Booklet of Abstracts

Summary

International Workshop on Photoionization &
Resonant Inelastic X-ray Scattering
IWP-RIXS 2017
Aussois, France
26th - 31st of March 2017

Conference organization:

SOLEIL SYNCHROTRON

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Welcome!

The International Workshop on Photoionization & Resonant Inelastic X-ray Scattering workshop series have been organized every three years since 1992. The last three ones were held near Uppsala (Sweden) in 2008, in Las Vegas (US) in 2011 and Erice (Italy) in 2014.

The 2017 edition of IWP/RIXS takes place in Aussois, France from **March 26th to 31st, 2017**.
Aussois is a beautiful authentic ski resort nested in Savoie in the French Alpes.

The scientific program is tailored in such a way that some time will be devoted to the exploration of the nearby slopes (skiing) and/or hills (hiking).

The joint IWP/RIXS2017 workshop aims at covering a broad field related to photoionization/RIXS processes on diluted matter: atoms, molecules, ions, transient species, molecular complexes, clusters, nanoparticles and liquid interfaces. Both experimental and theoretical approaches should be covered as well as new methodologies associated with synchrotron radiation and with short-wavelengths and/or short pulses sources such as FELs and HHG. We intend also to foster interfaces with chemistry, life sciences, and nanosciences.

Bienvenue !

L’International Workshop on Photoionization & Resonant Inelastic X-ray Scattering workshop s’est tenu tous les trois ans depuis 1992. Les trois dernières éditions ont été organisées près d’Uppsala (Suède) en 2008, à Las Vegas (USA) en 2011 et à Erice (Italie) en 2014.

L’édition 2017 de IWP/RIXS se déroule à Aussois (France) du **26 au 31 Mars 2017**.
Aussois est une charmante station de ski nichée en Savoie dans les Alpes françaises.

Le programme scientifique est ajusté de façon à laisser du temps pour explorer les pentes (ski) et/ou les vallons (randonnées).

Le workshop combiné IWP/RIXS2017 ambitionne de couvrir un large domaine lié aux processus de photoionisation et de RIXS de la matière diluée : atomes, molécules, ions, espèces transitoires, complexes moléculaires, agrégats, nanoparticules et interfaces avec les liquides. Les approches expérimentales et théoriques sont au programme de même que les nouvelles méthodologies associées au rayonnement synchrotron, et aux sources ultra-brèves et/ou à courtes longueurs d’onde telles que les LELs et les sources harmoniques (HHG). Nous explorerons aussi les interfaces avec la chimie, les sciences de la vie et les nanosciences.

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International Workshop on Photoionization & Resonant Inelastic X-ray Scattering
IWP-RIXS 2017

Aussois, France

26th - 31st of March 2017

Programme

Sunday, March 26th

17:00 - 19:30 Registration

19:30 - 21:30 Welcome reception

Monday, March 27th

08:30 - 08:45 Welcome

Session 1
FEL Non equilibrium matter

Chairperson: **Linda Young**

08:45 - 09:15 **Invited Talk**
Stimulated X-ray Raman scattering in molecular targets – A critical study of the building block of coherent nonlinear X-ray spectroscopy
Nina Rohringer *- MPSD, Hamburg, Germany*

09:15 - 09:45 **Invited Talk**
Non-equilibrium Processes within X-Ray FEL Generated Plasmas
Beata Ziaja-Motyka *- CFEL DESY, Hamburg, Germany*

09:45 - 10:15 **Invited Talk**
Femtosecond response of polyatomic molecules to intense soft and hard X-rays
Rebecca Boll *- DESY, Hamburg, Germany*

10:15 - 10:45 *Coffee break*

Session 2
Atto and Ultra-fast processes

Chairperson: **Nina Rohringer**

10:45 - 11:15 **Invited Talk**
Attosecond dynamics through Fano resonances
Fernando Martin *- Universidad Autónoma de Madrid, Spain*

11:15 - 11:45 **Invited Talk**
Observing atoms and molecules change their shape in short and strong laser fields
Thomas Pfeiffer *- MPIK, Heidelberg, Germany*

11:45 - 12:15 **Invited Talk**
Tracking in real-time attosecond inelastic scattering in dielectrics
Francesca Calegari *- CNR-IFN, Milano, Italy*

12:15 - 12:45 **Invited Talk**
Attosecond electron dynamics in molecules and liquids
Hans-Jacob Wörner *- ETH, Zürich, Switzerland*

13:00 - 14:30 *Lunch*

Session 3
RIXS 1

Chairperson: **Yoshihisa Harada**

14:30 - 15:00 **Invited Talk**
Mapping potential energy surfaces and dynamics around selected atoms with RIXS
Alexander Föhlisch *- BESSY, Berlin, Germany*

15:00 - 15:30 **Invited Talk**
Symmetry breaking in soft X-ray resonant inelastic scattering on molecules
Jan-Erik Rubensson *- Uppsala University, Sweden*

15:30 - 16:00 **Invited Talk**
Electron and nuclear dynamics in deeply core-excited molecules
Tatiana Marchenko *- UPMC, Paris, France*

16:00 - 16:20 Theory of RIXS of water
Faris Gel'mukhanov *- KTH Stockholm, Sweden*

16:20 - 16:40 Excited state proton transfer in aqueous 2-mercaptopyridine studied with RIXS
Jesper Norell *- Stockholm University, Sweden*

16:40 - 17:00 *Coffee break*

17:00 - 19:00 Poster Session

20:00 - *Dinner*

Tuesday, March 28th

Session 4
Chirality and Exotic polarization

Chairperson: **Kiyoshi Ueda**

08:30 - 09:00 **Invited Talk**
Photoelectron circular dichroism measured by multiphoton ionization
Thomas Baumert *- Kassel University, Germany*

09:00 - 09:30 **Invited Talk**
Toward femtochemistry with circularly polarized pulses
Valérie Blanchet *- CELIA, Bordeaux, France*

09:30 - 09:50 Bi-elliptical high-harmonic spectroscopy as a probe of matter: From atomic orbitals to chiral molecules
Denitsa Baykusheva *- ETH Zurich, Switzerland*

09:50 - 10:10 Complete polarization state of high order harmonics generated from bicircular counter-rotating ω and 2ω fields and probed by molecular frame photoemission
Danielle Dowek *– ISMO, Orsay, France*

10:10 - 10:30 *Coffee break*

10:30 - 16:30 *Ski or Snowshoes*

16:30 - 17:00 *Coffee break*

Session 5
Multielectron processes

Chairperson: **Steve Manson**

17:00 - 17:30 **Invited Talk**
Photoionization as probe of dynamical processes
Piero Decleva *- Universitá di Trieste, Italy*

17:30 - 18:00 **Invited Talk**
$K^{-2}V$: A new spectroscopic tool
Stéphane Carniato *- LCPMR, CNRS & UPMC, Paris, France*

18:00 - 18:30 **Invited Talk**
Multiple inner shell vacancies and collective Auger decay processes
Raimund Feifel*, Gothenburg University, Sweden*

18:30 - 18:50 Hybrid basis close-coupling interface to quantum chemistry packages for the treatment of ionization problems
Markus Klinker *- Universidad Autónoma de Madrid, Spain*

18:50 - 19:10 Multi electron spectroscopy: Auger decays of the rubidium 3d hole
Jérôme Palaudoux *– LCPMR, CNRS & UPMC, Paris, France*

20:00 *Savoyard Dinner*

Wednesday, March 29th

Session 6
ICD et clusters

Chairperson: **Arnaldo Naves de Brito**

08:30 - 09:00 **Invited Talk**
Multicoincidence studies of molecular photoionization – Entanglement and wavefunction imaging
Reinhard Dörner *- Frankfurt University, Germany*

09:00 - 09:30 **Invited Talk**
ICD and ICD cascades in multiply excited clusters
Alexander I. Kuleff *- Heidelberg University, Germany*

09:30 - 09:50 On the computations of decay widths of Fano resonances
Tsveta Miteva *– LCPMR, CNRS & UPMC, Paris, France*

09:50 - 10:10 Size-resolved photoemission anisotropies of neutral water clusters and predictions for liquid water
Sebastian Hartweg *- ETH Zurich, Switzerland*

10:10 - 10:40 *Coffee break*

Session 7
Liquid jets

Chairperson: **Paul Morin**

10:40 - 11:10	**Invited Talk** Local and non-local electronic and nuclear relaxation processes in aqueous solutions ***Bernd Winter*** *- Fritz-Haber-Institut, Berlin, Germany*
11:10 - 11:40	**Invited Talk** *A superficial look at water* ***Olle Björneholm*** *- Uppsala University, Sweden*
11:40 - 12:10	**Invited Talk** From distillation to biomolecules in aqueous surface: Revelations from electron spectroscopy ***Arnaldo Naves de Brito*** *- UNICAMP, Campinas, Brazil*
12:10 - 12:30	High energy photoemission as a probe of ultrafast charge transfer in KCl aqueous solution ***Denis Céolin*** *– Synchrotron SOLEIL, Gif-sur-Yvette, France*
12:30 - 12:50	Optical luminescence from liquid water after excitation with Synchrotron Radiation ***Christian Ozga*** *- Kassel University, Germany*
13:00 - 14:30	*Lunch*

Session 8
Chemistry and Nanosystems

Chairperson: **Fernando Martin**

14:30 - 15:00	**Invited Talk** Capturing the fastest charge and spin dynamics in nanosystems using high harmonic beams ***Margaret Murnane*** *- JILA, Boulder, USA*
15:00 - 15:30	**Invited Talk** Ultrafast non equilibrium dynamics induced by attopulses ***Françoise Remacle*** *- Liège University, Belgium*
15:30 - 16:00	**Invited Talk** Double imaging coincidences techniques for product determination in gas phase complex mixtures ***Gustavo Garcia*** *- Synchrotron SOLEIL, Gif-sur-Yvette, France*
16:00 - 16:20	Isolated nanoparticles' surfaces and interfaces probed by soft X-ray photoelectron spectroscopy ***Mina Patanen*** *- University of Oulu, Finland*
16:20 - 16:40	Selective dissociation upon core-electronic excitation in unsaturated hydrocarbons ***Shabnam Oghbaie*** *- Lund University, Sweden*
16:40 - 17:00	*Coffee break*
17:00 - 19:00	Poster Session
20:00 -	*Dinner*

Thursday, March 30th

Session 9
Atto and Ultra-fast processes 2

Chairperson: **Matjaž Žitnik**

08:30 - 09:00	**Invited Talk** Photoionization dynamics: Transition and scattering delays ***Richard Taïeb*** *- UPMC, Paris, France*
09:00 - 09:20	What can we learn from electronic-state lifetime interference in atoms and molecules? ***Ralph Püttner*** *- Berlin University, Germany*
09:20 - 09:40	Photodamage and photostability of halogenated uracils under XUV HH radiation ***Raluca Cireasa*** *– ISMO, Orsay, France*
09:40 - 10:00	Attosecond interferometry with self-amplified spontaneous emission of a free-electron laser ***Tim Laarmann*** *– DESY, Hamburg, Germany*
10:00 - 10:20	Role of electron-nuclear coupled dynamics on charge migration induced by attosecond pulses in glycine ***Manuel Lara-Astiaso*** *- Universidad Autónoma de Madrid, Spain*
10:20 - 10:40	*Coffee break*
10:40 - 16:30	Ski or visit of “Haute-Maurienne” village
16:30 - 17:00	*Coffee break*

Session 10
RIXS 2

Chairperson: **Alexander Föhlisch**

17:00 - 17:30	**Invited Talk** X-ray Raman spectroscopy ***Simo Huotari*** *- Helsinki University, Finland*
17:30 - 18:00	**Invited Talk** Interference effects in high-resolution X-ray spectra ***Matjaž Žitnik*** *- Jožef Stefan Institute, Ljubljana, Slovenia*
18:00 - 18:30	**Invited Talk** Soft X-ray experiments of samples under atmospheric pressure: X-ray emission studies of liquids, solutions, gases and interfaces at SPring-8 BL17SU ***Takashi Tokushima*** *- RIKEN, Saitama, Japan*
18:30 - 18:50	Probing the trans-and Cis-isomerization of azobenzene with RIXS ***Zhong Yin*** *- Max Planck Institute, Göttingen, Germany*
18:50 - 19:10	*Hydrogen-bonding network of water confined in a polyelectrolyte brush* ***Kosuke Yamazoe*** *- University of Tokyo, Japan*
20:00 -	*Conference Dinner & Best poster award (sponsored by Elsevier)*

Friday, March 31st

Session 11

Ions

Chairperson: **Maria Novella Piancastelli**

08:30 - 09:00 **Invited Talk**
Multi-electron electron effects in inner-shell ionization of ions
Stefan Schippers *- Giessen University, Germany*

09:00 - 09:30 **Invited Talk**
One- and two-color photoionization of atomic ions formed within an intense free-electron laser pulse
Michael Meyer *- XFEL, Hamburg, Germany*

09:30 - 10:00 **Invited Talk**
Photoionization of ions stored in traps : From small carbonated systems to large biopolymers
Alexandre Giuliani *- INRA, Nantes / Synchrotron SOLEIL, Gif-sur-Yvette, France*

10:00 - 10:20 Dissociation dynamics of energy-selected methyl halide ions (CH_3X^+, X=F, Cl, Br) investigated by Synchrotron photoelectron photoion coincidences
Xiaofeng Tang *- Chinese Academy of Sciences, Hefei, China*

10:20 - 10:50 *Coffee break*

Session 12

FEL multiphoton

Chairperson: **John Bozek**

10:50 - 11:20 **Invited Talk**
Coherent control experiments with the fully coherent free electron laser FERMI
Kevin Prince *- Elettra, Trieste, Italy*

11:20 - 11:50 **Invited Talk**
Hard X-ray photonics with intense X-ray laser pulses
Hitoki Yoneda *- University of Electro-Communications, Tokyo, Japan*

11:50 - 12:20 **Invited Talk**
X-ray pump -- X-ray probe spectroscopy
Antonio Picón *- ANL, Argonne, USA*

12:20 - 12:40 Molecular femtodynamics at FERMI
Maria Novella Piancastelli *- LCPMR, CNRS & UPMC, Paris, France / Uppsala University, Sweden*

12:40 - 13:00 Control of H_2 dissociative ionization in the non-linear regime using EUV femtosecond pulses @ FERMI
Fabian Holzmeier *– ISMO, Orsay / Synchrotron SOLEIL, Gif-sur-Yvette, France*

13:00 - *Lunch and Departure*

ABSTRACTS

Monday, March 27th, 2017

SESSIONS 1, 2 & 3

IWP-RIXS 17

Monday, March 27th

Chairpersons: L. Young, N. Rohringer, Y. Harada

IT-01	Stimulated X-ray Raman scattering in molecular targets – A critical study of the building block of coherent nonlinear X-ray spectroscopy *N.Rohringer*
IT-02	Non-equilibrium Processes within X-Ray FEL Generated Plasmas *B. Ziaja-Motyka*
IT-03	Femtosecond response of polyatomic moleculesto intense soft and hard X-rays *R. Boll*
IT-04	Attosecond dynamics through Fano resonances *F.Martin*
IT-05	Observing atoms and molecules change their shape in short and strong laser fields *T. Pfeiffer*
IT-06	Tracking in real-time attosecond inelastic scattering in dielectrics *F. Calegari*
IT-07	Attosecond electron dynamics in molecules and liquids *H.J. Wörner*
IT-08	Mapping potential energy surfaces and dynamics around selected atoms with RIXS *A. Föhlisch*
IT-09	Symmetry breaking in soft X-ray resonant inelastic scattering on molecules *J.E. Rubensson*
IT-10	Electron and nuclear dynamics in deeply core-excited molecules *T. Marchenko*
OC-01	Theory of RIXS of water *F. Gel'mukhanov*
OC-02	Excited state proton transfer in aqueous 2-mercaptopyridine studied with RIXS *J. Norell*

Stimulated X-ray Raman Scattering in Molecular Targets – A Critical Study of the Building Block of Coherent Nonlinear X-ray Spectroscopy

N. Rohringer

DESY Deutsches Elektronen-Synchrotron, 22607 Hamburg, Germany
University of Hamburg, 22607 Hamburg
Max Planck Institute for the Structure and Dynamics of Matter, 22761 Hamburg

ABSTRACT

In the soft x-ray range, coherent amplification of spontaneous x-ray emission [1] and stimulated resonant inelastic x-ray scattering (SRIXS) [2] have been demonstrated in Neon. A next crucial step for advancing time resolved spectroscopy is the transfer of stimulated emission and SRIXS to the hard x-ray domain that would allow single-shot spectroscopy in chemically and biologically relevant samples. Here, we present results of amplified spontaneous K-α emission in Manganese salts in solutions [3]. Coherent amplification of the Mn K-α emission by four orders of magnitude and saturation of the signal has been observed in $MnCl_2$. More excitingly, the chemical shifts of $MnCl_2$ and $KMnO_4$ is maintained in the strongly spectrally sharpened stimulated K-α emission spectra.

A more comprehensive technique for the study of chemical structure is SRIXS. Although demonstrated in Neon [2], the realization of SRIXS in molecular targets is more difficult to achieve [4-6] due to a smaller gain-cross section, that is distributed over many electronic, vibrational and rotational channels. We present two experimental studies, that were specifically developed to achieve vibrationally resolved SRIXS in CO. In a first attempt [4], the XFEL was operated in a two-color self-amplified spontaneous emission (SASE) scheme, with one frequency band tuned to the Oxygen π^* resonance, and the other band overlapping with the Stokes-shifted frequencies. This setting would allow for high-resolution SRIXS spectra by covariance analysis[5], experimentally, the spectra are, however, contaminated by absorption features of molecular ions generated in competing processes. In a second experiment[6], the SASE pump pulse was replaced with a self-seeded, narrow-band pulse at considerably lower pulse energy that resulted reducing the background. A comparison with theory shows that the experimental conditions were at the onset of an observable signal, but so far, no statistical evidence is seen, to confidently report the demonstration of SXRIS in a molecular target. We present an experimental protocol that allows for the detection of small SRIXS signals with highly fluctuating XFEL spectra. The challenges and the necessary experimental parameters to ultimately reach the conditions for stimulated x-ray emission spectroscopy in chemically relevant targets will be critically assessed.

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Non-equilibrium Processes within X-Ray FEL Generated Plasmas

B. Ziaja-Motyka

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& 2) Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152,
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ABSTRACT

Plasma representing the fourth fundamental state of matter is abundant in the universe. Dense plasmas can be found in all types of stars, within giant planets, and are commonly created under laboratory conditions during experiments involving high-power light sources. In my talk I will give an overview of our recent theoretical investigation how the unique properties of X-ray free-electron laser radiation can be employed to create and investigate dense plasmas. I will present: (i) modeling of nanoplasmas created from finite systems such as atomic clusters or macromolecules, and (ii) modeling of plasmas created from bulk systems. In both cases I will discuss in detail their non-equilibrium evolution stage, with an outlook for its ab-initio treatment.

