, RABBIT experiments of gas and liquid phase water are compared in the 31 to 40 eV photon energy range. The possibility to float an under vacuum liquid jet with electric potentialsallowed for measurements of the two contributions separately[3]. Our experimental scheme employs a two-foci geometry developed for robust referencing with the simultaneous acquisition of a RABBIT measurement in an atomic reference [4]. The results obtained for gas phase water agree well with published theoretical estimation [5], while results obtained for the liquid phase present discrepancies with previous experimental work [6]. This highlights the complexity of performing RABBIT experiments in condensed matter and the need for theoretical simulations to unravel physical effects affecting the measurements.



a) Experimental RABBIT traces of neon (reference) and liquid water (sample) obtained with the two-foci gometry setup: red corresponds to sidebands and blue to harmonics oscillations. b) Difference between the extracted RABBIT delays of gas and liquid phase water, compared with previous literaure experimental results.

References

[1] Borrego-Varillas, R., et al. (2022). Rep. Prog. Phys.**85**: 066401
[2] Signorell, R. and Winter, B. (2020). Phys. Chem. Chem. Phys.**24**: 13438-13460
[3] Siegbahn, H., et al. (1982). Journal of Electron Spectroscopy and Related Phenomena**28**: 135-138
[4] Locher, R., et al. (2014). Rev. Sci. Instrum.**85**: 013113
[5] Serov, V. V. et Kheifets, A. S. (2017), J. Chem. Phys. **147**: 204303
[6] Jordan, I., et al. (2020). Science**369 :** 974-979

Attohallen – A New Attosecond Science Facility in Sweden

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Attohallen, a new attosecond science facility located at the University of Gothenburg, Sweden will be presented with focus on its main specifications and unique aspects as well as the science cases behind it. This facility is equipped with cutting-edge femtosecond laser sources.

The main source is an OPCPA-HE laser developed by Light Conversion for ELI-ALPS in Szeged based on the concepts shown in Ref. [1]. It can deliver CEP-stabilized sub-10 fs 50 mJ pulses at a repetition rate of 100 Hz. This high energy output feeds a beamline that has been designed for the generation of attosecond pulses of high flux, which is primarily achieved by utilizing a loose focusing configuration (f = 10 m) [2]. This new attosecond beam line, which now is completed by an interferometer for attosecond time-resolved experiments, will be used for ultrafast electron-ion correlation spectroscopy on dilute targets. The detection of the electrons and ions created upon photon interaction is performed using a magnetic bottle spectrometer, for which we have installed a new 5.6 m instruments, offering exceptionally high spectral resolving power (~ 120), akin to the original Oxford instrument of that type [3]. A typical electron spectrum of Xenon using Argon as medium for generating the XUV radiation and overlayed with the fundamental infrared laser beam utilizing our new grazing incidence interferometer is shown in Fig. 1. It reflects photoelectron peaks corresponding to the harmonic energies H11 – H23, which are observed for all delays, and sidebands S12 – S22 which are generated only when the two pulses overlap in time.

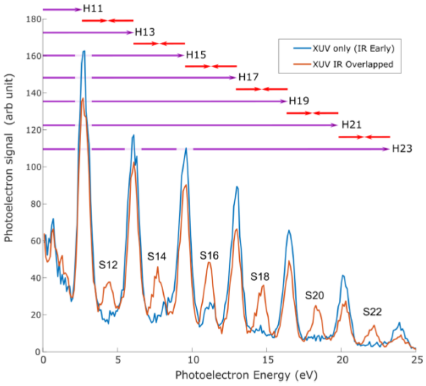

Figure 1. Sideband generation in Xe using XUV + IR using our grazing incidence interferometer. Photoelectron peaks corresponding to the harmonic energies (H11-H23) are observed for all delays, whereas sidebands (S12-S22) are generated only when the two pulses overlap in time.

Another output of the OPCPA laser has reduced pulse energy but a substantially higher repetition rate of 10 kHz. It will be used for driving a second beam line which is in its design phase for generating isolated attosecond pulses.

References

[1] Budriūnas, R. et al., 2017, Opt. Express 25, 5797.
[2] Heyl, C.M. et a.,l 2016 Optica 3, 75.
[3] Eland J.H.D et al., 2003 Phys. Re.v Lett. 90, 053003

Ionization delays in iodine-containing molecules

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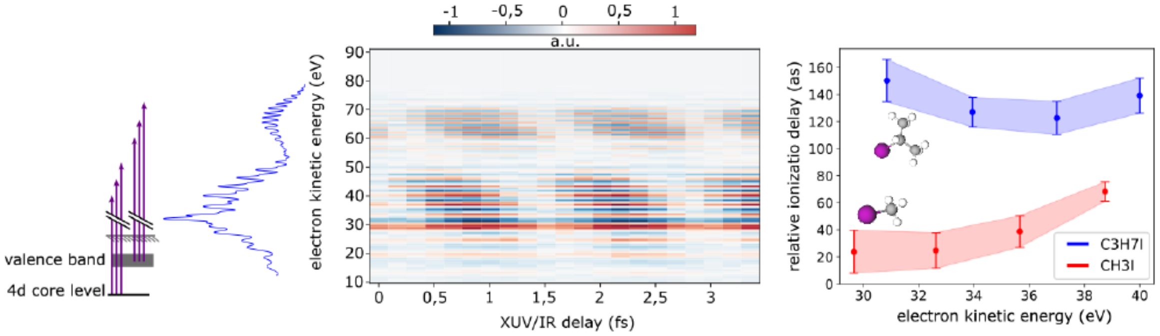
Photoionization is not an instantaneous process and ionization delays measurements act as a fine probe of molecular electronic potential. While pioneering ionization delays studies have been done in readily accessible valence atomic shells [1], we can now reach core shells of high Z atoms, such as Iodine 4d levels, with XUV attosecond pulses generated by High Harmonic Generation (HHG). These core levels are of interest as they act as localized electron sources on one particular atom (here Iodine) in the molecular frame.

With these measurements, we managed to establish the influence of the length of the carbon chain attached to the Iodine atom on the ionization delay.

Core shells ionization delays have been measured using streaking method either with HHG based experiments [2] or at XFELs [3], which principal drawback is a poor spectral resolution (> 5eV). Our approach is based on RABBBIT (Reconstruction of Attosecond Beating By Interference of two-photon Transitions) spectroscopy, combining good temporal and spectral resolutions. We were able to measure relative delays in 4d I shell between different molecules using a two foci configuration [4], in which two RABBITTs are performed in parallel, one probing the molecules of interest, the other acting as an absolute timing and XUV spectral phase (attochirp) measurements. We measured a visible delay offset of 125±60 attoseconds (as) for 30eV 4d photoelectrons electrons between Iodomethane (CH3I) and Iodopropane (C3H7I)



CH3I photoelectron spectra resulting of XUV/IR cross correlation (RABBITT) (left) and extracted relative ionization delays in 2 Iodine containing molecules (right). XUV was generated by HHG 800 nm Ti:Sa laser, focused in Ne gas cell

References

[1] Isinger et al., Science (2017)
[2] Biswas et al., Nature Physics. (2010)
[3] Driver et al., Nature (2024)
[4] Locher et al., Rev. Sci. Instrum (2014)

Ultrafast Spectroscopic Investigation on the Effect of Electron-donating Substituent Group on Excited State Dynamics of Oxindole Photo-switches

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The E-Z photo-isomerization of a C=C double-bond is the central mechanism present in a variety of synthetic photo-switches and photo-motors currently under developmen[1]. With the example of oxindole photo-switch, we have recently demonstrated that the photo-switching quantum yield (ΦISO) could be significantly modified by adding electron-donating groups to the chromophore[2]. In a follow-up investigation, we aim to uncover how such chemical modifications influence the excited state dynamics, which would ultimately reveal the causality between the chemical modification and the photo-switching behaviors, paving the way for a unified theoretical guide for the molecular photo-switch design. We present 4 variants of oxindole switches, differing in the electron-donating group on the para- position of the benzene ring (Fig. 1 a). Their ΦISO increases with the electron-donating strength (value of σp). The transient absorption (TAS) and the fluorescence up-conversion (FLUPS) experiments have been conducted to probe the dynamics. From both experiments, variants with –CF3 and -H manifest a slower decay compared with -OH and –NO2 (Fig. 1 b). For all variants, the lifetime analysis has indicated the existence of a sub-picosecond decay component and a 10 ps decay component for all variants. For 3tE and 3aE, an extra decay component of 40 ps could be found in the TAS experiment. No significant correlation was confirmed between the electron-donating strength (σp) and the lifetimes, while in a similar research on another photo-switch such correlation is solid[3]. We envision performing the time-resolved XPS. Thanks to the advantage of XPS, we expect that the energistic nature of each decay component will be identified with certainty, complementing our depiction of the excited state dynamics from TAS and FLUPS.

