Molecular Physics and Physical Chemistry with Advanced Photon Sources

739. WE-Heraeus-Seminar

30 January - 03 February 2022

hybrid

at the Physikzentrum Bad Honnef, Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 739. WE-Heraeus-Seminar:

Broadly tunable photonsources (light sources) like storage rings (synchrotron radiation, SR) and Free Electron Lasers (FEL) that went into operation in the last decade provide radiation of high brilliance. They open exciting prospects for molecular spectroscopy and dynamics in several spectral regions that were traditionally difficult to access. It is therefore timely to address the potential of advanced photon sources for molecular physics and physical chemistry and review the state of the art in the research fields that already or potentially will benefit from these sources, among them combustion science, astrophysics, and atmospheric chemistry.

In this seminar, we will bring together scientists from light source facilities, who are involved in beamline development and the implementation of new applications, with present and prospective users inmolecular physics and physical chemistry, who are interested in the opportunities that such light sources provide now and especially in the near future. In particular, we wish to emphasize the opportunities that arise from combining the properties of different light sources in a single research program. We wish to promote discussions between beamline scientists and users, to utilize the full potential of ongoing developments and to establish new collaborations. It is a further goal to motivate young scientists to present work that uses advanced photon sources or would potentially benefit from it, because fresh ideas of young scientist are critical for the development of the field. The program will therefore constitute a mix of plenary, invited, and contributed lectures as well as ample time for a poster session. Sufficient time for discussions will be scheduled after the talks. In addition we schedule a round table discussion that addresses questions by young scientists concerning careers in science. The focus on the interaction between advanced and junior researchers will distinguish this seminar from other meetings in the field

Scientific Organizers:

Prof. Dr. Ingo Fischer	Universität Würzburg, Germany E-mail: ingo.fischer@uni-wuerzburg.de
Dr. Laurent Nahon	SOLEIL, France E-mail: laurent.nahon@synchrotron-soleil.fr
Dr. David L. Osborn	Sandia Natl Lab, USA E-mail: dlosbor@sandia.gov

Introduction

Administrative Organization:

Dr. Stefan Jorda
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Registration:

Elisabeth Nowotka (WE Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (17:00 h – 21:00 h) and Monday
morning

Program

Sunday, 30 January 2022

17:00 – 20:00	Registration	
18:00	*BUFFET SUPPER and informal get-together*	
20:15 – 20:30	Scientific organizers	**Welcome words**

Chair: Laurent Nahon

20:30 – 21:30	Wim Ubachs	**Precision measurements of molecular hydrogen in search for new physics**

Program

Monday, 31 January 2022

08:00	*BREAKFAST*	

Chair: Christa Fittschen

09:00 – 10:00	Majed Chergui	**Perpectives in ultrafast X-ray spectroscopy**
10:00 – 10:40	Zhandong Wang	**Recent progress of autoxidation chemistry by advanced mass spectrometry**
10:40 – 11:00	*COFFEE BREAK*	
11:00 – 11:40	Patrick Hemberger	**New mechanistic insights into catalytic processes by detection of highly reactive intermediates**
11:40 – 12:20	Tina Kasper	**Pollutant formation in energy conversion processes**
12:20 – 12:40	Dusan Bozanic	**Velocity Map Imaging VUV Angle-Resolved Photoemission on Isolated Plasmonic Nanostructures**
12:40 – 12:45	**Conference Photo** (in the front of the lecture hall)	
13:00	*LUNCH*	

Program

Monday, 31 January 2022

Chair: Majdi Hochlaf

15:00 – 15:40	Daniel Rolles	**Gas-phase photochemistry studies with free-electron lasers**
15:40 – 16:20	Tatiana Marchenko	**Ultrafast dynamics in molecules without ultrafast light sources**
16:20 – 16:40	Danylo Matselyukh	**Decoherence and revival in attosecond charge migration driven by non-adiabatic dynamics**
16:40 – 17:00	*COFFEE BREAK*	
17:00 – 17:40	Olivier Pirali	**High-resolution molecular spectroscopy in the THz region using synchrotron radiation**
17:40 – 18:40	Stephen Pratt	**Multiple probes of photoionization dynamics**
18:40 – 19:00	Stefan Jorda	**About the Wilhelm and Else Heraeus-Foundation**
19:30	*DINNER*	
20:30	**Poster session on site**	

Program

Tuesday, 01 February 2022

08:00	*BREAKFAST*	

Chair: Gustavo Garcia

09:00 – 09:40	Berenger Gans	**VUV photoionization spectroscopy of free radicals with synchrotron- and laser-based experiments**
09:40 – 10:20	Xiaofeng Tang	**Vacuum ultraviolet photochemistry of peroxy radicals in the gas phase**
10:20 – 10:40	Diksha Garg	**Ultrafast fragmentation and relaxation dynamics of fluorene observed on femtosecond timescales**
10:40 – 11:00	*COFFEE BREAK*	
11:00 – 12:30	**Poster session I online**	
13:00	*LUNCH*	

Chair: tba

15:00 – 15:40	Christine Joblin	**Studying the properties of astro-PAHs under VUV synchrotron radiation**
15:40 – 16:00	Lyna Bourehil	**Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy**
16:00 – 16:20	Domenik Schleier	**Kinetics of 1- and 2-Methylallyl + O_2 reaction, investigated by photoionisation using synchrotron radiation**
16:20 – 16:35	*BREAK*	
16:35 – 18:00	**Poster session II online**	
19:30	*DINNER*	

Program

Wednesday, 02 February 2022

08:00	*BREAKFAST*	

Chair: Olle Björneholm

09:00 – 09:40	Fabian Holzmeier	**Dissociative photoionization of EUV lithography photoresist models**
09:40 – 10:20	Ruth Signorell	**Photon sources for the study of aerosol formation and photochemistry**
10:20 – 11:00	Bernd Winter	**Advances in liquid-jet photoelectron spectroscopy**
11:00 – 11:20	*COFFEE BREAK*	
11:20 – 12:00	Sadia Bari	**Soft X-ray absorption spectroscopy of isolated biomolecules**
12:00 – 12:20	Florian Trinter	**Ultrafast temporal evolution of interatomic Coulombic decay in NeKr dimers**
12:20 – 12:40	Deependra Jadoun	**Time-resolved photoelectron spectroscopy of conical intersections with attosecond pulse trains**
13:00	*LUNCH*	

Program

Wednesday, 02 February 2022

Chair: tba

15:00 – 15:40	Carlo Callegari	**Molecular physics and physical chemistry FERMI/LDM beamline**
15:40 – 16:00	Dennis Mayer	**Following excited-state chemical shifts in molecular ultrafast x-ray photoelectron spectroscopy**
16:00 – 16:20	Laura Carlini	**A gas-phase study of cyclo-dipeptides containing an aromatic side chain: photoemission and state-selected fragmen**
16:20 – 16:40	Jacopo Chiarinelli	**Unveiling inter- and intra-molecular intera in homogeneous and hydrated uracil clust**
16:40 – 17:00	*COFFEE BREAK*	
17:00 – 17:40	Rebecca Caravan	**Direct studies of an elusive reactive intermediate: understanding the chemistry of Earth's lower atmosphere using synchrotron-coupled mass spectrometry**
17:40 – 18:20	Kevin Wilson	**Probing gas-surface reactions in aerosols using synchrotron radiation**

19:30 *HERAEUS DINNER*
(social event with cold & warm buffet with complimentary drinks)

Program

Thursday, 03 February 2022

08:00	*BREAKFAST*	

Chair: Ingo Fischer

09:00 – 10 :00	Jos Oomens	**FEL-based IR ion spectroscopy for molecular structure identification in mass spectrometry**
10:00 – 10:40	Francesca Calegari	**Realtime tracking of the electron dynamics in complex molecules**
10:40 – 11:00	*COFFEE BREAK*	
11:00 – 11:20	Gabi Wenzel	**Infrared spectroscopy of isomers formed in the –H dissociative ionization of methyl-PAHs**
11:20– 11:40	Rémi Dupuy	**Photoelectron angular distributions from surfactants at the liquid-vapor interface**
11:40	Scientific organizers	**Closing remarks**
12:30	*LUNCH*	

End of the seminar and departure

NO DINNER for participants leaving on Friday morning

Posters

Posters session Tuesday 11:00 h – 12:30 h CET

Dina Atwa Khalil	**Synchrotron radiation based investigations of colored layers binding materials and resins of the god Ptah-Sokar-Osiris wooden statuette and its mummified falcon which are dating back to 26th Pharaonic dynasty**
Björn Bastian	**XUV coincidence spectroscopy of helium nanodroplets**
Thorsten Bernhardt	**Insight into sustainable catalysis with advanced light sources**
Olle Björneholm	**Non-local core-hole decay process in aqueous inorganic ions**
Laura Carlini	**A gas-phase study of cyclo-dipeptides containing an aromatic side chain: photoemission and state-selected fragmentation**
Yan Chen	**N–N bond fission dynamics of the N_2O^+ cation in the $C^2\Sigma^+$ state: competition between the NO^+ and N^+ fragment ion formation pathways**
Mayara da Silva Santos	**Study of chemical bonds in metal-oxygen systems based on X-ray absorption spectroscopy**
Franziska Dahlmann	**Strong ortho/para effects in the vibrational spectrum of $Cl^-(H_2)$**
Sambit Kumar Das	**Excited state dynamics in the photolysis of phenyl azide**
Robert Donovan	**Exotic chemical and physical processes involving heavy Rydberg states.**
Christa Fittschen	**Chemistry and spectroscopy of $CH_3C(O)O_2$ radicals**
Max Flach	**Quantifying energy shifts in high resolution x-ray spectroscopy to peer at transition metal 3d population beyond the oxidation state**

Posters session Tuesday 11:00 h – 12:30 h CET

Nadav Genossar	**Ring opening and tunneling inversion in the cyclopropyl radical and cation**
Marius Gerlach	**Auger spectroscopy of fulminic acid, HCNO**
Majdi Hochlaf	**State-to-state dissociative photoionization of molecular nitrogen: The full story**
Seb Jackson	**Ultrafast molecular spectroscopy by time-resolved photoelectron imaging**
Yining JIANG	**Characterization of radiolysis-induced post-translational modifications (PTMs) in modeled systems by IRMPD and UVPD spectroscopy**
Pavle Juranic	**Generation and measurement of ultra-short x-ray pulses at SwissFEL**
Emil Karaev	**Threshold photoelectron spectra of fragments of AsMe3 and SbMe3**
Juliette Leroux	**Performance and first results of a versatile home-built tandem mass spectrometer dedicated for experiments at advanced light sources**
Fabiano Lever	**Data fusion for photoelectron spectroscopy @FLASH: a GPU accelerated approach**
Jochen Mikosch	**Sensitivity of inner-shell photoelectron spectroscopy to non-Born-Oppenheimer and photodissociation dynamics in polyatomic molecules**
Marcel Mudrich	**Probing intermolecular decay processes in superfluid helium nanodroplets by tunable and ultrafast XUV radiation**
Archna Sharma	**X-ray absorption spectra of hydrocortisone and betamethasone**

Posters session Tuesday 11:00 h – 12:30 h CET

Stephan Thürmer	**How shake-up and shake-off satellites can reveal ultrafast charge delocalization in liquid water**
Akansha Tyagi	**All reflective delay line for dispersion-less ultrafast measurements**

Posters session Tuesday 16:30 h – 18:00 h CET

Sara Gallarati	**Investigation of oxidation reaction products of Acetyl Acetone using synchrotron photoionization**
Deb Pratim Mukhopadhyay	**Photoelectron spectroscopy of reactive low-valent organophosphorus compounds, $P\text{-}CH_3$, $H\text{-}P{=}CH_2$ and $P{=}CH_2$: A study of coincidence measurement using synchrotron radiation**
Richarda Niemann	**Infrared super-resolution wide-field microscopy using sum-frequency generation**
Behnam Nikoobakht	**New Insight into the Photodissociation Dynamics of formaldehyde oxide CH_2OO**
Fabio Novelli	**Nonlinear terahertz spectroscopy on liquid water**
Zhangatay Nurekeyev	**Tracking chemical dynamics with time-resolved X-ray spectroscopy and scattering**
Michael Odelius	**Excited state molecular dynamics simulations of the photodissociation of ironpentacarbonyl**
Zeyou Pan	**On the absolute photoionization cross section and threshold photoelectron spectrum of two reactive ketenes in lignin valorization: fulvenone and 2-Carbonyl Cyclohexadienone**
Maximilian Paradiz DomÍnguez	**Time-resolved near-edge soft X-ray absorption spectroscopy as a new tool in organic photochemistry**
Lassi Pihlava	**Photodissociation dynamics of halogenated aromatic molecules: the case of core-ionized tetrabromothiophene**
Heidy Mayerly Quitián-Lara	**Astrochemistry of small-sized polycyclic aromatic hydrocarbons in X-ray-dominated regions**
Lorenzo Restaino	**Probing nonadiabatic dynamics with attosecond pulse trains and soft X-ray Raman spectroscopy**

Posters session Tuesday 16:30 h – 18:00 h CET

Marvin Reuner	**Theoretical description of time-resolved momentum microscopy probing excited-state dynamics of pentacene on a silver substrate**
Daniel Rösch	**High-resolution multiplexed double velocity map imaging PEPICO for gas phase reaction kinetics**
Madhusree Roy Chowdhury	**Photoionization of cyano-PAHs**
Carles Serrat	**Perspectives for hard X-ray selective cancellation of the active center of biomolecules**
Yashoj Shakya	**Revealing ultrafast proton transfer dynamics in ionized aqueous urea solution through time-resolved x-ray absorption spectra and ab initio simulations**
Denis Tikhonov	**PAHs under extreme ultraviolet exposure: Theory and experiment**
Jens Uhlig	**Looking on ultrafast dynamics from many ways**
Eliane van Dam	**Stripping away ion hydration shells in electrical double layer formation: water networks matter**
Christian van der Linde	**IR multiple photon dissociation spectroscopy of MO_2^+ (M = V, Nb, Ta)**
Ivo Vinklárek	**Pickup of hydrogen bonding molecules by benzene nanoparticles: growing ice-mantles in interstellar space medium**
Ru-Pan Wang	**A setup for FLASH liquid-phase ultrafast X-ray spectroscopy (FLUXS)**
Christian Weigelt	**Ultrafast wettability alteration: The decisive moments of adsorption on supported particles**

Posters session Tuesday 16:30 h – 18:00 h CET

Cuihong Zhang	**Absolute absorption cross-section of $C_2H_5O_2$ Radical and Kinetics of its self-reaction: Rate constant and branching ratio**

Abstracts of Talks

(in alphabetical order)

Soft X-ray absorption spectroscopy of isolated biomolecules

S. Bari[1,2]

[1]Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany
[2] Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

Biomolecules are the building blocks of life and it is important to understand how exactly their physical properties are responsible for their functionality and responses to stressors. A very suitable method is to study isolated biomolecules with cutting-edge mass spectrometry techniques at advanced light sources to unravel their intrinsic properties, i.e. in an environment-free and controlled chemical state. In particular, Near-Edge X-ray Absorption Mass Spectrometry (NEXAMS), which is an action-spectroscopy technique based on fragment-resolved absorption upon resonant photoexcitation of core atomic levels, has been of growing interest in recent years for investigating the spatial and electronic structure of biomolecules.

In this talk, I will present the latest results from NEXAMS studies on peptides [1, 2] and related molecules like porphyrins [3]. Not only spatial and electronic structures, but also damage processes, site-selective dissociation and orbital-dependent deexcitation pathways will be discussed.

References

[1] S. Dörner, L. Schwob, K. Atak, K. Schubert, R. Boll, T. Schlathölter, M. Timm, C. Bülow, V. Zamudio-Bayer, B. von Issendorff, J. T. Lau, S. Techert and S. Bari, J. Am. Soc. Mass Spectrom. **32**, 670 (2021)

[2] L. Schwob, S. Dörner, K. Atak, K. Schubert, M. Timm, C. Bülow, V. Zamudio-Bayer, B. von Issendorff, J. T. Lau, S. Techert and S. Bari, J. Phys. Chem. Lett., **11**, 1215 (2020)

[3] K. Schubert, M. Guo, K. Atak, S. Dörner, C. Bülow, B. von Issendorff, S. Klumpp, J. T. Lau, P. S. Miedema, T. Schlathölter, S. Techert, M. Timm, X. Wang, V. Zamudio-Bayer, L. Schwob, S. Bari, Chem. Sci. **12**, 3966 (2021)

Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy

<u>Bourehil Lyna</u> [1,2], Héloïse Dossmann[1], Gustavo Garcia[2], Denis Lesage[1]

1 Institut Parisien de Chimie Moléculaire (IPCM) - Sorbonne Université UPMC Paris VI, CNRS : UMR8232 - 4 Place Jussieu 75252 Paris Cedex 05, France

2 Synchrotron SOLEIL (SOLEIL) - Centre National de la Recherche Scientifique : UR1-France

Organometallic complexes are key compounds in homogenous catalysis and their reactivity is closely related to the steric and electronic effects of the ligands within the complex. [1, 2] Photoelectron spectroscopy (PES) may be used as a fine probe of the electronic interaction between the ligand and the metal centre[3] . This method has been applied here to study tricarbonyl iron complexes of the type ($Fe(CO)_3L$) with L being substituted cyclopentadiene ligands. Such complexes take part in hydrogen alkylation reactions[4] and reduction reactions[5].

The experiments were carried out on the DESIRS beamline at the synchrotron SOLEIL facility, using e^-/i^+ coincidence techniques to obtain mass-selected PES of jet-cooled complexes. These spectra provide access to the ionisation energies and state-selected Fe-CO dissociation energies. Rationalization of the experimental results is further made using density functional theory and bond description methods to get information on the electronic structure of the complex and thus on the metal-ligand interaction.