Femtosecond Response of Polyatomic Molecules to Intense Soft and Hard X-rays

R. Boll

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ABSTRACT

X-ray free-electron lasers (FELs) offer unique opportunities for investigating the structure and dynamics of biomolecules and complex systems, as well as holding the prospect of single particle imaging. At FELs, imaging experiments often rely on the fact that light elements such as carbon and hydrogen have very low absorption cross sections for high-energy photons, and that radiation damage can thus be neglected, or, in other words, that the well-known “diffract before destroy” approach holds. However, the response to very short (<30fs) pulses of hard X-rays (>6keV), focused very tightly (100nm) to reach extremely high peak intensities (>10^{20}W/cm^2), as is the case at the Coherent X-ray Imaging (CXI) beamline of the Linac Coherent Light Source (LCLS), is not yet well understood on the atomic level.

Although biomolecules consist predominantly of light elements, they can also contain heavier atoms, such as sulfur or selenium. Here, we demonstrate that the presence of a single heavy atom can lead to a very high degree of ionization in a polyatomic molecule.[1] Following multi-photon absorption, the initially localized charge spreads rapidly to the molecular environment, finally leading to the emission of more than 54 electrons from a single small molecule, iodobenzene, within the X-ray pulse. We map in detail the time-dependent electronic and nuclear dynamics by a combined experimental and theoretical analysis.

The interplay between multiphoton absorption and subsequent charge rearrangement considerably differs from earlier observations for soft X-rays[2-4] or for weaker hard X-rays. The level of ionization is significantly enhanced in extended systems, as compared to isolated heavy atoms at extremely high peak intensities. This indicates that considerable radiation damage can occur already on very short timescales, originating from heavy atom absorption sites, as has also been shown recently for iron and sulfur containing ferrodoxin proteins.[5]

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Attosecond Dynamics through Fano Resonances

F. Martín[1,2,3]

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ABSTRACT

A popular approach to time resolve the ultrafast electron dynamics that occurs in atoms and molecules is RABITT (reconstruction of attosecond beating by interference of two-photon transitions). In this technique, a pump extreme-ultraviolet attosecond-pulse train (XUV-APT) is used in association with a compressed infra-red (IR) probe pulse to ionize the target atom or molecule and the photoelectron spectrum, which is composed of harmonic and sideband peaks, is recorded as a function of the pump-probe time delay. RABBIT has been widely used to reconstruct the APT from the harmonic phases, when the atomic phases are known, and, conversely, to recover the atomic phases, when the APT shape is known. For simplicity, at its origins, RABITT was exclusively applied to regions of the photoelectron spectra that are free from resonances, but, in more recent times, it has been extended to regions where autoionizing states are present [1,2]. Autoionization introduces additional energy-varying phases, which must therefore be taken into account when analyzing RABITT spectra and invalidate the usual interpretation schemes applied to non-resonant ionization.

To help in the interpretation problem, we have developed an analytical time-resolved model [3,4], based on Fano's autoionization theory, which, from a minimum set of parameters, is able to reproduce with high accuracy the RABBIT spectra that from either ab initio calculations or experiments. The method has been successfully used to interpret recent RABBIT measurements on He [2] and Ar [1] in the vicinity of the 2s2p and $3s^{-1}3p^{6}4p$ autoionizing resonances, respectively, and to time resolve the electron wave packet dynamics that results from ionizing the He atom in the vicinity of the 2s2p resonance [2].

In this talk, I will review the basic ingredients of the model and the above-mentioned applications, and will present its extension to interpret recent angularly resolved photoelectron spectra, which can provide a much more detailed information on the autoionization dynamics.

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Observing Atoms and Molecules Change their Shape in Short and Strong Laser Fields

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ABSTRACT

Atoms are commonly regarded as fundamental, well-defined and rigid quantum systems, even operated as clockworks in the most precise time-pieces ever build for applications in temporal and frequency metrology. However, as atoms and small molecules interact with intense electric fields, their charged constituents (electrons, nuclei) and their natural quantum dynamics are significantly altered. As a consequence, the intrinsic properties of atoms and molecules, their spectroscopic (energy levels) and spatial (electronic/nuclear wavefunctions/positions) structure, can change dramatically.

High-frequency radiation such as extreme ultraviolet (XUV) and x-ray light is ideally suited to examine atoms and molecules as they change their natural structure and shape in strong laser fields. For attosecond spectroscopy, high harmonics generated by intense optical lasers are of great use, whereas for the imaging of tiny molecular sizes one can employ coherent femtosecond-pulsed x-ray light delivered by free-electron lasers (FELs).

This talk will cover some of our recent experiments on spectral and spatial modifications of small quantum systems *during* their interaction with short pulsed light fields. It will be shown how optical methods (absorption spectroscopy and x-ray scattering) are ideally suited to serve as *in-situ* time-resolving probes. They can provide amplitude and phase information of excited state wavefunctions in atoms and molecules [1,2], and thus allow to reconstruct and control two-electron wavepackets in helium [3], and drive complex dynamics in solution-phase molecules [4]. By operating at very high intensities, it is possible to use optical laser pulses to cut off the natural evolution of fundamental quantum phenomena, enabling the recent time-resolved measurement of the buildup of a Fano resonance [5].

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Tracking in Real-time Attosecond Inelastic Scattering in Dielectrics

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ABSTRACT

Scattering of electrons in dielectric materials is at the heart of laser nanomachining, light-driven electronics, and radiation damage. Electron propagation in a solid is typically accompanied by elastic and inelastic collisions with the lattice and other electrons that result in changes of the electron momentum and energy. The average distance between consecutive collisions is on the sub-nm to nm scale and direct access to electron scattering dynamics therefore requires attosecond time resolution. So far theoretical and experimental studies have focused on electron photo-emission and -transport in metals [1-3] or adlayer-covered metals [4]. The accumulative charging of dielectrics exposed to intense laser pulses has hitherto prevented the application of attosecond photoelectron spectroscopy. Here, we avoid this problem by using nanoscopic dielectric targets in a beam, which replaces the targets between laser shots and present the first measurements of electron dynamics in dielectric nanoparticles following ionization by an attosecond pulse.

A stream of isolated aerodynamically focused SiO_2 nanoparticles of 50-nm diameter was delivered into the laser interaction region. Photoemission was initiated by an isolated 250 as pulse at 35 eV and the electron dynamics was traced by attosecond streaking using a delayed few-cycle laser pulse at 720nm. Electrons were detected by a kilohertz, single-shot velocity-map imaging (VMI) spectrometer, permitted to separate frames containing nanoparticle signals from frames containing the response of the reference gas only. This unique tool allowed us to obtain nanoparticle and reference streaking spectrograms from the very same experimental data set and for identical laser conditions.

The streaking trace for nanoparticles was found to be delayed compared to the one from the gas reference by ~100 as. To interpret the experimental results we performed semi-classical Monte-Carlo trajectory simulations taking into account the near-field distributions around the nanoparticles as obtained from Mie theory. The simulations indicate that the delay originates from scattering of the photoelectrons inside the nanoparticle and that the measurements permit to clock the inelastic scattering time.

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Attosecond Electron Dynamics in Molecules and Liquids

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ABSTRACT

Photoionization and electron transport in the condensed phase are phenomena that entirely take place on the attosecond time scale. I will present our recent experimental and theoretical work investigating photoionization dynamics of molecules [1, 2]. We have measured relative photoionization delays between the two outermost valence shells of two polyatomic molecules, H_2O and N_2O. Whereas the measured delays are all below 50 as in the case of H_2O, delays reach up to 160 as in the case of N_2O [1]. These large delays are shown to originate from the transient trapping of the photoelectron in shape resonances that have calculated lifetimes on the order of 100 as [2]. We have moreover extended attosecond science from gases to liquids by coupling an attosecond beamline with a liquid microjet [3]. This advance has enabled us to perform the first attosecond time-resolved measurements on liquids. We have studied the relative photoemission delays between the highest-occupied molecular orbitals of gas-phase and liquid-phase water molecules. The measured delays are on the order of 30-50 as. Our analysis shows that these delays reflect the effects of solvation on the water molecules and the signatures of elastic scattering *delays* during electron transport [4]. Finally, I will report on our very recent realization of the first time-resolved X-ray absorption experiment in the water window [5], which brings attosecond transient absorption experiments on solvated molecules within reach.

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Mapping Potential Energy Surfaces and Dynamics around Selected Atoms with RIXS

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ABSTRACT

Chemistry as well as materials' functionality are determined by the potential energy surface of a systems electronic ground state and its excited states. This makes the potential energy surface a central and powerful concept in physics, chemistry and materials science. However, direct experimental access to the potential energy surface around selected atomic centers and to its long-range structure are lacking. Sub-natural linewidth resonant inelastic soft x-ray scattering at vibrational resolution is utilized to determine ground state potential energy surfaces locally and detect long-range changes of the potentials [1]. Even directional cuts through a complex potential energy surface are possible due to highly defined wave packet dynamics during the core-excited state. In a next step, the investigation of excited state dynamics at the transform limit in energy and time will become accessible combining Anti-Stokes features with potential energy mapping [2]. This will allow to determine also the potential energy surfaces of excited states and their crossings. Examples of selective bond modifications as well as charge separation will be discussed.

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[2] *Anti-Stokes resonant x-ray Raman scattering for atom specific and excited state selective dynamics*
Kristjan Kunnus, Ida Josefsson, Ivan Rajkovic, Simon Schreck, Wilson Quevedo, Martin Beye, Sebastian Grübel, Mirko Scholz, Dennis Nordlund, Wenkai Zhang, Robert W Hartsock, Kelly J Gaffney, William F Schlotter, Joshua J Turner, Brian Kennedy, Franz Hennies, Simone Techert, Philippe Wernet, Michael Odelius, Alexander Föhlisch New Journal of Physics **18** (10), 103011 (2016)

Symmetry Breaking in Soft X-ray Resonant Inelastic Scattering on Molecules

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ABSTRACT

The dipole approximation dictates strict selection rules in resonant inelastic X-ray scattering (RIXS). For molecules with inversion symmetry this implies that the parity of the initial and final state must be the same. With vibronic coupling transitions to *electronically* forbidden final states can be populated, and for small molecules it is predicted that that the total electronic-vibronic wavefunction still obeys the dipole selection rules. Only recently has high-energy resolution made it possible to test this prediction experimentally, and it still remains a question to what extent decoherence in the scattering process plays a role when larger molecules and violent dynamics like ultrafast dissociation are investigated. These issues are discussed by comparing spectra of homonuclear diatomics (N_2, O_2) to spectra larger symmetric molecules (CO_2, SF_6), and molecular ions in solution (CO_3^{2-}). Results from the ADRESS beamline at SLS, the SEXTANTS beamline at SOLEIL, and BL07LSU at SPring-8 are presented. New opportunities for liquid and gas-phase RIXS at the upcoming VERITAS beamline at MAX IV are briefly discussed.

Electron and Nuclear Dynamics in Deeply Core-excited Molecules

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ABSTRACT

Excitation of a molecule with a high-energy photon leads to an ultrafast dynamic response involving nuclear and electronic degrees of freedom. Alternatively to the time-resolved measurements using ultrafast laser sources, the nuclear and electron dynamics can be successfully studied in the x-ray energy domain using a technique known as “core-hole clock” spectroscopy (CHCS) based on core-level excitation and decay. The decay of an excited molecule occurs through emission of an Auger electron or an x-ray photon. The corresponding core-hole clock techniques are referred to as resonant Auger electron spectroscopy and resonant inelastic x-ray scattering (RIXS).

Our work demonstrates the feasibility of application of CHCS to the study of attosecond electron and nuclear dynamics in isolated molecules. In gas-phase iodomethane CH_3I we show a large sensitivity of RIXS spectroscopy to nuclear and electronic rearrangement in a core-excited molecule on sub-femtosecond time scale determined by the natural lifetime of the iodine L-shell core hole (~ 0.2 fs) [1]. Similar observations in CH_3I have been made recently using resonant Auger spectroscopy at HAXPES high-energy high-resolution electron spectrometer installed on the GALAXIES beamline at the SOLEIL synchrotron facility.

Furthermore, we have demonstrated that RIXS spectroscopy in isolated carbon disulfide CS_2 molecules can provide access to X-ray-induced electron dynamics in a molecule occurring on attosecond time scale [2]. At large photon-energy detuning below the first absorption resonance, the excitation-energy dependence of the RIXS profile is dominated by the onset of electron dynamics triggered by a coherent excitation of multiple electronic states. The RIXS profile is determined by the interplay of the effective scattering duration and the characteristic time of the electron wave packet evolution.

Our study demonstrates the potential of CHCS as a promising technique for the studies of electron dynamics in molecules excited at the deep core shells.

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Theory of RIXS of Water

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ABSTRACT

In this study we use the gas-phase water to demonstrate how different intermediate core-excited states in ultra-high resolution resonant inelastic X-ray scattering (RIXS) may act as selective gates to specific vibrational modes by means of spatially selective nuclear dynamics in the core-excited state. The alignment of the wave packet along the OH bonds and between the bonds for the $|1a^{-1}4a^{1}\rangle$ and $|1a^{-1}2b^{1}\rangle$ states, respectively, allows to probe vibrational states aligned preferentially along these directions and to map the potential energy surface. The combination of experiment with state-of-the-art ab initio calculations allows to explain this selectivity and observed propensity rule with a detailed analysis of the potential energy surfaces (PESs) of the ground and core-excited states and by making use of the time-dependent wave packet picture [1]. We show that the RIXS technique makes it possible to probe extended regions of the ground state PES along each internal degree of freedom and to study the regime of normal-to-local mode transitions for symmetric molecules A_2B. We show that the use of frequency detuning and isotope substitution can act as additional tools to finetune information about the ground state, in both cases by altering the wave packet dynamics in the core-excited state. Our study of the isotopomer HDO shed light on the process of the wave function collapse-a cornerstone principle in the the theory of light-mater interaction [2]. We outline also the current stay of our simulations of RIXS and REXS of liquid water.

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Excited State Proton Transfer in Aqueous 2-mercaptopyridine Studied with RIXS

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ABSTRACT

Excited State Proton Transfer (ESPT) is a fundamental and ubiquitous process of importance for energy transfer and photo-stability in e.g. biological systems[1-2].

We study[3] ESPT in the model system 2-Mercaptopyridine, in aqueous solution, with nitrogen N1s Resonant Inelastic X-ray Scattering (RIXS) to investigate drivers, pathways and timescales.

By combining high level quantum chemical calculations with static and time-resolved measurements we are able to disentangle optically and X-ray induced dynamics which favors defragmentation along different coordinates. This demonstrates the strength of the combined modeling, and indicates how deformation of chemical bonds with varied photon energies could allow for selective control of molecular structures.

We identify a fingerprint for the deprotonation of the nitrogen site and benchmark the process to take place at femtosecond timescale, demonstrating RIXS as a viable probe for ESPT studies.

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ABSTRACTS

Tuesday, March 28th, 2017

SESSIONS 4 & 5

IWP-RIXS 17

Tuesday, March 28th

Chairpersons: K. Ueda, S. Manson

IT-11	Photoelectron circular dichroism measured by multiphoton ionization *T. Baumert*
IT-12	Toward femtochemistry with circularly polarized pulses *V. Blanchet*
OC-03	Bi-elliptical high-harmonic spectroscopy as a probe of matter: From atomic orbitals to chiral molecules *D. Baykusheva*
OC-04	Complete polarization state of high order harmonics generated from bicircular counter-rotating ω and 2ω fields and probed by molecular frame photoemission *D. Dowek*
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IT-15	Multiple inner shell vacancies and collective Auger decay processes *R. Feifel*
OC-05	Hybrid basis close-coupling interface to quantum chemistry packages for the treatment of ionization problems *M. Klinker*
OC-06	Multi electron spectroscopy: Auger decays of the rubidium 3d hole *J. Palaudoux*

Photoelectron Circular Dichroism Measured by Multiphoton Ionization

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ABSTRACT

The photo electron circular dichroism (PECD) [1,2], i.e. a striking forward / backward electron emission with respect to the light propagation of a light beam ionizing randomly oriented chiral molecules, was extended to the resonance enhanced multi photon ionization (REMPI) regime with femtosecond laser pulses [3-5] and studied as a function of absorbed photons [6,7]. The effect is in the ten percent regime and sub one percent sensitivity to enantiomeric excess was demonstrated [8]. Besides a discussion of the published experiments I will highlight the current status of our experiments with a special focus on coherent control techniques to study and control the coupled electron nuclear motion [9,10] in chiral potentials.

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Toward Femtochemistry with Circularly Polarized Pulses

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ABSTRACT

Each molecule can be recognized by its chemical composition and its structural conformation that dictates how it will interact with other molecules. Life has found an extra parameter to stock durably information: chirality. This asymmetry property appears at the molecular level when two molecules have the same chemical composition and structure but cannot be superimposed to each other by a mirror transposition. The two mirror images are called enantiomers. Enantiomers are able to regulate different biological mechanisms through their handedness. This chiral recognition is the key element in how we perceive odor and taste and is as well as of major importance in many mechanism for drug action. Chirality is as such, one of the most subtle example of broken symmetry with a huge impact in chemistry, pharmacology and biochemistry and even the origin of life.

In the photoionization of randomly-oriented pure enantiomers by circular polarization light, an asymmetry of the emitted photoelectron is observed along the photon propagation axis. This forward/backward asymmetry can reach several percentage and reverses with the handedness of the enantiomer or the helicity of the light polarization.[1] By comparing different ionization mechanisms, all using femtosecond pulses, we found that PECD exists in all regimes (single photon, multiphoton, tunneling).[2] On the basis of these experiments, we have performed the first (to our knowledge) experimental investigation on time-dependent chiral dynamics. The molecular dynamics investigated are vibronic coupling from Rydberg states in Fenchone and Camphor ($C_{10}H_{16}O$). These two molecules are isomers of each other.[3] The time-resolved approach opens new horizons and questions on what are the most important dynamical aspects of the scattering of an electron in chiral potential that is as well evolving.

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Bi-elliptical High-harmonic Spectroscopy as a Probe of Matter: From Atomic Orbitals to Chiral Molecules

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ABSTRACT

Development of coherent ultrashort XUV sources with tuneable polarization will enable the study of phenomena such as spin polarization[1], molecular symmetry-breaking[2], or chiral light-matter interactions[3] on an ultrafast time scale. One appealing scheme for generating highly elliptical high-harmonic radiation consists in combining a circularly polarized fundamental field with its counter-rotating second harmonic[4]. The resulting spectrum is composed of pairs of harmonics (*3q+1*) and (*3q+2*) of opposite helicities while every third (*3q*) harmonic is absent in a three-fold symmetric medium. Static bi-circular measurements of the harmonic emission from a series of noble gases (Ne, Ar, Kr, Xe) performed at different wavelengths (800 – 2000 nm) of the fundamental reveal that the relative strength between the (*3q+1*) and (*3q+2*) peaks is a characteristic signature of the atomic orbital. Furthermore, this ratio is very sensitive to the presence of destructive interferences in the photoionization cross section such as Cooper minima.