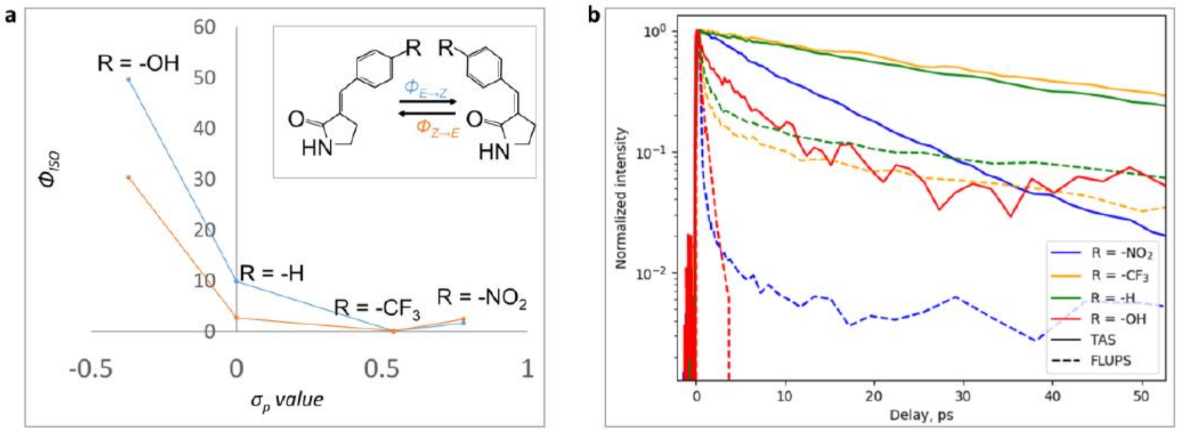

Figure 1: a. Four oxindole switches and their photoswitching quantum yields; b. The kinetic traces of TAS and FLUPS at their maximum signal wavelength.

References

[1] Z. L. Pianowski, "Molecular photoswitches: chemistry, properties, and applications," Wiley-VCH GmbH, 2022.
[2] D. Doellerer, D. R. Pooler, A. Guinart, S. Crespi, and B. L. Feringa Chem. Eur. J. 2023 p. e202301634.
[3] Conyard, Jamie; Cnossen, Arjen; Browne, Wesley

A high repetition HHG source of ultrafast XUV pulses for the SXP instrument at the European XFEL

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This contribution presents the concept of establishing a compact table-top high harmonic generation (HHG) source with high repetition rates at the Soft X-ray Port (SXP) instrument by utilizing the existing laser infrastructure at the European XFEL, including the central pump-probe laser as well as a fully synchronized 60 W standalone fiber laser system. The compact implementation will enable studies in the extreme ultraviolet (XUV) range at the SXP interaction point using the existing instrumentation, complementary to those conducted with the XFEL beam between 0.3 keV and 3 keV. This project will facilitate unique optical pump - XUV probe experiments, contribute to the development of a robust research program at the SXP instrument, and provide opportunities for other European XFEL groups as well as the international user community.

The first implementation of the HHG source will utilize an Yb fiber-based laser, currently commissioned at the SXP instrument, delivering 300 fs short and 150 µJ strong laser pulses at a repetition rate of 333 kHz. The second laser system, the intense 1030 nm SASE 3 pump probe laser, will also be employed once the HHG source is commissioned. Recent advancements have demonstrated its excellent suitability for this purpose, producing pulses with a duration of less than 40 fs and energies exceeding 2 mJ, with an intra-bunch repetition rate of 1.1 MHz. By this means, ultrashort XUV pulses will be generated via laser-driven HHG, offering coherent pulses with less than 10 fs duration and pulse energies around 10 nJ in the Al window, spanning the 20 eV to 72 eV photon energy range. This spectral range aligns with the M absorption edges of most 3d transition metals, facilitating studies crucial for various applications, including quantum information technologies and energy materials.

In the long run, the implementation of the HHG source will expand the SXP research capabilities, offering opportunities for attosecond science and novel experimental possibilities. By adjusting pulse duration and laser wavelength of the laser driver, the HHG spectrum can be tailored to specific research needs. Moreover, synchronization with the European XFEL will enable ultrafast pump-probe experiments and multicolor studies on the same sample, positioning SXP as a unique and versatile scientific instrument.

Femtosecond dynamic of CO_2 Activation Mechanisms on Copper-Based Catalysts

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The catalytic conversion of CO_2 into value-added fuels and chemicals has garnered increasing attention due to its significant environmental and economic implications. Size-selected clusters, studied in a controlled environment, offer ideal model systems for investigating the adsorption and activation of CO_2 molecules on copper-based catalysts. We recently setup a cryogenic linear ion trap tandem mass spectrometer together with a femtosecond laser system to investigate femtosecond pump-probe spectroscopy involving with a negative-neutral-positive excitation scheme, to characterize the structure and vibrational wave-packet dynamics of mass-selected clusters in their neutral charge states[1, 2]. Our current research focuses on elucidating the nature of activated copper clusters, unraveling the dynamics of CO_2 activation and adsorption, and examining the influence of charge states and cluster size on these reaction pathways. Here, we present vibrational wave-packet dynamic of Cu_5 clusters, confirming planar trapezoidal geometries by the frequency analysis of the oscillatory transients. Ion trap reactions of copper cluster anion with CO_2 reveals the gas-phase reactivity and provide potential candidate CO_2 complexes for femtosecond dynamic studies. This study aims to advance the understanding of catalytic processes at the atomic level, paving the way for the rational design of high-performance catalytic systems.

References

[1] J. Jin, M. Grellmann, K. R. Asmis. (2023). "Nuclear quantum dynamics on the ground electronic state of neutral silver dimer $^{107}Ag^{109}Ag$ probed by femtosecond NeNePo spectroscopy" Phys. Chem. Chem. Phys. **25**(36): 24313-24320.

[2] M. Grellmann, M. DeWitt, D. M. Neumark, K. R. Asmis J. Jin. (2024). "Vibrational wave-packet dynamics of the silver pentamer probed by femtosecond NeNePo spectroscopy" Phys. Chem. Chem. Phys. **26**(8): 6600-6607.

Vibrational spectroscopy and dynamics of Cu complexes bound with hydrogen isotopes

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Transition metal (TM) clusters can serve as model systems for investigating the binding behaviour and other properties of adsorbed gases at metal centres, thus assisting the design of advanced porous materials for hydrogen isotope separation. For an in-depth understanding of the selective and binding nature of the adsorbates at the metal site, vibrational action spectroscopy of well-defined and isolated gas-phase clusters can be used to study the reaction dynamics. In the present study, we reported infrared photodissociation (IRPD) spectroscopic and theoretical investigations on Cu^{+1} clusters tagged with hydrogen isotopes, highlighting the strong binding behaviour of the metal centre with H^2 and D^2[1]. In brief, the observed vibrational bands (in the range 2500 cm-1 - 4400 cm-1) are attributed to vDD / vHH stretches and combination modes involving the metal-adsorption site. Furthermore, ion-yield measurements of $[Cu(H2O)]^+$ -H2/D2 at different temperatures aid in characterizing the preferential nature of isotope adsorption at the hydrated metal centres .

Complementing the approach, pump-probe experiments on such gas-adsorbed Cu clusters would help unravel the reaction dynamics and short-lived, transition-state intermediates. Moreover, vibrational wave-packet dynamics can reveal the cluster structure as well as the low frequency metal-adsorbate vibrations[2]. Such transient measurements can also indicate isotopic effects associated with photodissociation of metal-H2/D2 but to further disentangle the dynamics at different charge and spin states, high energy XUV probe pulses are required.

References

[1] Dongmo, E.G., et al. (2024). "*Direct evidence for ligand-enhanced activity of Cu(I) sites*". Chem. Sci.,**15**,14635-14643.

[2] Grellmann, M., et al. (2024). "*Vibrational wave-packet dynamics of the silver pentamer probed by femtosecond NeNePo spectroscopy*". Phys. Chem. Chem. Phys., **26, 6600-6607.**

Table-top high-flux coherent XUV source for spectroscopy applications

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High-harmonic generation (HHG) driven by ultrashort laser pulses is an established process for the generation of coherent extreme ultraviolet (XUV) to soft X-ray radiation, which has found widespread use in various applications [1]. In recent years photon-hungry applications such as time-resolved photoelectron spectroscopy [2,3] and or imaging applications based on statistical analysis [3] have required more powerful HHG sources employing higher repetition rates. This need can be addressed by using high-average-power fiber lasers as the HHG drivers [4]. Here, we present HHG-based XUV sources providing a large photon flux and a remarkable brightness across a wide range between 20 eV and 150 eV. They are driven by commercial ultrafast fiber lasers with optional post-compression consisting of up to hundreds of Watts of average power while providing pulse energies up to the multi-mJ level yet maintaining <300-fs pulse durations. A post-compression unit is often part of the devices to shorten the pulses to ~35 fs or even less. These turnkey sources provide unprecedented photon flux at the source point of >1010 photons/s in each harmonic between 80 eV and 140 eV. Using a tuneable monochromator, any individual harmonic with a defined spectral bandwidth can be selected. The spectral and temporal properties of the XUV pulses can be optimized for the respective applications.