References:

1. Constable, E.C., *In Metals and Ligand Reactivity*. 2005. 22-45.
2. Zecchina, A.C., S., Eds. , *The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology.* John Wiley and Sons, 2017.
3. Dossmann, H. Gatineau, D. Clavier, H. Memboeuf, A. Lesage, D. Gimbert, Y., *Exploring Phosphine Electronic Effects on Molybdenum Complexes: A Combined Photoelectron Spectroscopy and Energy Decomposition Analysis Study.* J Phys Chem A, 2020. 124(42): p. 8753-8765.
4. Bettoni, L.G., S. Renaud, J. L., , *A phosphine-free iron complex-catalyzed synthesis of cycloalkanes via the borrowing hydrogen strategy. .* Chem. Commun. , 2020,. 56(85): p. 12909−12912.
5. Moulin, S.D., H. Pagnoux-Ozherelyeva, A. Gaillard, S. Poater, A. Cavallo, L. Lohier, J.-F. Renaud, J.-L., , *Bifunctional (Cyclopentadienone) Iron−Tricarbonyl Complexes: Synthesis, Computational Studies and Application in Reductive Amination.* Chem. Eur. J., 2013. 19: p. 17881−17890.

Velocity Map Imaging VUV Angle-Resolved Photoemission on Isolated Plasmonic Nanostructures

Dušan K. Božanić[1,2], Gustavo A. Garcia[1], Laurent Nahon[1]

[1]Synchrotron SOLEIL, l'Orme des Merisiers, St. Aubin, BP48, 91192 Gif sur Yvette Cedex, France

[2]Department of Radiation Chemistry and Physics, "VINČA" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

Aerosol photoelectron spectroscopy is an important method for studying the electronic structure of submicrometer particles, free from the influence of substrate or solvent [1, 2]. This technique comprises the interaction of focused beam of particles (typically ~100 nm in size) with ionizing radiation under high vacuum conditions. In this approach the aerosol particles can be directly produced from a solution or a colloidal dispersion, which opens a possibility for investigations of a variety of hybrid nanosystems that can be produced by conventional wet chemistry methods. The photoelectrons formed in the particle/photon beam interaction can be detected and discriminated according to their momenta using VUV velocity map imaging photoemission spectroscopy (VUV VMI-PES). This technique is typically used for measuring of valence photoemission spectra of gas-phase species, as it enables simultaneous evaluation of kinetic and angular distributions of all emitted photoelectrons. In the case of nanosystems, due to attenuation of the incident radiation, the electron images obtained by VUV VMI-PES are asymmetric with respect to the direction of propagation of the photon beam. This leads to additional symmetry restrictions in the reconstruction of the 3D electron momentum distribution, which is necessary to obtain the photoelectron spectrum. In our recent study [3], we introduced a new methodology to extract the photoelectron spectrum, the anisotropy parameter, and the asymmetry parameter from the electron images of a nanosystem as a function of the electron energy. In this report, we describe the methodology and present the results of the VUV VMI-PES studies of different isolated plasmonic nanostructures, obtained by atomization of the hydrocolloids of neat and functionalized noble metal nanoparticles.

[1] K. R. Wilson, H.Bluhm, and M. Ahmed, Aerosol Photoemission, in Fundamentals and Applications in Aerosol Spectroscopy, ed. by R. Signorell and J. P. Reid, CRC Press 2011.
[2] L. Ban, B. L. Yoder, and R. Signorell, Annu. Rev. Phys. Chem. **71**, 315 (2020).
[3] D.K. Božanić, G.A. Garcia, O. Sublemontier, J. Pajović, V. Djoković, L. Nahon, J. Phys. Chem. C **124**, 24500 (2020).

Realtime tracking of the electron dynamics in complex molecules

F. Calegari[1,2]

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[2]Institut fur Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

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

Here, I will give a few examples on how attosecond/few-femtosecond technology can be used to observe purely electronic processes initiated in complex targets. At first, I will present a time-resolved study of the correlation-driven charge migration process occurring in the DNA nucleobase adenine after ionisation by a 15-35 eV attosecond pulse. Our most intriguing observation is that a stable dication of the parent molecule can be produced if the probing NIR pulse is delayed of 2.3 fs from the XUV pulse. The delayed creation of the dication is the signature of a many-body effect resulting in a charge migration mechanism occurring on a sub-3 fs time scale [3].

I will then present a novel setup combining sub-2fs UV pulses [4] with few-fs IR and attosecond XUV pulses. We recently have combined linearly polarized UV pulses with circularly polarized IR pulses to perform time-resolved Photo Electron Circular Dichroism (PECD) in Methyl-lactate and Ethyl-lactate with sub-5 fs resolution. We demonstrate that the broadband UV pulse can excite a coherent superposition of Rydberg states. The resulting coherent electron dynamics can be used to modulate the chiral response of the molecule on a sub-15 fs time scale.

References

[1] F. Calegari et al. **49**, J. Phys. B 062001 (2016)
[2] F. Calegari et al **336**, Science 346 (2014)
[3] E. Månnson et al, (Nature) Commun. Chem. **4**, 73 (2021)
[4] M. Galli et al, Optics Letters, 44, 1308 (2019)

Molecular physics and physical chemistry at the FERMI/LDM beamline

C. Callegari[1]

[1]*Elettra – Sincrotrone Trieste S.c.p.A., 34149 Basovizza Trieste, Italy*

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

The Low Density Matter (LDM) beamline at FERMI has been serving the atomic, molecular and cluster science community since its opening at the end of 2012 [2]. Through the use of interchangeable supersonic jet sources, it offers the possibility of studying atoms and molecules (including aligned ones), as well as more exotic systems such as superfluid helium droplets or metallic nanoparticles. Ion and electron spectroscopies (time-of-flight; velocity map imaging) and coherent diffraction imaging are available in one of the few different standard configurations of the endstation. Users’ equipment can be accommodated as well, and several experiments have also been performed in non-standard configurations. A synchronized infrared laser (with second-, third-, and fourth harmonic generation capability) is available for optical+FEL, and a split-and-delay line for FEL—FEL, pump-probe experiments. The LDM beamline has worked in close synergy with the Machine Physics team to help characterize FERMI, and develop new modes of operation.

In this talk I will present the results of a few case studies performed at the LDM beamline as Users’ experiments or as internal research and development, recent instrumental upgrades, and prospects for the physical chemistry community.

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

References

[1] E. Allaria et al., Nat. Photon. **6**, 699 (2012); ibid. **7**, 913 (2013)

[2] V. Lyamayev et al., J. Phys. B **100**, 164007 (2013);
C. Svetina et al., J. Synchrotron Radiat. **22**, 538 (2015)

Direct studies of an elusive reactive intermediate: understanding the chemistry of Earth's lower atmosphere using synchrotron-coupled mass spectrometry

R.L. Caravan

Chemical Sciences and Engineering Division,
Argonne National Laboratory, Lemont, IL, USA

Earth's lower atmosphere is highly chemically complex. Understanding and predicting its chemistry requires a combination of complementary studies that span scales of time and chemical complexity. One key component of this is studies of reactive intermediates—short-lived species that drive chemical change through their reactions. Carbonyl oxides (known as Criegee intermediates) are an important class of reactive intermediates that are formed in Earth's atmosphere from the ozonolysis of alkenes. Until just over a decade ago, carbonyl oxides had eluded direction detection. The advent of photolytic methods to directly generate carbonyl oxides has facilitated direct studies of their reactivity, which have revealed that the reactivity of carbonyl oxides is far more complex than we thought. The first of these studies, and many thereafter, have been conducted using a powerful combination of photoionization mass spectrometry and tunable VUV synchrotron radiation. When coupled to the tuneable-VUV output of the Chemical Dynamics Beamline at the Advanced Light Source (Lawrence Berkeley National Laboratory), the Sandia Multiplexed Photoionization Mass Spectrometer instrument (MPIMS) acquires 3-D datasets (mass, kinetic time, and photoionization energy), that facilitate direct and unambiguous chemical kinetics and mechanistic studies of carbonyl oxides. In this talk, I will discuss the exciting insights into the reactivity of carbonyl oxides that this technique has provided, and how these results have impacted our understanding of their role in Earth's lower atmosphere.

This material is based in part on research at Argonne supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Contract No. DE-AC02-06CH11357. This research used resources of the Advanced Light Source, a U.S. DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

A gas-phase study of cyclo-dipeptides containing an aromatic side chain: photoemission and state-selected fragmentation

L Carlini[1*], E Molteni[1], P Bolognesi[1], D Sangalli[1], G Mattioli[1], P Alippi[1], A Casavola[1], M Singh[2], C Altucci[2], M Valadan[2], M Nisoli[3,4], Y Wu[3], F Vismarra[3,4], R Borrego Varillas[4], R Richter[5], J Chiarinelli[1], M C Castrovilli[1] and L Avaldi[1]

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[2]Università degli Studi di Napoli Federico II, Dipartimento di Fisica, Napoli, Italy
[3]Politecnico di Milano, Dipartimento di Fisica, Milano, Italy
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Peptides, i.e. molecules built by linking a series of aminoacids via the peptide bonds, play a central role in several scientific as well as practical areas , from the study of the origin of life, to the development of self-assembled nanostructures with peculiar properties. Linear (*l*-) and cyclo (*c*-) dipeptides obtained by linking two aminoacids are the smallest and simplest peptides. Among the *c*-dipeptides, the ones containing an aromatic aminoacid in the side chain are of interest for the study of the dynamics involving energy and charge transfers [1], relevant processes in bio-systems.

In this work we report a combined experimental and theoretical study of the electronic structure and the state-selected fragmentation of cyclo-dipeptide cations (*c*-GlyPhe, *c*-TrpTrp and *c*-TrpTyr) containing aromatic aminoacids. A systematic *ab-initio* study allowed to explore geometry, energy levels, electronic wave-functions and optical properties of these dipeptides, while valence photoemission (PES), mass spectrometry (MS) and photoelectron-photoion coincidence, PEPICO, measurements performed at the CIPO beamline [2] of the Elettra synchrotron radiation facility at 60 eV provided information on the photoelectron energy distribution and state selected fragmentation [3]. The comparison between the calculated density of states (DOS) and the experimental PES spectra points out some general characteristics, typical fingerprints due to the presence of an aromatic side chain appears in all the three samples. From the PEPICO measurements, the partial ion yield of the main fragments as a function of the binding energy (BE) has been extracted, giving insight into the molecular fragmentation. By comparing the most probable fragmentation pathways for the three samples we found that when the dipeptide contains the Trp aminoacid, independently of the ionized orbital, the charge migrates always to the Trp aromatic terminal, which is then lost as a charged fragment during fragmentation.

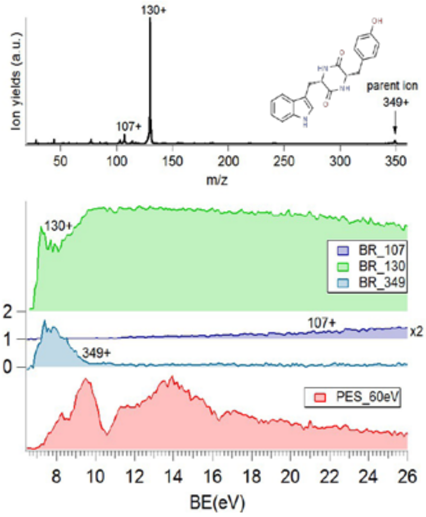

Figure 1. The mass spectrum (top panel), the partial ion yield of the main fragments (central panel) and the PES spectrum (bottom panel) of c-TrpTyr molecule obtained at 60 eV incident radiation.

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Perpectives in ultrafast X-ray spectroscopy

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The past ten years have witnessed a revolution in science with the advent of X-ray free electron lasers (XFEL) and table-top sources of short-wavelength radiation. XFELs in particular provide pulses of ultrashort time duration, high fluxes, high coherence, polarization control, etc., which allow novel methods to be implemented. Among these are photon-in/photon-out methods such as X-ray emission spectroscopy (XES), resonant Inelastic X-ray scattering (RIXS), or non-linear X-ray optical methods. I will show an example of recent studies on the dynamics of haem proteins captured by fs-XES. [1,2] I will then dwell on the perspectives for X-ray circular and helical dichroism studies of molecular systems. [3] I will finish by presenting the state-of-the-art of non-linear X-ray studies and give an example of hard X-ray transient grating spectroscopy, [4] as well as subsequent developments.

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Unveiling inter- and intra-molecular interactions in homogeneous and hydrated uracil clusters

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X-ray photoemission spectroscopy, XPS, is a very suited tool to probe the chemical environment of a specific atom in a system. In this work XPS has been used to study the different molecular interactions (H-bond, π-stacking, dispersion interactions) at work in homogeneous and hydrated uracil (U) clusters in the gas phase. The measurements have been performed at the Pleiades beam line [1] of SOLEIL synchrotron using a gas aggregation source, developed at CNRS-CIMAP [2] and coupled to an end station equipped with a Scienta R4000 photoelectron spectrometer. The measured C, N and O 1s XPS spectra of the clusters display a shift with respect to isolated uracil molecules [3] due to the variation of the molecular connections in the clusters. DFT-based simulations to calculate the binding energy of each atom in the cluster and molecular dynamics simulations to determine the cluster structure have been performed. The strategy of the simulation [4,5] is based on a bottom-up approach that selects aggregates with increasing numbers of uracil (2-50) and water (0-60) molecules to disentangle the effects of the different interactions in the cluster. In the case of the homogeneous clusters it was found that the formation of large clusters is driven by the anisotropic distribution of H-bond donor and acceptor sites, which can be also modulated by weaker dispersion forces [4]. In the mixed clusters the presence of hydrophobic moieties lead to the formation of a core-shell-like supramolecular organization in clusters of increasing size, where water forms tightly packed cores and uracil forms a shell around these cores [5].

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Photoelectron angular distributions from surfactants at the liquid-vapor interface

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Liquid-vapor (especially aqueous-vapor) interfaces play a major role in atmospheric science, for example in the interaction of oceans with the atmosphere, in aqueous aerosols where they govern important chemical reactions, or in the evaporation of lakes and reservoirs. Sparely soluble, amphiphilic organic molecules (e.g. long chain fatty acids) tend to accumulate at the surface of aqueous solutions and can change dramatically the properties of the interface. One of the crucial steps towards a better understanding of the effect of surfactants is to obtain molecular-scale information on the arrangement and behavior of these molecules at the interface.

Here we present an investigation of fatty acids in aqueous solutions, where photoemission spectroscopy is coupled with a liquid microjet. Measurements at synchrotron beamlines equipped with an elliptically polarizing undulator offer the possibility to measure photoelectron angular distributions (PADs) from such systems. I will discuss how the measurement of PADs, a so far little explored parameter in liquid XPS, can offer new insights on the characterization of surfactants at the liquid-vapor interface. PADs reflect the degree of elastic scattering experienced by photoelectrons before leaving the aqueous surface, and can thus be related to the relative positions of different molecules, or functional groups within molecules, on the surface normal axis. It is thus possible to use them as a new tool in photoemission studies.

VUV photoionization spectroscopy of free radicals with synchrotron- and laser-based experiments

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The photoionization spectroscopy of free radicals is a difficult task mainly because it implies the use of efficient radical sources and of tunable VUV radiations.

In this talk, I will describe two different techniques employing either the threshold photoelectron spectroscopy (TPES) coupled with synchrotron radiations or the pulsed-field-ionization zero-kinetic-electron photoelectron spectroscopy (PFI ZEKE PES) coupled with a tunable VUV laser.

In the first part of the talk, I will briefly present a few results obtained on C_2 [1] and SiH [2], in collaborations (mainly with J.C. Loison, G. Garcia, *et al.*), using a flow tube reactor coupled with the DELICIOUS 3 spectrometer of the DESIRS beamline of the SOLEIL synchrotron.

In the second part, I will introduce a recent laser experiment that we built at ISMO to perform high-resolution PFI-ZEKE spectroscopy of free radicals. Preliminary results will be presented [4,5].

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Ultrafast fragmentation and relaxation dynamics of fluorene observed on femtosecond timescales.

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Polycyclic aromatic hydrocarbons (PAHs) is an important class of astrochemically relevant molecules, that constitutes more than 20% of the galactic carbon. Recently, substituted PAHs have been identified in the molecular clouds and their formation mechanism is yet to be understood [1]. To understand the chemical processes occurring in the interstellar medium (ISM), studying fragmentation dynamics of these molecules is crucial.

We analyze the dissociation and fragmentation dynamics for the PAH, fluorene ($C_{13}H_{10}$) after they interact with XUV and Vis radiation. Since electronic transitions happen on femtosecond (fs) time scales, we employed fs pump-probe spectroscopy with free electron laser (FEL, XUV photons, 30.3 nm) and a table-top laser (UV photons, 405 nm) to study the dynamics of these molecules. The experiments were performed in a beamtime at the Free-Electron Laser (FEL) FLASH in Hamburg using the CAMP endstation [2]. This work reports the relaxation lifetimes of the fluorene monocation and the dication. Effect of using different probes will also be briefly discussed.

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New mechanistic insights into catalytic processes by detection of highly reactive intermediates

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Catalysts are the drivers for many chemical reactions and responsible for almost all large-scale industrial process from ammonia synthesis to valorization of alkanes and biomass or crude oil cracking. Usually process optimization is performed by variation of the reaction conditions like pressure, temperature, concentration, or the catalyst. However, if these trial-and-error approaches fail, mechanistic insights are much-needed. Reactive intermediates such as radicals or ketenes are responsible for the branching of a chemical reaction. If we understand their fate, we can unveil the chemistry behind the reactive systems and can actively take control on the process.