We interpret our results with the aid of an adapted version of the quantum-orbit model[5] by decomposing the temporal structure of the harmonic emission into complex electron trajectories. Our results reveal that the observed differences arise from interfering quantum paths on the one hand and from different recombination amplitudes to the p_+- and p_--components of the atomic ground state on the other.

Bi-circular, or more generally bi-elliptical fields enable efficient HHG at large ellipticities of the driving fields, thus opening the path towards dichroism studies[3]. In a second series of measurements, we follow the high-harmonic amplitude of an isotropic ensemble of chiral molecules subject to a bichromatic field (950+1900 nm) as the polarization of each frequency component is varied from linear to nearly circular[6]. The observed difference in the response of the *(R)*- and *(S)*-enantiomers of methyl oxirane amounts to ~3%, a value that is by one magnitude smaller than recently predicted by theory[6].

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Complete Polarization State of High Order Harmonics Generated from Bicircular Counter-rotating ω and 2ω Fields and Probed by Molecular Frame Photoemission

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ABSTRACT

Elliptically and circularly polarized ultrashort XUV sources are of particular interest since they constitute key tools to perform dynamical studies of the chiral properties of matter in dilute[1] and condensed[2] phase. In this context, different high-order harmonic generation (HHG) schemes with inherent symmetry breaking, based on the polarization of the generating beam (elliptical or bicircular counter-rotating fields) or on an anisotropic medium (e.g. aligned molecules), have been proposed. Nevertheless characterizing the polarization state of this XUV light remains challenging, and only a partial retrieval is achieved most of the time.

In the present work, the so-called molecular polarimetry (MP) method[3] relies on measuring molecular frame photoelectron angular distributions (MFPADs) in dissociative photoionization (DPI) processes induced by the XUV harmonic radiation, using coincidence electron-ion 3D momentum spectroscopy. MP takes advantage of the remarkable property that the complete polarization state of the ionizing light is encoded in the MFPAD in terms of the three Stokes parameters (s_1, s_2, s_3), equivalent to the polarization ellipse parameters *and* the degree of polarization of the light. This method was recently applied to determine the polarization state of harmonics generated in SF_6 molecules by elliptically polarized IR laser[4].

Here we present the first complete characterization of the polarization state of quasi-circular high order harmonics generated in argon by using bicircular counter-rotating ω (800 nm) and 2ω (400 nm) fields, a scheme with a high potential towards the control of elliptically polarized attosecond pulses[5,6]. The experiments were performed at the PLFA facility (CEA-SLIC).

The results will be discussed in particular for 3m+1 and 3m-1 HHs in the 21-32 eV range, involving DPI of the NO molecule in the region of the $NO^+(4\sigma^{-1})c^3\Pi$ state shape resonance, where s_3, derived from the molecular frame circular dichroim, provides the signed helicity of the ionizing light, (s_1, s_2) are extracted from the field frame angular distributions of the fragments, and the degree of depolarization s_4 is subsequently obtained for each harmonic.

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Photoionization as Probe of Dynamical Processes

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ABSTRACT

Time resolved photoelectron spectroscopy is a powerful probe of dynamical processes, typical of pump-probe experiments. Although ionization energies are already very informative, maximal information is conveyed by angularly resolved photoemission. Anisotropy in the molecular orientation is obtained from the pump pulse or by previous alignment. A full simulation of the spectra requires an efficient yet accurate approach, capable to relatively large molecules, both valence and core ionizations in a variety of electronic states, following the time evolution of the wavepacket.

We shall illustrate the capabilities of the present Dyson orbital / static-exchange DFT formulation [1,2] in different systems, to highlight the quality of the information that is in principle accessible both regarding nuclear and electronic motion. Development towards a full simulation in different contexts will be discussed.

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$K^{-2}V$: A New Spectroscopic Tool

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ABSTRACT

In the last few years, double core hole (DCH) or K^{-2} states have been studied by single photon ionization on synchrotron centers [1] and by multiple photon ionization [2] on X-ray free electron lasers (XFELs).

Closely related to double core ionization, the single photon process where a core electron is ionized while another core electron is excited simultaneously has been also observed. This $K^{-2}V$ spectroscopy that provides a new insight on double core-hole states combines the characters of both XPS and near-edge X-ray absorption fine structures (NEXAFS) spectroscopy.

As shown recently [3-7], theoretical investigations revealed interesting properties on the formation mechanisms of $K^{-2}V$ states. Studies of the C_2H_{2n} (n=1-3) series [3], N_2 [4], H_2O [5] and more recently on centrosymmetric CO_2 [6] molecule and Neon atom [7] demonstrated that two competing channels appear with comparable intensities. The first one corresponds to the dipolar ionization of a core electron accompanied by monopolar excitation (direct shake-up) of the remaining core electron. The second one corresponds to the dipolar excitation of a core electron to a vacant orbital accompanied by monopolar shake-off of the other core electron (conjugate shake-up process).

After a presentation of the various specificities of $K^{-2}V$ vs $K^{-1}V$(NEXAFS)/ K^{-1}(XPS) spectroscopies, perspectives on free electron laser light sources achieved for the study of K^{-2}/$K^{-2}V$ processes in complement to synchrotron radiation sources will be suggested.

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Multiple Inner Shell Vacancies and Collective Auger Decay Processes

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ABSTACT

In this contribution, a progress report on very recent investigations of multiple inner shell vacancies and new class of decay processes will be given.

Advances in X-ray instrumentation have made it possible to measure the spectra of an essentially unexplored class of electronic states associated with double inner shell vacancies at unprecedented ease, using the technique of single-electron spectroscopy[1]. As an example, spectra of double *K*-shell pre-edge states in CS_2 and SF_6 will be presented and interpreted with the aid of a high-level theoretical model, which gives excellent agreement with the experiment. The results illustrate the important distinction between direct and conjugate shake-up in a molecular context.

A new class of many-electron Auger transitions in atoms was initially proposed over 40 years ago[2], but the first tentative evidence for its real existence was only adduced by Lee *et al*.[3] in 1993, on the basis of the resonant Auger spectrum of Kr. Using a multi-electron coincidence technique with synchrotron radiation, it was unambiguously shown very recently[4] that the transition suggested by Lee *et al*.[3] in Kr really does take place, but with a rather small branching ratio. Related inter-atomic three-electron transitions in rare gas clusters were predicted some years ago by Averbukh and Kolorenc[5] and demonstrated by Ouchi *et al*.[6]. From consideration of the energy levels involved it seems that the basic three-electron process could occur in molecules too, wherever a double inner-valence shell vacancy lies at a higher energy than the molecular triple ionisation onset. Experiments on CH_3F reveal for the first time[7] the existence of this new decay pathway there, and calculations show that despite its three-electron nature, its effective oscillator strength is orders of magnitudes higher than in atoms, allowing an efficient competition with both molecular dissociation and two-electron decay channels on the ultrafast few femtosecond time scale. The dramatic enhancement of the molecular three-electron Auger transition can be explained in terms of a partial breakdown of the molecular orbital picture of ionisation.

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OC-05

Hybrid Basis Close-coupling Interface to Quantum Chemistry Packages for the Treatment of Ionization Problems

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ABSTRACT

The theoretical description of observables in attosecond pump-probe experiments requires a good representation of the system's ionization continuum. For polyelectronic molecules, however, this is still a challenge due to the complicated short-range structure of correlated electronic wave functions. Whereas Quantum Chemistry Packages (QCP), implementing sophisticated methods to compute bound electronic molecular states, are routine calculations nowadays; comparable tools for the continuum are not yet widely available.

To tackle this problem we present a new approach developed in our group, which, by means of a hybrid Guassian-B-spline (GABS) basis [1] (see Fig. 1), interfaces existing QCPs with close-coupling scattering methods [2]. To illustrate the viability of this approach, we report results for the multichannel ionization of molecular Hydrogen that prove to be in excellent agreement with existing accurate benchmarks. Building on this we present results for molecular Nitrogen, the ionization of which cannot be easily treated by existing methods, thereby showcasing our method's usefulness in the study of ionization in polyelectronic, molecular system.

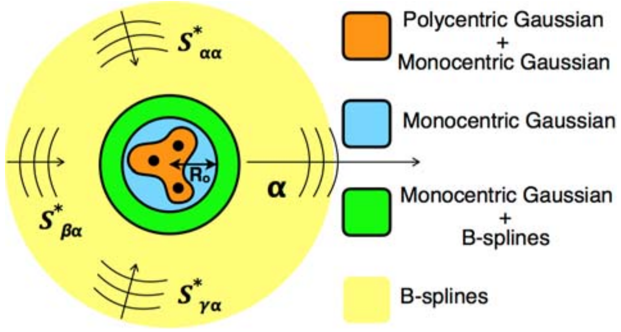

Figure 1 : Schematic depiction of GABS Basis

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Multi Electron Spectroscopy: Auger Decays of the Rubidium 3*d* Hole

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ABSTRACT

The emission of one or two Auger electrons, following 3*d* inner-shell ionization of Rubidium atoms by synchrotron light, has been investigated both experimentally and theoretically.

$$\begin{aligned} \mathrm{Rb} + h\nu \rightarrow \mathrm{Rb}^{+*}\,(3d^{-1}) + e^{-}_{ph} &\rightarrow \mathrm{Rb}^{2+} + e^{-}_{A} \\ &\rightarrow \mathrm{Rb}^{3+} + e^{-}_{A1} + e^{-}_{A2} \end{aligned}$$

All the electrons emitted in the process are detected in coincidence and analyzed in energy thanks to a magnetic-bottle electron time-of-flight spectrometer (MB-TOF) [1, 2]. Rubidium vapor was produced by a homemade resistively heated oven and ionized by soft X-ray region synchrotron radiation from the PLEIADES beamline of the SOLEIL facility.

In a first step [3], the combination of our experimental results with our calculations has enabled, similarly to our previous study on Hg [4], the full determination of the decay pathways and branching ratios. This allowed us to probe the strong electron correlation effects which are specific to the Rb 3*d* Auger decay, due to the presence of the external 5*s* electron of the Rb atom. We also found evidence that shake-down transition can occur during Auger decay. The experimental findings were analyzed by Dirac-Fock configuration interaction calculations using the Grasp2k package and its supporting program libraries.

In a second step, we implemented electron retardation in our MB-TOF in order to improve the resolution on fast Auger electrons. The efficiency of the method was first tested on an atom (Kr) and on a molecule (N_2O), by resolving the Kr $3d_{5/2}^{-1}$ and $3d_{3/2}^{-1}$ Auger spectra [2] and each site-specific N $1s^{-1}$ Auger spectra (from the central or terminal N atoms of the N_2O molecule) with higher resolution than in the present literature [5]. Using this retardation technique, the Rb Auger spectra was recorded with a good resolution, similar to that of the non-coincident Rb 3*d* Auger from the literature [6], giving access to a full identification of the $3d^{-1} \rightarrow 4p^{-2}$ Auger decays.

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ABSTRACTS

Wednesday, March 29th, 2017

SESSIONS 6, 7 & 8

IWP-RIXS 17

Wednesday, March 29th

Chairpersons: A. Naves de Brito, P. Morin, F. Martin

IT-16	Multicoincidence studies of molecular photoionization – Entanglement and wavefunction imaging *R. Dörner*
IT-17	ICD and ICD cascades in multiply excited clusters *A.I. Kuleff*
OC-07	On the computations of decay widths of Fano resonances *T. Miteva*
OC-08	Size-resolved photoemission anisotropies of neutral water clusters and predictions for liquid water *S. Hartweg*
IT-18	Local and non-local electronic and nuclear relaxation processes in aqueous solutions *B. Winter*
IT-19	A superficial look at water *O. Björneholm*
IT-20	From distillation to biomolecules in aqueous surface: Revelations from electron spectroscopy *A. Naves de Brito*
OC-09	High energy photoemission as a probe of ultrafast charge transfer in KCl aqueous solution *D. Céolin*
OC-10	Optical luminescence from liquid water after excitation with Synchrotron Radiation *C. Ozga*
IT-21	Capturing the fastest charge and spin dynamics in nanosystems using high harmonic beams *M. Murnane*
IT-22	Ultrafast non equilibrium dynamics induced by attopulses *F. Remacle*
IT-23	Double imaging coincidences techniques for product determination in gas phase complex mixtures *G. Garcia*
OC-11	Isolated nanoparticles’ surfaces and interfaces probed by soft X-ray photoelectron spectroscopy *M. Patanen*
OC-12	Selective dissociation upon core-electronic excitation in unsaturated hydrocarbons *S. Oghbaie*

Multicoincidence Studies of Molecular Photoionization – Entanglement and Wavefunction Imaging

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ABSTRACT

We will show recent highlights of multiparticle coincidence experiments on photoionization performed with a COLTRIMS Reaction Microscope. We will discuss single photo double ionization of H2 and He where fundamental questions, like the mechanism of double ionization, the role of the photon momentum can be answered and the entanglement between the two emitted electrons can be seen.

We will also show an example of ultrafast dissociation, where the emitted electron allows to visualize the transition from a molecular orbital to an atomic orbital upon fragmentation.

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   Phys.Rev.Lett. 117, 263001 (2016)
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   Phys.Rev.Lett. 116, 043001 (2016)

ICD and ICD Cascades in Multiply Excited Clusters

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ABSTRACT

Exposing atomic or molecular clusters to intense laser pulses will typically result in a multiple ionization of the cluster, even in the cases when the single-photon energy is not enough to directly ionize the cluster constituents. The atoms or molecules of the clusters can absorb more than one photon and use the accumulated energy to eject an electron in a process known as multiphoton ionization. It has been first predicted theoretically [1] and recently confirmed experimentally [2] that if the photon energy of the pulse is on resonance with the lowest excitation of the cluster constituents, another very efficient pathway for multiple ionization of the cluster becomes open. Due to the resonant transition, the cluster first gets multiply excited and then relaxes by emitting electrons via a process in which a pair of neighboring cluster constituents undergoes an interatomic (intermolecular) Coulombic decay (ICD) [3] where one of the species de-excites to its ground state, transferring its energy to ionize another excited species.

It will be shown in the present talk that tuning the laser to a higher resonant transition, a previously unknown type of ICD, intra-Rydberg ICD occurs. In this process, de-excitation of a cluster constituent to a lower-lying excited state leads to electron emission from another neighboring excited species. Moreover, systems multiply excited to higher Rydberg states will decay by a cascade of such processes, producing even more ions compared to the direct ICD transition to the ground state. First experimental observation [4] of the intra-Rydberg ICD and the ICD cascades in multiply excited neon clusters will also be presented and discussed.

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On the Computations of Decay Widths of Fano Resonances

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ABSTRACT

A resonance state of an atom or a molecule is a metastable state with a finite lifetime and sufficient energy to break up into subsystems [1]. In the case of the Auger and interatomic Coulombic decay (ICD) processes, the metastable states can be considered as bound states interacting with a continuum of states [2]. The total decay width of such resonances can then be calculated as a sum of the partial decay widths expressed as coupling elements between the bound Ψ and the continuum parts $\chi_{\beta,\epsilon_\beta}$ of the resonance

$$\Gamma = 2\pi \sum_{\beta=1}^{N_c} \left| \left\langle \Psi \middle| \hat{H} - E_r \middle| \chi_{\beta,\epsilon_\beta} \right\rangle \right|^2$$

The available methods for the calculation of decay widths of Fano resonances are applicable to relatively small systems, such as small rare-gas and metal-water clusters [3, 4]. In order to extend the methodology to larger systems, we present a novel approach to the calculation of decay widths of resonances in singly-ionised systems. In our approach, the bound part of the resonance, Ψ, is approximated at the zeroth order as a one-hole configuration. The final states of the decay, $\chi_{\beta,\epsilon_\beta}$, are obtained after diagonalisation of the Hamiltonian matrix in the space of all two-hole-one-particle (2h1p) configurations with a fixed virtual orbital.

The Fano-CI method can be applied to the computation of both total and partial decay widths. Furthermore, it has fairly low computational costs and can thus be employed for investigating medium-sized atomic and molecular systems. To check the validity of our method, we present benchmark calculations of Auger and ICD widths of small rare-gas and hydrogen-bonded clusters. Comparison with available theoretical and experimental data shows that a satisfactory estimate of the decay width can be achieved with a relatively small basis set, which is of importance for the application of the method to larger systems.

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Size-resolved Photoemission Anisotropies of Neutral Water Clusters and Predictions for Liquid Water

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ABSTRACT

A detailed understanding of low energy electron scattering is of fundamental importance for the modelling of radiation damage in biological systems [1] as well as for an in-depth description of the solvated electron in chemistry [2]. The comprehension of electron scattering in liquids is also crucial for a quantitative interpretation of liquid-jet photoelectron spectra.

We present the first measurements of size-resolved photoelectron angular distributions for the valence orbitals ($1b_1$, $3a_1$ and $1b_2$) of neutral water clusters $(H_2O)_n$ with $1 \leq n \leq 20$ [3]. The measurements were performed over a photon energy range from 12.5 to 35 eV using a photoelectron photoion double imaging coincidence (i^2PEPICO) spectrometer [4, 5]. For a given photon energy, we find a systematic decrease of the photoelectron anisotropy up to a cluster size of 5-6 molecules and convergence of the anisotropy for larger clusters. We suggest that this remarkable convergence results from a local short-range scattering potential that is fully described by a unit of 5-6 molecules. Photoemission anisotropies for liquid water are predicted from the experimental cluster data and accurate scattering calculations. We find reasonable agreement with available experimental liquid microjet data.

The mass-resolved photoelectron imaging data for the water dimer provide new insight into the electronic structure of the water dimer. We are able to distinguish photoionization of the 'monomer-like' $1b_1$ orbital of the hydrogen bond donor from the ionization of the delocalized a_1/b_1 orbital that participates in hydrogen bonding. The observed differences agree well with expectations from theory [6] and previous measurements [7].

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Local and Non-local Electronic and Nuclear Relaxation Processes in Aqueous Solutions

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ABSTRACT

Applications of resonant and non-resonant core-level photoelectron (PE) spectroscopy to liquid microjets for the study of the electronic structure of liquid water and aqueous solutions are presented. Our focus is on the core-level photoemission / relaxation spectroscopy, and especially on the shape of Auger / autoionization electron spectra. The important spectral feature is the high-kinetic energy tail of the Auger spectrum, which has no gas-phase analogue, and hence reflects the participation of solvent water in the relaxation process. For instance, O1s Auger electron spectroscopy from liquid water reveals a novel electronic de-excitation process of core-level ionized water in which a pairs of cations form, either $H_2O^+\cdots H_2O^+$ or $OH^+\cdots H_3O^+$. [1] These reactive species are the delocalized analogue to H_2O^{2+}, formed in a localized on-site Auger decay, and are expected to play a considerable role in water radiation chemistry and biodamage. Both cationic pairs form upon autoionization of the initial ionized water molecule. Isotope measurements show that autoionization also occurs from a series of transient Zundel-type structures evolving from proton transfer, from the ionized water molecule to a neighbor molecule, within a few femtoseconds. The actual autoionization is either through intermolecular Coulombic decay (ICD) or Auger decay.[1,2] These so-called proton-transfer mediated charge separation (PTM-CS) processes are found to also occur in other and similarly hydrogen-bonded solute molecules such as NH_3 (aq), NH_4^+ (aq), or H_2O_2 (aq).[3] Their probabilities strongly correlate with the hydrogen-bond strength which makes autoionization spectroscopy suitable for the characterization of hydration structure. Cationic NH_4^+ (aq) is of particular interest as the relaxation can involve a double-proton transfer to the water solvent which can be understood as a very fast complete chemical reaction.