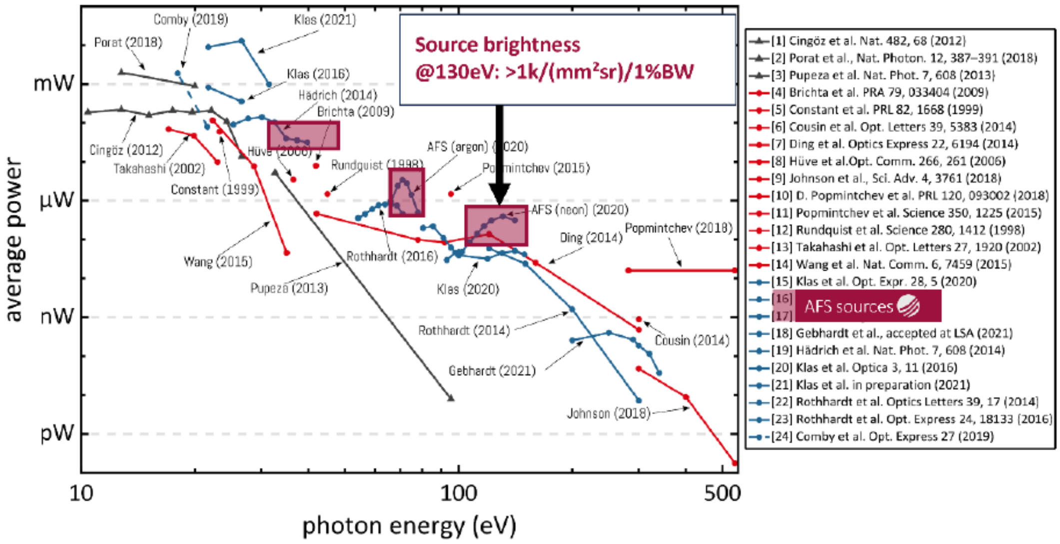

Figure 1: Comparison of different driver laser technologies (blue: fiber lasers, black: enhancement cavity, red: Ti:sa lasers) with respect to the XUV average power at different XUV photon energy [5]

Over the time span of one hour, the photon flux is as stable as ~1% RMS in the spectral range around 70 eV and 120 eV, respectively. Currently, further scaling towards even higher photon fluxes at 90eV is ongoing by using ultrashort pulses at 515nm. We will present the current status of these experiments.

References

[1] T. Popmintchev et al. Nat Phot. 4, 822–832 (2010).
[2] M. Keunecke et al. Rev. Sci. Instrum. 91, 063905 (2020)
[3] M. Reutzel et al. Advances in Physics: X 9 (1) 2024.
[4] S. Hädrich, et al. J. Phys. B At. Mol. Opt. Phys. 49, 172002 (2016).
[5] 1. Robert Klas, "Efficiency Scaling of High Harmonic Generation using Ultrashort Fiber Lasers," Dissertation, (2021).

Low-Energy Electron Scattering Cross Sections for Nanoconfined Water

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Nanoconfined water occurs in a wide variety of natural forms where it controls biological functions (e.g. protein stability, transport through ion channel), geological (e.g. transport through porous rocks) and atmospheric processes (e.g. freezing of droplets), and processes in cosmic environments; e.g. chemical reactions in interstellar dust grains [1–3]. Nanoconfined water has significantly different structural and dynamic properties than bulk water, some of which have already been extensively investigated experimentally and theoretically [1,2]. Experimental investigations into low-energy electron scattering in nanoconfined water systems are a challenge and seem to be essentially limited to photoelectron studies on nanoscale water clusters [4–6]. While condensed and gas phase electron scattering cross sections are reported for water, analogous data for scattering in water clusters was missing so far.

In the presented work, we combine velocity map photoelectron spectroscopy (PES) of clusters with a detailed electron scattering model based on a Monte Carlo solution of the transport equation to retrieve cluster cross sections for electron transport scattering in water clusters with nanoconfinement in the range of ~ 1.0 and 2.5 nm (~ 25 to 250 molecules per cluster) and electron kinetic energies (eKE) below ~32 eV. A cluster-size and energy-dependent function is determined to parametrize the deviation of simulation to experiment. With this, cross sections for electron scattering in water clusters are extracted, cf. Figure 1. We find larger electron scattering cross sections for clusters than for the condensed phase, in agreement with the results of ref. [4], likely due to reduced dielectric screening in clusters.

Exploring the Impact of Chemical Substitution on the Non-Adiabatic Dynamics of Benzaldehyde via Time-Resolved UV-XUV Photoelectron Spectroscopy

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The ultrafast non-adiabatic dynamics of organic cyclic compounds are key to numerous biological and chemical photoprocesses, where Conical Intersections (CIs) govern energy transfer by coupling electronic and vibrational degrees of freedom [1]. This study employs sub-20-fs extreme ultraviolet (XUV) time-resolved photoelectron spectroscopy (tr-PES) to study how selective chemical substitution impacts the excited state relaxation dynamics in benzaldehyde [2]. Using an ultraviolet pump (4.5 eV) and an XUV probe (39.5 eV) [3], we map the ultrafast dynamics of BZA and its methylated derivatives after excitation to the bright S2 excited state (Fig. 1a). As an example, the experimental photoelectron trace measured for 2-methylbenzaldehyde (2MBZA) is shown in Fig. 1b, revealing the ultrafast passage from the S2 state to the S1 state. Notably, the decay time of the S2 feature of the various compounds decreases as the methyl group approaches the aldehyde (Fig. 1c), suggesting a non-inertial effect of the methylation on the dynamics. This finding aligns with our theoretical simulations, which indicate that methyl proximity to the aldehyde reduces a barrier present on the S2 potential energy surface, thereby accelerating the dynamics. Moreover, the high temporal resolution of our experiment allows us to track the coherent vibrational oscillations activated along the relaxation pathways (Fig. 1d), including phenyl-CHO stretching, C-C stretching, and ring bending-twisting, which closely align with the known vibrational modes of excited BZA [4]. Our results offer significant insights into the ultrafast processes underlying BZA photochemistry and illustrate the capability of tr-PES to uncover complex dynamics within photochemical systems.

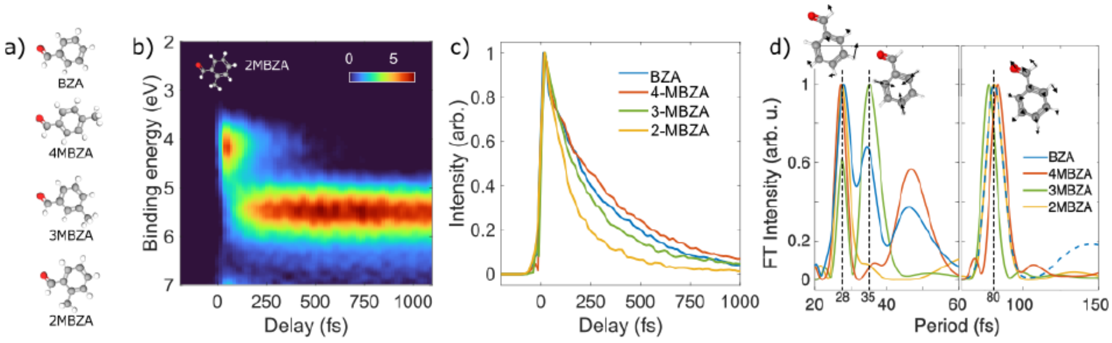

Figure 1: a) Molecular structures of BZA and its methylated derivatives under study. b) Experimental photoelectron spectrogram of 2MBZA. c) Energy-integrated photoelectron signals around the S_2 feature between 3.4 eV and 4.6 eV. d) Fourier transform of the center of mass of the S_2 signal (left) and S_1 signal (right), with corresponding vibrational modes [4].

References

[1] Schuurman, M., Stolow, A. (2018). “Dynamics at Conical Intersections” Ann. Rev. Phys. Chem. **69**: 427.

[2] Lee, S. H., et al. (2002). “Substituent Effects in Molecular Electronic Relaxation Dynamics via Time-Resolved Photoelectron Spectroscopy: ππ* States in Benzenes” J. Phys. Chem. A **106**(39): 8979.

[3] Crego, A., et al. (2024). “Sub-20-fs UV-XUV Beamline for Ultrafast Molecular Spectroscopy” Sci. Rep. **14**: 26016

[4] Silva, C. R., Reilly, J. P. (1996). “Theoretical Calculations on Excited Electronic States

Attosecond coincidence spectroscopy in small molecules

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Attosecond photoelectron interferometric techniques have been extensively employed over the past decade to investigate dynamics in molecular systems following photoionization. These techniques provide valuable insights into electron correlation effects and coupled electronic-nuclear dynamics [1]. Additionally, the combination of two-colour interferometric techniques with photoelectron-photoion coincidence spectroscopy enables angle-resolved studies in the recoil frame, unveiling information about the anisotropy of the molecular potential [2].