In this talk we utilize photoelectron photoion coincidence spectroscopy (PEPICO) with vacuum ultraviolet synchrotron radiation from the Swiss Light Source (SLS). PEPICO combines both mass spectrometry and photoelectron spectroscopy as a reaction microscope to explore mechanisms in catalysis.[1]

We discuss how this state-of-the-art detection tools gained new insights into catalytic fast pyrolysis (CFP) of lignin model compounds, such as benzenediols over zeolites. While resorcinol (m-benzenediol) and hydroquinone (p-benzenediol) possess similar reactivity, catechol (o-benzenediol) sticks out and can uniquely dehydrate to form the reactive fulvenone ($c\text{-}C_5H_4{=}C{=}O$) intermediate.[2] This ketene rapidly hydrogenates to form resonantly stabilized phenoxy radicals ($C_6H_5\text{-}O$), which undergo a branching towards phenol or yield cyclopentadienyl radicals ($c\text{-}C_5H_5$) upon decarbonylation. The latter radicals are hydrogenated to form cyclopentadiene ($c\text{-}C_5H_6$), which can dimerize in a Diels-Alder reaction to yield dicyclopentadiene. The dimer can decompose in different pathways to yield fulvene, benzene, toluene, and xylenes, or dehydrogenate multiple times to form naphthalene. These pathways provide compelling evidence for coke formation mechanisms, which are responsible for the deactivation of the catalyst.

If time permits, we will also dive into catalytic C-H activation chemistry of alkanes, where detection of methyl, ethyl and propyl radicals shed new light on the dehydrogenation or coupling reaction mechanism and the formation of the first aromatic ring, benzene.

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Dissociative photoionization of EUV lithography photoresist models

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The dissociative photoionization of model molecules for extreme ultraviolet (EUV) lithography photoresists used in the production of integrated circuits was investigated to get mechanistic insights that are important for improving photoresists materials and developing better electronic devices. The semiconductor industry has recently adopted EUV lithography to enable sub-10 nm features on wafers. However, stochastic print failures are often decreasing the efficiency in the manufacturing process. The origin of these defects is not definitively clear since little is known about the chemical mechanism in photoresist materials that is induced by interaction with EUV light. Since those materials are complex compositions and the complete reaction mechanism involves photoionization, radiation chemistry by secondary electrons and diffusion in the thin film, it is best to disentangle the sub-steps and investigate them independently at first. We studied the interaction of photoresist prototype compounds using EUV synchrotron radiation and employing photoelectron spectroscopy and photoelectron-photoion coincidence detection at the GasPhase beamline at Elettra Sincrotrone Trieste. These gas phase experiments complement parallel research on thin films conducted at imec using time-averaged and time-resolved spectroscopic techniques. First of all, however, they give unique insights into the initial step in EUV lithography, photoionization, for a better understanding of the mechanism, necessary to make EUV lithography more profitable.

Time-resolved Photoelectron Spectroscopy of Conical Intersections with Attosecond Pulse Trains

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Abstract

Conical intersections (CIs) are believed to be ubiquitous in molecules and mediate various important processes such as photosynthesis, photoisomerization in the process of vision, etc. Ultrafast decay channels, which appear in the vicinity of CIs, funnel the molecule from one state to another. The population transfer near a CI creates a superposition of electronic states, thus giving rise to electronic coherence. Probing the electronic coherence can be considered a unique signature of the CI in a molecule. Time-resolved photoelectron spectroscopy (TRPES) has been proposed to observe the occurrence of CIs in a molecule. The electronic coherence can be observed in the TRPES spectrum when ultrashort probe pulses with adequate temporal resolution are used. The features of electronic coherence in the TRPES spectrum fade away when the pulse width of the probe pulse is increased such that the spectral resolution is improved. Although, the enhanced spectral resolution helps monitor the increasing energy separation between the electronic states after the passage through CI. The restriction of observing one phenomenon over the other comes from the fact that the spectral and temporal widths of the isolated pulses are Fourier conjugates of each other. We propose to overcome the Fourier restriction by performing TRPES with an attosecond pulse train (APT) as a probe [1]. TRPES spectrum with APT as a probe contains electronic coherence features and hints of increasing energy separation between the electronic states. Therefore, it is possible to partially lift restrictions on temporal and spectral resolutions in TRPES with APTs.

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Studying the properties of astro-PAHs under VUV synchrotron radiation

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In star forming regions, polycyclic aromatic hydrocarbons (PAHs) are strongly coupled to VUV irradiation. This interaction leads to various molecular processes that impact the physical and chemical conditions in these environments. Ionisation leads to gas heating by thermalisation of the emitted electrons. Photodissociation mainly governs the chemical evolution of these astro-PAHs and their contribution to the production of small molecules such as H2 and hydrocarbons. Radiative cooling affects the dissociation yield and leads to the well-known aromatic IR emission bands (AIBs), which constitute the only direct diagnosis we have so far for the presence of astro-PAHs. The unique capabilities in terms of sensitivity, spectral, and spatial resolutions offered by the imminent James Webb Space Telescope should bring further observational insights into these aspects.

In the laboratory, these molecular processes need to be quantified in order to accurately feed astronomical models [1]. To do so, one has to take into account both the broad distribution of VUV photons and the extreme isolation conditions that occur in astrophysical environments. We performed action spectroscopy on trapped PAH cations [2,3] and imaging photoelectron photoion coincidence spectroscopy on neutral PAHs and PAH clusters [4,5] using the available set-ups at the VUV undulator beamline DESIRS of SOLEIL. We also performed complementary experiments in cryogenic ion traps and storage devices, which allow us to access timescales (ms, s) relevant for radiative cooling [6,7]. The next step will be to couple the latter instruments with the VUV synchrotron light.

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Pollutant formation in energy conversion processes

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The goal of curbing climate change requires a reduction in greenhouse gas emissions and forces the transition to CO_2-neutral technologies in the electricity, mobility, industry and building sectors. Combustion for energy and heat conversion is an advanced and reliable technology, which can help mitigate the risks of this transition. One short- to mid-term strategy is to defossilize the fuel used in combustion processes, e.g., by using hydrogen, or synthetic and biomass-derived carbon-containing fuels. Consequently, the reduction of pollutants and the improvement of the efficiency of combustion processes remains an important task. Predictive process simulation of fuel conversion can overcome empiric process optimization and requires a detailed understanding of the reaction pathways and chemical kinetics.

The work presented here, aims at improving our understanding of the interaction of NOx with hydrocarbon ignition chemistry at low temperatures and of the oxidation of toluene during combustion. The ignition chemistry is studied in a flow reactor and the oxidation in premixed laminar low-pressure flames. Both experiments are well suited for probe-sampling and subsequent qualitative and quantitative gas analysis by photoelectron photo ion coincidence spectroscopy (PEPICO). VUV radiation produced by the VUV beamline at the Swiss Light Source was used for near-threshold photoionization. With the PEPICO technique isomers can be identified and their signals separated for the quantitative analysis. For both systems the analysis focusses on the role of intermediates in the process: The interaction of NOx with hydrocarbon fuels leads to the formation of nitrogenated intermediates, which influence ignition kinetics and NOx pollutant formation. For toluene oxidation, key intermediates of the fuel destruction pathway, e.g., benzyl radicals and C_5H_5CCH were detected. Regarding the formation of aromatic pollutants in the flames, the experiments show that these species are not formed from the fuel, but from small resonantly stabilized radicals such as propargyl and allyl radicals. In addition, the limitations of the isomer specific detection of these intermediates are discussed.

Ultrafast dynamics in molecules without ultrafast light sources

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Ultrafast relaxation of core-excited molecules involves electron-electron correlation effects as well as correlations between nuclear and electronic motion occurring on femtosecond (1 fs=10^{-15} s) and attosecond (1 as=10^{-18} s) time scales. Investigation of these effects requires a detailed study of the electronic structure evolving in time along with the nuclear dynamics. This information remains inaccessible for direct time-resolved measurements due to the broad bandwidth of the ultrafast radiation sources resulting in a limited resolution in the energy domain. Alternatively to the time-resolved measurements, the dynamical effects can be successfully studied through high energy-resolution electron and X-ray spectroscopy using synchrotron radiation.

I will present an overview of our selected studies performed in the last few years at ESRF and SOLEIL synchrotron facilities demonstrating how the electron and nuclear dynamics in molecules can be extracted from the experiments without using short light pulses [1-4]. Few examples of our experiments performed at FEL facilities with the focus on the dynamical effects in small molecules will also be presented.

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Decoherence and Revival in Attosecond Charge Migration Driven by Non-adiabatic Dynamics

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Recent developments in table-top and accelerator-based light sources have brought the direct observation of purely electronic dynamics of molecules within reach [1,2]. Nevertheless, how such electronic charge migration interacts with structural dynamics, how fast electronic coherence is lost and whether it can revive has so far not been experimentally characterized.

Here, we report a combined theoretical and experimental study of silane (SiH_4) using attosecond transient-absorption spectroscopy. Our results reveal a 690-attosecond charge migration and show, for the first time, how adiabatic and non-adiabatic structural dynamics influence such dynamics on a femtosecond time scale. We used a 5-fs VIS/NIR pump-pulse to prepare a superposition of electronic states in the silane molecule and probed the created coherences with a time-delayed attosecond X-ray pulse through transient absorption at the well-characterized silicon $L_{2,3}$-edge [3]. The experimental results are interpreted through a detailed comparison with Multi-Configurational Time-Dependent Hartree (MCTDH) simulations, which treat the electronic and vibrational degrees of freedom fully quantum mechanically.

Excellent agreement between theory and experiment has been achieved, showing that the observed loss of electronic coherence over the first ~10 fs is due to the loss of overlap of the vibrational wavepackets in the symmetric stretch vibrational mode and is not compromised by non-adiabatic population transfer. After ~50 fs a revival of the electronic coherence revival is observed, due to the return of spatial and momentum overlap of the vibrational wavepackets in different electronic states.

These results (i) show how charge migration can be prepared and observed in neutral molecules, (ii) confirm that electronic coherence can be rapidly lost due to structural dynamics, but (iii) that it can nevertheless revive even tens of femtoseconds later. Our work thus sheds new light on several founding paradigms of attosecond chemistry.

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Following excited-state chemical shifts in molecular ultrafast x-ray photoelectron spectroscopy

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Light-induced relaxation processes in molecules are accompanied by a charge redistribution over the molecule. In a recent experiment, we could observe the charge motion within the excited-state relaxation on a specific site of a molecule using time-resolved x-ray photoelectron spectroscopy (TR-XPS). A shift in the ionisation potential of a core electron can be connected to the local charge change within the framework of a potential model. With this, we extend the concept of the static chemical shift from conventional XPS [1, 2] to an excited-state chemical shift which allows to invert TR-XPS to dynamic charge at a specific site of the molecule.

We demonstrate the capabilities of TR-XPS with a study of the UV-excited dynamics of 2-thiouracil conducted at the FLASH free electron laser in Hamburg, Germany [3]. By probing sulfur 2p core electrons, we discover that a significant part of the excited-state population relaxes to the ground state within 220-250fs. Additionally, we observe a 250fs oscillation in the kinetic energy of the excited-state population which reveals a coherent population exchange among electronic states.

* For the full list of authors see [3].

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FEL-based IR ion spectroscopy for molecular structure identification in mass spectrometry

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Mass spectrometry (MS) is one of the cornerstones of analytical chemistry, especially in the analysis of complex mixtures: samples that contain thousands of molecular components in varying concentrations. Both sensitivity and resolving power of MS are unparalleled by other analytical methods. However, determination of molecular structures on the basis of MS data is challenging, as a single molecular weight value may correspond to many structural isomers.

The FELIX free-electron laser provides new opportunities here, as it enables the integration of MS with infrared (IR) spectroscopy. IR spectra can be recorded with the selectivity of MS, i.e. for individual components in the complex mixture [1]. In contrast to a mass spectrum, an IR spectrum provides diagnostic information on the molecular structure. The IR spectra may be related to molecular structure via reference spectra, either from actual physical reference compounds, but also from computed IR spectra paving the way towards reference-free molecular structure identification.

A prominent example of complex mixture analysis involves patients’ body fluid samples that may contain metabolites that can serve as valuable biomarkers for pathological condition. We will show examples of how we apply this method to identify new biomarkers for metabolic diseases [2]. With the molecular structure information, new strategies for diagnostics, e.g. in newborn screening, and therapeutics may be developed [3].

The method of infrared ion spectroscopy (IRIS) is also applicable in fields beyond metabolomics. Molecular structure identification of unknown compounds is for instance also relevant environmental studies (e.g. drinking water contaminants), pharmaceutical sciences (drug metabolism) and forensic investigations (molecular structure of uncontrolled “designer” drugs), etc.

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High-resolution molecular spectroscopy in the THz region using synchrotron radiation

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Our team exploits the synchrotron radiation extracted by the AILES beamline of SOLEIL synchrotron facility to study different molecular physics problematics in the far-IR and THz spectral ranges. The experimental set-ups, associated to the high-resolution Bruker interferometer of the beamline, allow to record rotationally resolved spectra of a large number of molecules. In this talk, I will present few studies to illustrate the capabilities (and the instrumental limitations) offered by the beamline concerning high-resolution molecular spectroscopy. I will also detail our recent instrumental progresses, which consists of mixing synchrotron radiation with different laser sources. These new spectrometers allow for sub-MHz resolution spectroscopy in the THz and far-IR ranges [1] and open new perspectives for molecular physics studies at the AILES beamline of SOLEIL synchrotron.

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Multiple Probes of Photoionization Dynamics

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In recent years, photoionization mass spectrometry, electron spectroscopy, and coincidence techniques have become powerful analytical tools for the study of chemical reactivity and dynamics.[1-3] The improvement of these tools has also allowed significantly more detailed studies of the photoionization process itself. In this talk, I will present results obtained using multiple techniques in an attempt to unravel the complex spectroscopy and dynamics near the first ionization threshold of molecular nitrogen. I will also discuss potential new experiments to elucidate electronic autoionization processes and the interactions that drive them, with a particular emphasis on transitions from inner-valence/outer-core orbitals.

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Gas-phase photochemistry studies with free-electron lasers

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X-ray free-electron lasers provide intense, short-pulse, short-wavelength radiation that can be used to study ultrafast electronic and structural dynamics in gas-phase molecules with unprecedented spatial and temporal resolution. I will present recent examples of time-resolved experiments utilizing a variety of different techniques such as time-resolved photoelectron spectroscopy [1], Coulomb explosion imaging [2,3], and ultrafast X-ray scattering [4]. These methods and results will be compared to similar experiments performed with other ultrafast techniques such as ultrafast electron diffraction and strong-field ionization based experiments with near-infrared laser sources in order to highlight strengths and limitations of each technique.

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Kinetics of 1- and 2-methylallyl + O_2 reaction, investigated by photoionisation using synchrotron radiation

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The advent of biofuels has proven that combustion will remain an important pillar of the energy sector in the future.[1] These new fuels have a largely different composition than fossil fuels, and require the constant improvement of combustion models. Bimolecular rate constants are one important component of these models and are needed to quantify the importance of different pathways at various temperatures and pressures. Up to now rate-constants of different radical isomers could only be measured when both could be generated separately. However, isomerizations can occur significantly faster than bimolecular reactions and thus, a new *in situ* method is needed to distinguish between isomers in order to obtain isomer-selective rate constants. We have recently proven that bimolecular rate constants can be determined using photoelectron/photoion coincidence (PEPICO) spectroscopy,[2] a technique that simultaneously offers the possibility to distinguish between several isomers by their threshold photoelectron (TPE) signal.

Here we will present a way to measure isomer-selective rate constants of several branched hydrocarbon radicals with oxygen. For this we selected different methylallyl (C_4H_7) radicals and measured their bimolecular rate constants at distinct pressures. The radicals were produced inside a slow-flow reactor by photolysis of their halide precursors at 213 nm and consequently detected by ionisation through synchrotron light. Since 1-methylallyl (1-MA) has two different isomers, E- and Z-1-MA, we used different photon energies to distinguish between the two forms. The pressure dependence of the investigated C_4H_7 radicals can be compared to the parent allyl radical (C_3H_5) and explained by their chemical structure.

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Photon sources for the study of aerosol formation and photochemistry

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The formation of new particles through condensation from the gas phase is an important source of atmospheric aerosols. It is known that volatile vapor components can increase nucleation rates of other, less volatile vapor components by orders of magnitude. In the Earth's atmosphere, water vapor acts as such a mediator. The mechanism behind nucleation enhancement has so far been unknown because direct experimental observations of the very first steps of nucleation were missing. We have recently developed a new nucleation instrument based on Laval expansions combined with soft cluster ionization, which allows us to probe the molecular clusters that are formed in the very first step of nucleation. This provides insight into the molecular mechanism behind nucleation enhancement and reveals that the mediator catalyzes nucleation by forming transient, hetero-molecular clusters with the nucleating species [1].

Photochemical processes have been recognized as a major contributor to the degradation and oxidation of matter in atmospheric aerosols. Compared with photochemical reactions in extended condensed matter, photochemistry in aerosols is additionally influenced by optical confinement effects, thereby accelerating photochemical reactions in aerosol particles. We used X-ray spectro-microscopic imaging of single aerosol particles combined with modelling to elucidate and quantify the acceleration of in-particle photochemistry [2].

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Vacuum ultraviolet photochemistry of peroxy radicals in the gas phase

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Peroxy radicals (RO_2) are key reaction intermediates in the low temperature oxidation of organic compounds and play essential roles in combustion and atmospheric chemistry. In this talk, I will present our recent research progress on the vacuum ultraviolet (VUV) photochemistry of peroxy radicals by using synchrotron radiation-based photoionization mass spectrometry (PIMS, at Hefei) and double imaging photoelectron photoion coincidence spectroscopy (i^2PEPICO, at SOLEIL). Peroxy radicals are generated in a microwave discharge flow tube through the reactions of alkyl radicals with oxygen, initiated with fluorine atoms. Two kinds of alkyl cations, originating from direct photoionization of alkyl radicals, and from dissociative photoionization of peroxy radicals whose cations are not stable, have been observed and separated through their different ion kinetic energies. The precursors of the latter, the isomers/rotamers of peroxy radicals are individually identified and assigned in photoionization spectra or mass-selected threshold photoelectron spectra (TPES) with the aid of computed adiabatic ionization energies (AIEs) and Franck-Condon factors.