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A Superficial Look at Water

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ABSTRACT

Water is of key importance for life itself and in numerous environmental and technical processes. Despite its importance and its simple molecular structure, the behavior of liquid water remains enigmatic. Molecules at interfaces have different environments compared to those in bulk water, resulting in various interface-specific phenomena. These are highly challenging to investigate, and our understanding of the water interfaces is therefore in many respects even more incomplete than for bulk water. In addition to their fundamental importance, water interfaces are also crucial in e.g. environmental sciences, biology and technology.

In this talk, I will present some results on aqueous solutions obtained by x-ray photoelectron spectroscopy. First I will exemplify how the aqueous surface differs from the bulk, including both fundamental properties, and examples relevant to atmospheric sciences. Second, I will discuss the possibilities offered by tender x-rays, including decay processes after deep core ionization.

From Distillation to Biomolecules in Aqueous Surface: Revelations from Electron Spectroscopy

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ABSTRACT

The molecular surface of aqueous solutions may show not only physical but chemical properties surprisingly different from the bulk[1]. In this presentation we would like to bring to your attention two topics: ethanol-water distillation and the behavior of biomolecules, such as amino acids, at aqueous interfaces. Distillation started by Greek alchemists in the 1st century AD[2]. One of the key points in distillation is the knowledge of the partial vapor pressure of the ethanol-water mixture as a function of the ethanol molar percentage. Far from linear, the ethanol partial vapor pressure shows a rich behavior [3], which cannot be fully rationalized unless the surface structure on a molecular scale is understood. We plan to show surprising new findings both at low, see fig. 1, and high ethanol concentration obtained with electron spectroscopy. Amino acids, the building blocks of proteins, are of fundamental importance to bio interfaces, but they also play a role in atmospheric aerosols, where they occur due to e.g. decomposition of biomaterial. Amino acids constitute an important fraction of the water-soluble organic nitrogen (WSON) compounds in both marine and continental aerosols, and are involved in many processes in the atmosphere. In the Amazon Basin, the world largest amount of carbon in vegetation, during wet season, aerosols, present in clouds, resembles those from marine environment. MD simulations shows that amino acids may be connected to their effects on surface tension, an important parameter for cloud drop activation. These effects on surface tension depend on the surface density of the amino acids. We plan to show how the presence of key amino acids at the surface change according to the side chain length and other properties. Furthermore we will show that new protonated species of amino acids may be present at the surface but not in the bulk.

Figure 1. Amino acids at aqueous interface and Ethanol-Water surface structure on a molecular scale.

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High Energy Photoemission as a Probe of Ultrafast Charge Transfer in KCl Aqueous Solution

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ABSTRACT

I will present the first high energy photoelectron spectroscopy (HAXPES) experiment performed in the liquid phase at the GALAXIES beamline (SOLEIL Synchrotron, France) [1-2]. We used the recently developed in-vacuum microjet setup specifically designed for our photoemission station in order to measure Auger spectra of a potassium chloride aqueous solution. Associated to calculations, these results allow us to highlight an ultrafast electron transfer occurring on a ~fs timescale. The KLL Auger spectrum of potassium – contrary to chloride – exhibits an obvious large extra structure that is described by configurations corresponding to delocalized states between water and potassium. These states originate from a charge migration from the solvent to the core-ionized potassium ion induced by the photoionization step and occurring on the K-shell core-hole lifetime.

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Optical Luminescence from Liquid Water after Excitation with Synchrotron Radiation

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ABSTRACT

The observation of emitted photons from dense media upon excitation with soft X-rays produced by synchrotron radiation facilities is a valuable method to study their inner structure. It provides not only complementary data to established methods (e.g charged particle detection [1]) but can be included in the toolkit of methods used for the search for liquid water in the universe and therefore extraterrestrial life.

Here, we present an overview of the recent results obtained by a combination of a liquid microjet with a photon spectrometer suited for the detection of photons in the ultraviolet to extreme ultraviolet regime. In particular we could find a broad emission band originating from the liquid phase as well as an interface effect between the liquid phase and the surrounding gas phase. This effect is caused by the Auger electrons ejected from the outer molecular layers of the liquid water phase which excite the gas phase molecules and therefore produce gas phase fluorescence with liquid water like excitation behavior.

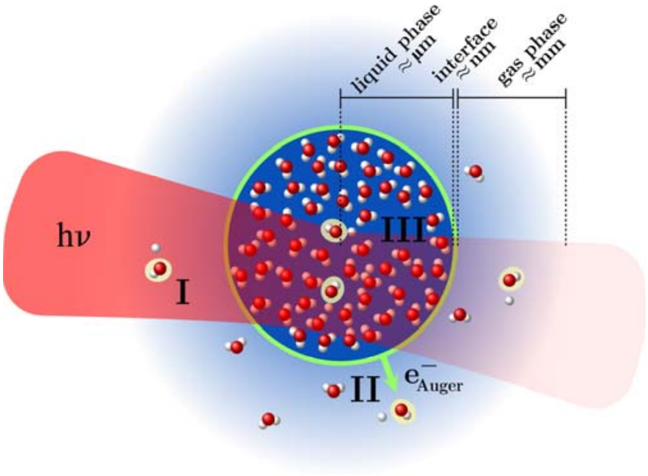

Illustration of the different processes :
(I) Direct excitation of the gas phase water by soft X-Rays leads to known atomic emission lines (II) Gas phase molecules excited by Auger electrons produced in the liquid phase produce molecular emission lines with liquid like excitation behavior (III) Transient species originating from the impinging of soft X-Rays produce a broad luminescence band

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Capturing the Fastest Charge and Spin Dynamics in Nanosystems using High Harmonic Beams

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ABSTRACT

High harmonic generation (HHG) is a unique quantum light source with fundamentally new capabilities – producing fully spatially and temporally coherent beams with linear or circular polarization throughout the extreme ultraviolet (EUV) and soft X-ray region, all on a tabletop. This talk will review recent developments in HHG sources, as well as exciting advances in imaging and spectroscopy of materials.[1-5] It is now possible to image below the wavelength limit in the EUV/x-ray region for the first time, by combining HHG sources with coherent diffractive imaging (CDI) techniques. Moreover, in recent work we measured the shortest lifetime of any state to date, at 212±30 attoseconds, corresponding to an excited state in the band structure of a material. More recently, In particular, a new technique called attosecond-ARPES (angle resolved photoemission) harnesses HHG pulse trains to measure the fastest electron dynamics intrinsic to materials, making it possible to distinguish sub-femtosecond electron scattering and screening for the first time. Finally, bright, phase matched, circularly and linearly polarized HHG now span from the EUV to the soft X-ray region at kHz repetition rates, ideally suited for a host of applications in science and technology.

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Ultrafast Non Equilibrium Dynamics Induced by Attopulses

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ABSTRACT

The recent developments in the generation of optical attopulses suggest that it will soon become experimentally feasible to induce and subsequently directly probe ultrafast charge transfer between the end moieties of modular molecules. One ultrafast pulse creates a non-stationary state of the neutral or of the cation, that can be probed by a second pulse. Such experiments would allow characterizing a purely electronic time scale, before the coupling to the nuclei takes place. This is a pre Born-Oppenheimer regime where the electronic states are not stationary.[1] Our next goal is to investigate how the onset of nuclear motion and subsequently the fate of a chemical reaction can be controlled through the non equilibrium electronic density resulting from the interaction with a strong ultra short excitation pulse.

We will report on the simulation of realistic pump probe experiments that monitor the ultrafast non equilibrium electronic dynamics using a coupled equation scheme that includes the ionization continua and field effects in LiH,[2] in the medium size bifunctional molecule PENNA ($C_{10}H_{15}N$)[3], in C_{60}[4] and in ICCH.[5] We will then discuss the role of nuclear motion in the diatomic molecule LiH using full electron–nuclei quantum dynamics computation.[6] These computations show that the ultrafast beatings of the electronic coherences in space and in time are modulated by the different periods of the nuclear motion but survive for a large number of vibrational periods, see Figure. Our results also show that dissociation to specific asymptotes can be controlled through the CEP phase of an essentially one cycle IR pulse. Recent simulations on the non equilibrium dynamics for two nuclear degrees of freedom in HCN show that the electronic coherences persist for several vibrations as well.

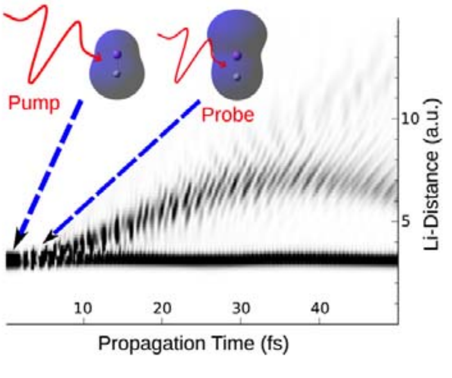

Figure. Heatmap of the time evolution and space localization of the vibronic wave packet pumped by a single cycle IR pulse (800 nm) in the LiH molecule. The time and space localization of electronic coherence created between the GS and the 1st excited Σ state is modulated by the vibrational motion on these two potentials.

Acknowledgments: This work is supported by FRFC 2.4545.12, FRFC T.0132.16 and DoE AMOS DE-SC0012628.

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Double Imaging Coincidences Techniques for Product Determination in Gas Phase Complex Mixtures

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ABSTRACT

Full detection of all products involved at any given time on a chemical reaction is considered as the ultimate goal, leading to a complete description of the reaction mechanism and therefore to its control. Optical methods, although very sensitive, lack the required universality needed for complex determinations. Because every species can be ionised, mass spectrometry also appears as a method of choice, however extensive fragmentation due to the high energy ionisation sources in commercial spectrometers, and the inability to differentiate structural isomers limit its usability. In the past decade, several groups have combined mass spectrometry with VUV tuneable sources in order to minimise fragmentation by ionising close to the first threshold (soft ionization), and to record the photoion efficiency (PIE) curves as a function of photon energy, which provide structural information, as demonstrated in complex systems such as low-pressure flames.[1]

Because the amount of structural information contained in the PIEs is limited, a more recent development that increases sensitivity and isomer differentiation will be discussed here. Although photoelectron-photoion coincidence (PEPICO) techniques have been applied extensively to acquire detailed knowledge on photoionisation processes since the early seventies, it is only recently that are being applied for advanced product detection in complex gas phase media.[2,3]

I will present examples of application of modern double imaging PEPICO (i^{2}PEPICO) techniques in combination with tuneable VUV synchrotron radiation for the study of complex systems of environmental interest such as low-pressure flames,[4] secondary organic aerosol formation,[5] isoprene oxidation, and enantioselective analysis of essential oils, such as pepper oil.

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Isolated Nanoparticles' Surfaces and Interfaces Probed by Soft X-ray Photoelectron Spectroscopy

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ABSTRACT

The electronic structure of unsupported nano-objects has long been of fundamental interest, as abrupt changes and surprising quantum phenomena appear when single atom properties evolve to the collective electronic properties of infinite solids. However, also from the applied point of view the investigation of free-standing nano-sized matter is now more timely than ever: their unique, size-scalable properties are exploited in industrial applications like in fluorescent quantum dots, and nano-objects have been found to be ubiquitous in nature with impact on human health and climate. In either their use for catalysis applications or in naturally occurring chemical reactions of atmospheric nano-aerosols, the electronic structure of the surface critically determines their chemical reactivity. Therefore, studying the structure of the first layers of nanomaterials is of utmost importance, when it comes to surface sensitive techniques probing the electronic structure of matter, there is no other like soft X-ray photoelectron spectroscopy. In this progress report, we will describe some recent soft X-ray spectroscopy studies of unsupported nano-matter carried out at the PLEIADES beamline at the Synchrotron SOLEIL (Saint-Aubin, France). We have been able to follow the oxidation of Si nanocrystals of different sizes in ambient air [1] and *in situ* when nanocrystals were exposed to a thermal treatment (heating) in flight. As a second example, we will present the surface characterization of carbon dots. Being highly biocompatible and fluorescent, they are promising alternatives to metal-based quantum dots for biomedical applications, but there is still a lack of understanding of their structure and of the origin of their fluorescence.

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Selective Dissociation upon Core-electronic Excitation in Unsaturated Hydrocarbons

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ABSTRACT

The influence of a localized core hole on subsequent electronic processes of molecules has long been debated, where the role of symmetry breaking and the competition between electronic decay and nuclear dynamics are major factors determining whether the memory of the initial core hole is retained. We investigate the fate of core hole localized at different sites and bonds by using tunable synchrotron radiation to selectively excite core electron to valence orbital. Dissociative double ionization using synchrotron radiation, ion-ion coincidence imaging spectroscopy [1], and *ab-initio* quantum calculation are studied to disentangle nuclear dynamics preceding dissociation channels [2,3], by which we pinpoint the significance of core hole symmetry breaking on the subsequent dynamics [4].

Study of site-selective C1s to π^* excitation in butadiene, a prototype for polyene molecules, shows localized dissociation after terminal carbon excitation, while no strong localization effect is visible after central carbon excitation. It appears that out-of-plane symmetry breaking around the terminal carbon and nuclear wave packet dynamics of the core hole state are mechanisms enhancing the ultrafast hydrogen migration and asymmetric C-C bond dissociation. The site-selective symmetry breaking is justified due to different bonding character of the occupied π^* orbital on the terminal and central sites. Since in polyene molecules this character alternates between successive carbon atoms, inner-shell spectroscopy studies on larger polyenes should shed light on other factors that can affect symmetry breaking, site-selective or statistical dissociation dynamics.

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ABSTRACTS

Thursday, March 30th, 2017

SESSIONS 9 & 10

IWP-RIXS 17

Thursday, March 30th

Chairpersons: M. Žitnik, A. Föhlisch

IT- 24	Photoionization dynamics: Transition and scattering delays *R. Taïeb*
OC-13	What can we learn from electronic-state lifetime interference in atoms and molecules? *R. Püttner*
OC-14	Photodamage and photostability of halogenated uracils under XUV HH radiation *R. Cireasa*
OC-15	Attosecond interferometry with self-amplified spontaneous emission of a free-electron laser *T. Laarmann*
OC-16	Role of electron-nuclear coupled dynamics on charge migration induced by attosecond pulses in glycine *M. Lara-Astiaso*
IT-25	X-ray Raman spectroscopy *S. Huotari*
IT-26	Interference effects in high-resolution X-ray spectra *M. Žitnik*
IT-27	Soft X-ray experiments of samples under atmospheric pressure: X-ray emission studies of liquids, solutions, gases and interfaces at SPring-8 BL17SU *T. Tokushima*
OC-17	Probing the trans-and Cis-isomerization of azobenzene with RIXS *Z. Yin*
OC-18	Hydrogen-bonding network of water confined in a polyelectrolyte brush *K. Yamazoe*

Photoionization Dynamics: Transition and Scattering Delays

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ABSTRACT

Resolving electron motion in atoms and molecules on its natural attosecond (as) scale is way beyond the temporal resolution of available detection devices. The techniques developed to achieve such attosecond resolution thus rely on interferometric setups [1]. In fact, the reported times are actually group delays derived from phase measurements, involving coherent photoemission processes. Therefore, the analysis of the experimental data and the related theoretical development ask for rigorous and unambiguous definitions and interpretations of these phases, and of the inferred group delays [2].

It is now accepted that a "scattering delay" [4] affects the dynamics of any photoemission process. However, the simplicity of the underlying physics is not fully recognized yet. Formally, such delays are imprinted in the phase shifts of the photoelectron wave-functions, which are commonly expressed on the basis of incoming waves. In this framework, the "scattering phase" associated to photoemission appears as the argument of the transition amplitude, thus obscuring the significance of the delay - which may be misinterpreted for example as a transition duration.

Here, we will present the benefits of working with the continuum wave-functions selected by the transitions (scwf) [3], which (i) carry all the information related to the continuum reached by photoabsorption, (ii) are defined independently of the arbitrary basis one chooses to work with and (iii) are real valued for single-photon transitions. They provide a clear-cut interpretation of the scattering delays.

In higher order processes, the scwf comes with an additional complex phase, as soon as the transition is resonant. We will show that the group delay associated with that phase can now be interpreted as a "transition delay", and how it can be accessed experimentally in a straightforward reinterpretation of the rabbit interferometric technique, initially designed for the characterization of coherent xuv pulses.

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What can we Learn from Electronic-state Lifetime Interference in Atoms and Molecules?

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ABSTRACT

Core excitation and subsequent resonant Auger processes that populate the same final state via two or more different core-excited intermediate states cause electronic-state lifetime interference (ELI) if the different excitation and decay pathways are experimentally indistinguishable. This prerequisite is fulfilled in case of strongly overlapping core-excited states, i.e. processes that involve deep core holes with short lifetimes, and can be observed in the partial cross sections leading to a given Auger final state.

The contributions of ELI to the partial cross sections are described by the lifetime interference terms that contain the product of the matrix elements for excitation and decay of two indistinguishable ways that lead to the same final state. Due to the absence of squares of the matrix elements these lifetime interference terms can have positive or negative signs. We present a fit model that allows determining the electronic-state lifetime interference terms in the $2p^{-2}nl$ partial cross sections formed during the resonant Auger decay subsequent to $1s^{-1}$ excitations. We apply this model to Ar 1s core-excited states [1] as well as Cl 1s core-excited states of the molecules HCl and CH_3Cl [2].

For Argon the sign of the lifetime interference term depends on the overlap integral of the excited state orbital in the core-excited and the final state. In particular, the sign is positive when the final state is populated via spectator or shake-down Auger decay and negative for shake-up Auger decay. This observation is in line with results for resonant Kr $3d^{-1}nl$ excitations [3]. For argon we were also able to determine the probabilities of different decay channels from a given intermediate state. For molecules, this fit model allows us to disentangle overlapping core-excited states with different symmetry. In particular, we were able to determine the intensity ratios of the overlapping states Cl $1s^{-1}4p\pi/1s^{-1}4p\sigma$ in HCl and Cl $1s^{-1}4pe/1s^{-1}4pa_1$ in CH_3Cl. The experimental value for HCl is compared with theoretical results showing satisfactory agreement [4].

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Photodamage and Photostability of Halogenated Uracils under XUV HH Radiation

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ABSTRACT

In the last decade, the high harmonic generation (HHG) has emerged as a new photon source capable to provide structural and dynamical information, including (sub)-femtosecond arrangements of nuclei and electrons. Currently, the HH radiation is also used for investigating more complex molecules of interest for chemistry and biology.