In our studies, we investigate photoionization dynamics in small molecules, such as CH_4-CD_4 isotopologues and CO_2, utilizing attosecond coincidence spectroscopy. The absorption of an extreme ultraviolet (XUV) photon originating from an attosecond pulse train populates a manifold of cationic states. An additional absorption or emission of an infrared (IR) photon gives rise to a two-colour photoionization spectrogram. A collinear configuration, presenting an attosecond stability, is utilized to control the relative delay between the XUV and the IR pulses, which co-propagate into a reaction microscope where they interact with the gas target [3].

The investigation of the mixture of CH_4 - CD_4 using attosecond photoelectron interferometry gives access to the nuclear response of the two isotopologues, since the electronic properties of the two molecular systems are not significantly affected by the two-colour field. By looking into the angle-integrated amplitude and contrast of the oscillations of the photoelectron peaks, we obtain information regarding the nuclear dynamics upon photoionization, as well as the effect of nuclear motion on the correlated electronic-nuclear dynamics [4]. Additionally, we investigate the angle-resolved phase of the photoionization process by fitting the oscillating component and the phase of the two-colour signal using complex asymmetry parameters [5].

Our studies extend also in CO_2, presenting photoionization time delays while considering the influence of field-induced coupling between ionization channels. Furthermore, we show time-resolved photoelectron angular distributions in the recoil frame by measuring the ejected electrons in coincidence with the O^+ dissociation fragments.

References

[1] a) G. Sansone *et al.*, Nature **465**, 763 (2010); b) R. Pazourek, S. Nagele, and J. Burgdörfer, Rev. Mod. Phys. **87**, 765 (2015); c) M. Nisoli *et al.*, Chemical reviews **117**, 10760 (2017);
[2] a) J. Vos *et al.*, Science **360**, 1326 (2018); b) H. Ahmadi *et al.*, Nat Commun **13** (2022); c) X. Gong *et al.*, Phys. Rev. X **12** (2022);
[3] D. Ertel *et al.*, The Review of scientific instruments **94** (2023).
[4] a) X. Gong *et al.*, Nat Commun **14**, 4402 (2023); b) D. Ertel *et al.*, Sci. Adv. **9**, eadh7747 (2023);
[5] a) D. Ertel *et al.*, J. Phys. Chem. A **128**, 1685 (2024); b) S. Saha *et al.*, Phys. Rev. A **104** (2021);

Pump probe measurements on SYLOS LONG beamline

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High-order Harmonic Generation in Gasses (GHHG) remains the state-of-the-art method to produce light pulses that are able to capture and eventually manipulate the fastest processes in various forms of matter down to the attosecond time scale. It has been the core technology of the field of attosecond sciences since its discovery over two decades ago. Despite the development of sophisticated techniques such as phase-locked XUV-IR pump-probe able to retrieve electron dynamics with few ten attosecond resolution, the dream of pure XUV pulse experiments (i.e. nonlinear interaction schemes) has not quite materialized. The main obstacle is the intrinsically low conversion efficiency of GHHG preventing the production of sufficiently high XUV pulse energies.

With the advent of modern OPCPA technology, TW class lasers with kHz repetition rates and few cycle duration are now available, promising to overcome this obstacle. Building a GHHG beamline that can harness these merits means entering new territory and it is not at all straightforward. While the path of upscaling has been described in theory [1,2], only an experiment can tell how these goals can be reached in practice.

We will report on pump-probe measurements carried with argon and liquid water. We plan to demonstrate the current capabilities which can be access by users.

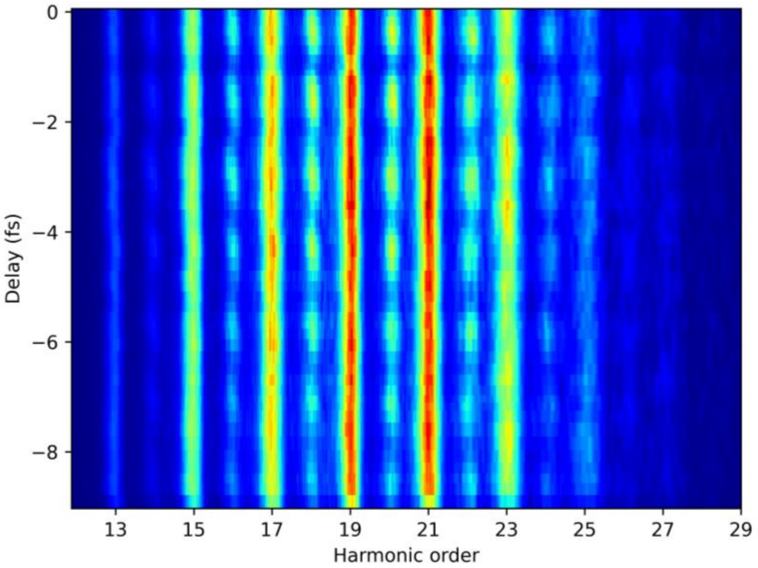

Figure 6: Recorded RABBIT trace with the beamline with argon

References

[1] Heyl C M et al 2016 Optica 3 75
[2] Rudawski P et al 2013 Rev. Sci. Instrum. 84 073103

Unravelling the Influence of Bridging Lengths in the Ultrafast Isomerization Dynamics of Bridged Azobenzenes in a Molecular Beam

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Bridged azobenzenes have drawn considerable attention in the last decade due to their superior photochemical properties compared to conventional azobenzene (AB), providing for higher isomerization yields and bidirectional switching abilities upon irradiation in the visible region of the electromagnetic spectrum [1]. In this study, the ultrafast isomerization dynamics of two of bridged azobenzenes, archetype -C2H2-bridged diazocine (Dz) and -CH2-bridged diazepine (Dzp), were investigated using time-resolved time-of-flight mass spectrometry, photoelectron imaging and photoionization-photofragmentation spectroscopy aided by quantum chemical calculations.

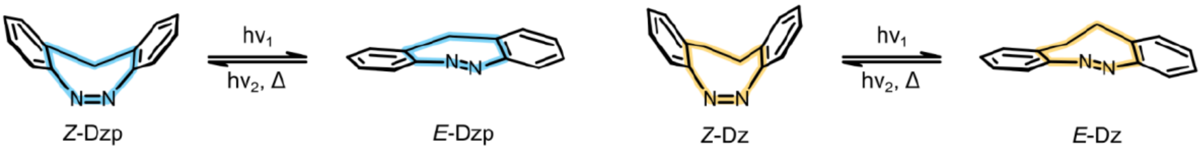

Figure 1: Isomerization scheme of diazepine (Dzp) and diazocine (Dz)

After S1 (nπ*) excitation at λpump = 400 nm, transient ion yield measurements revealed a prolonged decay for Dzp (τ1 = 38 ± 7 fs, τ2 = 680 ± 96 fs) opposed to Dz (τ1 < 38 ± 1 fs) at λprobe = 800 nm. Based on quantum chemical calculations, this was attributed to a consecutive isomerization pathway in Dzp consisting of an unfolding motion followed by CNNC increase in contrast to a concerted motion for Dz.

Further, single-color photoelectron imaging at the pump and probe wavelength revealed two competing ionization pathways. For Dz, the ionization pathway depends on the chosen ionization wavelength. The initially excited molecules undergo an unfolding motion in the S1 state to reach the CI to the ground state with τ1 < 38 ± 1 fs. Thus, an ultrafast rearrangement during the ionization (90 fs fwhm) is proposed, allowing for adiabatic transitions close to the D0 minimum rather than the FC region.

In the photoionization-photofragmentation experiments, a pronounced oscillation was found in the parent ion yield depletion of both Dzp and Dz. In combination with quantum chemical calculations, the motion was assigned to the so called butterfly vibration with ṽ = 50 cm-1 and 32 cm-1, respectively. This vibrational motion is therefore highly excited upon ionization and resembles the path from the FC region to the minimum in the D0.

In summary, the photoinduced dynamics for Dzp and Dz of the first excited state S1 as well as the ionic ground state D0 were revealed by a combination of three experiments, elucidating the important role of the S1 state in the ionization of these molecules.

References

[1] Siewertsen, R., et al. (2011). "Superior Z → E and E → Z photoswitching dynamics of dihydrodibenzodiazocine, a bridged azobenzene, by S1(nπ*) excitation at λ = 387 and 490 nm" Phys. Chem. Chem. Phys. **13**: 1054.