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Ultrafast temporal evolution of interatomic Coulombic decay in NeKr dimers

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We investigate interatomic Coulombic decay in NeKr dimers after neon inner-valence photoionization [$Ne^+(2s^{-1})$] using a synchrotron light source. We measure with high energy resolution the two singly charged ions of the Coulomb-exploding dimer dication and the photoelectron in coincidence. By carefully tracing the post-collision interaction between the photoelectron and the emitted ICD electron we are able to probe the temporal evolution of the state as it decays. Although the ionizing light pulses are 80 picoseconds long, we determine the lifetime of the intermediate dimer cation state and visualize the contraction of the nuclear structure on the femtosecond time scale.

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Precision measurements of molecular hydrogen in search for new physics

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The hydrogen molecule has become a benchmark system for testing theory at the most fundamental level (quantum electrodynamics) and for probing physics beyond the Standard Model at the atomic/molecular scale: are there forces beyond the three included in the Standard Model of physics plus gravity, are there extra dimensions beyond the 3+1 describing space time ? Comparison of laboratory wavelengths of transitions in hydrogen may be compared with the lines observed during the epoch of the early Universe to verify whether fundamental constants of Nature have varied over cosmological time. In recent studies a variety of new results have been obtained:
(1) Dissociation limits of H_2 and D_2 are measured to 10-digit accuracy [1,2];
(2) Shape resonances or quasi-bound resonances have been observed leading to an accurate determination of the scattering length of H + H collisions [3];
(3) Measurements are being extended to radioactive tritium species [4];
(4) Precise vibrational splittings in the HD^+ molecular ion [5] as well as in the HD neutral [6] have been measured yielding the most accurate value for the proton-electron mass ratio.

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Recent progress of autoxidation chemistry by advanced mass spectrometry

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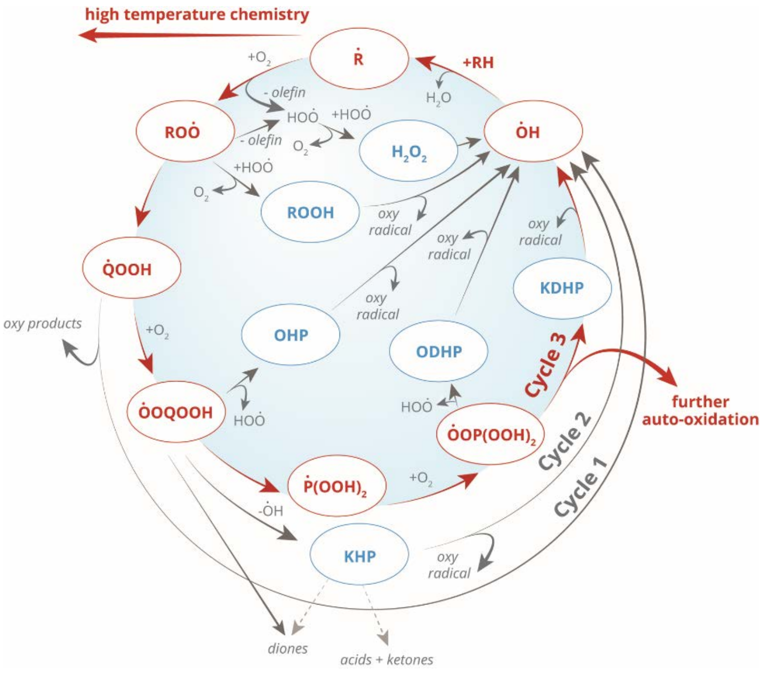
Autoxidation plays an important role in a wide range of chemical systems, contributing to the spoilage of food and wine, ignition in internal combustion engines, and formation of atmospheric organic aerosol from volatile emissions. In this talk, I will first present the recent progress for the autoxidation chemistry of organic compounds studied in jet-stirred reactors (JSR). These progress is based on the synchrotron radiation photoionization mass spectrometry (SVUV-PIMS) study at the Hefei light source in China, the advanced light source (ALS) in USA, and the SOLEIL in France. Besides the SVUV-PIMS, the atmospheric pressure chemical ionization mass spectrometry had also been utilized in the autoxidation chemistry study. In the second part of the talk, I will introduce the recent development of the atomic and molecular physics beamline (BL09U) at the Hefei light source on the gas phase chemistry study.



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Infrared spectroscopy of isomers formed in the –H dissociative ionization of methyl-PAHs

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Cationic benzylium and tropylium are two competitive isomers formed by dissociative ionization of methylbenzene (toluene) and infrared predissociation (IRPD) spectroscopy of ions tagged with neon has been established as a powerful tool in disentangling these cationic species [1]. Methylated polycyclic aromatic hydrocarbon (PAH) cations are expected to be abundant in space [2] and their dehydrogenation could lead to the formation of both the benzylium- (XCH_2^+) and tropylium-like (XC_7^+) cations, that are expected to be the two lowest-energy isomers [3] and whose isomerization process might impact their chemical evolution in photodissociation regions (PDRs). In this study, we consider three methyl-PAHs as precursors, namely 1-methylpyrene, 2-methylnaphthalene, and 2-methylanthracene. Their cationic –H fragments, $C_{17}H_{11}^+$, $C_{11}H_9^+$, and $C_{15}H_{11}^+$, were probed at the Free Electron Laser for Infrared eXperiments (FELIX) Laboratory using IRPD spectroscopy at the FELion cryogenic 22-pole ion trap [4]. Their strongest depletion band is located at about 1620 cm^{-1} revealing the predominance of the XCH_2^+ isomers. Saturation depletion measurements and spectral comparison to the theoretical anharmonic infrared spectra show that only this isomer is present in the case of $C_{17}H_{11}^+$, whereas at least two are present with a large abundance for the acene-derived species. Clear spectral evidence for the XC_7^+ isomer is found in the $C_{11}H_9^+$ case consistent with a relative abundance of 30 %. These results demonstrate the important role of steric hindrance in the formation of XC_7^+ species and reveal the potential of XCH_2^+ species to account for the aromatic infrared emission band (AIB) observed at 6.2 µm in astrophysical environments, e.g. the planetary nebula NGC 7027 and the PDR at the Orion Bar [5].

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Probing Gas-Surface Reactions in Aerosols using Synchrotron Radiation

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Developing accurate descriptions of the role that interfacial chemistry plays in the multiphase oxidation of organic aerosol and cloud droplet nucleation remains an outstanding challenge. One particularly difficult problem is connecting the uptake coefficients observed in an experiment, with the kinetics of individual elementary steps that couple reactivity across a gas/liquid interface. The relative rates and coupling of these steps can often yield new pathways or catalytic mechanisms, which are largely absent for reactions occurring solely in the gas phase. I will discuss some recent results, obtained using VUV and X-ray techniques at the Advanced Light Source, illustrating new reactive coupling between Criegee Intermediates and free radicals as well as how spectator molecules at the aerosol interface can act as phase transfer catalysts.

Advances in liquid-jet photoelectron spectroscopy

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We report on recent advances in liquid-jet photoelectron spectroscopy (PES) from water and aqueous solutions. The first part discusses the limits to the detection of photoelectron peaks undisturbed in shape and position by quasi-elastic electron-scattering processes, such as vibrational excitation, which strongly increase in probability below 10-15 eV kinetic energy.[1] Furthermore, quantitative analysis of the signal intensity of the low-energy electron-scattering tail strongly hints at so far unconsidered efficient scattering channels below the water ionization threshold. The second part focusses on a novel energy-referencing approach, based on condensed-matter concepts as opposed to the so-far common purely molecular framework, for measuring accurate vertical ionization energies from liquids.[2-3] This approach also enables access to solution–vacuum interfacial properties, such as the work function and surface potentials, then requiring explicit consideration of a solution's Fermi energy / electrochemical potential and its relation to measured quantities.

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Abstracts of Posters

(in alphabetical order)

SYNCHROTRON RADIATION BASED INVESTIGATIONS OF COLORED LAYERS , BINDING MATERIALS AND RESINS OF THE GOD PTAH-SOKAR-OSIRIS WOODEN STATUETTE AND ITS MUMMIFIED FALCON WHICH ARE DATING BACK TO 26TH PHARAONIC DYNASTY.

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The main goal of this work was to study the colour palette of a polychrome wooden statuette of the God Ptah –Sokr- Osiris from 26th dynasty of ancient Egypt (Figure 1a and 1b). The God Path – Sokar – Osiris models appeared at the end of the New Kingdom, and became a very common feature of elites' burials through late period until the roman one (1). Analysis of painted layered materials, preparation layers, resins and linen rolls samples have been performed using synchrotron radiation based µ (FT-IR) and (XRD) techniques. The application of SR techniques provided new and valuable information about the chemical nature of pigments, adhesives and binding materials that used by the ancient maker over other conventional spectroscopic techniques. In an attempt to evaluate the degree of statuette wood degradation, the wood sample was identified using the thin sections with SEM. SEM micrographs of wood allow identifying it as a (*Ficus sycamores*). The preparation layer was proved to be a mixture of calcite and quartz. The chromatic palette used in the statuette was identified as hematite, Egyptian blue, arsenic sulphides, possibly malachite and carbon from charred animal origin. The crystallinity of cellulose has been measured using Segal formula which indicates extreme degradation of the statuette wood. Figure 2 shows the pattern of SR-XRD analysis, crystallinity index of cellulose measured to be 66.6 % while the value of standard Ficus sycamores is 76.0%. Such study was mandatory in order to set the best strategies for preserving the statuette.

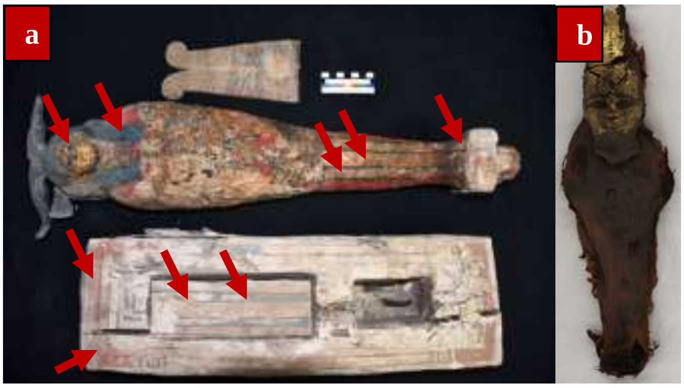

Figure 1a and b represents the images of the object including the positions of the samples.

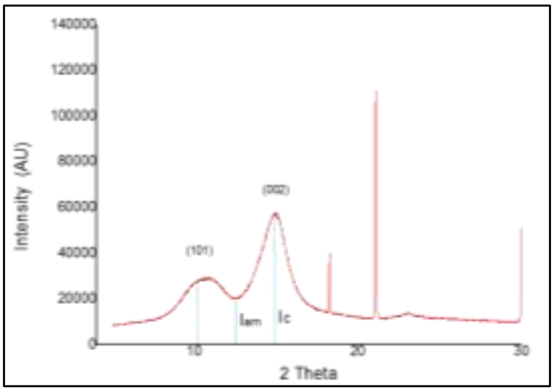

Figure 2 represents XRD pattern for the sample of wood.

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XUV coincidence spectroscopy of helium nanodroplets

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A new endstation at the AMO beamline of ASTRID2 synchrotron at Aarhus University allows to probe electronic decay processes in gasphase molecules and clusters by photoelectron-photoion coincidence (PEPICO) velocity-map imaging spectroscopy in the UV and XUV ranges. As an example, we present electron spectra and angular distributions of pure and doped superfluid helium nanodroplets recorded in coincidence with fragment photoions around the Fano resonance below the N=2 ionization threshold [1]. The aim is to disentangle different pathways to low kinetic energy electrons. The latter can either originate from inelastic scattering of photoelectrons in the droplet [2] or from interatomic Coulombic decay (ICD) [3] that competes with the autoionization of the double excited helium [4]. Synchrotron experiments are well suited to identify product channels and electronic energy levels and often form the basis for subsequent time-resolved measurements to unravel the dynamics of electronic processes [5].

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ICD and CAI in doped and pure helium nanodroplets irradiated by intense HHG XUV pulses

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Intense extreme-ultraviolet (XUV) pulses enable the investigation of highly nonlinear optical phenomena in unsupported molecules and nanosystems as well as potentially novel interatomic decay processes in weakly bound systems. Among these processes are heterogeneous interatomic Coulombic decay (ICD) and collective autoionization (CAI) mechanisms[1] which can play an important role in radiation damage through the production of radicals and low kinetic energy electrons[2]. Here, I will report systematic measurements on ICD and CAI of doped and pure He nanodroplet obtained at MAC-endstation[3] at ELI beamlines in Prague by employing a back-focusing geometry[4] of an intense XUV pulses generated by HHG laser pulses. To investigate ICD and CAI on pure and doped helium nanodroplets, the intense XUV laser is tuned at the $1s2p^1P$ absorption band of He nanodroplets using a new scheme based on consecutive SHG in a BBO crystal followed by HHG in a gas cell. These measurements on ICD and CAI show a good agreement with those obtained on pure and doped He nanodroplets using synchrotron radiation and free electron laser.

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Insight into sustainable catalysis with advanced light sources

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Sustainable catalytic processes require abundant, low-cost materials, energy efficient reaction pathways and high conversion rates. Our aim is to investigate chemical reactions that support green energy generation such as CO_2 reduction and H_2O conversion with well-defined model catalysts (metal oxides) that are based on readily available materials.

For this purpose, advanced light sources provide a completely new approach to tackle the intimate details of complicated catalytic reaction pathways and thus provide invaluable information for the design of new sustainable catalytic materials.

We apply the free electron laser FELICE in Nijmegen (The Netherlands) in cooperation with Joost Bakker and advanced femtosecond spectroscopy to unravel details of the molecular structure and dynamics of catalytic reactions on metal oxide nano-cluster model systems. Theoretical support of our work is provided by Uzi Landman from the Georgia Institute of Technology, USA.

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Non-local core-hole decay process in aqueous inorganic ions

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How do the solvating water molecules affect core-hole decay of aqueous ions? For Mg^{2+}, this has been predicted to result in non-local processes involving electrons on both the ion and the water molecules, such as Inter-Molecular Coulombic Decay (ICD) and Electron-Transfer Mediated Decay (ETMD) [1], see fig. 1. To experimentally test these predictions, the $1s^{-1}$ decay has been studied for a series of isoelectronic aqueous ions, Na^{+}, Mg^{2+} and Al^{3+}, using electron spectroscopy at the P04 beamline of PETRA III [2,3], combined with calculations.

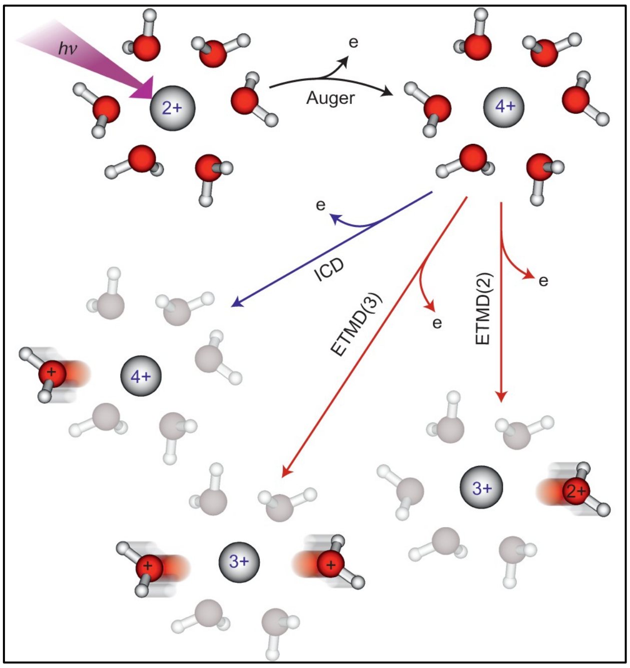

Fig. 1: Some possible decay processes following 1s ionization of solvated Mg^{2+} [1].

I will present results on non-local non-radiative $1s^{-1}$ decay channels, both ICD and ETMD [4]. The main decay channel, KLL Auger decay, is seen to be accompanied by non-local ICD-like decay involving solvation shell water molecules, resulting in states with one hole on the metal ion and one hole on a water molecule. The ICD intensity varies between the ions, and the ICD-signals consist of components corresponding to different water orbitals.

The KLL Auger decay results in ions lacking two valence electrons. These are not stable in water, and their decay must involve the surrounding molecules. In the Mg case, this has been predicted to occur via stepwise ETMD processes [1]. Experimentally, ETMD is observed for Al, but not for Mg.

Resonant excitation is seen to result in both localized and delocalized states, possibly suggesting ultrafast electron dynamics during the core-hole life time.

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A gas-phase study of cyclo-dipeptides containing an aromatic side chain: photoemission and state-selected fragmentation

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Peptides, i.e. molecules built by linking a series of aminoacids via the peptide bonds, play a central role in several scientific as well as practical areas , from the study of the origin of life, to the development of self-assembled nanostructures with peculiar properties. Linear (*l*-) and cyclo (*c*-) dipeptides obtained by linking two aminoacids are the smallest and simplest peptides. Among the *c*-dipeptides, the ones containing an aromatic aminoacid in the side chain are of interest for the study of the dynamics involving energy and charge transfers [1], relevant processes in bio-systems.

In this work we report a combined experimental and theoretical study of the electronic structure and the state-selected fragmentation of cyclo-dipeptide cations (*c*-GlyPhe, *c*-TrpTrp and *c*-TrpTyr) containing aromatic aminoacids. A systematic *ab-initio* study allowed to explore geometry, energy levels, electronic wave-functions and optical properties of these dipeptides, while valence photoemission (PES), mass spectrometry (MS) and photoelectron-photoion coincidence, PEPICO, measurements performed at the CIPO beamline [2] of the Elettra synchrotron radiation facility at 60 eV provided information on the photoelectron energy distribution and state selected fragmentation [3]. The comparison between the calculated density of states (DOS) and the experimental PES spectra points out some general characteristics, typical fingerprints due to the presence of an aromatic side chain appears in all the three samples. From the PEPICO measurements, the partial ion yield of the main fragments as a function of the binding energy (BE) has been extracted, giving insight into the molecular fragmentation. By comparing the most probable fragmentation pathways for the three samples we found that when the dipeptide contains the Trp aminoacid, independently of the ionized orbital, the charge migrates always to the Trp aromatic terminal, which is then lost as a charged fragment during fragmentation.