5-Halouracils (5-HaloU) belong to a particular class of biomolecules called radiosensitisers that enable to use radiation damage for therapeutic purposes. When utilised in combined chemo- and radio-therapy treatments to replace the Thymine in the DNA of the tumour cells, they enhance the lethal effects of the UV, X-ray, proton and γ radiation on these cells.

To study the dynamics underlying the photo-stability and the radiation damage of 5-HaloU (5FU and 5BrU) occurring under the XUV radiation, we have employed ultra-short XUV pulses produced by HHG and broadband 800 nm probe pulses. The XUV pulse durations were either 1.5 fs or 10 fs and their associated energy domain spectra corresponded to a modulated quasi-continuous spectrum or to a frequency comb where the harmonics were separated by 6 eV, respectively. The ensuing dynamics was detected by recording mass spectra as a function of the pump-probe delay. These mass spectra indicate that the parent ionisation is followed by complex dynamics involving ring opening reactions, proton/hydrogen transfer, multichannel and sequential dissociations. The dynamics extracted from different fragment ion signals suggest that the same photoprotection mechanisms as those conferring photostability to the neutral nucleobases and to the DNA appear to be activated. The molecules are excited to a state around 10.5 eV that undergoes an ultrafast relaxation on a timescale of 30 fs due nonadiabatic interactions followed sequentially by 2.3 ps internal conversion. [1] For both FU and BrU, proton migration dynamics were observed for the time dependences of couples of fragments separated by one mass unit. An ultrafast decay of about 40 fs was observed for the transient signal of m/z=43 (HNCO) and the complementary rising behaviour on the same timescale was observed for m/z=44, which can be only formed by H/H^+ transfer via tautomerisation. Similar behaviours, although slower, were measured for m/z=31 (FC) (~80 fs) and m/z=32 and for the equivalent BrU fragments. These dynamics may be associated tautomerisation and isomerisation processes where the difference in the H/H^+ transfer timescales is determined by the initial and final sites of the transfer and, in particular, to the involvement of the halogen atom.

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Attosecond Interferometry with Self-amplified Spontaneous Emission of a Free-electron Laser

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ABSTRACT

Science with short-wavelength free-electron lasers (FELs) has enabled multiple breakthroughs covering the broad range from basic research in life sciences to applications in material science and catalysis. Particularly, the high degree of spatial coherence of the light field allows for key applications such as serial-femtosecond X-ray crystallography using the well-established and robust self-amplified spontaneous emission (SASE) of FELs[1]. Recently, temporal coherence provided by seeded FELs moved into the focus of interest[2-4]. It has been shown that full control over the light phase allows for a new class of light-phase sensitive experiments in the short-wavelength limit[5-7], such as non-linear four-wave mixing[8] and attosecond (1 as = 10^{-18} s) coherent control[9]. These give novel opportunities to study and possibly control energy and charge migration in molecular systems of increasing complexity with unprecedented spatial and temporal resolution.

Here, we demonstrate attosecond phase control in a Michelson-type all-reflective interferometric autocorrelator using monochromatic SASE pulses at $\lambda = 38$ nm. The resulting fringe contrast monitors the field interference when varying the relative phase within the optical cycle, i.e. the FEL oscillation with a period of 129 ± 4 as. The successful transfer of a powerful table-top method towards FEL science and technology paves the way towards utilization of advanced nonlinear methodologies for watching the transformation of electronic orbitals in real time.

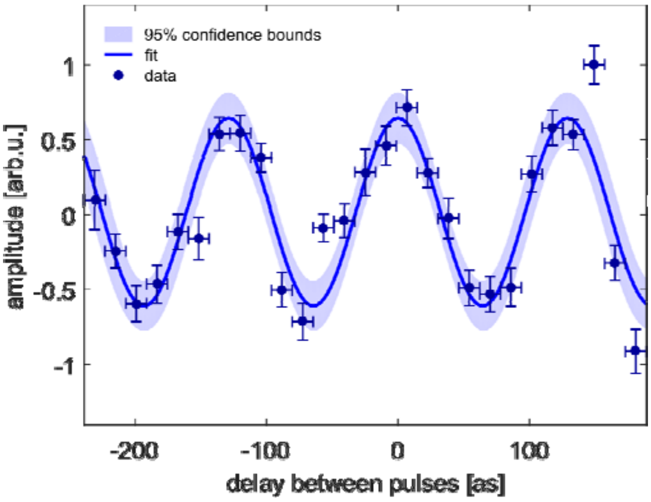

Fig. 1 Interferometric autocorrelation recorded with FEL (SASE) pulses.

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Role of Electron-nuclear Coupled Dynamics on Charge Migration Induced by Attosecond Pulses in Glycine

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ABSTRACT

Quantum Mechanics states that the expectation value of an hermitian, time independent operator will exhibit a temporal dependence if the system is described by a non-stationary state of that operator. In other words, any superposition of eigenstates of a given system leads to a time varying observable, such as the probability density. This lies at the core of the so-called ultrafast charge migration, concept introduced by Cederbaum and Zobeley in the nineties to describe the charge fluctuations occurring in the attosecond time scale upon sudden ionization of a molecule [1]. Investigations of ultrafast charge migration were partly inspired by the pioneering work of Weinkauf and coworkers on peptides chains [2]. However, the first experimental observation of this phenomenon obtained with attosecond resolution has only been achieved in 2014 for the amino acid phenylalanine [3]. These findings have drawn much attention of the scientific community and new theoretical approaches are being developed to provide a solid knowledge of these ultrafast processes that are ultimately responsible of the subsequent chemical response of the biological system. Most of existing methods describe the process by assuming that the ionization is triggered through a sudden transition from the ground state, avoiding the evaluation of ionization amplitudes [4]. And, even in those works where the ionization step is more accurately represented [3, 5], the nuclei remain frozen, which is expected to be a reasonable approximation in the first tens of femtoseconds [6]. In this conference, we will present our progresses to achieve a complete theoretical description of the ultrafast charge migration triggered in glycine molecule, which include both an accurate evaluation of the ionization step and the nuclear degrees of freedom in the time propagation. We employ a Static-exchange DFT-based approach [7] to extract reliable ionization amplitudes, while the correlated electron-nuclear dynamics of the ionic subsystem is obtained from a TDDFT-Ehrenfest simulation. We will also show recent simulations to demonstrate how the choice of the ionizing laser pulse modifies the ensuing charge dynamics, thus opening the door to the control of charge-directed reactivity in biologically relevant molecules.

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X-ray Raman Spectroscopy

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ABSTRACT

Non-resonant inelastic x-ray scattering from core-electron excitations is called x-ray Raman scattering (XRS). The process and information obtained from it is similar to that obtained by X-ray absorption spectroscopy (XAS) as well as by electron energy loss spectroscopy (EELS).

Soft-x-ray RIXS or XAS studies may sometimes encounter difficulties in certain cases when information from the bulk of materials, from buried systems is needed, or from samples that not compatible with vacuum. XRS spectroscopy offers alternative possibilities to study such cases. XRS lifts all constraints on the sample environment inherent to soft x-ray studies, and offers access to bulk-sensitive information on solids, liquids and gases as well as systems in enclosed sample environments such as high-pressure cells. For example the microscopic structure of water within the supercritical regime has been recently studied using the oxygen K-edge excitation spectra measured by XRS, yielding new information on the hydrogen-bond network of water in extreme conditions [1]. Another important feature of XRS is that it allows for other than dipole transitions to be studied, thanks to an practically unlimited range of momentum transfer offered by hard x-rays. These higher order multipole excitations can yield novel information on the electronic structure [2], not accessible by many other spectroscopies. The availability of XRS instruments at third generation synchrotron radiation sources has made highly accurate XRS measurements possible. XRS can be even used as a contrast mechanism in three-dimensional X-ray imaging [3]. New beamline is now available for XRS studies at the European Synchrotron Radiation Facility [4]. The capabilities of XRS and recent examples of novel studies allowed by it will be reviewed.

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Interference Effects in High-resolution X-ray Spectra

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ABSTRACT

For Rydberg series converging to a core-hole ionization threshold the emission spectrum is dominated by the spectator-type transitions. After photoemission process an electron most probably remains in initially unoccupied outer orbital enabling a specific intermediate state to evolves into a specific final state because for single core-hole states the configuration mixing is weak. The interference effects are therefore practically absent in the emission spectrum despite the fact that initial core-hole broadening is large enough to generate ambiguities about which intermediate state exactly was excited by photon absorption. However, this lack of knowledge does not upgrade to a sizeable interference effect because each final emission state is predominantly associated with only one intermediate state [1].

The situation changes dramatically when two electrons are excited into unoccupied orbitals. Since spectral density of two-electron-two-hole states is large, there are many overlapping resonances that are strongly mixed in the configuration space due to electron-electron correlations. A change of the potential, caused by the electron jump in the core redefines the active orbital set but still, many final states have considerable dipole matrix element with many different intermediate states. This means that several different absorption-emission paths from the ground to the specific final state can have comparable amplitudes making the transition probability strongly dependent on path interferences. Technically, in Kramers-Heisenberg equation the contribution of interference terms becomes important and photon in–photon out cross section cannot be factorized into the photoabsorption and photoemission part. The situation gets further complicated if emission dynamics involves an additional non-radiative electron jump – the radiative Auger decay [2].

The interferences modulate only the shape of the emission spectrum while its total intensity (as a function of photon-in energy) still follows the photoabsorption profile, provided the fluorescence branching ratio of the transition does not change [3]. A well-known advantage of high resolution x-ray spectroscopy is that it can remove core-hole broadening of the photoabsorption profile (HERFD). While this is efficiently done in point-to-point focusing configuration, a parallel accumulation of a given emission spectrum over a full range of emission energies is needed for RIXS interference studies [4]. We will present experimental and theoretical aspects of K-M emission from doubly photo-excited $K^{-1}M^{-1}V^2$ states in argon considering also the corresponding KM-M^3 radiative Auger decay [5].

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Soft X-ray Experiments of Samples under Atmospheric Pressure: X-ray Emission Studies of Liquids, Solutions, Gases and Interfaces at SPring-8 BL17SU

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ABSTRACT

Experiments using soft x-rays (around 400 to 1000eV) is normally considered to require vacuum condition because of strong absorption by oxygen and nitrogen molecules in air. However, owing to recent developments of experimental technique, soft x-ray spectroscopy is becoming one of a choice for experimental study of samples under atmospheric pressure.

For example, atmospheric pressure cell using ultra-thin (~150nm) film windows, which enable photon-in photon-out experiments of soft x-rays, becomes available for liquids and solutions. We have developed a liquid flow-through cell at SPring-8 BL17SU, and have studied liquids including water[1-3], acetic acid [4], aqueous solutions [5-7], binary mixtures [8, 9] and an ionic liquid[10] by means of x-ray absorption and emission spectroscopy in soft x-ray region. It is also possible to measure gas sample using the cell by flowing gaseous samples instead of liquids without large modifications. We have studied x-ray emission spectra of oxygen gas [11, 12] using the cell. Measurements of solids are possible by exchanging air by helium. We have developed a high temperature cell and succeeded to measure heating solid samples related to solid oxide fuel cell at 600°C under helium environments [13]. It is a large advantage that one can explorer electronic state with the same method for three forms of matter, i.e. gas, liquid and solid.

In the talk, our soft x-ray studies concerning liquids, solutions and gas molecules will be discussed. In addition, an ongoing project on liquid-solid interfaces of electrodes will be introduced.

ACKNOWLEDGMENTS

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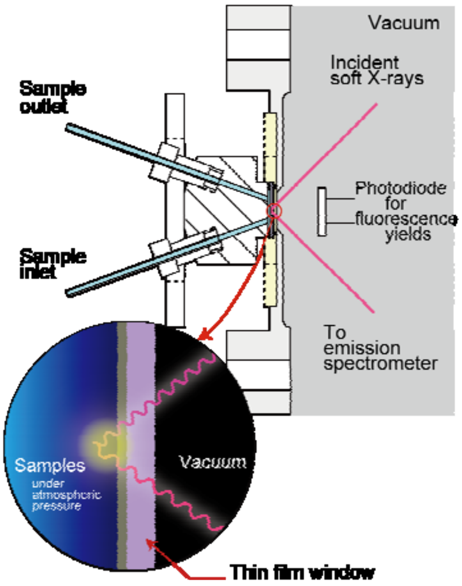

Figure 1 Schematic drawing of a liquid flow cell for soft x-ray spectroscopy.

Probing the *Trans*-and *Cis*-Isomerization of Azobenzene with RIXS

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ABSTRACT

Photo isomerizations are typical reactions in the field of photochemistry. Generally, they are of utmost importance in biochemistry as they are key step in the process of vision and they trigger the motion of biological entities towards light. Practically, they are being assessed in the growing field of organic electronics. Understanding photo isomerization is also essential for their successful application in various branches of material science like molecular switching devices or molecular diodes.[1-3]

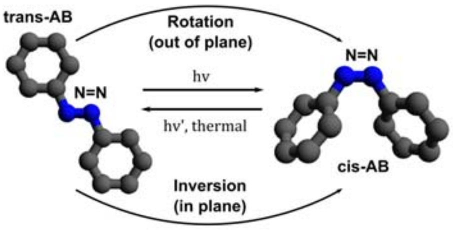

Figure 1: The *trans-cis* Azobenzene (AB) isomerization is proposed to either go through a torsional movement around the N=N double bond or through an in plane movement of the phenyl ring.

Though intensively investigated, so far no detailed study about the valence structure of *trans*- and *cis*- azobenzene exists. We report for the first time resonant inelastic X-ray scattering (RIXS) results of *trans*- and *cis* azobenzene dissolved in ethanol on the nitrogen K-edge.[4] The results reveal remarkable insights into the different pathways of the isomers after core-excitation. We observe a Raman like signal in the X-ray regime for *trans*- and *cis*-isomers. For the *cis*-isomer an additional peak arises, revealing a transition suppressed in the *trans*-state due to different hybridization thereby making the electronic structure of *trans*- and *cis*-isomers distinguishable. Optical dark states become visible utilizing RIXS.

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Hydrogen-bonding Network of Water Confined in a Polyelectrolyte Brush

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ABSTRACT

Unique hydrogen-bonding structure of water in the vicinity of polyelectrolytes should significantly affect the specific structure and functions of biomolecules[1], which consist of several biomolecular polyelectrolytes. Polyelectrolyte brushes[2], which represent high-density charged polymer chains immobilized on the substrate, are well suited for investigating the local structure of water that is not only in the vicinity of polyelectrolytes but also confined by these brushes.

In this study, soft X-ray absorption (XAS) and emission spectroscopy (XES) were used to investigate the hydrogen-bonding structure of water confined in a polyelectrolyte brush. XAS and XES are excellent tools for not only providing information about the strength of hydrogen-bonding but also characterizing local symmetry of the hydrogen-bonding. Detailed analyses of distinct electronic structures from XAS and XES spectra provide constructive information about the hydrogen-bonding network of water.

The polyelectrolyte brush was prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) on a 150 nm thick SiC membrane with a Au layer on the top (NTT-AT) according to a previously reported procedure[2]. O 1s XAS and XES experiments of water confined in the polyelectrolyte brush were performed at the SPring-8 synchrotron radiation facility using the BL07LSU HORNET station[3]. The polyelectrolyte brush was exposed to water vapor in order to absorb water into the bulk of the brush.

The XES spectrum of water confined in a poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC) brush was compared with those of the dry PMTAC brush in vacuum, bulk water and ice. The results indicated that the water confined in the PMTAC brush almost lacks the $1b_1$'' peak, which means the confined water is highly hydrogen bonded like ice. Slight enhancement of the $3a_1$ peak compared to ice may also indicate a uniform distortion of hydrogen bonds.

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ABSTRACTS

Friday, March 31st, 2017

SESSIONS 11 & 12

IWP-RIXS 17

Friday, March 31st

Chairpersons: M.N. Piancastelli, J. Bozek

IT-28	Multi-electron electron effects in inner-shell ionization of ions *S. Schippers*
IT-29	One- and two-color photoionization of atomic ions formed within an intense free-electron laser pulse *M. Meyer*
IT-30	Photoionization of ions stored in traps : From small carbonated systems to large biopolymers *A. Giuliani*
OC-19	Dissociation dynamics of energy-selected methyl halide ions (CH_3X^+, X=F, Cl, Br) investigated by Synchrotron photoelectron photoion coincidences *X. Tang*
IT-31	Coherent control experiments with the fully coherent free electron laser FERMI *K. Prince*
IT-32	Hard X-ray photonics with intense X-ray laser pulses *H. Yoneda*
IT-33	X-ray pump -- X-ray probe spectroscopy *A. Picón*
OC-20	Molecular femtodynamics at FERMI *M.N. Piancastelli*
OC-21	Control of H_2 dissociative ionization in the non-linear regime using EUV femtosecond pulses @ FERMI *F. Holzmeier*

Multi-electron Electron Effects in Inner-shell Ionization of Ions

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ABSTRACT

Experiments on photon-ion interactions are technically challenging because of the low particle densities of ionic targets which are orders of magnitude lower than the typical densities of neutral gas targets. The photon-ion merged-beams technique (see [1] for a recent introductory review) partly makes up for the low target density by providing an elongated interaction volume and a high detection efficiency of heavy photoproducts. In recent years, a consortium of German university groups has implemented the photon-ion merged-beams method at the world's currently brightest 3rd generation synchrotron light source, i.e., PETRA III at DESY in Hamburg, Germany. The PIPE[1] setup [2] started operating in 2013 and, since then, a number of studies have been carried out on inner-shell ionization of positively charged atomic ions [2-5], atomic anions [6] and endohedral fullerene ions [7,8]. Particular attention has been given to the determination of *absolute* cross sections for multiple ionization and, thus, to quantitatively map out the branching into the various final charge states resulting from the complex de-excitation cascades after the creation of a core-shell hole. For example, in K-shell ionization of singly charged carbon ions, the triple Auger process – a genuine four-particle interaction - could unambiguously be identified and the associated decay rate be determined with high precision [4]. In my talk, I will review the first results from the PIPE setup, which provide intriguing insight into the highly correlated many-particle dynamics that is initiated by the inner-shell ionization of ions.

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[1] Photon-Ion spectrometer at PETRA III

One- and Two-color Photoionization of Atomic Ions Formed within an Intense Free-electron Laser Pulse

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ABSTRACT

The availability of XUV and X-ray Free Electron Lasers (FELs) providing intensities up to 10^{16} W/cm^2 has enabled many investigations of non-linear processes in the short wavelength regime [1]. Sequential ionization was identified as the main mechanism driving the formation of highly charged states, which were observed using ion spectroscopy. A more detailed understanding of the underlying dynamics can be obtained by electron spectroscopy enabling the differentiation of ionization channels as well as of the processes photo-induced in different ions. Therefore, the detailed investigation of sequential ionization does not only allow to obtain insight into the multi-photon ionization dynamics, but also to perform dedicated photoionization experiments on ionic targets, including studies of the electron emission, which is often extremely challenging using other experimental configurations.