Measures of chirality for photoelectron spectra

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The advent of tightly-controlled polychromatic light sources has enabled the creation of a new and unusual form of radiation: synthetic chiral light [1], whose electric-field vector traces out a chiral curve over time, enabling strongly chiral interactions with matter which stay squarely in the dipole approximation, without relying on weaker magnetic-dipole or electric-quadrupole interactions. In highharmonic generation, synthetic chiral light promises a large step in enantiosensitivity, but it also holds significant potential in photoionization experiments, from enantiosensitive ionization yields to the creation of chiral signals in photoelectron spectra that can be tracked in time-resolved experiments. In order to track the chirality of a photoelectron spectrum, however, we need to be able to quantify that chirality, and here the theoretical tooling is lacking: there are currently no satisfactory universal measures of the chirality of a distribution which can be applied to photoelectron spectra [2]. In this contribution we present a family of such measures, which are built from the multipolar moments of the photoelectron distribution and arise naturally from the theory of quantized angular momentum [2]. Our measures are general, simple to use, and robust, and they can quantify the spectra from chiral molecules driven by achiral fields, as well as those from achiral systems driven by synthetic chiral light.

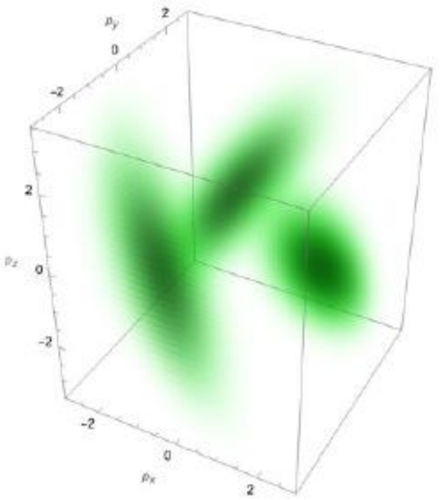

Figure 1: Toy-model chiral photoelectron spectrum consisting of three tilted gaussians. We can easily quantify the chirality of this, and a multitude of analogous distributions.

References

[1] Ayuso, D. et al. (2019). "Synthetic chiral light for efficient control of chiral light–matter interaction" Nature Photonics **13**: 866.
[2] Pisanty, E. et al. (2024), in preparation.

Probing the effect of relative humidity on salt aerosol nanoparticles and their ultrafast dynamics

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Aerosols are fine gas-phase particles suspended in the atmosphere, significantly impacting climate and public health by influencing cloud formation and atmospheric interactions [1]. The properties and effects of these particles on atmospheric processes depend on several parameters including the relative humidity, as they are often both hygroscopic and deliquescent. We study the NaCl nanoparticles as sea salt/desert dust aerosols samples, NaCl is most suitable model system for marine aerosols formed by sea spray or coastal desert dust, as chlorine is the most abundant anions in seawater, whereas Na+ is the most abundant cation. Their optical properties are of crucial importance for the radiation budget of the climate via direct effects, such as scattering and absorption of sunlight, as well as indirect effects, such as their contributions to serve as cloud condensation nuclei [3]. This project focuses on the formation and dissociation dynamics of free-flying salt aerosol sodium chloride (NaCl) nanoparticles, prepared at different humidity levels. By utilizing femtosecond laser pulses and the NanoTRIMS (Nano Target Recoil Ion Momentum Spectroscopy) technique available at AUS [Figure 1], we shall explore ultrafast reactions on aerosol nanoparticle surfaces and image their dissociation pathways. The NaCl nanoparticles are ionized in the focus of the laser (FM: focusing mirror), where the laser (z-axis) interacts with cross beam target NaCl-NPs (x-axis) as shown in Figure 4b. We measure the kinetic energy release in this ionization process by measuring the three-dimensional momentum of product ions. The results will be discussed during the meeting.

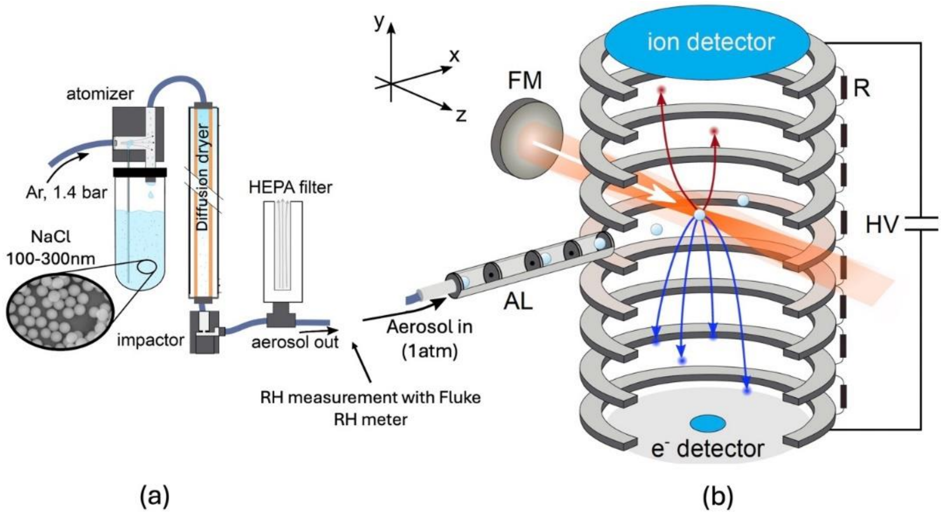

Figure 7 (a): Sea salt aerosol generation setups for NaCl nanoparticles. (b) NanoTRIM experimental setup using femtosecond laser for ultrafast studies at AUS, Sharjah.

References

[1] 1. Hallquist, M., et al. "H.; Seinfeld, JH; Surratt, JD; Szmigielski, R.; Wildt." Atmos. Chem. Phys 9.14 (2009): 5155-5236

[2] Lohmann, U., & Feichter, J. (2005). Global indirect aerosol effects: a review. Atmospheric Chemistry and Physics, 5(3), 715-737.

Ultrafast correlation dynamics of double ionization of atomic krypton

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The ELI Beamlines facility is an international research center within the Extreme Light Infrastructure ERIC, providing high-power lasers and laser-driven secondary sources for ultrafast user applications. The MAC end-station [1], at the high-harmonic (HHG) beamline [2], is a multi-purpose experimental station dedicated for the investigation of ultrafast dynamics in atoms, molecules, and nanoscale targets [3, 4]. We are presenting an overwiev of our recent developments and experimental results on ultrafast electron correlation dynamics in atomic krypton [3].

Electron correlation processes are of great importance for many material properties, chemical processes, and for autoionization events. At the MAC end-station at ELI Beamlines, we employ single harmonics at 29.6, 32.8, and 35.9 eV with atomic krypton as a target system for the study of ultrafast electron correlation dynamics. At this photon energy range, electron correlation may lead to the population of excited Kr+* satellite states above the 2s-1 state, which are probed by a synchronized femtosecond NIR pulse by further ionization to the Kr2+ final states. The detection of the transient Kr2+ ion yield provides a robust and straightforward method to discern the ongoing electron dynamics [3].

In this study we carefully adjust the NIR probe intensity, which reveals particular processes in the excited Kr+* satellite states (fig. 1). We show that it is possible to control the ratio of sequential and non-sequential two-color double ionization, or to selectively reveal or suppress (fig. 1 (a) and (d), respectively) quantum beating oscillations between coherently excited satellite states [3]. Our work thus demonstrate an effective way to probe and control the ionization dynamics of a multi-electron system by careful adjustment of the NIR probe pulse.

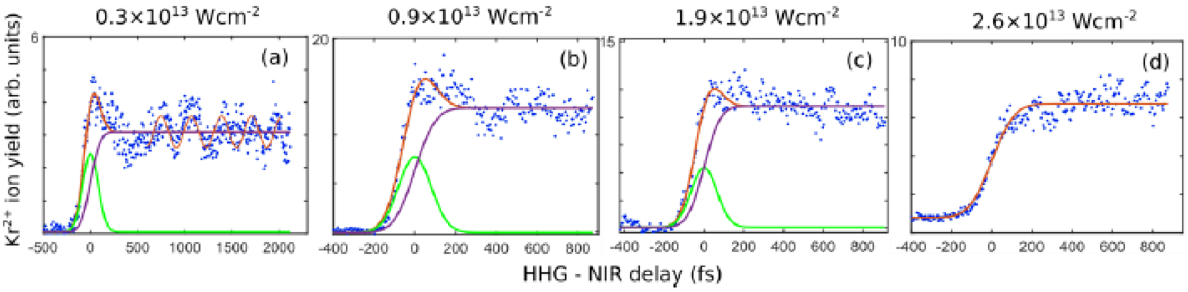

Figure 1: Kr2+ ion yield as a function of the XUV-NIR delay obtained at a photon energy of 32.8 eV and at variable NIR intensities (a)-(d). The blue dots represents experimetnal data, green lines fitted non-sequential ionization, and purple lines fitted sequential ionization. The red lines shows the total transient fitt to the data. Orange line in (a) shows an oscillation of quantum beating obtained from Fourier analyis.