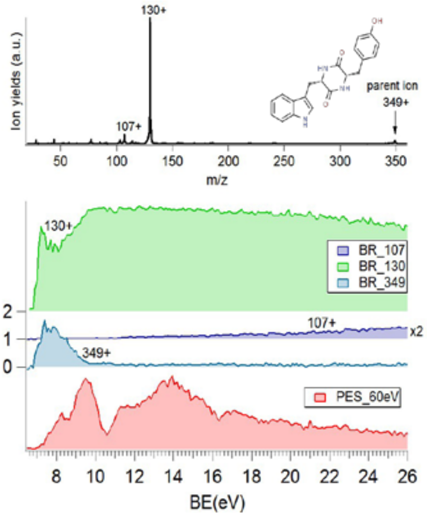

Figure 1. The mass spectrum (top panel), the partial ion yield of the main fragments (central panel) and the PES spectrum (bottom panel) of c-TrpTyr molecule obtained at 60 eV incident radiation.

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N–N bond fission dynamics of the N_2O^+ cation in the $C^2\Sigma^+$ state: competition between the NO^+ and N^+ fragment ion formation pathways

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The N–N bond fission is dominant for dissociation of N_2O^+ cation in the $C^2\Sigma^+$ state, producing two parallel fragmentation pathways of $NO^+(X^1\Sigma^+)+N(^2P)$ and $N^+(^3P_g)+NO(X^2\Pi)$. In addition to the well-studied former, the N^+ formation mechanism and dynamics remained unattended. Here we have performed a specific investigation on the N^++NO dissociation pathway from N_2O^+ cation in the $C^2\Sigma^+$ state using threshold photoelectron–photoion coincidence (TPEPICO) velocity map imaging, in comparison to our previous study of NO^++N channel. From the recorded N^+ images, the ro-vibrational populations of NO neutral fragments are derived for the different vibrational levels of $C^2\Sigma^+$, as well as the angular distributions. Unlike that only rotationally cold NO fragments are produced from the vibrationless $N_2O^+(C^2\Sigma^+)$ cations, some rotationally hot NO fragments are observed in dissociation of the vibrationally excited states like (1,0,0) and (0,0,1). With the aid of the calculated potential energy surfaces with the multiconfiguration second–order perturbation theory, the N^+ formation mechanism from the $N_2O^+(C^2\Sigma^+)$ cation is illuminated, where the spin–orbital couple to a bound linear $1^4\Pi$ state and the internal conversion to bent $D^2\Pi$ state both play determining roles in this N–N bond fission dynamics.

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Study of chemical bonds in metal-oxygen systems based on X-ray absorption spectroscopy

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In transition metal oxides, the way the oxygen atoms are bonded to the metal center is found to play a significant role in their reactivity, in view of different types of oxo-ligands and unusual oxidation states. [1,2] In this context, finding compounds that present unusual oxidation states elements and reactive oxygen species (superoxo, peroxo and oxyl) is of great scientific, technological and societal interests, since the application of this knowledge can go from industrial catalytic processes [2] to understanding the atmospheric chemistry [3], among other fields. [1,4]

Here, we use X-ray absorption spectroscopy (XAS) at the oxygen K and metal $L_{2,3}$ or $M_{2,3}$ edges of $[MO_n]^+$ systems (M = transition metal, n = integer) to identify the spectroscopic signatures of oxo-ligands and assign the oxidation state of the metal. The $[MO_n]^+$ species in the gas phase are produced by argon sputtering of a metal target in the presence of oxygen. The cationic species are mass selected using a quadrupole mass filter and then accumulated in a cryogenic ion trap. [5] X-ray absorption spectra of cold ions are recorded in partial ion yield mode with high sensitivity. Our ion trap instrument is installed at the undulator beamline UE52-PGM at the Berlin synchrotron radiation facility BESSY II.

XAS is, here, demonstrated to be an important tool to identify the spectroscopic fingerprint of oxo-ligands, offering direct access to element specific electronic structures..

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Strong ortho/para effects in the vibrational spectrum of $Cl^-(H_2)$

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The predissociation spectrum of the $^{35}Cl^-(H_2)$ complex is measured between 450 and 800 cm^{-1} in a multipole radiofrequency ion trap at different temperatures using the FELIX infrared free electron laser. Above a certain temperature, the removal of the Cl^-(*para*-H_2) *para* nuclear spin isomer by ligand exchange to the Cl^-(*ortho*-H_2) *ortho* isomer is suppressed effectively, thereby making it possible to detect the spectrum of this more weakly bound complex. At trap temperatures of 30.5 and 41.5 K, we detect two vibrational bands of Cl^-(*para*-H_2) at 510(1) and 606(1) cm^{-1}.[1] Using accurate quantum calculations, these bands are assigned to transitions to the inter-monomer vibrational modes (v_1, v_2, l_2) = (0, 2, 0) and (1, 2, 0), respectively.[2]

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EXCITED STATE DYNAMICS IN THE PHOTOLYSIS OF PHENYL AZIDE

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The photolysis of Aryl Azides is widely used to produce highly reactive Aryl Nitrenes, used actively in organic and inorganic synthesis as intermediates. This piece of work is focused on simulating the ultrafast dynamics involved in the photo-induced N_2 dissociation from Aryl Azides leading to the formation of Aryl Nitrenes. Phenyl Azide ($Ph\text{-}N_3$) can be considered to be a model system for a class of Aryl Azides.

The excited states and decay dynamics are studied with Complete Active Space Self Consistent Field (CASSCF) and complementary N-Electron Valence State Perturbation Theory (NEVPT2) calculations. Initial investigations from the potential energy surface scans motivated us towards large-scale MD simulations to generate a statistical overview of the excited state dynamics. Excited state MD simulations are carried out within the SHARC package from S_1, S_2, S_3, S_4, and S_5 acting as initial states. Preliminary studies of the simulated trajectories reveal an average dissociation time of 20-60 fs depending on the state from which the excited state simulation initiates. Analysis of the trajectories reveals a direct correlation between the splitting of the $N\text{-}N_2$ bond and the N-N-N bond angle which takes the dynamics beyond the single degree of freedom framework. The population analysis of the trajectories presents that irrespective of the initial state, it's the S_2 state in which the $N\text{-}N_2$ bond splits followed by Nitrene formation. The analysis also reveals an interesting oscillatory behavior in the population of the S_2 state.

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Exotic Chemical and Physical Processes involving Heavy Rydberg States.

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The physical, chemical, spectroscopic and theoretical properties of heavy Rydberg (HR) states and the ion-pair (IP) states that support them will be briefly reviewed. HR states are vibrational states in a potential that has long-range attractive Coulombic behaviour. This potential, combined with a repulsive core, results in extended vibrational amplitudes, particularly for higher vibrational levels that can reach ~100˚A and beyond [1,2]. Extreme chemical behaviour including enhanced chemical reactivity and efficient energy transfer is frequently encountered [3]. Our aim in the Seminar will be to discuss methods that could be used to observe the rapid changes in electronic and molecular structure that occur during reactions involving HR states.

Unusual physical properties result from the large dipole and transition dipole moments associated with IP states, will be reviewed in the context of the underlying electronic structure. Under collision-free conditions such states have a rich spectroscopy which can be analysed using the concept of the quantum defect, with an effective principal quantum number replacing the vibrational quantum number [2]. This approach will be illustrated with spectroscopic data in the UV and VUV that has previously been analysed in terms of Dunham coefficients but is better understood and described using HR analysis.

HR and electronic Rydberg states often occupy the same energy region and this, together with the high density of HR vibrational levels, leads to vibronic mixing and numerous perturbations that are a fertile field for analysis by multichannel quantum defect theory and reactive scattering calculations.

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Chemistry and spectroscopy of $CH_3C(O)O_2$ radicals

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Peroxy radicals, RO_2, are key species in the atmosphere. They are formed from a reaction of OH radicals with hydrocarbons:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O$$

In polluted environments, RO_2 radicals react predominantly with NO, leading to formation of NO_2, and eventually through photolysis of NO_2 to formation of O_3.

At low NO_x concentrations such as in the marine boundary layer or the background troposphere, the lifetime of RO_2 radicals increases and other reaction pathways such as self- and cross reaction with other RO_2 or with HO_2 radicals become competitive. To study these reactions, UV absorption spectroscopy has been employed in the past: this technique gives good sensitivity for peroxy radicals, but poor selectivity as these radicals have broad absorption features in the UV. We have established a technique allowing to follow peroxy radicals with a better selectivity compared to UV, but with still good sensitivity by coupling laser photolysis to cw-Cavity Ring Down Spectroscopy in the near IR.

Here, we will present results on the measurement of the rate constant of the self-reaction of the acetylperoxy radical, $CH_3C(O)O_2$. Studying this reaction is much complicated due to unavoidable secondary chemistry: the self-reaction leads to formation of CH_3O_2 radicals, which in turn react with $CH_3C(O)O_2$. This reaction has two different paths, one leading to stable products, the other to CH_3O_2 and HO_2 radicals. The HO_2 radicals from this reaction in turn react with both, $CH_3C(O)O_2$ and CH_3O_2 radicals, leading also to either stable products or recycling the radicals. Therefore, the branching ratios of both secondary reactions will influence the decay of the acetylperoxy radical and need to be determined.

Quantifying energy shifts in high resolution x-ray spectroscopy to peer at transition metal 3d population beyond the oxidation state

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Connecting physical charge distributions and formally derived oxidation states in transition metal complexes is of high interest to modern chemistry and material science. With this study we provide a systematic investigation of changes in the iron L-edge excitation energy depending on the charge distribution on the iron center of gas phase diatomic FeX^+ (X = F, Cl, Br, I) using high resolution x-ray absorption spectroscopy. A comparison of the iron halide samples with Fe^+ revealed a shift in excitation energy towards lower energies with respect to the Fe^+ and along the FeX^+ series. The experimentally determined excitation energy shifts correlate with the electronegativity of the halogen and are attributed to an increase in 3d derived orbital population as supported by charge transfer multiplet and density functional theory calculations. Hence, we show a general dependence of transition metal 3d derived orbital population connecting two oxidation states that by definition corresponds to integer occupation of atomic orbitals.

Investigation of Oxidation Reaction Products of Acetyl Acetone Using Synchrotron Photoionization

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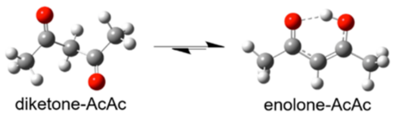
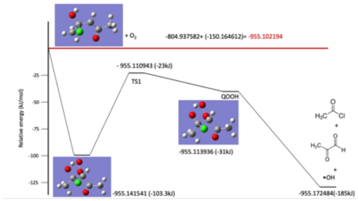
The photolytically Cl-initiated oxidation reaction of Acetyl Acetone (AcAc) was carried out at the Advanced Light Source (ALS) in the Lawrence Berkeley National Laboratory, a third-generation synchrotron facility. AcAc oxidation was studied through various methods due to its role in fuel combustion and its environmental significancy. Using a multiplex photoionization mass spectrometer coupled with the tunable vacuum ultraviolet radiation of the ALS, data are collected at low pressure (4 Torr) and room temperature (298 K). This atmospheric oxidation mechanism is intricate because it involves both the enolone and the diketone form and because it includes several secondary chemistry pathways [imagine A]. Reaction mechanisms for primary products are postulated using electronic structure calculations of the potential energy surface from both the addition of Cl to the double bond of the enolone form and the initial H abstraction radical of the diketone with O_2. We have identified m/z=72 (methyl glyoxal) as primary product result of the Waddington mechanism [image B], m/z=114 (2,3,4-pentantrione) as a product coming from the arrangement of the Russell Intermediate from a peroxy self-reaction [image C], m/z=42 (ketene), m/z=30 (formaldehyde) as products of primary chemistry [image D] and m/z=60 (acetic acid) as a product of secondary chemistry. Data analysis was performed via characterization of the reaction species photoionization spectra and kinetic traces. Products and reaction pathways are computed using the CBS-QB3 composite method.



A.



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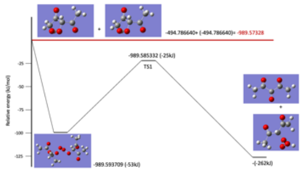

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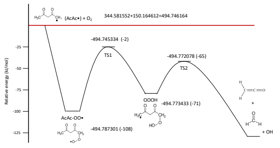

D.

Ring opening and tunneling inversion in the cyclopropyl radical and cation

Nadav Genossar[1,2], P. Bryan Changala[3], Marie-Aline Martin-Drumel[4], Bérenger Gans[4], Jean-Chrisophe Loison[5], Patrick Hemberger[6], Dana Bresker[1], Shani Har Lavan[1], Uri Zamir[1] and Joshua H. Baraban[1*]
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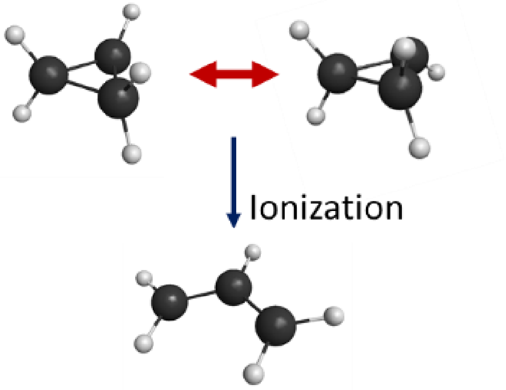
We report new measurements of the photoionization spectrum of the cyclopropyl radical (c-C_3H_5) and the appearance energy of the cyclopropyl cation at the SOLEIL and SLS synchrotrons, respectively. Utilizing the mass-selective and the double imaging capabilities of the photoelectron-photoion coincidence spectroscopy (PEPICO) setups at both synchrotrons, new threshold photoelectron spectra (TPES) were acquired, providing significant improvement over existing literature data, yielding new insights and allowing the extraction of various important chemical quantities.

This fundamental chemical system is of interest in various areas of study, including solvolysis reactions, radical clock reactions, and basic understanding of the properties of cyclic species. The cyclopropyl cation is especially unstable towards ring-opening to allylic geometries; this complicates analysis of the spectra while raising elementary questions regarding the observation of saddle points on the potential energy surface and their theoretical treatment.

Due to the large energy difference between the allylic equilibrium geometry and the unstable cyclic configuration on the cation PES, propagator-based methods that avoid the construction of cationic vibronic eigenstates were used to simulate the ionization spectrum. The results of our simulations compare well with the cyclopropyl TPES data. Further computational effort is underway to improve the simulations. Together with the dissociative ionization dynamics of cyclopropane, these allow determination of the unusual C-H bond dissociation energy of cyclopropane and the cyclization energies of the cyclopropyl radical and cation.



Auger spectroscopy of fulminic acid, HCNO

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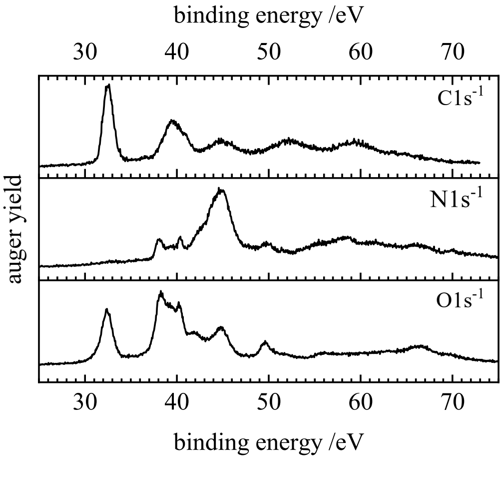
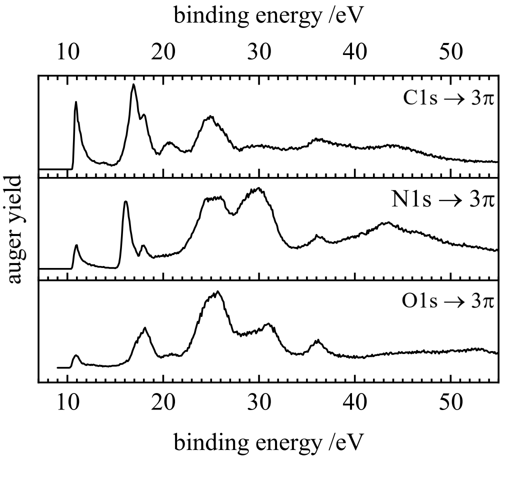
Fulminic acid, HCNO, was first detected in space in 2009 in the three starless cores B1, L1544 and L183.[1] The isomer isocyanic acid, HNCO, is also ubiquitous in interstellar systems.[2] Due to their composition of the atoms Hydrogen, Carbon, Oxygen and Nitrogen a prebiotic role has been suggested for these molecules. Investigating the interaction of these molecules with X-ray radiation is critical in understanding their fate in space.

As such, we present the gas phase auger electron spectra of fulminic acid which were recorded at the PLEIADES beamline at the Synchrotron SOLEIL in France. Fulminic acid was prepared by preparative pyrolysis of the precursor 3-phenyl-4-oximino-isoxazol-5(4H)-one as described by Wentrup et al..[3] Normal and resonant auger electron spectra as well as NEXAFS spectra were recorded at all three edges. To give further insights into the observed transitions we compare the spectra to the spectra of isocyanic acid, as well as theoretical simulations.