In a first series of experiments, intense XUV radiation from the FERMI FEL in Italy was combined with an NIR optical laser to study the photoionization of excited states in the He+ ion [2]. Using circularly polarized FEL pulses and tuning its wavelength to the 1s-3p excitation in the ion we were able to resonantly orient the He+ 3p(m=+1) magnetic substate and to control the population of this state by a helicity dependent AC Stark shift generated by an overlapped NIR laser. For the subsequent multi-photon ionization of this state by the NIR laser, the angular distribution of the produced low-kinetic energy electrons and the circular dichroism in the angular distribution (CDAD) for this process could be determined. The experimental results are well described by theoretical models based on solving the non-relativistic time-dependent Schrödinger equation (TDSE), which explains the strong intensity dependence of the dichroism as the result of a helicity dependent AC Stark shift. In this scenario, the NIR laser is used to control the excitation and the ionization of the excited states in the singly charged helium ion.

In a more recent experiment, the non-dipole effect in the photoionization of the Ar+ ion was investigated by angle-resolved photoelectron spectroscopy at FERMI [3]. Similar to the experiment on helium, the argon ions are produced during the sequential ionization induced by the intense FEL pulses. In the electron spectra, the ionization from the neutral ($\mathrm{Ar}\ 3p^6 + h\nu \rightarrow \mathrm{Ar}^+\ 3p^5 + \varepsilon l$) can be clearly distinguished from the ionization of the ion ($\mathrm{Ar}^+\ 3p^5 + h\nu \rightarrow \mathrm{Ar}^{2+}\ 3p^4\ (^1S,\ ^1D,\ ^3P) + \varepsilon l$) allowing a very detailed comparison with theoretical predictions [4]. The experimental data are in good qualitative agreement with theory demonstrating a clear non-dipole effect in the investigated energy region, but challenges also the theoretical models, since the strength of the effect exceeds the original theoretical predictions.

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Photoionization of Ions Stored in Traps : From Small Carbonated Systems to Large Biopolymers

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ABSTRACT

Until recently, spectroscopy of ions was performed in merged beam experiments. In these setups, the ions of interest are arranged in a beam, which is merged with probe particles, such as electrons [1] or photons.[2,3] Merged-beam experiments have been used to measure absolute photoionization cross sections of atoms and small molecules, such as CO or C_{60},[4] in the extreme UV and soft X-ray regime. However, a difficulty in the technique comes from the ion source, which produces targets under ground and metastable excited states. In the beginning of the century, ion traps have been started to be used for ion spectroscopy using synchrotron radiation at Elettra [5] and Bessy.[6] In these experiments, ions were produced respectively from electron impact ionization of the gaseous precursor or from sputtering. In order to reach for other precursors, we have coupled a linear ion trap with VUV [7] and soft-X ray beamlines at SOLEIL, which is fitted with various atmospheric pressure ion sources, such as electrospray ionization (ESI) and atmospheric pressure photoionization (APPI).

Thanks to the APPI source, the photoionization cross section of C_{60} has been reinvestigated.[8] The competitions between ionization and fragmentation has been studied for a large panel of polyaromatic hydrocarbons (PAH).[9] Using ESI sources, larger system have been brought into the gas phase, such as peptides and proteins. Especially, the dependence of the ionization energy of three proteins as a function of their charge state has been investigated.[10]

Ion trapping devices are very versatile, allowing various kinds of ion to be studied. The ability of traps to cool down precursor allows complementing efficiently the merged beams methods.

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Dissociation Dynamics of Energy-selected Methyl Halide Ions (CH_3X^+, X=F, Cl, Br) Investigated by Synchrotron Photoelectron Photoion Coincidences

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ABSTRACT

As one type of important chemical reagents and benchmark for high symmetry polyatomic molecules, methyl halide neutrals and ions have attracted a great deal of attention in the past. More concretely, the dissociation of methyl halide ions is fundamentally interesting since they usually undergo specific reactions into different products depending on the ions' state and halide substituent. In this talk, I will present our recent researches on vacuum ultraviolet photoionization and dissociative photoionization of methyl halides (CH_3X, X=F, Cl, Br) investigated by using two novel photoelectron photoion coincidence (PEPICO) setups, the DELICIOUS III double imaging PEPICO spectrometer at Synchrotron SOLEIL, France, [1,2] and the threshold PEPICO (TPEPICO) imaging spectrometer at National Synchrotron Radiation Laboratory (NSRL), China [3]. The low-lying electronic states of CH_3X^+ ions were prepared and analyzed and a series of fragment ions such as CH_2X^+, CHX^+, CH_3^+ and CH_2^+ were observed in experiments. Especially the high-resolution kinetic energy release distributions (KERDs) in the dissociation were acquired from electron and ion kinetic energy correlation diagrams or TPEPICO ion images. Then the detailed dissociation mechanisms of energy-selected CH_3X^+ ions, prepared in the low-lying electronic states, as well as outside the Franck-Condon region, have been analyzed and exhibit a state-specific character [4-6]. In addition, the performances of the two PEPICO setups at two synchrotron facilities and their different characters will be compared and discussed too.

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Coherent Control Experiments with the Fully Coherent Free Electron Laser FERMI

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ABSTRACT

Pulsed optical lasers are characterized by high intensity, ultrashort duration, variable polarization, transverse coherence and longitudinal coherence. The majority of short wavelength Free Electron Lasers (FELs) are based on Self-Amplified Spontaneous Emission (SASE) and have poor longitudinal coherence. However, many optical experiments required this coherence, for example, Schultze *et al*. [1] used an IR pulse of approximately 3 fs duration to measure a temporal delay of 21 attoseconds. This is only possible with high-precision phase locking, and without coherence and phase control, the time resolution at short wavelengths is limited to the temporal duration of the pulse.

The seeded FEL FERMI is the first FEL to produce fully coherent pulses. As well, commensurate wavelengths (different harmonics of the same seed wavelength) were predicted to be mutually phase coherent. We have demonstrated experimentally the longitudinal phase correlation between two colours (first and second harmonics), and applied it to coherently control a photoionization experiment [2]. Neon was ionized at wavelengths of 63.0 and 31.5 nm, and the asymmetry of the 2p photoelectron angular distribution (PAD) was manipulated by adjusting the phase, in a Brumer-Shapiro type experiment [3]. The outgoing 2p electrons, ionized by one (second-harmonic) photon or two (first-harmonic) photons interfere to give an asymmetric PAD whose asymmetry depends on the relative phase of the two photon fields. The relative phase of the two wavelengths was locked and tuned with temporal resolution of ~3 as. The extremely precise manipulation of the phase in the present experiment is based on the use of phase shifters located be-tween the radiators of FERMI.

Further two-colour results [5] will also be presented, showing that homodyne detection can be used to observe single-photon Laser Enabled Auger Decay [6], which has been predicted but not previously observed, and to coherently control the process.

The flexible design of FERMI permits new operating modes of the machine [4], for example to perform Tannor-Rice or pump-dump type experiments, and results will be shown.

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Hard X-ray Photonics with Intense X-ray Laser Pulses

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ABSTRACT

After the success of inner-shell-excited hard x-ray lasers, the x-ray emission from matter can also be controlled by induced emission. Recently we have demonstrated control of the branching ratio between Kα1 and Kα2 emission and have obtained a narrow Kα emission profile, smaller than the natural width, by controlling the seeding of a Kα laser. Now, we have also succeeded to control the temporal pulse shape, spectral broadening and to obtain a narrower spectrum of Kα emission for various material conditions. This controllability is a sign of realization of useful photonics in the hard x-ray region. The present talk will discuss application of these controlled hard x-ray laser pulses.

X-ray Pump -- X-ray Probe Spectroscopy

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ABSTRACT

Novel accelerator-based and laser-based sources allow the generation of femtosecond and attosecond x-ray/XUV pulses. This has opened new perspectives to track in "real time" molecular processes in the natural time scale of electron and nuclei motion. Molecular phenomena initiated by the absorption of an x-ray/XUV photon is one of the most challenging questions for these novel sources [1]. Two-color femtosecond x-ray pulses with controlled time delay enable the study of x-ray induced phenomena with x-ray probing. The site-specificity of those photons allow the excitation of inner-shell electrons in a particular site of the molecule and, with a controlled time delay, the probing of the induced intramolecular dynamics in another site of the same molecule [2]. Also, novel XUV/x-ray sources with a high spatio-temporal degree of coherence are suitable for quantum control schemes involving inner-shell electrons. In this talk, we present new theoretical and experimental results towards this direction and discuss the perspectives of this exciting field.

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Molecular Femtodynamics at FERMI

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ABSTRACT

To follow the dynamics of a molecular species interacting with electromagnetic radiation on a very short time scale is a sought–after goal. A novel method to achieve it will be illustrated [1]. The unique performances of the FERMI seeded free-electron laser (FEL) in Trieste, Italy, have been exploited to follow the photoexcitation-deexcitation and fragmentation dynamics of a complex molecule, acetylacetone, by pump-probe experiments on the 50-femtosecond (fs) time scale. Electron and ion spectra have been measured with a magnetic bottle spectrometer after pumping with a UV-vis laser at 266 nm and probing with the FERMI monochromatic beam at 19.23 eV, up to a total pump-probe delay of 200 picoseconds (ps). The main event revealed by the ion spectra is a fragmentation process leading to the ejection of the methyl group which subsequently undergoes further fragmentation until the carbon is stripped of all hydrogens. In the photoelectron spectra, the transition from the S_2 ($\pi\pi^*$) singlet state to the S_1 ($n\pi^*$) state and finally the relaxation to the T_1 ($\pi\pi^*$) state are clearly reflected by the evolution over time of the spectral features in the binding energy region corresponding to the ionization of the excited acetylacetone. The ultrafast photodynamics of acetylacetone has been enlightened in great detail, with the aid of state-of-the-art *ab initio* static and surface-hopping dynamics calculations. The novelty of our results consists of the achievement of valence photoelectron spectra with sufficient resolution to observe subtle electronic structure changes, coupled with complementary ion spectra obtained in the same conditions, and interpreted on the ground of state-of-the-art static and dynamic calculations. We intend to proceed along this new path by applying the same experimental and theoretical tools to the study of photochemical reactions.

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Control of H_2 Dissociative Ionization in the Non-linear Regime using EUV Femtosecond Pulses @ FERMI

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ABSTRACT

The unique properties of the FERMI free electron laser (FEL) delivering bright, coherent and tunable EUV femtosecond (fs) pulses were exploited to photoionize H_2 molecules in a non-linear 2-photon process via resonantly excited neutral intermediate states. Selective excitation of the vibrationally resolved $H_2^*(B\ ^1\Sigma_u^+$, v=8-17) and $H_2^*(C\ ^1\Pi_u$, v=2-4) states using 100 fs FEL pulses in the 12-15 eV range enabled us to investigate the influence of the nuclear degree of freedom (DOF) on the outcome of photoionization: depending on the intermediate state's internuclear distance expansion, absorption of the second photon leads to dissociative (DI) and/or non-dissociative ionization (NDI).

Time-of-flight (TOF) mass spectrometry, together with electron and ion velocity map imaging (VMI), were employed on the LDM beamline [1] to analyze the DI/NDI ratio, kinetic energy spectra and angular distributions of photoelectrons and H^+ fragment ions. A drastic enhancement of DI of about two orders of magnitude compared to one-photon ionization was demonstrated, as predicted by time-dependent Schrödinger equation calculations for 1-10 fs pulses and accounting for the DOF of electrons and nuclei [2,3]. Excitation of isolated $H_2^*(B\ ^1\Sigma_u^+$,v) levels even leads to situations where DI dominates NDI, which is very unusual for valence shell ionization. For such cases, the ion fragment energy spectra display clear oscillations, which reflect a projection of the intermediate state vibrational wave function onto the ionic $H_2^+(2p\sigma_u)$ dissociative state. Analogous structures are found in the photoelectron spectra for electrons correlated to DI. Those spectra moreover yield access to the vibrational distribution of the $H_2^+(X\ ^2\Sigma_g)$ ground state for NDI. The latter is quite sensitive to the vibronic intermediate state and therefore provides an additional probe of the induced nuclear dynamics. New calculations based on time-dependent second order perturbation theory, well adapted to the 100 fs EUV pulses as utilized in the experiment, are in progress.

The remarkable anisotropies observed in the ion and electron angular distributions complement the characterization of the photoionization dynamics. Furthermore, the electron angular distribution provides a sensitive means to characterize quantum interferences resulting from the coherent superposition of indistinguishable reaction paths. The results of a first experiment support the feasibility for coherent control [4] of NDI involving two-EUV-photon resonant and one-XUV-photon non-resonant channels, relying on the variable controlled phase available at FERMI between the fundamental and second harmonic FEL pulses.

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POSTER SESSION

List of Poster

PO-01	Bi-elliptical High-harmonic Spectroscopy as a Probe of Matter: From Atomic Orbitals to Chiral Molecules *D. Baykusheva*
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PO-03	About the Feasibility to Perform PES on Ionic Species *J-M. Bizau*
PO-04	Diffraction Effects in the Recoil-frame Photoelectron Angular Distributions of Fluoromethane *C. Bomme*
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PO-14	Interatomic Decay Mechanisms in Noble Gas Clusters Investigated by Photon Spectroscopy *A. Hans*
PO-15	Probing the OH Stretch in Different Local Environments in Liquid Water *Y. Harada*

PO-16	Relativistic Configuration Interaction Calculations for RIXS-MCD of 3d Transition Metal Oxides *H. Ikeno*
PO-17	Developments of Electrochemical Cell for Soft X-ray Spectroscopy *T. Ishihara*
PO-18	Imaging Ultrafast Molecular Wave-packets with a Single Chirped UV Pulse *D. Jelovina*
PO-19	X-ray versus Auger Emission Following Xe 1s Photoionization *L. Journel*
PO-20	Energy Sharing in the Triple Auger Decay of Potassium 2p Holes *M. A. Khalal*
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PO-23	Photoionization and Ionic Dissociation of the C_3H_3NS Molecule Induced by Soft X-rays Near the C1s And N1s Edges *A. F. Lago*
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PO-25	Relativistic Effects in the Photoionization of Outer and Near-outer Subshells of Free and Confined High-Z Atoms *S. T. Manson*
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PO-27	Role of the Super Atom Molecular Orbital (SAMO) Electronic States in the Photoionization of Fullerenes *B. Mignolet*
PO-28	Experimental and Theoretical High-energy Resolution X-Ray Absorption Spectroscopy: Implications for the Investigation of the Entatic State[1] *P. Müller*
PO-29	Measurement of Angularly Resolved Spectral Phase for the Fano Resonance in Argon *S. Nandi*
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PO-33	RIXS on $Ba_3M_{2-x}Ir_{1+x}O_9$ *A. Revelli*
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PO-36	Hard-X-ray-induced multistep ultrafast dissociation: multistep core-hole-clock approach *O. Travnikova*
PO-37	Rescattering Electron Spectroscopy And Geometric Structure Retrieval On C_2H_4 Molecules *K. Ueda*
PO-38	Time-resolved Observation of XFEL Induced Dynamics in CH_2I_2 Molecule *K. Ueda*
PO-39	Nanoplasma Produced by a Femtosecond Hard-X-ray Laser Pulse in Xenon Clusters *K. Ueda*
PO-40	Sequence-specific Ionization Potentials of Oligonucleotides Correlated with VUV-induced DNA Strand Breaks *S. Vogel*
PO-41	Mean Free Paths of Slow Electrons from Velocity Map Imaging of Aerosol Particles *B. L. Yoder*
PO-42	Picosecond X-ray Tracking of Optically Driven Molecular Dynamics *L. Young*

Bi-elliptical High-harmonic Spectroscopy as a Probe of Matter: From Atomic Orbitals to Chiral Molecules

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ABSTACT

Development of coherent ultrashort XUV sources with tuneable polarization will enable the study of phenomena such as spin polarization[1], molecular symmetry-breaking[2], or chiral light-matter interactions[3] on an ultrafast time scale. One appealing scheme for generating highly elliptical high-harmonic radiation consists in combining a circularly polarized fundamental field with its counter-rotating second harmonic[4]. The resulting spectrum is composed of pairs of harmonics (*3q+1*) and (*3q+2*) of opposite helicities while every third (*3q*) harmonic is absent in a three-fold symmetric medium. Static bi-circular measurements of the harmonic emission from a series of noble gases (Ne, Ar, Kr, Xe) performed at different wavelengths (800 – 2000 nm) of the fundamental reveal that the relative strength between the (*3q+1*) and (*3q+2*) peaks is a characteristic signature of the atomic orbital. Furthermore, this ratio is very sensitive to the presence of destructive interferences in the photoionization cross section such as Cooper minima.

We interpret our results with the aid of an adapted version of the quantum-orbit model[5] by decomposing the temporal structure of the harmonic emission into complex electron trajectories. Our results reveal that the observed differences arise from interfering quantum paths on the one hand and from different recombination amplitudes to the p_+- and p_--components of the atomic ground state on the other.

Bi-circular, or more generally bi-elliptical fields enable efficient HHG at large ellipticities of the driving fields, thus opening the path towards dichroism studies[3]. In a second series of measurements, we follow the high-harmonic amplitude of an isotropic ensemble of chiral molecules subject to a bichromatic field (950+1900 nm) as the polarization of each frequency component is varied from linear to nearly circular[6]. The observed difference in the response of the *(R)*- and *(S)*-enantiomers of methyl oxirane amounts to ~3%, a value that is by one magnitude smaller than recently predicted by theory[6].

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Laser-driven Attosecond Dynamics in Photoionization of Hydrogenic Molecules

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ABSTRACT

High-harmonic generation techniques are nowadays commonly employed to generate ultrashort pulses that are able to retrieve real-time information of electron dynamics in matter. State-of-the-art experimental set-ups have recently provided images of electron motion upon photoionization of atoms and molecules with unprecedented attosecond resolution, capable of capturing the build-up of Fano profiles in He [1] or a charge migration process in a biomolecule [2]. In this framework, measurements of photoionization time delays have also attracted great interest, using pump-probe protocols to estimate the elapsed time between the photon absorption and the electron emission that follows. Experimentally, this information can be retrieved using attosecond electron streaking schemes, using a XUV attosecond pulse with a phase-controlled IR field [3], or from the RABBITT (reconstruction of attosecond beating by interference of two-photon transitions) spectrum resulting after the interaction of trains of attosecond pulses with IR radiation [4]. Atomic targets have been used in most existing works [3,4]. In molecules, however, the presence of the nuclear degrees of freedom enriches the available information, but also complicates its extraction, as evidenced by recent controversial discussions [5,6].

We will present our progress on photoionization of H_2 using XUV-IR pump-probe schemes to extract attosecond electron dynamics information from the resulting photoelectron-photoion coincident spectra. First, in the context of electron streaking, we analyze the signature of autoionization in the dissociative and non-dissociative ionization channels. We study the features associated to these highly correlated electronic states and to the nuclear motion. We extract fully angle and energy-differential photoelectron distributions. These are asymmetric as a consequence of the coherent population of states of different parity, which can be associated to the same or to different ionic states left behind [7]. In either case, the asymmetry can be solely induced by the IR-field or mediated by the delayed autoionization event. We will show the dependence of the relative contribution of these two mechanisms in the resulting asymmetry as a function of the time-delay between the XUV and the IR field. Secondly, we aim to elucidate the distinct features obtained when using trains of attosecond pulses instead of an isolated pump pulse, and present ab initio calculations and simple models to retrieve the molecular photoionization time delays in each context.