References

[1] E. Klimešová, O. Kulyk, Z. Hoque et al., Eur. Phys. J. Spec. Top. **230**, 4183—4194 (2021).
[2] O. Hort, M. Albrecht, V. E. Nefedova et al., Opt. Express **27**, 8871–8883 (2019).
[3] A. H. Roos, Z. Hoque, E. Klimešová et al., New J. Phys. **25**, 013038 (2023).
[4] L. Jurkovičová, L. B. Ltaief, A. H. Roos et al., Comm. Phys. **7**, 26 (2024).

Nonequilibrium phase transitions and terahertz field effects on 1TTaS$_2$ probed by time-resolved photoemission spectroscopy

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Photoexcitation of materials with complex ground states can drive them into new out-of-equilibrium phases. The team at Nova Gorica studied the properties of these phases and the associated dynamics in the charge density wave (CDW)-Mott insulator 1T-TaS2, using time- and angle-resolved photoemission with XUV probe energies, which I will present here. We observe strong similarities between the band structures of the transient phase and the structurally undistorted equilibrium phase, with evidence for the coexistence of insulating and metallic phases. We also reveal a strong coupling between the recovery of Mott and CDW phases. During recovery, a metastable phase, driven by the CDW lattice order, emerges only in the strong photoexcitation regime and is a commensurate CDWMott insulating phase but with a reduced CDW amplitude.

In addition, the research work in Duisburg, where we studied the terahertz field induced electron dynamics in 1T-TaS2, using the THz-pump UV-probe photoemission spectroscopy setup recently built in Duisburg, will be presented. If an electric field component of incident THz pump pulses lies along the sample surface normal, then energy streaking of photoelectrons is observed due to interaction of emitted electrons with THz field in vacuum. We also observed time-dependent changes in the momentum component along the sample surface. This could be either due to momentum streaking in vacuum or acceleration of electrons by the THz field inside the material or both. For an electric field component of incident THz pump pulses lying along the sample surface, neither energy streaking nor time-dependent changes in the in-plane momentum are observed.

References

[1] Saha, T., et al. (2023). Physical Review B. **108,** 035157.
[2] Hellmann, S., et al. (2012). Nat. Commun. **3**, 1069.
[3] Petersen, J. C., et al. (2011). Phys. Rev. Lett. **107**, 177402.
[4] Sohrt, C., et al. (2014). Faraday Discuss. **171**, 243.
[5] Ligges, M., et al., (2018). Phys. Rev. Lett. **120**, 166401.
[6] Reimann, J., et al. (2018). Nature **562**, 396.
[7] Dreyhaupt, A., et al. (2005). Appl. Phys. Lett. **86**, 121114.

Probing UV-induced dynamics of phenanthridine with time-resolved X-ray absorption and X-ray photoelectron spectroscopy

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Modifying polycyclic aromatic hydrocarbons (PAHs) by replacing a carbon by a nitrogen atom introduces nπ* states into the molecules, in addition to existing ππ* states. nπ* states result from the excitation of non-bonding electrons at the nitrogen atom. Their introduction into the molecule leads to an alteration in optoelectronic properties making PANHs promising candidates e.g. for organic photovoltaic devices.[1]

In this experiment we investigated the excited state dynamics of the PANH phenanthridine after UV excitation at 268 nm into the S3 state (ππ* character). Using the Maloja endstation at the free electron laser SwissFEL time-resolved X-ray absorption and photoelectron spectra were recorded near the N1s edge. In recent experiments on thiouracil Mayer et al. found a strong dependence of the chemical shift on the character of the excited electronic states and thereby introduced the concept of the excited-state chemical shift.[2] For phenanthridine we expect the N1s binding energy to be particularly sensitive towards nπ* states due to the localized character of the core orbital at the nitrogen atom allowing to investigate the role of nπ* states in the deactivation pathway of UV excited phenanthridine. Significant shifts are observed both in the time-resolved X-ray photoelectron and X-ray absorption spectra and time constants for the deactivation process can be derived. For the X-ray absorption spectra, spectral features of the excited states and time constants are compared to theoretical results from surface hopping dynamics simulations combined with TDDFT calculations.

References

[1] V. Lami et al., Sol. RRL, 20171, 1700053.
[2] D. Mayer et al., Nature Communications, 2022, 13, 198.

Time-resolved resonant soft X-ray photoelectron spectroscopy of metal-oxide nanoparticles dissolved in aqueous solution

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Significant effort is being invested to find abundant, catalytically active and stable (photo)electrocatalysts, with transition metal oxides being an associated promising material class. The issues of efficiency and stability are due to related electronic-structure processes driving the oxygen evolution reaction and hydrogen evolution reaction at the solid-liquid interface between the electrocatalyst and the electrolyte. I will present our spectroscopic results on hematite (α-Fe2O3) nanoparticles dissolved in water,[1] which mimic the interface of this model (photo)electrocatalyst for water splitting in their true environment and were obtained using soft-X-ray synchrotron photoemission spectroscopy in combination with the liquid microjet technique at BESSY II. The method is shown to be sufficiently sensitive for the detection of adsorbed hydroxyl species, resulting from H2O dissociation at the nanoparticle surface in aqueous solution. We obtain signals from surface OH from resonant, non-resonant, and so-called partial-electron-yield X-ray absorption (PEY-XA) spectra. An observed intensity variation of the pre-edge peak, when comparing the PEY-XA spectra for different iron Auger electron decay channels, can be assigned to different extents of electron delocalization. From the experimental fraction of local versus non-local autoionization signals we infer an ultrafast, ~1 fs, charge transfer time from interfacial Fe3+ to the environment, see Figure 1.

I will also present an introduction to the recently started ERC-funded project WATER-X, which focuses on soft X-ray spectroscopic investigations of the <4 ns-timescale processes that occur in photocatalytic water-splitting at the metal-oxide nanoparticle–water interface using the liquid-jet technique. The novel element of this research will be the use of resonant, time-resolved soft X-ray photoelectron spectroscopy, whereby a combination of ultrashort UV/Vis pump pulses and tunable soft X-ray probe laser pulses with photon energies up to 600 eV will be used to investigate transient oxygen species via their resonant-Auger electron spectroscopic fingerprints at the metal-oxide nanoparticle surface in a bulk water environment.

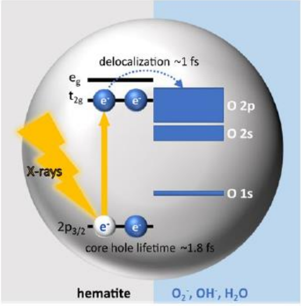

Figure 1: Sketch of the fast charge delocalization process at the hematite nanoparticle–water interface. Within the 1.8 fs core-hole lifetime, ~40 % of all iron 2p core-to-valence excited electrons delocalize into its (oxygen-dominated) environment (water, OH-, O2-).

References

[1] Ali, H., Winter, B., Seidel, R. (2023). "The Metal-Oxide Nanoparticle-Aqueous Solution Interface Studied by Liquid-Microjet Photoemission" Accounts of Chemical Research (56): 1687-1697

Generation of broad-bandwidth deep ultraviolet pulses with achromatic second harmonic generation

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The generation of deep ultraviolet optical pulses featuring broad spectral bandwidth and short pulse durations is a challenging task, especially when using high repetition rate (> 100kHz) laser systems that provide low pulse energies to drive the nonlinear conversion processes. We present a scheme based on second harmonic generation of the output of a non-collinear optical parametric amplifier. To increase the bandwidth and efficiency of the second harmonic generation we employ achromatic phase matching [1]. First results will be presented.

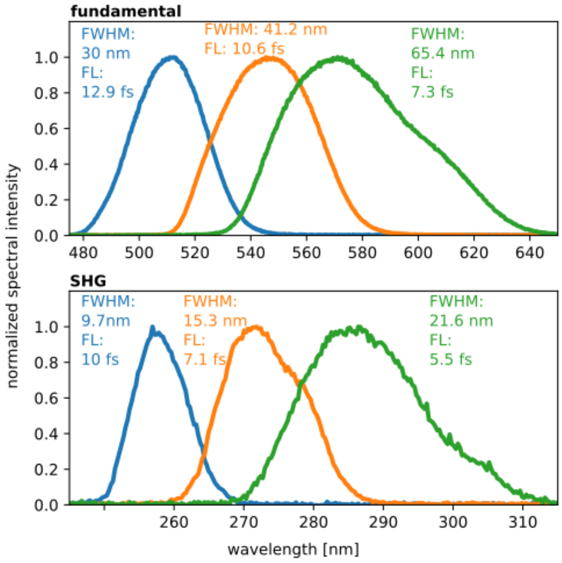

Figure 1: Conversion of broad bandwidth VIS pulses to the UV spectral domain.

References

[1] P. Baum, S. Lochbrunner, and E. Riedle, Opt. Lett. 29, 1686 (2004).