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State-to-state dissociative photoionization of molecular nitrogen: The full story

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N_2 is a major constituent of Earth and planetary atmospheres. First, evidenced in 1952, the dissociative photoionization of molecular nitrogen, N_2, plays an important role in the species abundance, out of equilibrium evolution, and chemical reactivity of diverse media including upper atmospheres (the so-called ionospheres) and plasma. Many scenarios were proposed for rationalizing the dissociative ionization mechanisms and exit channels, which are reviewed here, mainly involving the $N_2^+(C^2\Sigma_u^+, v^+)$ vibrational levels state-to-state dynamics on which we focus. We show, however, that previous studies are not comprehensive enough for fully shedding light on the complex undergoing processes. As a complementary global work, we used state-of-the-art quantum chemistry, time-dependent and independent theoretical approaches associated to advanced experimental techniques to study the unimolecular decomposition of the N_2^+ ions forming the $N^+ + N$ products. In addition to the already suggested spin-orbit induced predissociation of the cationic $C^2\Sigma_u^+$ state, we documented a new mechanism based on vibronic coupling and tunneling dissociation. [1] Besides, the quantum processes highlighted here should be also in action in the dynamics of electronically-excited larger molecular systems involved in physical and chemical phenomena in plasma and in various natural environments on Earth and beyond.

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Ultrafast Molecular Spectroscopy by Time-Resolved Photoelectron Imaging

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Photochemical Carbon-Sulfur Bond Cleavage via *Rydberg-to-Valence Evolution in Thioethers:* Time-resolved photoelectron imaging and supporting *ab initio* quantum chemistry calculations were used to investigate non-adiabatic excess energy redistribution dynamics operating in a series of saturated thioethers. In all cases, molecular fragmentation occurs predominantly on an ultrafast (<100 fs) timescale following 200 nm excitation, driven by the evolution of Rydberg-to-valence orbital character along the S-C stretching coordinate. The C-S-C bending angle was also found to be a key coordinate driving initial internal conversion through the excited state Rydberg manifold, although only very small angular displacements away from the ground state equilibrium geometry are required. Through use of a high intensity 267 nm probe, we were also able to detect the presence of some initial photoproducts.

Increasing Temporal Resolution by use of Hollow Capillary Fibres to generate Few-Femtosecond Deep-Ultraviolet Laser Pulses: Femtosecond pulses in the vacuum ultraviolet spectral region permit extended observation of non-adiabatic dynamics in gas-phase molecules.[1] When used as a probe in time-resolved photoelectron spectroscopy, such pulses project deeply into the ionisation continuum and allow the evolution of excited state population to be monitored across multiple potential energy surfaces. Extremely short ultraviolet and vacuum-ultraviolet laser pulses may be achieved by resonant dispersive wave emission in hollow waveguides.[2] Soliton dynamics in hollow capillary fibres allow for high infrared to ultraviolet conversion efficiency (~15%) and continuously tunable emission spectra; however, despite initial progress in this area,[3] their full potential has not yet been realised in time-resolved molecular spectroscopy. In this work, we demonstrate - for the first time - non-resonant photoionisation of 1,3-butadiene revealing a 10 fs cross-correlation using deep-ultraviolet resonant dispersive wave emission from hollow capillary fibres. This extremely high time resolution presents exciting new opportunities for the study of extremely fast molecular dynamics.

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Characterization of radiolysis-induced post-translational modifications (PTMs) in modeled systems by IRMPD and UVPD spectroscopy

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Oxidative stress induced by an excess of free radicals in the cellular environment may cause deleterious effects affecting the normal biological conformation of proteins, which can be accumulated with age to lead to pathology such as Alzheimer's disease [1]. For a better comprehension of post-translational modification (PTM) in Met-residue, a series of study have been launched from a single Met to various linear and cyclic Met-containing peptides by using tandem mass spectrometry (MS2) and IRMPD spectroscopy performed at CLIO and Felix IR FELs [2-4]. The goal of the present work is to further advance this research in more complex Me-containing models in order to understand different factors in Met oxidation process.

Similar to Met, another sensible target of reactive oxygen species (ROS) is nucleobase. Nucleobases are the fundamental building blocks of nucleic acids in natural DNA and RNA nucleosides, which gives it a vital status in the continuation of biological life. The research on DNA lesion can be traced back decades. With the rise of IRMPD spectroscopy technology, a serious of nucleobases in their protonated or deprotonated forms have been characterized. However, the oxo-forms of these molecules remain untouched. In this work, the objective is to use MS^2-CID coupled with IRMPD spectroscopy as an emerging characterization tool to give a new understanding of the lesion of nucleobases and their derivatives in aqueous solution induced by γ-radiolysis.

Preliminary results on Me-Containing peptides and DNA nucleobases, nucleotides and nucleotides have also been obtained at Synchrotron Soleil in France. The experiments have been performed employing the linear quadrupole trap SRMS2 set-up coupled to the DESIRS beamline using photons for activation by UVPD spectroscopy in the 4-14 eV range.

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Generation and measurement of ultra-short x-ray pulses at SwissFEL

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The drive for measuring ultrafast processes in atoms and molecules drives the development of new methods to generate and measure ultra-short x-ray pulses at free electron lasers (FELs). Here we describe the effort conducted at the SwissFEL facility at PSI to push the X-ray light source to enable this kind of research.

SwissFEL used non-linear compression schemes to generate single and two-color attosecond pulses [1], which were indirectly characterized with a high-resolution single-shot spectrometer. Moreover, PSI has developed a passive streaker [2] able to measure the FEL power profile with femtosecond resolution. Finally, we have developed a new photoionization streaking method and algorithm to characterize ultra-short x-ray pulses [3], which we plan to test at SwissFEL or another x-ray FEL facility in the near future.

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Threshold Photoelectron Spectra of fragments of AsMe3 and SbMe3.

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Our group already investigated the pyrolysis products of methylated group V compounds X = N[1], P[2], Bi[3]. While for the single methylated isomers of nitrogen we observed H-N-CH_2, N-CH_2 and H-N-CH, bismuth showed only Bi-CH_3. For phosphorus the isomers H-P-CH_2, P-CH_3 and P-CH_2 were detected. To complete our investigation of the 5th main group, trimethylarsenic and trimethylantimony were pyrolyzed. The emerging reactive species were characterized with the PEPICO setup of the VUV beamline of the synchrotron SLS in Switzerland. The resulting mass-selected threshold photoelectron spectra were interpreted using quantum chemical calculations and Franck-Condon simulations.

Our results show that antimony behaves similarly to bismuth, forming among others Sb-CH_3. Arsenic on the other hand showed H-As-CH_2, As-CH_3 and As-CH_2, which is analogous to phosphorus. The following table provides an overview of our work on methylated group V compounds.

E	ECH_3	$HECH_2$	ECH_2	HCEH
N	–	X	X	X
P	X	X	X	–
As	X	X	X	–
Sb	X	–	–	–
Bi	X	–	–	–

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PERFORMANCE AND FIRST RESULTS OF A VERSATILE HOME-BUILT TANDEM MASS SPECTROMETER DEDICATED FOR EXPERIMENTS AT ADVANCED LIGHT SOURCES

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The first experiments combining tandem mass spectrometers with synchrotron beamlines have been carried out 10 years ago in order to probe the electronic structure and radio-induced damage of electrosprayed biomolecules. Since then, vacuum-ultraviolet (VUV) and soft X-ray light have received growing interest from the mass spectrometric community thanks to their high potential for exploring physicochemical processes and properties of systems such as peptides, oligonucleotides, PAHs or metal-organic compounds. However, these experiments still remain very challenging to perform due to the relative low target density and the low absorption cross section of these molecules in the concerned energy ranges. Additionally, there is currently a lack of dedicated end-stations at synchrotron facilities worldwide.

A new tandem mass spectrometer has been recently built in our group in order to face these challenges and answer the growing demand for performing such experiments. The instrument has been specially conceived to easily interface with any advanced light sources' beamlines, including synchrotrons and free-electron lasers, as well as tabletop lasers. Briefly, the instrument consists of a high throughput electrospray ionization source, a quadrupole mass filter, an ion Paul trap and a reflectron time-of-flight. The performance of the instrument will be detailed.

The first results obtained on custom-made peptides where the electronic signature of the protonation sites by means of near-edge X-ray absorption mass spectrometer (NEXAMS) across the nitrogen K-edge have been studied, will be presented. These peptides have been recently measured at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany).

Data fusion for photoelectron spectroscopy @FLASH: a GPU accelerated approach

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We present a collection of data analysis techniques that are used to extract information from the large amount of data produced at the URSA-PQ instrument at FLASH. Data fusion procedures are used to combine together information from diverse sources, providing a more unified picture of the physical process under study. Graphical processing units (GPU) accelerated computing is used to increase the efficiency of the data processing algorithms.

Sensitivity of inner-shell photoelectron spectroscopy to non-Born-Oppenheimer and photodissociation dynamics in polyatomic molecules

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The ultrafast photodynamics of the linear CS_2 molecule, excited by an ultraviolet (200nm wavelength) pump photon, is studied. It is probed by inner-shell photoelectron spectroscopy and Coulomb explosion imaging initiated by intense soft X-ray probe pulses from the FLASH Free Electron Laser. CS_2 exhibits complex photochemical dynamics which involves vibrational mode coupling, internal conversion and intersystem crossing. Most notably, its dissociation proceeds via a combined excitation of the asymmetric stretch and bend vibrations, which entails a characteristic quantum beat. Here we explore the sensitivity and selectivity of the FEL probe, which leads mainly to site-specific inner shell photoionization of the sulphur atom in the molecule, to the non-Born-Oppenheimer dynamics in CS_2. We exploit the capabilities offered by the CAMP instrument at FLASH to simultaneously investigate the delay-dependent yield, kinetic energy release, and angular correlations of photoelectrons and various ionic fragments formed after inner-shell photoionization and subsequent Auger decay. In order to observed correlations between different ionic species, a timestamping camera is utilized, thus allowing the ion time-of-flight spectra and three-dimensional velocity distributions to be recorded simultaneously for all fragments. The observed time-resolved ion and photoelectron spectra are examined alongside *ab-initio* calculations of the excited state dynamics, including the simulation of observables for direct comparison with the experiment.

Probing intermolecular decay processes in superfluid helium nanodroplets by tunable and ultrafast XUV radiation

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Pure and doped superfluid helium nanodroplets are particularly attractive targets for both tunable XUV radiation generated by synchrotrons, and for ultrafast XUV and X-ray pulses generated by free-electron lasers (FELs). The extremely weak binding of helium atoms and the simple electronic structure of the helium atom renders electron spectra simple and easy to interpret. The quantum fluid properties of helium droplets, and their ability to pick up virtually any foreign atom or molecule without chemically interacting with it, makes them ideal test beds for probing XUV-induced correlated electronic decay processes in heterogeneous condensed phase systems.

In recent synchrotron experiments, we have investigated interatomic Coulombic decay (ICD) and related processes by resonantly exciting the droplets [1,2], by directly photoionizing them [3,4], and by simultaneously ionizing and exciting them [5]. In this way, we have evidenced new intermolecular decay mechanisms such as electron-transfer mediated decay (ETMD), ICD induced by electron-helium scattering and electron-ion recombination, and double-ionization ICD. In recent XUV-FEL experiments we have traced the ultrafast relaxation of resonantly excited helium nanodroplets [6,7] and the time-evolution of ICD in multiply excited helium nanodroplets [8]. We found that ICD is crucially determined by a peculiar nano-fluid dynamics initiated by resonant excitation of the droplet. Furthermore, we observed a massive enhancement of above-threshold ionization (ATI) of XUV-excited helium nanodroplets due to collective coupling of excitations [9]. In my contribution, I will briefly review these recent advances and I will point out intriguing prospects for the research on free clusters and nanodroplets using advanced photon sources.

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Photoelectron spectroscopy of reactive low-valent organophosphorus compounds, P-CH_3, H-P=CH_2 and P=CH_2: A study of coincidence measurement using synchrotron radiation

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Determination of accurate ionization energy, finding the nature of the electronic ground state and isomeric preferences are always crucial for any reactive intermediate as they help to understand multistep complex chemistry as well as catalytic processes. Organophosphorus compounds are widely used in flame retarders, plasticizers and anti-foaming agents in a variety of industries. Here, we report the mass-selected photoelectron spectra (PES) of low valent reactive species of phosphorus, P=CH_2, H-P=CH_2 and P=CH_3, measured using i^2PEPICO spectrometer coupled with synchrotron radiation provided by SOLEIL beam line facility. All three species were generated in a flow-tube reactor from $P(CH_3)_3$ by H-abstraction using fluorine atoms produced via F_2 microwave discharge. Vibrational structures of the measured PES were correlated with spectral simulation, done by calculating Franck-Condon (FC) factors between neutral and cationic states. For methylated pnictogen, the isomeric preference between E-CH_3 and H-E=CH_2 (E=N-Bi) is reversed along with the group due to the inherent reluctance to undergo hybridization and consequently multiple bonding for higher pnictogen. From our measured PES we have identified both isomers of PCH_3, P-CH_3 (I.E-8.91 ± 0.04 eV) and H-P=CH_2 (I.E-10.07 ± 0.03 eV) while for N and Bi, only H-N=CH_2 and Bi-CH_3 were identified. We have also found that like Bi-CH_3, the ground electronic state of P-CH_3 is also triplet and biradical in nature.[1]

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Infrared super-resolution wide-field microscopy using sum-frequency generation

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Nonlinear optical imaging with a spatial resolution well below the Abbe diffraction limit of light, such as stimulated emission depletion (STED) microscopy, has enabled many ground-breaking discoveries. In the infrared (IR) spectral range, however, no comparable schemes exist, and high-resolution IR imaging has so far been restricted to scanning probe techniques such as scattering near-field optical microscopy.

Here, we demonstrate sum-frequency generation (SFG) microscopy as a new IR super-resolution imaging technique, which can additionally provide interface-specific signals through the selection rules of the nonlinear-optical process.

To demonstrate the concept, we study an IR nanophotonic system based on localized phonon polaritons in sub-diffractional nanostructures made from Silicon Carbide.[1,2] For our experiments, we use the IR free-electron laser (FEL) at our institute as a unique high-power IR light source.[3] Previous SFG microscopy results[4] by scanning tightly focused beams demonstrated the principle, but also revealed laser-induced damage. We have now implemented a wide-field SFG microscope to overcome this disadvantage.

Our SFG microscope clearly resolves phonon polariton modes in individual sub-diffractional nanostructures, providing a resolution of ~1.4 µm at a resonant imaging wavelengths in the range of λ_{IR} = 10-12 µm, i.e., we achieve a spatial resolution of ~λ_{IR}/9. Full spectral mapping over the whole SiC Reststrahlenband allows the spectroscopic identification of polariton resonances, while the high spatial resolution allows the microscopic identification of the origin of the SFG light. We are able to identify different polariton modes in SiC nanopillars, i.e. monopole and dipole modes[1] as well as edge modes in square arrays of the pillars. In SiC nanorods we find length dependent polariton resonances and compare the microscope images with electric field simulations calculated in COMSOL.

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New Insight into the Photodissociation Dynamics of formaldehyde oxide CH_2OO

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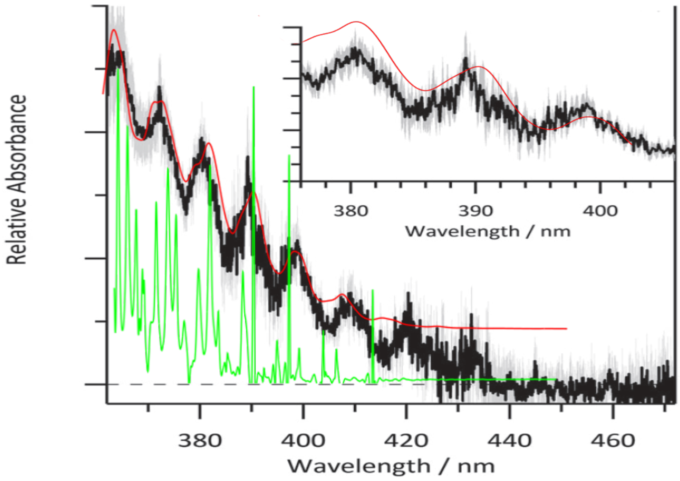
An extended theoretical analysis of the photodissociation of the smallest Criegee intermediate CH_2OO following excitation to the B state is presented. It relies on explicitly correlated multireference electronic wavefunctions combined with a quantum dynamical treatment for two interacting (B-C) electronic states and three coupled nuclear degrees of freedom. The 3D model relies on PESs along the O-O and C-O stretching as well as C-O-O bending modes for the two lowest excited states with A' symmetry, and is sufficiently accurate to reproduce the experimental \$$B^1A'$-$X^1A'$ absorption spectrum, especially at the low-energy range to unprecedented accuracy. The existence of a deep well on the (diabatic) B state causes a considerable amount of the wavepacket to be reflected by the B state well, which can explain the vibronic structures appearing in the long wavelength range of 360-470 nm of the spectrum. The main progression appearing in the energy range from 360 to 470 nm is assigned to the O-O stretching mode while finer details are affected by couplings to the C-O stretching and C-O-O bending modes. The weakly avoided crossing between the B-state and C-state potential energy surfaces appearing near 3.1 eV excitation energy causes considerable disturbance in the vibronic fine structure of the bands. The description of the latter is quite strongly affected by the type of electron correlation treatment adopted, either fully variational (MRCI type) or perturbation theoretic (RS2 type). The results give novel insight into the complex interactions governing that intriguing process.



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Nonlinear terahertz spectroscopy on liquid water

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Water is one of the most studied and least understood liquids[1]. While several anomalies in the thermodynamic, macroscopic properties of liquid water are well documented[2], on the microscopic scale water is characterized by a dynamical, tetrahedral network of hydrogen bonded (HB) molecules rearranging on the picosecond timescale[3]. Thus, terahertz (THz) spectroscopy represents a possible experimental approach to study the dynamics of the HB water network.