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About the Feasibility to Perform PES on Ionic Species

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ABSTRACT

Up to now, all the attempts performed to study the photoionization of ionic species using photoelectron spectroscopy (PES) and synchrotron radiation have encountered limited success. The main reason is the very low density of the ionic targets which can be focused into the source volume of an electron spectrometer, typically five or six orders of magnitude lower than what is usually achieved in experiments on gas phase targets. Since the few pioneering experiments in the 90's [1,2], only the high brilliance of the free electron lasers (XFEL) has allowed to obtain electron spectra on ionic species [3-5].

We will present at the conference the first results we have obtained on the photoionization of xenon [6] and silicon ions by inserting on the merged beam setup of the PLEIADES beam line at SOLEIL a cylindrical mirror analyzer (CMA) electron spectrometer [7].

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Diffraction Effects in the Recoil-frame Photoelectron Angular Distributions of Fluoromethane

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ABSTRACT

We have measured the recoil-frame photoelectron angular distributions (RF-PADs) for inner-shell photoionization of the halomethanes CH_3F for photoelectrons up to 280 eV in the gas-phase. For these high kinetic energies, the RF-PADs are dominated by diffraction effects that encode information on the molecular geometry in the RF-PADs.

Molecular-frame photoelectron angular distributions (MF-PADs) provide deep insights into the molecular photoionization process that give access to an unprecedented level of detailed information such as phases of photoelectron waves [1, 2], localization of core holes [3], and double-slit interference [4,5]. When interpreting MF-PADs in terms of photoelectron diffraction [6,7], direct information on the geometric and electronic structure of the molecule can be obtained , e.g., by comparing the measured diffraction patterns and MF-PADs to single and multiple scattering calculations [8, 9,10, 11, 12].

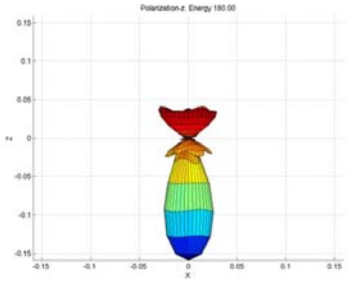

Figure 1: MSXa calculation of MF-PADs after F(*1s*) photoionization of CH_3F for 180eV photoelectron kinetic energy. Light propagation axis and molecular C-F axis are parallel(along z axis).

For these high kinetic energies of 100eV and above, the Recoil Frame Photoelectron Angular Distributions (RF-PADs) are dominated by diffraction effects that encode information on the molecular geometry in the RF-PADs. In order to illustrate this in more detail, we are now in the process of comparing our experimental results to single and MSXa multiple scattering calculations [11,12] .

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VUV Photoionization Study of Freestanding Graphene Nanoflakes Produced by an Aerosol Source

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ABSTRACT

Graphene nanoflakes (GNFs) are monolayers of up to few hundred carbon atoms arranged in a honeycomb lattice with hydrogen- or hydroxyl-terminated edge carbons. As a consequence of their finite dimensions, electronic and optical properties of GNFs depend on the number of constituent carbon atoms, the arrangement of the lattice (i.e. armchair or zigzag), and their chemical environment.

In this contribution, we present the results of the valence photoelectron spectroscopy of freestanding GNFs using VUV synchrotron radiation. The GNFs were produced by fragmentation of the graphene oxide aerosol particles of 130 nm average size impinging on a heated porous tungsten thermodesorber tip and investigated *in situ* by photoelectron/photoion coincidence (PEPICO) spectroscopy at 10 and 12 eV photon energies. The experiments were performed in the SAPHIRS chamber equipped with the DELICIOUSIII electron/ion imaging coincidence spectrometer of the DESIRS beamline at Synchrotron SOLEIL [1].

The mass spectra revealed the presence of m/z=504, 578, and 652 GNFs in the system that match the nanoflakes with up to 42, 48, and 54 carbon atoms, respectively. The changes in the valence band structure of the freestanding GNFs with the change in their molecular mass were followed by analyzing the photoelectron spectra corresponding to the specific nanoflake of the given mass owing to the PEPICO detection scheme. The performed PEPICO experiments coupled with appropriate theoretical calculations [2] would open up a possibility of associating the recorded valence photoelectron spectra of gas phase GNFs with their lattice organization.

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Robust Control of Molecular Excitation using Chirped Airy-pulses

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ABSTRACT

We report on adiabatic population control in molecules using intense shaped femtosecond laser pulses. The laser pulses employed are spectrally phase-shaped using a combination of second and third order dispersion, resulting in chirped Airy-pulses[1]. These pulses offer a variety of different temporal amplitude and phase shapes to optimally adapt to the laser-induced intramolecular excitation dynamics[2,3]. Third order dispersion (TOD) results in temporally asymmetric Airy-pulses featuring gentle slopes as well as rapidly varying amplitude profiles. Group delay dispersion (GDD) provides time-dependent frequency sweeps -chirps -being essential for adiabatic control scenarios[4]. In our experiments, we investigate the interaction of GDD-TOD-shaped pulses with potassium molecules serving as a prototype system for coherent control scenarios. We support our experimental studies by quantum dynamics simulations in order to model the interaction processes and extract the quantum control mechanisms at play.

Chirped temporal Airy-pulses offer a wide range of different temporal pulse shapes. The combination of fast and slow varying features of the amplitude and time dependent instantaneous frequency of the electric field offer the possibility of fast, efficient and robust control over the electronic populations in molecules. First results on the potassium dimer reveal the selective addressing of different molecular states. The measured landscapes are nicely reproduced by simulations, taking into account volume and orientation averaging. Further simulations at higher intensities suggest a robust topology of the measured photoelectron yield landscapes. In ongoing experiments, we explore this regime of higher pulse intensities and expand the parameter range. In addition, we investigate numerically the effect of the instantaneous frequency of the laser pulse and the molecular resonance frequency on the wave packet dynamics and the final population distribution.

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Attosecond Transition Dynamics in Two-photon Ionization

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ABSTRACT

Attosecond science has recently allowed revisiting the fundamental concept of photoemission in the time domain, revealing ionization delays ranging down to few attoseconds in the gaz, solid and liquid phases[1].

All these experiments were performed using attosecond XUV pulses to initiate the 1-photon process and IR pulses to probe it, in the so-called RABBIT (attosecond pulse train, APT) or streaking (single attosecond pulse, SAP) regimes. In such schemes, the interpretation of the measurements is only possible if one properly accounts for the contribution of the IR probe to the phase accumulated by the photoelectron, from which the 1-photon ionization group delay is derived.

Here, we show how the phase accumulated during the transition precisely characterizes the dynamics of photoelectrons produced in *2-photon* (XUV-IR) transitions, by means of numerical experiments on simple model systems. We further show how the transition group delay can be accessed in different reinterpretations of the RABBIT setup, at various levels of accuracy[2,3,4], and point out the links with non-resonant[5] and resonant[6,7] 1-photon delay measurements using APTs.

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Gamma Radiation Effect on Debye Temperature and Exciton-phonon Coupling in InGaAs/GaAs/AlGaAs(δ-Si) HEMTs

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ABSTRACT

In this work, we investigate the gamma radiation effects on the optical properties of δ-Si-doping InGaAs/GaAs/AlGaAs **High Electron Mobility Transistors (**HEMT) grown by molecular beam epitaxy on (100) oriented GaAs substrates. Photoluminescence measurements are used to determine electron and hole relaxation process in the InGaAs/GaAs/AlGaAs (δ-Si) HEMTs. Low and room temperatures PL spectra show the optical transitions that occur between the fundamental states of electrons to holes in the InGaAs and GaAs channels. For more information about the carriers dynamics in the examined structures, we studied their interactions with the crystal lattice, energy level defects, the energy level thermal activation through the analysis of the PL spectrum evolution depending on the temperature. Gamma radiation has affected the Debye temperature and Exciton-Phonon Coupling in δ-Si-InGaAs/GaAs/AlGaAs structures.

Keywords: Gamma radiation, Debye temperature, Exciton-Phonon Coupling, Photoluminescence.

Ab Initio Calculations of Multidimensional Potential Energy Surfaces of H2O and H2S for K-edge Resonant Inelastic X-ray Scattering

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ABSTRACT

Insight into the potential energy landscape is crucial for understanding chemical properties, dynamics and reactions of molecules and molecular systems. The potential energy surfaces are in general multidimensional and anharmonic. Theoretially this means that we need to move past the framework of the harmonic approximation and combine molecular degrees of freedom to accurately model the potential energy surfaces.

High-resolution resonant inelastic X-ray scattering (RIXS) makes it possible to selectively probe the electronic environment and ultrafast nuclear dynamics at the core-excited atom. When the electronic broadening is quenched, as in the case of quasi-elastic K-edge RIXS, we can obtain a detailed mapping of the ground state potential energy surface [1], even with vibrational selectivity introduced by the dynamics in the core-excited states [2]. Probing the KL-edge RIXS we can get a picture of the local electronic energy landscape of the final core-excited state as well as dynamical information [3].

To help pinpoint the mechanisms active in the RIXS process, theoretical tools can help give further us insight into the details of the experimental spectra, e.g. by generation of accurate multidimensional potential energy surfaces. For calculation of the initial, intermediate and final state potential energy surfaces, the multi-configurational restricted active space approaches (RASPT2) are particularly powerful. Using RASPT2, we can model the ground state as well as target specific core-excited states, during dissociation and including relativistic effects. In two separate studies of H2O (g) and H2S (g) we have used the RASPT2 method to accurately compute multidimensional potential energy surfaces of the ground state and core-excited state for quasi-elastic K-edge scattering in H2O and ground state, core-excited state and final state for $K_{\alpha,\beta}$-edge RIXS in H2S.

The aim of this presentation is to highlight and discuss the similarities and interesting differences in the potential energy landscapes for these two systems. I will present a sophisticated theoretical methodology for calculating multidimensional potential energy surfaces and compare the theoretical findings to high-level RIXS measurements.

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Electronic Structure of Pyrochlore $Lu_2V_2O_7$ Studied by Resonant Inelastic X-ray Scattering

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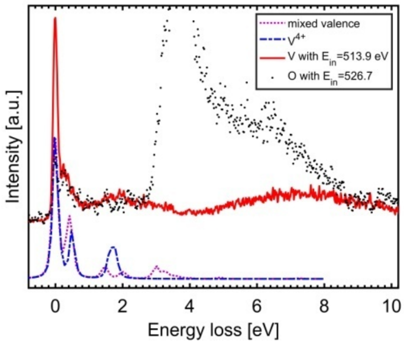
ABSTRACT

The specific structure of pyrochlore leads to the presence of the geometrical frustration. With the orbital ordering towards the centre of tetrahedron, the ferromagnetic interaction between neighbours arise this frustration, e.g. ferromagnetic $Lu_2V_2O_7$. Certain prototypes of frustrated magnets possess a thermal Hall conductivity.[1] In the case of $Lu_2V_2O_7$, it displays the magnon Hall Effect, and harbors the similar thermal Hall conductivity. [2] By using resonant inelastic X-ray scattering (RIXS) technique[3], we have studied the electronic structure of V L_3 (2p-3d) and O K (1s-2p) edges on single crystal $Lu_2V_2O_7$ with orientation [111]. With the high overall energy resolution (140 meV), the d-d excitations on these RIXS spectra dose not illustrate the theoretically discrete feature peaks from V^{4+}; instead presence of continuous spectral shape and additional peak from other formal valence which imply that initial ground state should depend on time evolution. Measured orbital excitations with similar peak positions in both V L_3 and O K data originate from the high 2p3d orbital hybridization. Considered single formal valence states (V^{3+}, V^{4+}, and V^{5+}), the crystal-field multiplet calculations[4] performed for vanadium ions are consistent with the measured spectra. These phenomena indicate that spin current induced electric field[5] results in the dynamic mechanism of itinerant electron confined in the cluster Mott-insulator[6].



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A Beamline for Attosecond UV Pump - XUV Probe Experiments: Towards Tracking Electron Dynamics in DNA Bases

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ABSTRACT

Upon UV photo-exposure, DNA nucleobases become electronically excited. This process potentially favors mutagenic miscoding of the DNA sequence[1]. Our goal is to investigate with attosecond time resolution the UV-induced electron dynamics in DNA bases and to understand the role of this ultrafast dynamics in the photochemical processes occurring at later times.

To this end a versatile attosecond beamline has been designed for UV-pump XUV-probe experiments. Few-fs UV pulses are used to resonantly excite the biomolecules, while XUV isolated attosecond pulses are used to probe the following dynamics via photo-fragmentation.

Near-infrared (NIR), 5-fs pulses with 2.5 mJ energy, 1 kHz repetition rate, and a residual single-shot CEP fluctuation of ~200 mrad (rms) are obtained by hollow-core fiber compression of 25 fs, 6 mJ, 800 nm pulses[2]. A first portion of the NIR beam is used to generate 220-as XUV pulses via high order harmonics generation[3,4]. A second portion of the NIR beam is used to temporally characterize the XUV pulses[5]. Finally, the remaining portion of the NIR beam is used to generate broadband UV pulses (sub-5fs) with 100-nJ energy per pulse in a high-pressure gas cell, exploiting the third harmonic generation process. The three beams are properly recombined and collinearly focused in the experimental chamber.

A biomolecular source has also been developed in order to produce a molecular beam of DNA bases. The source is based on the combination of a pulsed valve operating at 100 Hz with an oven. The molecules produced by evaporation are efficiently transported to the experimental chamber by the buffer gas. This source provides a sufficiently dense target to perform UV-pump XUV-probe photo-fragmentation experiments.

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K-Shell Photionization of Oxygen Ions: Experiment and Theory

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ABSTRACT

Single and multiply ionization stages of C, N, O, Ne and Fe have been observed in the ionized outflow in the planetary nebulae NGC 4051, measured with the satellite XMM-Newton [1] in the soft-x-ray region. Multiply ionization stages of O and Fe are also seen in the XMM-Newton spectra from the Seyfert galaxy NGC 3783, in-cluding UV imaging, x-ray and UV light curves, the 0.2–10 keV x-ray continuum, the iron K-emission lines, and high-resolution spectroscopy in the modelling of the soft x-ray warm absorber [2].

We present detailed measurements of the absolute K-shell single photoionization cross sections for O^+ to $O5^+$ were measured for the first time by employing the ion-photon merged-beam technique at the PLEIADES beam line, SOLEIL synchrotron-radiation facility [3] Theoretical predictions are made from the SCUNC, MCDF and RMPS methods to compare with the measurements. These calculations enable the identification and characterization of the very strong 1s→2p and up to the K-edge region in most of them. The first measurements in the isonuclear sequence of these ions on O^{3+} [4], the experimental and theoretical data of O^+ and O^{2+} [5] and the data for the O^{4+} and O^{5+} is published recently (Online: Nov. 22, 2016) [6]. I will present the data in the conference with comparison with previous measurements on N and C data as will with the evidence comparison with the astrophysical observed data.

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PECD of Amino-acid Proline: Free Gas Phase Molecule and Homochiral Nanoparticles

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ABSTRACT

The studies of photoelectron circular dichroism (PECD) on chiral systems, including biomolecules, has been a subject of rapidly increasing interest and activity. This chiroptical effect leads to very pronounced forward/backward asymmetries in the photoelectron angular distribution (PAD) with respect to the light's propagation's axis when using circularly polarized light. PECD has been used to probe absolute configuration, electronic and static (isomers, conformers) and dynamical (vibrational effects) molecular structures [1]. In addition, a possible link with the origin of homochirality of life has been reported [2].

In the course of my PhD project, and after the complete study of the simplest chiral amino-acid alanine [3], we are extending the PECD study to a particular alpha-amino-acid: Proline, which is the only naturally occurring amino acid containing a pyrrolidine (secondary amine) side chain. This provides proline-rich proteins with specific structural properties.

Free proline was brought into the gas phase by aerosol thermodesorption (TD) to study its PECD over a large VUV range with a double imaging electron/ion coincidence (i^2PEPICO) spectrometer. Several temperatures were used in order to vary the Boltzmann conformer population of the nascent Pro in order to perform a complete conformer analysis with the help of CMS-Xα calculations [3]. A large asymmetry of 12% at the Lyman α (10.2 eV) energy was found for the HOMO orbital, which is 3 times larger than alanine, but interestingly of the same sign. In the future, we will use a complementary method which is the resistive heating (RH) coupled to an adiabatic expansion which provides higher signal and better resolution, and the comparison with TD-method will allow to identify and discard any possible spurious decomposition compounds.

I will also present preliminary studies on proline chiral nanoparticles where two effects may compete: first the forward/backward asymmetry related to PECD which is also observed in the measured angle-resolved PAD, and second the shadowing effect due to the large particle size compared to the ionizing wavelength and to the finite escape depth of the photoelectrons [4].

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Interatomic Decay Mechanisms in Noble Gas Clusters Investigated by Photon Spectroscopy

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ABSTRACT

In recent years, several non-local autoionization and related processes like Interatomic Coulombic Decay (ICD), Electron Transfer Mediated Decay (ETMD), and Radiative Charge Transfer (RCT) were found to be the dominant decay channels of excited weakly bound clusters [1]. Because of the genotoxicity of slow electrons – a typical decay product of such processes – they attracted attention and were investigated extensively in theory and experiment. Whether the impact of these mechanisms plays an important role for natural chemical and biological processes is currently under discussion.

Noble gas clusters, with weak van-der-Waals bounds, are prototypical systems for both theory and experiment, and were investigated for different sizes and compositions by various methods. While most early experiments used the spectroscopy of charged particles, the detection of photons can give additional, complementary information and has the benefit of large escape lengths of photons from dense samples. Recently, we demonstrated the possibility of detecting resonant ICD by measuring fluorescence in different spectral ranges [2,3, see figure].

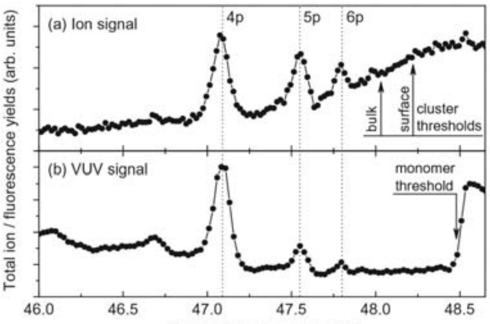

Figure: The occurrence of resonant ICD was unambiguously proven by the direct correspondence of emitted vacuum-ultraviolet photons and energetic ions after resonant 2s-*n*p excitation of neon clusters [3]. Also the characteristic slow ICD-electrons were detected (not shown here) [2].

Here, we report on the progress in the investigation of interatomic decay mechanisms using photon detection. We demonstrate the first determination of absolute cross sections of an ICD-process following photon absorption. Using time resolved detection, we show the efficient discrimination between atomic and cluster signal in a partially condensed jet.