Major upgrades to the Artemis facility open new doors for ultrafast XUV science

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The Artemis facility, a part of the UK's Central Laser Facility (CLF), provides ultrafast laser sources, utilising High Harmonic Generation (HHG), producing tuneable XUV light (10 eV to 100 eV), for the UK and international community. The research program at Artemis focuses on ultrafast dynamics experiments on gas, liquid and solid materials as well a coherent diffractive imaging techniques.

Recently, the CLF was awarded a £17M investment under the HILUX project [1] to provide a transformative upgrade to Artemis and ULTRA facilities. As part of this upgrade, Artemis will be replacing its 20W 1 KHz Ti:Sapphire system with a 500 W 100 KHz Yb-based laser system which primarily supports Artemis' AMO and ptychography work. Crucially, this new high average power laser allows experiments to take advantage of the 100-fold increase in data acquisition rates afforded, by the 100 KHz laser repetition rate, dramatically improving the data quality.

In addition to this, HiLUX is also funding systematic upgrades to all the Artemis endstations, including a (a) new gas phase end-station which will offer dual electron and ion coincidence spectrometers alongside gas-jet and laser-desorption sources, (b) new £2.1 million material science end station, which will offer a momentum microscope, hemispherical analyser and spin resolution for PEEM and ARPES on devices in operando and 10 micron-scale samples, (c) a new solution phase transient x-ray absorption spectroscopy endstation, and (d) an upgraded ptychography endstation. These upgrades will be completed by Q1 2027.

References

[1] https://www.clf.stfc.ac.uk/Pages/HiLUX.aspx

Dynamics of photoionization-induced processes in laser-prepared gas- and aqueous-phase samples

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In this contribution, I will present an outlook on upcoming studies aiming to combine both a cold target recoil ion momentum spectroscopy (COLTRIMS) [1] and a liquid-jet photoelectron spectroscopy (LJ-PES) [2] apparatus with a modern, high-average-power, synchronized laser system employing beamline P04 of synchrotron PETRA III as an ionizing probe. P04 is a unique light source offering a broad soft X-ray photon-energy range of 250-3000 eV, an exceptionally high photon flux of up to 1014 ph/s, a high repetition rate of 5.2 MHz, and ~100 ps on-target X-ray pulse duration for world-wide unique, high-data-collection-rate measurements.

The aim is to investigate two different projects, one on gas-phase and one on liquid-phase experiments, having in common the preparation of the different samples by laser pulses. In more detail, this will cover

- Studying X-ray-induced photoemission processes and their dynamics in laser pre-aligned gasphase molecules in a reaction microscope.
- Observing and controlling bimolecular chemical reactivity and kinetics, involving aqueousphase radicals (such as OH), hydrated electrons, and a range of co-reactants using the liquidjet, picosecond-time-resolved photoemission spectroscopy technique.

To achieve this, a versatile and state-of-the-art high-average-power laser system of up to 1 MHz repetition rate, 0.2-200 picoseconds pulse-duration range, and 200-2500 nm wavelength range will be combined and synchronized with the P04 beamline.

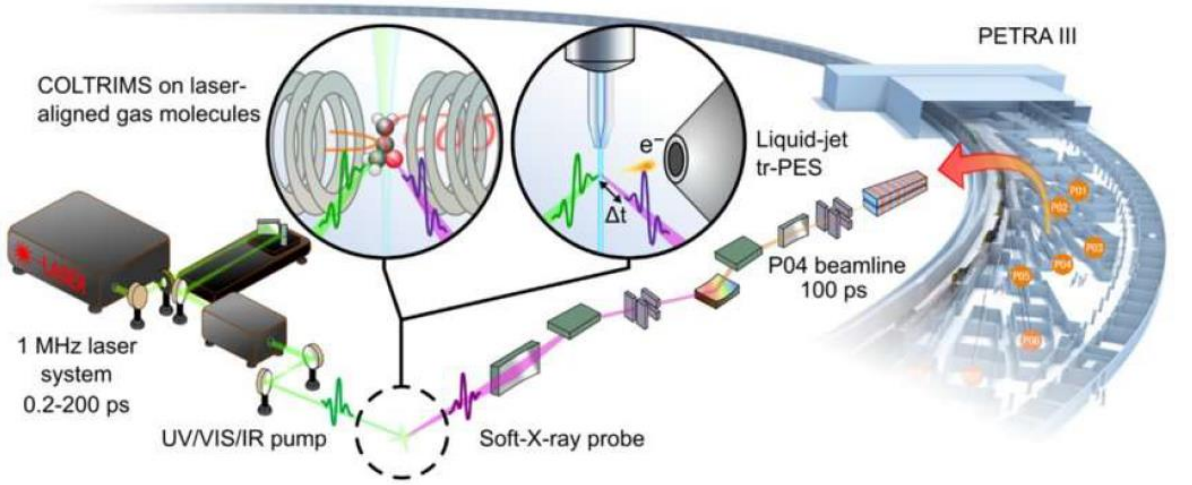

Figure 1: Experimental setup.

References

[1] Dörner, R., et al. (2000). Phys. Rep. 330(2-3): 95.
[2] Winter, B. and Faubel, M. (2006). Chem. Rev. 106(4), 1176.

Single-shot electron spectroscopy of individual clusters

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The development of short wavelength free-electron lasers (FELs) and intense lab-based high harmonic generation (HHG) sources has revolutionized the structural investigation of individual nanometre-sized specimens [1] like viruses [2] or clusters [3]: Using coherent diffractive imaging (CDI), high spatial resolution on the nanometre scale can be achieved. The diffraction image contains information about size, geometric shape, and exposure intensity. Providing short-wavelength attosecond light pulses, FELs [4] and HHG sources [5] open the door to so far unexplored ultrafast dynamics. In this context, atomic and molecular clusters are an excellent model system for studying light-matter interaction. We produce them from a large range of materials and can easily scale their size. Their simple composition and structure offer reduced complexity, making theoretical modeling feasible.

The direct measurement of electrons and their kinetic energies is a powerful method to gain insights into the ultrafast dynamical processes induced in the cluster, such as ionization processes and nanoplasma formation. Usually, the analysis suffers from averaging effects over different particle sizes and intensity fluctuations. In our new setup, we combine electron spectroscopy with single-shot CDI, enabling the investigation of individual rare gas and simple molecular clusters, thus disentangling size and focal intensity effect. This allows us to investigate how electron spectra from single clusters correlate to the material or composition, the size and shape of the clusters, and the irradiation intensity. With such experiments, we intend to gain a deeper understanding of energy exchange processes during nanoplasma formation, consolidating our knowledge about laser-matter interaction.

References

[1] H. Chapman et al., Nature Phys. 2, 839–843 (2006)
[2] M. Seibert et al., Nature 470, 78–81 (2011)
[3] D. Rupp et al., Nat. Commun 8, 493 (2017)
[4] J. Duris et al., Nat. Photonics 14, 30–36 (2020)
[5] P.M. Paul et al., Science 292, 5522 (2001)

New AMO end station for ultrafast XUV science at the Artemis facility

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The Artemis laboratory at the UK's Central Laser Facility (CLF) is a user facility offering access to high-average power femtosecond laser systems and high-harmonic generation (HHG) sources for a variety of ultrafast XUV experiments on both solid samples and gas-phase small molecules. The existing atomic, molecular, and optical physics (AMO) end station for gas-phase experiments offers velocity-map imaging or electron time-of-flight spectrometry capabilities and a variety of pulsed and effusive gas sources. Recent experiments have used time-resolved XUV photoelectron spectroscopy to map the reaction dynamics of small molecules such as CS2 [1] and 1,2-C2H2Cl2 [2], observe the roaming dynamics in CH3CHO [3], and study molecular-frame photoelectron angular distributions on aligned molecules [4]. However, time-resolved studies of ultrafast processes occurring in more structurally complicated molecules remain a challenge: for example, the signal arising from processes of interest can be obscured by the substantial background signal associated with dominant events such as ground state ionisation. A more sophisticated beamline and end station are necessary to overcome the difficulties intrinsic to next-generation experiments involving larger, more chemically complex molecules.

The CLF's ultrafast facilities have recently secured funding for a £17M major upgrade [5], HiLUX, which aims to increase the repetition rate of the facilities and develop end stations that can take full advantage of the consequential increased data rates. The upgrade to the Artemis AMO beamline will offer a 100 kHz Yb-based laser system, with 1.5 mJ, <50 fs pulses at 1 micron for HHG, and tunable <50 fs pulses from 235 nm to 10 microns. A new AMO end station (DYNAMO) will offer dual electron and ion coincidence spectrometers, equipped with delay-line detectors, and new gas-jet and laser desorption sources to facilitate multiple experimental regimes with improved discrimination of time-resolved signals. The upgrade is due to be completed by Q1 2027 and accessible to UK academics and their collaborators, and through Laserlab-Europe.