The first results detailing the nonlinear response of water in the THz frequency range are recent[4–9], and the molecular interpretation is a matter of ongoing discussion. Tcypkin *et al.*[4,5], Novelli *et al*.[6], and Ghalgaoui *et al.*[7], all found that the third-order nonlinear response of water at ~1 THz has a similar magnitude ($\chi^3 \sim 10^{-13}$ cm^2/V^2), but proposed different explanations. For example, the third-order signal in the THz range was assigned to cascaded second-order anharmonicity of the intramolecular O–H stretching modes[4]; to the THz field induced ionization of water[7]; or to the resonant excitation of molecular reorientations[8].

In order to address this issue, we performed a series of single color pump-probe experiments at 12.3 THz on liquid water at infrared FEL facilities[8,9]. Recently[9], by comparing results obtained on a static sample and a free-flowing water jet, we were able to disentangle the distinct contributions by thermal, acoustic, and nonlinear optical effects. We found that our results[8,9] suggest that the THz excitation could resonate with the rotationally damped motion of HB water molecules, resulting in enhanced transient anisotropy. This mechanism could help to rationalize the non-linear response of water in the whole frequency range between about 1 and 20 THz.

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Tracking chemical dynamics with time-resolved x-ray spectroscopy and scattering

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The light-triggered electronic excitation of molecules leads to several fundamental processes involving electronic and structural dynamics. Extreme light sources allow sub-ns (Synchrotron) and sub-ps (X-ray free electron laser) time-resolved x-ray spectroscopy and scattering investigations to study the electronic and geometric structural changes in reacting chemicals.

Using this approach, we studied the light-driven solute ionization of aqueous halides generating nascent halogen radicals in solution. This leads to a reorganization of the solvent shell on the sub-ps time scale, which we detect with fs Wide-Angle X-ray Scattering (WAXS), and thus structurally benchmark pure solvation dynamics. We follow the electronic and structural dynamics after photoionization of Iodide with 400 nm at LCLS using fs time-resolved X-ray Absorption Spectroscopy (XAS). The kinetic behavior, governed by geminate recombination of solvated electrons with the parent radical, has been monitored for the first time within the first picosecond via ultrafast XANES, which we compare to the currently conflicting theoretical descriptions of this process.

In a different series of experiments, we investigated transition metal coordination compounds – [Cu(phen)(DPEphos)]+ and [Cu(dmp)(DPEphos)]+ – model systems with relevance for photocatalysis and solar energy applications. A combination of Transient Absorption Spectroscopy and ps time-resolved XAS and WAXS for a series of heteroleptic copper complexes revealed – after Metal-to-Ligand-Charge-Transfer optical excitation – a strong correlation between the excited state dynamics and the ligand structure in these correlated electron molecular complexes. Overall, the more fundamental investigation on Iodide photodetachment aides our analysis of the photophysics of transition metal complexes. With these tools we can engage in studying different systems covering the emergent behavior in photocatalysts, photoswitches and other photoactivatable systems.

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Excited state molecular dynamics simulations of the photodissociation of ironpentacarbonyl

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Theoretical excited state molecular dynamics simulations of the initial non-adiabatic transitions after photoexcitation of ironpentacarbonyl reveal an intricate ultra-fast dynamics. Coupled electron-nuclear dynamics involving metal-to-ligand charge-transfer (MLCT) excitations and dissociative metal-centered excited states results in a gradual transition from coherent bond oscillatory motion to reoccurring bursts of carbonmonoxide release [1]. These initial events set the stage for sequential CO release in gas phase [2] and complex pathways in ethanol solution [3] as experimentally observed in X-ray photoelectron spectroscopy (XPS) and iron L-edge resonant inelastic X-ray scattering (RIXS). Theoretical simulations of gas phase XPS and solution RIXS spectra based on multi-configurational quantum chemistry has allowed for kinetic modeling of the processes on different time-scales. The impact and challenges for explicit dynamical modeling of time-resolved X-ray spectra are discussed.

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On the Absolute Photoionization Cross Section and Threshold Photoelectron Spectrum of two Reactive Ketenes in Lignin Valorization: Fulvenone and 2-Carbonyl Cyclohexadienone

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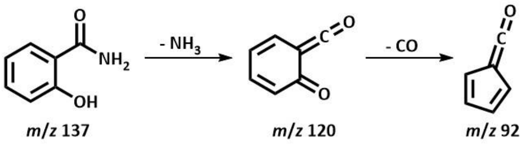
Fulvenone is an elusive and crucial ketene intermediate in lignin catalytic pyrolysis.[1,2] It is not only responsible for the branching of the reaction pathways, but also escapes from conventional detection methods such as GC/MS and NMR. Thanks to sensitive photoelectron photoion coincidence techniques, we clearly catched the fulvenone during the catalytic pyrolysis of lignin model compounds.[1,3] This is, however, not enough and quantification is much-needed for deeper mechanistic understanding and reliable kinetics of the lignin catalytic pyrolysis process. The absolute photoionization cross section (PICS) is widely applied for quantification, especially in flame chemistry[4] and relates the signal in a mass spectrum to the mole fraction during a chemical reaction:

$$\frac{S_{C_5H_4=C=O}}{S_{Ref}} = \frac{[C_5H_4 = C = O]}{[Ref]} \times \frac{\sigma_i^{C_5H_4=C=O}}{\sigma_i^{Ref}} \times \frac{A_{C_5H_4=C=O}}{A_{Ref}}$$

Where S are the photoion signal intensities, [C_5H_4=C=O] and [Ref] are the concentrations of both reaction products, σ_i are the respective ionization cross sections and A represents the apparatus function. Salicylamide is an excellent fulvenone (m/z 92) precursor, simultaneously yielding NH_3 and CO (as shown below).[5]

Ammonia is not only the reaction product, but is also used as a reference, because its PICS is well known.[6] Here we investigate the pyrolysis of salicylamide at different conditions and observed another ketene intermediate at m/z 120. We characterized the ketene at m/z 120 utilizing photoion mass-selected threshold photoelectron spectroscopy (ms-TPES). At higher pyrolysis temperatures m/z 120 could be almost fully converted to the fulvenone ketene (m/z 92). By optimizing parameters (temperature and concentration), photoionization spectra of both (m/z 92 and m/z 120) were recorded and the photon energy dependent cross section was determined.



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Time-resolved NEXAFS as a new tool in organic photochemistry

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The field of X-ray photon sources is rapidly advancing, and only recently have time-resolved pump-probe experiments using X-ray probe pulses become possible for liquid samples.
In these experiments, the sample is first excited by a pulse of visible laser light, and changes in the X-ray absorption are measured as a function of time in a timescale of picoseconds to nanoseconds. We have applying this technique to solve questions in photochemistry that have until remained unsolved. For the present work, I am analyzing how the X-ray absorption at the nitrogen and oxygen K-edges of pyridine N-oxide and pyridazine N-oxide change during the dynamics subsequent to their absorption of an ultra-violet photon. By relating these spectral changes to the spectra predicted by quantum chemical calculations, I hope to be able to elucidate what the different intermediates are, and the rate at which they transform into each other. This work serves as an example of how this novel time-resolved technique can be used to extract structural information about the chemical intermediates that form during a light-driven chemical transformation.

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Photodissociation dynamics of halogenated aromatic molecules: the case of core-ionized tetrabromothiophene [1]

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Photoresponse of halogenated organic molecules has been actively studied in recent years, in particular in the realm of multiphoton x-ray absorption. We investigated photodissociation of tetrabromothiophene (figure) upon single-photon core ionization by using energy-resolved multiparticle coincidence spectroscopy at the MAX IV synchrotron facility. Ionizing various core-orbitals selectively allowed us to observe ionization site dependent aspects of the ensuing dynamics. Based on detailed study upon Br 3d ionization, we propose a general dissociation model in which dicationic tetrabromothiophene dissociates in sequential steps. Dissociation usually starts with neutral Br loss after which the charges separate into two cations. One of the cations is often bromine. This charge separation may sometimes be followed by secondary dissociation. Comparison between ion yields upon Br 3d, C 1s and S 2p ionization showed ionization site dependency although the effects were mostly minor. An especially strong effect was found in the yield of the intact parent dication: after C 1s and S 2p ionization there is respectively ten and five times more stable parent dication than after Br 3d ionization. We interpret this effect, using first-principles calculations and molecular dynamics simulations of core-hole states, as likely caused by the geometry changes during the core-hole lifetime. Thus, even in a molecule with no hydrogen and ultrafast molecular dynamics, our results suggest that the nuclear relaxation in the core-hole state could play a key role in specific aspects of the eventual molecular dissociation.

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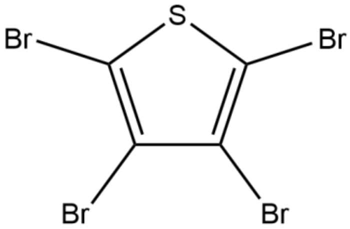

Figure: Structure of tetrabromothiophene

Astrochemistry of small-sized polycyclic aromatic hydrocarbons in X-ray-dominated regions

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The infrared signatures of polycyclic aromatic hydrocarbons (PAHs) are observed in a variety of astrophysical objects, including the interstellar medium (ISM), Planetary Nebulae (PNe), and the circumnuclear medium of active galactic nuclei (AGNs). These are sources of highly energetic soft and hard X-ray photons (0.2–10 keV), which expose the PAHs to a harsh environment. In this work, we examine experimentally the photoionization and photostability of PAH-related compounds, such as benzene (C_6H_6, the basic unit of PAHs), naphthalene ($C_{10}H_8$), biphenyl ($C_{12}H_{10}$), and cyclohexane (C_6H_{12}), the latter as a prototype of super-hydrogenated PAHs, upon interaction with photons of soft and hard X-rays. The measurements were performed at the Brazilian Synchrotron Light Laboratory (LNLS) and were analyzed using time-of-flight mass spectrometry. We estimate the lifetime of these molecules in photon-dominated regions of selected PNe and AGNs. We discuss distinct processes that may enhance the lifetime of small-sized PAHs in such astrophysical environments. Our results suggest that a more sophisticated interplay between PAHs and dust grains should be present in order to circumvent molecular destruction. Furthermore, we suggest that super-hydrogenation is a possible auxiliary mechanism for the protection of the carbon skeleton of PAHs. Finally, we suggest that the enrichment of multiply charged ions caused by X-ray photoionization and photodissociation processes could occur in distinct astrophysical objects.

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Probing Nonadiabatic Dynamics with Attosecond Pulse Trains and Soft X-ray Raman Spectroscopy

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When a photoexcited wave packet passes through a conical intersection, it generates ultrafast electronic coherences which can be detected by linear off-resonant X-ray Raman techniques. With such techniques, a pair of femtosecond or attosecond probe pulses is commonly used to excite the system and stimulate the emission of the signal photon, with both fields being components of a hybrid pulse scheme.

In this study, we explore how attosecond pulse trains, produced by High Harmonic Generation processes, perform as probe pulses in the framework of this spectroscopic technique, instead of single Gaussian pulses. We investigate the strengths and weaknesses of different combination schemes for the probe pulse, as well as the impact of parameters of the pulse trains on the signals. We employ two different model systems, which represent molecules of different symmetry, and quantum dynamics simulations to analyze the spectra. The results suggest that such pulse trains are well fit to capture the electronic coherence fingerprints.

Theoretical description of time-resolved momentum microscopy probing excited-state dynamics of pentacene on a silver substrate

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We theoretically describe time-resolved momentum microscopy of excited-state dynamics of pentacene molecules adsorbed on a silver substrate as a bilayer [1]. In particular, we calculate photoelectron momentum maps (PMM) obtained by an XUV photoionizing probe pulse and compare them to experimental data obtained at the Free-Electron Laser FLASH in Hamburg. We reveal that the electronic excitation leads to a geometry rearrangement of molecules in the top pentacene layer similar to an isolated pentacene molecule. We also find that the interaction of bottom-layer pentacene molecules with the substrate leads to additional features in PMMs.

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High-resolution multiplexed double velocity map imaging PEPICO for gas phase reaction kinetics

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Our high resolution double velocity map imaging photoelectron photoion coincidence (PEPICO) spectrometer is a new instrument for studying fundamental gas phase reactions with transient species pertinent to combustion and atmospheric chemistry. PEPICO spectroscopy yields multidimensional data sets consisting of ion mass spectra, photoionization spectra, mass-selected photoelectron spectra and kinetic time profiles of all species. Mass-selected photoelectron spectra are powerful molecular fingerprints to enable studies of isomers that cannot be distinguished by conventional photoionization mass spectrometry.

This new instrument is designed to give high mass and energy resolutions and can handle high ionization count rates. I will present results from commissioning experiments using a molecular beam as well as reaction kinetic experiments utilizing a side sampled slow flow reactor. These experiments were performed at Sandia using a gas discharge lamp and at the Advanced Light Source in Berkeley.

The new spectrometer has a large ion optics electrode stack, separating linear fields at the ionization point for good mass resolution from curved fields at the ends for velocity map imaging, enabling very high mass resolution with $m/\Delta m > 6000$.

To test the time-resolved capabilities of our instrument we studied the photodissociation of SO_2 with 193 nm light via the $\tilde{C}(^1B_2) \leftarrow \tilde{X}(^1A_1)$ transition. This reaction forms $O(^3P_j) + SO(^3\Sigma^-)$, but we also observed direct evidence for a small yield of $S(^3P_j) + O_2\ (^3\Sigma_g^-)$ that has not been reported in the literature previously.

This work was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), US Department of Energy (USDOE).

Photoionization of cyano-PAHs

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Polycyclic aromatic hydrocarbons (PAHs), made of benzoidal rings of *sp*^{2} hybridized C atoms, are ubiquitous in the interstellar medium (ISM) playing an important role in the physics and chemistry of the ISM [1]. With the recent detection of three cyano-PAHs in the ISM [2,3], it is of prime interest to study the photodynamics of these molecules in vacuum ultraviolet (VUV) spectral regions, especially in terms of photoionization and cation fragmentation processes. The experimental investigations are carried out at the VUV DESIRS beamline at Synchrotron SOLEIL, on a molecular beam chamber equipped with the double imaging electron/ion coincidence spectrometer DELICIOUS 3 [4]. The present work will be performed for the three cyano-PAH derivatives, cyanobenzene (benzonitrile) and 1- and 2-cyanonaphthalene to measure :

1- The high resolution threshold photoelectron spectrum (TPES) over a wide range of photon energies, to be benchmarked with ab initio calculations. The associated photoion yields will be recorded which might present autoionization features usable as spectroscopic fingerprints.
2- The state-selected fragmentation (TPEPICO) as a function of photon energy, to be compared with the case of highly-stable unsubstituted PAHs.
3- The photoelectron kinetic energy distribution as a function of the photon energy which provides information about the photoelectric heating for any given incoming photon spectrum distribution. These are expected to provide important input for photochemical models which lacks such information since the PAHs dominate the heating of the ISM via photoelectric heating.

The detailed results for the three cyano derivatives will be presented during the meeting.

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Perspectives for Hard X-Ray Selective Cancellation of the Active Center of Biomolecules

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The newly developed free-electron laser sources allow the extension of nonlinear processes to the hard X-ray regime, presently delivering up to 20-25 keV photon energy brilliant ultrashort light pulses. Above 30 keV photon energy radiation highly penetrates in the human body and interacts with the single atoms. It was reported that exposure to laser-produced hard X-ray pulses with relatively high peak intensities does not lead to increased harm to mammalian cells compared with the harm induced from exposure to hard X-rays with the same dose from conventional medical sources, concluding that the use of high-power laser facilities for medical imaging is justified [1]. X-ray absorption spectroscopy (XAS) is an element-specific probe of the local structural environment of a molecule. The X-ray spectra include X-ray absorption near edge structures (XANES), which give information on the atomic geometry and oxidation state, and extended X-ray absorption fine structures (EXAFS), which give information on the bond-lengths. The X-ray spectra obtained from XAS provide a unique fingerprint of the state of a particular molecule. Selective resonant excitation near a chosen core atomic ionization edge follows a rapid redistribution of charge that can begin in less than a femtosecond via Auger processes, so that multiple charged molecular ions are formed and the molecule generally becomes unstable with respect to charge separation and dissociates. In this context, we propose to investigate nonlinear selective core excitation of atoms in molecules by means of highly penetrating hard X-rays, in particular by resonantly-enhanced difference-frequency generation (re-DFG), taking advantage from the selective core resonances involved in XANES and EXAFS absorption spectra. The essential in the re-DFG hard X-ray approach is that the two-color (Ω_1, Ω_2) pulses are highly penetrating in bulk, while the core resonant re-DFG signals $\Omega_2 - \Omega_1$ are not. As a proof of principle, we present simulations of the spectral selectivity of re-DFG excitation of the oxygen K-edge (537 eV) by illumination of a single gas phase water molecule with two-color (3Ω, 4Ω) X-ray pulses of different photon energies and durations [2]. Studies with more complex biomolecules are in progress. The ultimate goal of the present research is to corroborate that efficient nonlinear processes can be produced locally and with high spectral selectivity in the core states of atoms in biologically relevant molecules using ultrashort hard X-ray pulses with medical harmless doses (mGy). This may determine a new unique tool for selectively inactivating pathogens directly in the human body, to be used in the large list of virus and bacterial human infectious diseases, and to the control of cancer and senescent cells, or for the treatment of the Alzheimer's disease, among others.

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Revealing ultrafast proton transfer dynamics in ionized aqueous urea solution through time-resolved x-ray absorption spectra and *ab initio* simulations

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Probing the early dynamics of chemical systems following ionization is essential for our understanding of radiation damage. The advent of FELs and advances in high harmonic generation (HHG) has shown that time-resolved x-ray absorption spectroscopy (TRXAS) on a femtosecond timescale can provide crucial insights into the ultrafast processes occurring upon ionization due to its element-specificity. However, to get a clear interpretation of the dynamical features in the spectra, one often has to reply on theoretical simulations.