References

[1] Smith, A. et al. (2018) 'Mapping the Complete Reaction Path of a Complex Photochemical Reaction' Phys. Rev. Lett. 120, 183003

[2] McGhee, H. G. et al. (2024) 'Ultrafast photochemical processes in 1,2-dichloroethene measure with a universal XUV probe' Phys. Chem. Chem. Phys.

[3] Alba, G. L. et al. (2024) 'Direct Observation of a Roaming Intermediate and Its Dynamics' J. Am. Chem. Soc. 146, 18, 12595-12600

[4] Woodhouse, J. L. et al. (2024) 'Quantitative analysis of aligned molecule photoelectron angular distributions' Submitted

[5] https://www.clf.stfc.ac.uk/Pages/HiLUX.aspx

Investigation of the interaction between organic dopants and a helium nanodroplet environment with time-resolved photoelectron spectroscopy

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Embedding molecules in ultracold helium nanodroplets allows us to study molecular processes in a superfluid environment [1]. Here, we apply time-resolved photoelectron spectroscopy to study the dynamics of dopants embedded in helium nanodroplets. Droplet size-dependent photoelectron spectra [2] have been established as an appropriate technique for studying interactions between organic dopants and the helium environment. Probing helium droplets doped with selected organic molecules, we present a study of the evaporation and ejection dynamics upon laser excitation (see figure 1). Both phenomena have been observed previously in helium nanodroplets for different dopants [1,3,4]. Additionally, static photoelectron spectra of tetracene embedded in helium nanodroplets were recorded (see figure 2). First results will be presented.

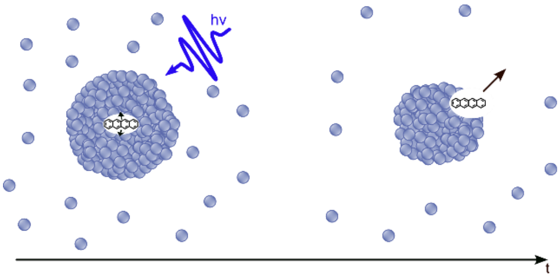

Figure 8: Helium evaporation and dopant ejection upon excitation

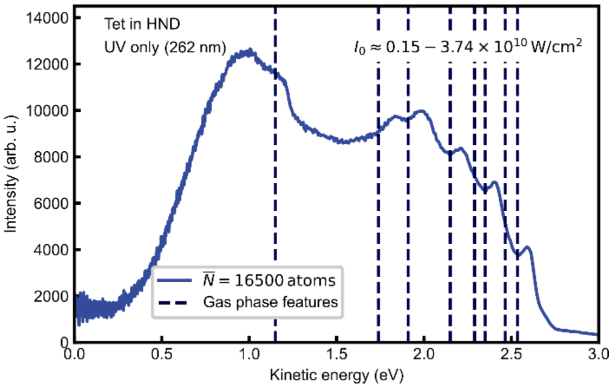

Figure 2: Static photoelectron spectrum of tetracene in helium nanodroplets

References

[1] Toennies, J.P. and Vilesov, A. F. (2004), Angew. Chem. In. Ed. **43**(20): 2622-2648
[2] Loginov. E. et al. (2005), Phys. Rev. Lett. **95**(16): 163401
[3] Thaler, B. et al. (2018), Nat. Commun. **9**(1):4006
[4] Meyer. M. et al. (2019), EPJ Web Conf. **205**: 06005

Alignment Frame Photoelectron Imaging in the XUV

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Photoelectron angular distributions (PADs) are dependent on both the symmetry of the ionization transition and the molecular geometry, thus making them a sensitive probe of molecular structure and dynamics.[1] However, in a laboratory frame measurement, much of the quantitative detail of the PAD is lost through averaging over a molecular sample with a random distribution molecular axes. Molecular frame information may be recovered by recording PADs of molecules which have been fixed in space prior to ionization, such that the molecular axis along which ionization takes place can be selected, so-called alignment frame photoelectron angular distributions (AFPADs).[2,3] Here, we present a quantitative comparison of experimental and theoretical alignment frame PADs for rigorous benchmarking of cutting-edge theoretical methods which modelling the ionization dynamics of molecules.

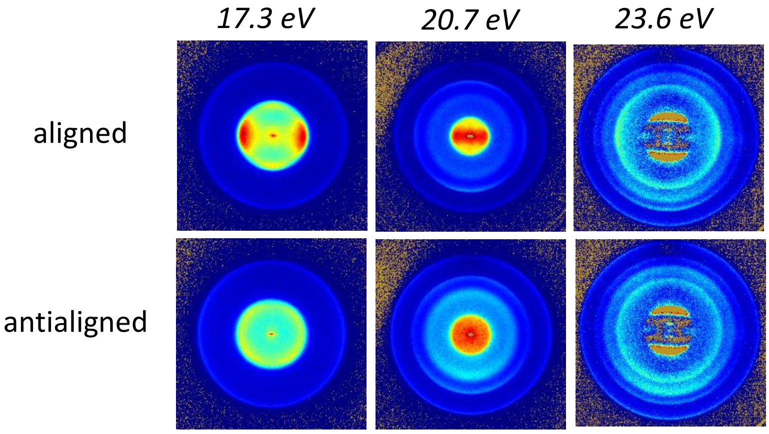

Figure 9 : Photoelectron images following ionization of nonadiabatically aligned N2O molecules with monochromated high harmonics at the specified photon energies

References

[1] K. L. Reid, Mol. Phys., 2012, 110, 37–41

[2] K. L. Reid and J. G. Underwood, J. Chem. Phys., 2000, 112, 3643–3649

[3] C. Marceau, et al., Phys. Rev. Lett., 2017, 119, 1–6

XUV Double-Ionisation of Thymine, Pyridine and their Complexes with Water – Distinguishing Local and Non-Local Secondary Ionisation

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Studying the photoionisation of biomolecules, such as amino acids and nucleobases, in the gas phase allows detailed insights into energetics and dynamics at the molecular level. As in-vivo biomolecular systems exist in the condensed phase, studying complexes of these biomolecules with water gives greater insight into decay channels that are available in biological systems, while still allowing the application of typical gas phase experimental approaches such as electron-ion coincidence spectroscopy.

An electron-ion-ion coincidence study of pure and micro-solvated thymine and pyridine ionised by XUV radiation above and below their double ionisation potential, will be presented. The coincidence detection scheme enables isolation of signals arising from double ionisation events and allows for correlation of (di)cationic states to certain fragmentation pathways. Above the double-ionisation potential, molecular fragmentation channels differ from single ionisation processes with intramolecular proton transfer reactions stabilising the cationic fragments. The fragmentation patterns of pure pyridine and thymine differ clearly from the corresponding micro-solvation complexes. In the latter, different auto-ionisation processes such as the non-local intermolecular Coulombic decay (ICD) and electron transfer mediated decay (ETMD), and local Auger-Meitner decay can be distinguished. These processes are important to the field of radiation chemistry since the production of low energy electrons can trigger reactions which damage biological material.

The reduction of molecular complexity in bio-relevant precursor molecules, such as pyridine, reduces the number of possible auto-ionisation pathways which can help to increase the understanding of the fundamental processes.

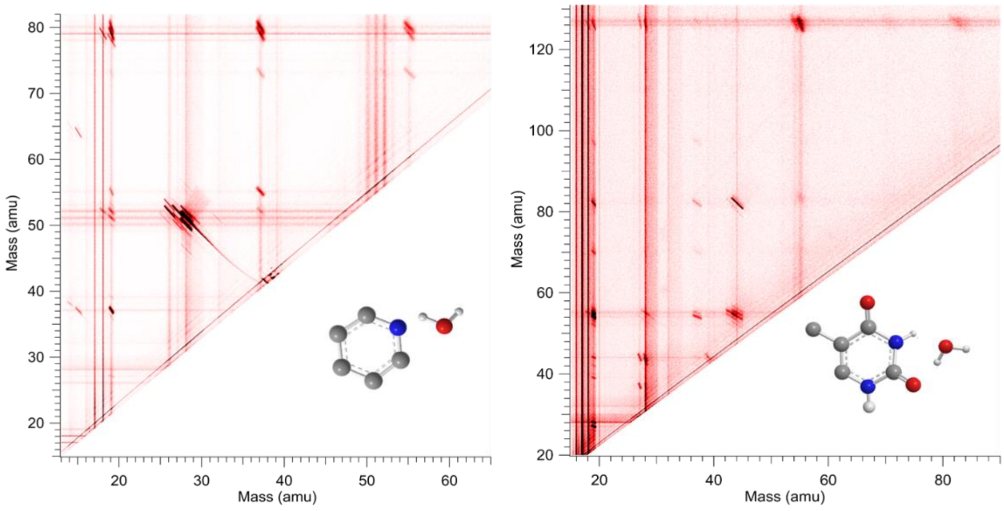

Figure 10: Left (right) ion-ion coincidence map of pyridine (thymine) – water complexes.

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