In this theoretical study, we investigate the response of urea in 10M aqueous solution to ionizing radiation and how it can be probed via TRXAS. We are able to interpret the temporal variation in the carbon (C) *K*-edge resonance signal as an effect of proton transfer between two hydrogen bonded ureas through our *ab initio* simulations. These simulated trajectories are obtained using a similar methodology presented in ref. [1, 2] employing Tully's fewest switches surface hopping algorithm within the quantum mechanics / molecular mechanics (QM/MM) scheme. Koopmans' theorem is used to describe the valence-ionized system. The ability of TRXAS to reveal rich insights into the ionization-induced dynamics of aqueous urea, in particular to follow the progress of proton transfer, at the C *K*-edges is hence shown. Our results are in good agreement with recent pump-probe experiments using strong field ionization, followed by x-rays generated from HHG on 10M aqueous urea solution.

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X-ray absorption spectra of hydrocortisone and betamethasone

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Synchrotron radiation is used to analyze the soft X-ray absorption spectroscopic investigations of two corticosteroids [1], hydrocortisone ($C_{21}H_{30}O_5$) (HC) and betamethasone ($C_{22}H_{29}FO_5$) (BM), at Indus-2, RRCAT, Indore, India. As illustrated in Figure 1, the K-edge and L-edge absorptions for HC and BM have been discovered. Quantum mechanical calculations are performed at the B3LYP/6-311G(d,p) level of theory. The optimized geometries and charge distributions of the ground and excited states are compared. The apparent charge shifts between atoms are correlated with an increase in the C1=C4 bond length and a corresponding decrease in the C1-C2 bond length. In the case of HC, the predicted electronic excitation energy is 5.02 eV. During the conference, details of the experimental and theoretical discoveries, as well as their correlation, will be presented.

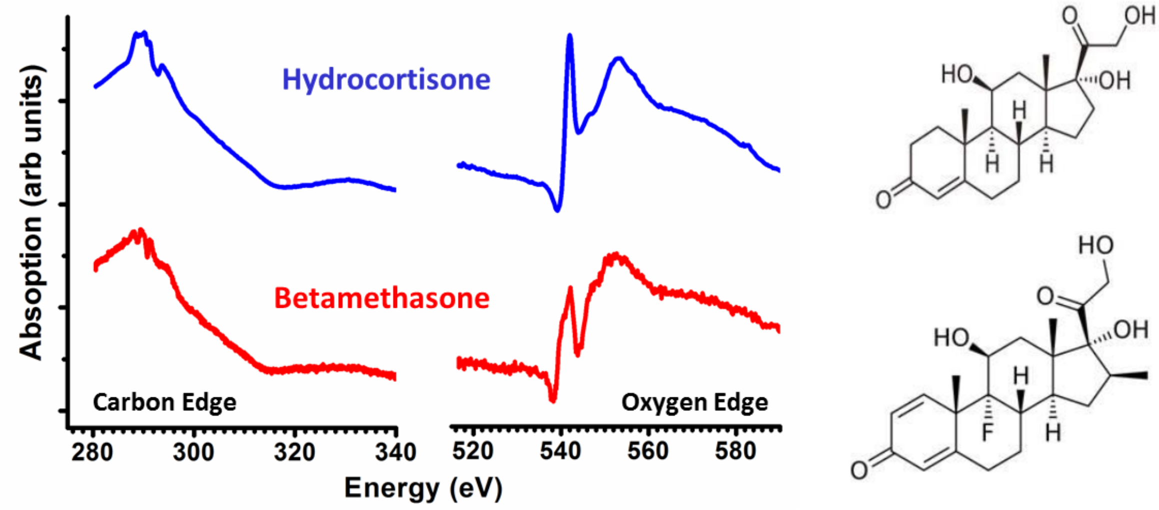

Figure 1: X-ray absorption edges due to Carbon (left) and Oxygen (right) atoms in Hydrocortisone and Betamethasone.

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How shake-up and shake-off satellites can reveal ultrafast charge delocalization in liquid water

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Probing decays of molecular systems after core ionization, either via Auger electrons from non-radiative decay or via photons in the radiative decay channel, gives insight into nuclear dynamics as well as charge and energy transfers on the timescale of the core-hole lifetime. In particular, Auger studies on liquid water have revealed ultrafast proton dynamics in liquid water, driven via hydrogen bonding [1]. It is well known that core ionization with sufficient energy can be accompanied by the additional promotion of a valence electron into an unoccupied orbital or into the continuum, termed shake-up and shake-off, respectively. The former produces an excited, doubly ionized state, while the latter yields a triply ionized species. While these processes and the resulting spectral satellite structures have been studied intensively since the 1970s, so far, they remain unexplored in the liquid phase. Furthermore, due to the increased computational complexity, the energetics of shake-up processes have been described far less. Studying shake-up and shake-off satellites in liquid water promises to give new insight into ultrafast charge- and energy-transfer processes during these alternative decay pathways. For example, electrons residing in the lowest unoccupied orbital are known to have a high probability of delocalizing into the liquid. Also, a triply charged species may have the ability to drive bond elongation and proton transfers much more strongly. Here, it is useful to explore both X-ray and Auger emission channels, as the latter involves a change in charge state of the remaining ion and is much more sensitive to the different energetics of shake-up and shake-off processes. We systematically studied shake-up satellites in gaseous and liquid water for the first time, and show that satellite states can be used to identify novel charge-transfer channels in the liquid phase. Our results will give new insight into the mechanism of proton-transfer dynamics in liquid water.

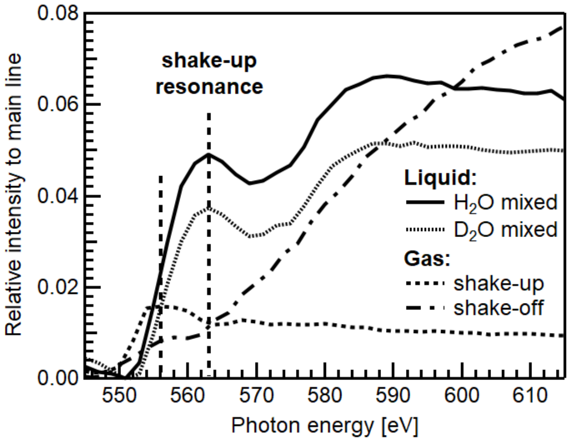

Fig. 1. Relative satellite intensities for liquid and gas. In the latter, shake-up and shake-off signals are clearly separated. The liquid has a more complex behavior, indicating intermixing of shake-up / shake-off channels via charge delocalization.

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PAHs under extreme ultraviolet exposure: theory and experiment

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Polycyclic aromatic hydrocarbons (PAHs) are common species in the interstellar medium, containing around 10% of the total galactic carbon [1]. Therefore investigation of their dynamics under the influence of the harsh ionizing radiation present in the ISM is crucial for astrochemical models. Here, we present theoretical modeling of the different photochemical processes occurring in the three-ringed PAH, fluorene (FLU), under the influence of the extreme ultraviolet (XUV) radiation with 41 eV of photon energy. We performed several types of molecular dynamics (MD) simulations to support the interpretation of the experimental data obtained at the permanent end station CAMP at the FLASH free-electron laser at Hamburg. The ultrafast pump-probe experiments used 30.3 nm XUV pump pulses and 810 nm probe pulses from a Ti:Sa laser system. [2]

FLU shows prominent ionization and fragmentation dynamics. To model the observed ultrafast relaxation observed in the ionization pathways, we have performed trajectory surface hopping MD, extracting electronic lifetimes of neutral FLU and near-ionization threshold FLU+ in agreement with experimentally measured values. [2] The fragmentation kinetic energy release patterns were modeled with augmented Born-Oppenheimer MD. Electronic excitation is present as an energy reservoir (internal excess energy), constantly pumping energy to the vibrational degrees of freedom in this approach. [3,4] The resulting patterns were compared with the experimental observations obtained from the recoil-frame covariance measurement from ion images recorded by a multi-mass imaging PImMS sensor. [5]

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All reflective delay line for dispersion-less ultrafast measurements

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Ultrashort pulse measurement is a key requirement in studying ultrafast dynamics from hundreds of femtoseconds up to attosecond time scale [1]. The dispersion less splitting of measuring pulse is a difficult task with conventional whole beam and transmission grating based interferometers. All reflective split mirror or diffraction grating based delay lines has been used for dispersion less measurements from NIR to near- UV spectral range [2,3]. These delay lines are difficult to align, suffers drift in beam position at focus and do not allow easy manipulation of both beams individually. In order to overcome these limitations, we have developed an all reflective prism mirror-based delay line, which is ideal for measurement of hundreds of femtoseconds up to tens of femtosecond pulses in near-IR to visible spectral range. It is based on symmetrical splitting of measuring pulse providing two separate arms for both split beams which make it more versatile for wide range of applications in ultrafast measurements

We have validated our delay line with NIR –femtosecond pulse measurement centred at 800 nm using linear and nonlinear Autocorrelation technique. The delay line serves easy recording of time zero signal as well interferometric autocorrelation and allows beam manipulation of individual split beams which can be further use for IR-IR controlling for High harmonic generation as well as for ultrafast pump-probe measurements [4]. The delay line is dispersion free, compact, easy to align and provides attosecond stability and precision.

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Looking on ultrafast dynamics from many ways

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With the recent advances in the development, performance and availability of ultra-short x-rays pulses it has become possible to use element selective spectroscopy as a regular tool in sample characterization. In the field of light sensitization and light activated catalysis these tools are increasingly used to study model complexes and learn the principles behind the observed dynamics. Understanding these principles in turn has led to the development of extraordinary new complexes capable of harvesting and using solar energy.

We will show examples in which x-ray spectroscopy was combined with optical spectroscopy and advanced modelling to understand the charge and structural dynamic inside complex molecule. The steric arrangement of the ligands has a profound effect on the electronic configuration. By identifying electronic and structural components of the re-arrangement we can disentangle this complex behaviour. Essential to this progress is our recently developed Data-Analysis suite KiMoPack that we will after 8 years of development present to scientific community and that allows the simultaneous optimization analysis of various types of data.

Stripping away ion hydration shells in electrical double layer formation: water networks matter

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The electrical double layer at the electrode/electrolyte interface is a key concept in electrochemistry. We present an experimental study combined with simulations, providing a molecular picture of the formation of the electrical double layer under applied potential. Using THz spectroscopy with ultra-bright synchrotron light as a source, we are able to follow for the first time the stripping away of the cation/anion hydration shells for electrolytes such as aqueous NaCl and KCl solutions. For Na+ we observe that the ion is attracted toward the electrode at the smallest applied negative potentials, while stripping of the Cl- hydration shell is observed only at higher potential values.[1] Recently, we have also performed these measurements for KCl solutions. These phenomena are directly measured by THz spectroscopy and rationalized by accompanying molecular-dynamics simulations and electronic-structure calculations.

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IR multiple photon dissociation spectroscopy of MO_2^+ (M = V, Nb, Ta)

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The Fourier-transform ion cyclotron resonance mass spectrometer at the beamline of the free-electron laser for intracavity experiments (FELICE) was equipped with a laser vaporization cluster ion source.[1,2]

Metal dioxides are very strongly bound systems and certainly require high laser energies to dissociate. The group 5 gas phase metal oxide cations VO_2^+, NbO_2^+, and TaO_2^+ are formed in the new ion source as examples for strongly bound triatomic species and are spectroscopically characterized using IR multiple-photon dissociation spectroscopy.[3] All ions fragment via the loss channel of atomic oxygen. The loss of atomic oxygen requires to overcome fragmentation energies in the range of 3 eV – 6 eV.

Bands for all MO_2^+ fundamental modes were observed: Those are the symmetric and anti-symmetric v_1 and v_3 stretching modes in the 900 cm^{-1} – 1000 cm^{-1} range and the v_2 bending mode in the 300 cm^{-1} – 450 cm^{-1} range. The spectra of the bending vibrations show a remarkable substructure, which is at least partly due to the rovibrational substructure.

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Pickup of hydrogen bonding molecules by benzene nanoparticles: growing ice-mantles in interstellar space medium

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Astronomical observations revealed surprisingly plethora of molecules in interstellar space medium (ISM), some of them very complex, which ask for a complex interstellar chemistry. [1] One of the proposed pathways is heterogenous chemistry occurring on the dust particles and clusters abundant in ISM. The clusters can be composed from polyaromatic hydrocarbons (PAHs), which are considered to store around 10% of all carbon in ISM.[1] In our pickup experiments, we generate the PAH clusters in supersonic expansion and investigate their uptake ability of other astronomically relevant molecules.[2] The outcome is probed by ToF mass spectrometry, which allows us to study the molecular pickup, coagulation, nanoparticle growth or electron-triggered reactions. We selected several representatives of PAH family, e.g.: benzene, naphthalene, phenanthrene, pyrene and compounds containing 5-member ring like fluoranthene and indene, which are expanded into clusters. Recently, we have mainly focused on uptake of the hydrogen bonding molecules represented by methanol, ethanol and water on benzene clusters, which mimics a crucial step in the growth of icy mantel on the dust particles. The results point out on the high mobility of these molecules on the clusters, which can coagulate within milliseconds. The character of generated clusters was probed by theoretical simulations combined with the analysis of mass spectra series by Poisson statistics. The calculated relative pickup probabilities showed that there is 30% lower probability to uptake water molecule compared to the alcohols. Our experiments can provide elementary data for the modelling of condensation of molecules on dust particles in ISM.

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A setup for FLASH Liquid-phase Ultrafast X-ray Spectroscopy (FLUXS)

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The presented project aims at building a versatile liquid-phase spectroscopic instrument for advanced ultrafast solution-phase spectroscopy in the soft X-ray regime (< 1000 eV) to provide unique experimental opportunities to the worldwide user community at FLASH, the XUV and soft X-ray free-electron laser at DESY in Hamburg. By constructing a flexible system, in combination with beam splitting techniques for referenced detection, the end station is able to conduct (i) self-referenced X-ray absorption spectroscopy (XAS) with monochromatized X-rays pulses, (ii) pink-beam post-sample self-referenced dispersive X-ray absorption spectroscopy (dXAS) in transmission mode, (iii) partial fluorescence yield (PFY) absorption spectroscopy for low-concentration samples, and (iv) resonant inelastic X-ray scattering (RIXS) with moderate energy resolution across the whole photon energy range of FLASH.

The spectrometer aims for an intermediate energy resolution (E/ΔE≈ 1000) for ultrafast molecular science, which allows for a compact and flexible design. It gives an opportunity to switch between transmission and scattering schemes (see Fig. 1). In transmission, measurements can be referenced by a using transmission grating beam splitter to create reference beams for Io measurements. Such a referencing scheme is vital for normalization at SASE XFELs with fluctuating spectral content and thus indispensable for dispersive transmission spectroscopy. We have successfully tested this experimental approach at FLASH using the two first-order beams of a soft X-ray transmission grating guided through or past a liquid flat jet, respectively [1].

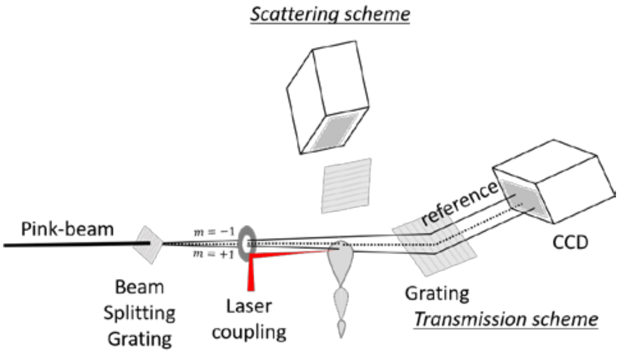

Figure 1. The experimental schemes.

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Ultrafast wettability alteration: The decisive moments of adsorption on supported particles

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The detection of intermediate species during photoinduced surface chemical reactions and the ability to correlate their ultrafast dynamics with the morphology and electronic structure of the surface is crucial to fully understand and control photoinduced or photocatalytic reactions.

In this investigation, the ultrafast photodissociation dynamics of CH3Br molecules on variable size Au clusters grown on MgO/Mo(100) has been investigated using the pump-probe femtosecond-laser mass spectroscopy technique [1]. Collaborative photoemission investigations in conjunction with femtosecond extreme ultraviolet laser pulses are employed to sensitively detect the changes in the electronic structure of the Au clusters as they are grown on MgO/Mo(100) [2].

Further prospective research directions aim at the investigation of catalytic water splitting facilitated by supported manganese oxide clusters. In this respect, previous comparative gas phase catalytic model systems provide an extremely promising perspective [3].

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Absolute Absorption Cross-Section of $C_2H_5O_2$ Radical and Kinetics of Its Self-Reaction: Rate Constant and Branching Ratio

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Ethane is one of the most abundant non-methane hydrocarbons in the atmosphere, and its atmospheric oxidation leads to the formation of the ethyl peroxy radical, $C_2H_5O_2$. A reliable detection of this radical is therefore highly desirable for studying its reactivity and thus understanding its embedded chemistry.

$C_2H_5O_2$ radicals were generated from pulsed 351 nm photolysis of C_2H_6/Cl_2 mixture in presence of 100 Torr O_2 at T = 295 K. The absolute absorption cross-section of the ethyl peroxy radical $C_2H_5O_2$ in the $\tilde{A} \leftarrow \tilde{X}$ electronic transition with the peak wavelength at 7596 cm-1 has been determined by the method of dual wavelengths time resolved continuous wave cavity ring down spectroscopy. $C_2H_5O_2$ radicals were detected on one of the CRDS paths. Two methods have been applied for the determination of the $C_2H_5O_2$ absorption cross-section, both methods lead to the same peak absorption cross-section for $C_2H_5O_2$ at 7596 cm-1 of $\sigma = (1.0 \pm 0.2) \times 10^{-20}$ cm^2.

The self-reaction of ethyl peroxy radical ($C_2H_5O_2$) has been studied with the obtained absorption cross-section. The rate constant for the self-reaction has been found at k1 = 1.0 ×10-13 cm3s-1 with the branching fraction of the C_2H_5O radical production channel being $\alpha = 0.31$. This finding is in contradiction with the recommendation of IUPAC, but confirms the most recent measurement (Noell et al, JPCA, 2010) and indicates that the current recommendation for this reaction should be revised.

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