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Probing the OH Stretch in Different Local Environments in Liquid Water

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ABSTRACT

We use X-ray absorption spectroscopy (XAS) to selectively excite different structural subensembles in liquid water. With improved sensitivity we resolve vibrational losses in the subsequent X-ray emission (XES)[1-3] and connect the thus observed OH-stretch vibrational frequencies[4] with the different parts of the OH-stretch optical Raman spectrum and can thus assign these to molecules in specific structural environments in the liquid. The present study proposes a unified interpretation of X-ray and vibrational spectroscopic data in line with a picture of two classes of structural environments in the liquid at ambient conditions with predominantly close-packed, high-density liquid (HDL) and occasional local fluctuations into strongly tetrahedral, low-density liquid (LDL).

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Relativistic Configuration Interaction Calculations for RIXS-MCD of 3*d* Transition Metal Oxides

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ABSTRACT

Resonant inelastic x-ray scattering (RIXS) is a rapidly developing spectroscopic technique to observe the element specific electronic structure in materials. RIXS is a *photon-in/photon-out* spectroscopy, thus it contains much richer information compared to the x-ray absorption spectroscopy (XAS), which is the first-order optical process. The magnetic circular dichroism of RIXS (RIXS-MCD) has also attracted attentions for a promising technique for investigating the magnetic structure of compounds. Recent developments of high-resolution monochromator and detector enable us to measure the RIXS spectra in high-energy resolution. On the other hand, the role of theoretical calculations for the interpretation for spectra is incomparably important. On the other hand, the role of theoretical calculations for the interpretation for spectra is incomparably important.

In this work, we developed the fully relativistic configuration interaction (CI) method for simulating the transition metal (TM) $L_{2,3}$-edges and *K*-pre-edge RIXS, which enable us to directly probe the 3d electrons playing dominant role on wide range of properties of TM compounds. Similar to the case of TM-$L_{2,3}$ XAS, the shape of those RIXS spectra are dominated by the multiplet effects arising from the strong electronic-correlations between core-2p and 3d electrons. In this method, the 2p-3d multiplet effects are explicitly taken into account by expanding the many-electron wavefunctions as linear combinations of Slater determinants corresponding to all possible electronic configurations among those orbitals. The relativistic effects are fully taken into account by solving the Dirac equation instead of Schödinger equation. This approach has already been applied for reproducing TM-$L_{2,3}$ XAS and XMCD[1-3]. The differential scattering cross-section of RIXS in arbitrary scattering geometries and photon polarization can be calculated following the Kramers-Heisenberg formula[4] using the CI wavefunctions corresponding to the initial, intermediate, and final states of RIXS process. The origin of peaks appearing in RIXS spectra can be interpreted in terms of the compositions of electronic configurations in each multiplet state.

In this presentation, some benchmarking results and recent application the relativistic CI method for RIXS-MCD will be shown.

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Developments of Electrochemical Cell for Soft X-ray Spectroscopy

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ABSTRACT

We have developed an electrochemical cell for X-ray spectroscopy in soft X-ray region as a expansion of our liquid flow cell which successfully used for soft X-ray measurement such as studies of liquid structure of water [1, 2] and electronic structure of solute molecules [3, 4]. To realize soft X-ray observation of electrochemical reaction, a new electrochemical cell was designed to use a deposited metal layer on the thin-film window as working electrode. According to durability tests of thin-film window with metal coating, electroconductive SiC was chosen as a material of thin-film. Cyclic voltammetry measurements was carried out using the newly developed electrochemical cell to confirm functionality as an electrochemical cell.

To confirm functionality as a cell for X-ray spectroscopy, we observed reaction of Pb electroplating in aqueous Pb(II) acetate. Figure 1(a) shows fluorescence yield X-ray absorption (FY-XAS) spectrum. The intensity of obtained spectrum were decreased by increasing the total application time of -600 mV. In terms of spectral shape, variation is almost negligible except for peak around 533 eV. The peak at around 533 eV becomes small as increasing total time. Figure 1(b) shows X-ray emission (XES) spectra at 533 eV excitation. According to peak shape, 533 eV peak in FY-XAS can be assigned to acetate anion, which is probably coordinated on Pb cation.

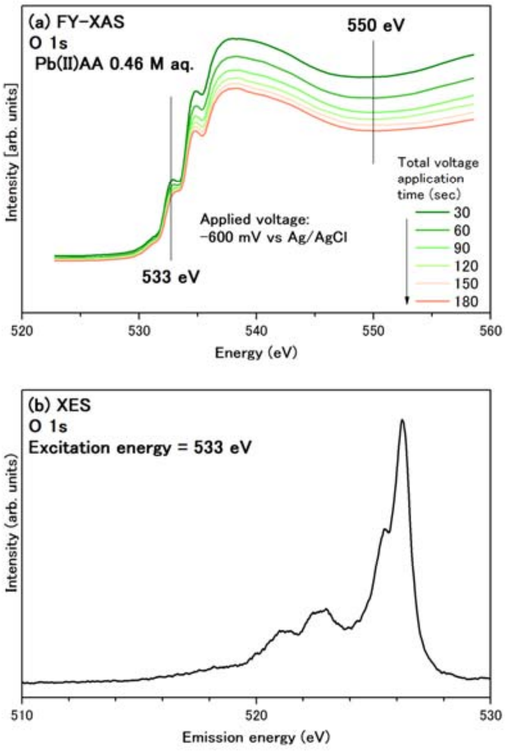

Figure 1
(a) FY-XAS spectrum of 0.46 M lead acetate at -600 mV. Voltage was applied 30sec intermittently, and XAS was measured while voltage is off. By repeating this sequence, spectral variation of XAS with respect to the total applied time (30, 60, 90, 120, 150, 180 sec) was investigated.
(b) XES spectra of 0.46 M lead acetate excited at 533 eV.

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Imaging Ultrafast Molecular Wave-packets with a Single Chirped UV Pulse

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ABSTRACT

Coherent control of ultrafast dynamics in atoms and molecules has been already experimentally demonstrated by shaping the phase, amplitude and polarization of ultrashort pulsed radiation [1-3]. Here, we present a theoretical work based on ab initio simulations on small molecules, where we propose the use of a single frequency-chirped sub-femtosecond pulse to manipulate molecular ionization yields. We introduce a quadratic frequency chirp that is experimentally achievable even in pulses with durations as short as a few hundreds of attoseconds [4]. We use H_2^+ as a benchmark target and numerically solve the full-dimensional time-dependent Schrödinger equation. The wave function is represented using a finite element discrete variable representation [5], including both electronic and nuclear degrees of freedom.

By varying the chirp parameter in a UV sub-femtosecond pulse, we observe that the two-photon ionization probability can be enhanced by more than one order of magnitude for a wide range of atomic and molecular targets. Moreover, we show how the vibronic (vibrational+electronic) wave packet pumped in the singly excited molecule can be simultaneously probed through the ionization fragments generated by the same pulse. In this way, the proposed approach mimics standard pump-probe techniques, with the chirp parameter encoding the time delay between the pump and probe frequencies. Extracting time images with attosecond resolution using a single pulse avoids many of the technical difficulties that make pump-probe experiments using two attosecond pulses so challenging.

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X-ray versus Auger Emission Following Xe 1s Photoionization

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ABSTRACT

Xe 1s photoelectron spectra have been measured at SPring-8, Japan. The core-hole lifetime broadening has been extracted from a fit of the photoelectron peak, and found to be 9.6 eV, corresponding to a core-hole lifetime of ~68 attoseconds. The amount of radiative versus non radiative decay after the creation of such a deep electron vacancy has been assessed by recording Auger LMM decay spectra below and above the K-edge. Below the K-edge, L vacancies are produced only by direct photoionization, while above the K-edge some of such vacancies are mainly produced by KL emission following 1s photoionization. Due to the dipole selection rule for x-ray emission, we are able to directly observe the dominant role of the KL relaxation process by a careful comparison of the Auger spectra below and above the K-edge.

Ab initio theoretical calculations allow to determine the percentage of radiative decay. A good agreement between experimental and calculated LMM spectra provides an unprecedented experimental proof of the dominance of radiative decay for heavy systems.

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Energy Sharing in the Triple Auger Decay of Potassium 2p Holes

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ABSTRACT

Electron correlation plays a key role in single photon multiple ionization of atoms. To study such processes, we use a magnetic bottle time of flight spectrometer to collect in coincidence almost all the electrons emitted in the full 4π solid angle [1–3]. Kinetic energies are determined with a resolution $\Delta E/E \approx 1.5\%$ and the detection efficiency for electrons $\eta \sim 50\text{-}70\%$ allows the effective detection of four electrons in coincidence.

We investigated multiple Auger decay in potassium atoms following 2p inner-shell ionization. The experiment was carried out at the PLEIADES beamline of the SOLEIL synchrotron facility. Relative abundances of K^{2+}, K^{3+} and K^{4+} ions produced by the Auger decay of the 2p holes are determined. In addition, we looked for the energy correlation among the electrons emitted in triple Auger decay leading to K^{4+} final state. A Dalitz plot [4] is used to represent the energy sharing between these three electrons.

These results are compared with the 2p triple Auger decay of argon [5]. We can thus determine the role of the valence electron 4s in the decay process of potassium.

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Rotationally Resolved Fluorescence Excitation Map of Molecular Hydrogen and Deuterium

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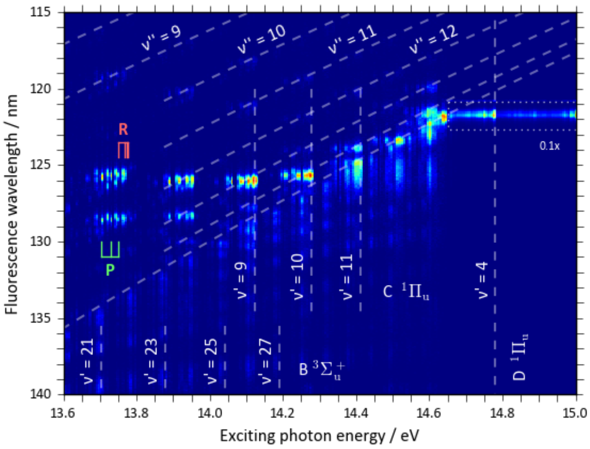
ABSTRACT

As the most abundant molecule in the universe hydrogen plays the role as the most fundamental prototype system in molecular physics and spectroscopy. Especially in astrophysics the exact knowledge of its properties is extremely important for observation and calculations [1]. The variety of crossings of individual electronic states in the singly excited regime of hydrogen makes this energy region an active field of research [2-4].

Synchrotron based photon-induced fluorescence spectroscopy (PIFS) combines the ultra-high resolution and tunability of modern synchrotron radiation with a high secondary fluorescence resolution, resulting in rotational resolution in excitation and relaxation. Hence, the full process from excitation to final radiative deexcitation can be monitored. This includes molecular fluorescence with vibrational progression, predissociative resonances coupling different electronic states, and continuous emissions from relaxation into the vibrational continuum of the electronic ground state. The individual effects were investigated in the last decades. Here however we present a detailed but conclusive overview of all possible transitions and their relations. Thus it includes the only scarcely explored continuum emissions, i.e. the Condon diffraction bands [5,6]. The main purpose, of course, is the benchmark of ever improving calculations, and the evaluation of theoretical methods. The strong influence of the nuclear mass becomes obvious if the complete map is considered. The oscillator strengths are impressively encoded the intensities of the transitions, while the potential energy landscape can be extracted from the energetic positions. In combination with the additionally recorded ionization yield the quantum mechanical hydrogen and deuterium molecule can be extracted from the data presented here.



This portion of the rotationally resolved fluorescence excitation map of hydrogen shows the vibrational progression of the C-state, as well as some of the dissociation continuum transitions if the C-state beyond the threshold. Clearly visible is the cutoff as soon as the atomic Lyman series is energetically allowed.

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Regio-selective Fragmentation of Nitroimidazoles and its Significance in Radiosensitization

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ABSTRACT

Electron-ion coincidence measurements of dissociation of three valence-ionized nitroimidazoles (Figure 1) revealed a remarkable regio-selectivity. Transferring the nitro (NO_2) group from the C2 carbon of the imidazole ring to the C4 or C5 carbon reduces fragmentation pathways and stabilizes the molecule. Still, regardless of the nitro group placement, the fragmentation always begins with the ejection of nitric oxide. The experiment showed that by varying the attachment position of the NO2 group, the NO yields, especially that of the cation NO^+, can be controlled by a significant degree.

The ability to control the $NO^{(+)}$ production from nitroimidazoles is significant from the viewpoint of radiosensitization[1]. While the use of oxygen has not led to significant success in enhancing the effect of radiation therapy, NO has shown a great potential in radiosensitization[2] and it has been estimated that NO can be a more effective radiosensitizer than oxygen.To shed more light onto the underlying mechanisms of this region-selectivity, and to potentially help to select more efficient NO-based radiosensitizer molecules, a series of MP2 and CASSCF/MCQDPT calculations were performed and are compared with the experiment.

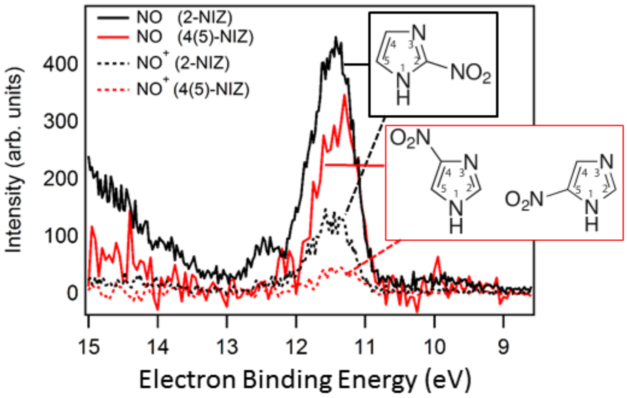

Figure 1. Yields of nitric oxide in coincidence with valence photoelectrons from 3 nitroimidazoles, showing strong regio-sensitivity.

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Photoionization and Ionic Dissociation of the C_3H_3NS Molecule Induced by Soft X-rays Near the C1s And N1s Edges

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ABSTRACT

The thiazole (C_3H_3NS) molecule and its derivatives belong to a special subclass of heterocyclic compounds, which is attracting increasing interest due to their wide spectra of chemical, biological and industrial applications. Knowledge of the electronic structures, physical and chemical properties of these building block compounds is essential to understand their chemical structure, stability, reactivity, and provide reliable data for new scientific and industrial applications.

The present work is concerned to the results from the experimental investigation involving the photoabsorption and dissociative photoionization of the gas phase C_3H_3NS molecule induced by soft X-rays synchrotron radiation covering the photon energy range of the C1s and N1s core edges. TOF-MS, photoelectron photoion coincidences and ion yield techniques were employed.

The experiments were undertaken at the spherical grating monochromator (SGM) beamline from the Brazilian Synchrotron Light Laboratory (LNLS-CNPEM) located in Campinas, Brazil. Soft X-rays photons, ranging from 270 eV to 450 eV, were employed to interact perpendicularly with the molecular gas jet. The resulting photoionization ion products were collected and identified by TOF-MS/PEPICO techniques.

From the analysis of the PEPICO, PIY and TIY spectra, as well as *ab initio* and DFT calculations for the species observed in the results, we have been able propose the main photodissociation pathways for this molecule as a function of the photon energy. The production of fragment ions of lower mass to charge ratio is substantially enhanced following core excitation/ionization as compared to the processes occurring in the valence region [1]. It has also been observed from our spectra that some ion species exhibit different core shell ionization dependences to the dissociation patterns.

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Role of Electron-nuclear Coupled Dynamics on Charge Migration Induced by Attosecond Pulses in Glycine

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ABSTRACT

Quantum Mechanics states that the expectation value of an hermitian, time independent operator will exhibit a temporal dependence if the system is described by a non-stationary state of that operator. In other words, any superposition of eigenstates of a given system leads to a time varying observable, such as the probability density. This lies at the core of the so-called ultrafast charge migration, concept introduced by Cederbaum and Zobeley in the nineties to describe the charge fluctuations occurring in the attosecond time scale upon sudden ionization of a molecule [1]. Investigations of ultrafast charge migration were partly inspired by the pioneering work of Weinkauf and coworkers on peptides chains [2]. However, the first experimental observation of this phenomenon obtained with attosecond resolution has only been achieved in 2014 for the amino acid phenylalanine [3]. These findings have drawn much attention of the scientific community and new theoretical approaches are being developed to provide a solid knowledge of these ultrafast processes that are ultimately responsible of the subsequent chemical response of the biological system. Most of existing methods describe the process by assuming that the ionization is triggered through a sudden transition from the ground state, avoiding the evaluation of ionization amplitudes [4]. And, even in those works where the ionization step is more accurately represented [3, 5], the nuclei remain frozen, which is expected to be a reasonable approximation in the first tens of femtoseconds [6]. In this conference, we will present our progresses to achieve a complete theoretical description of the ultrafast charge migration triggered in glycine molecule, which include both an accurate evaluation of the ionization step and the nuclear degrees of freedom in the time propagation. We employ a Static-exchange DFT-based approach [7] to extract reliable ionization amplitudes, while the correlated electron-nuclear dynamics of the ionic subsystem is obtained from a TDDFT-Ehrenfest simulation. We will also show recent simulations to demonstrate how the choice of the ionizing laser pulse modifies the ensuing charge dynamics, thus opening the door to the control of charge-directed reactivity in biologically relevant molecules.

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Relativistic Effects in the Photoionization of Outer and Near-outer Subshells of Free and Confined High-Z Atoms

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ABSTRACT

At high-Z photoionization cross sections of atoms are affected by relativistic effects in a variety of ways. To begin with, wave functions for both initial and final states are altered by relativity. And threshold energies can be altered significantly. In addition, the spin-orbit interaction becomes important at high Z and that splits both initial and final states into the various $j = l \pm 1/2$ components which increase the number of photoionization channels considerably. Furthermore, the addition of channels and the altered threshold can result in rather large changes in the many-body electron-electron correlation (interchannel coupling) in the final continuum states of the photoionization process. To include both relativistic interaction, as well as a significant amount of correlation, the relativistic random-phase approximation (RRPA) methodology has been employed [1]; since it is based on the Dirac Equation, RRPA includes relativistic effects on an *ab initio* basis, along with both initial discrete state correlation, and interchannel coupling in the final states.

Using RRPA, calculations have been performed for the photoionization cross sections of four heavy atoms, Hg (Z=80, Rn (Z=86) Rn (Z=88) and No (Z=102), focusing on the outer and near-outer subshells. In addition, the photoionization of each of these atoms confined in a C_{60} molecule has also been investigated; these are labelled Hg@C_{60}, etc. The effects of the C_{60} cage on the encapsulated atoms is modelled by an attractive spherical annular "square-well" potential of depth 0.302 a.u., inner radius 5.8 a.u. and width 1.9 a.u. [2-4], which has been found to be a reasonable approximation in many cases [2-5].

The results show that, indeed, the relativistic interactions have a significant upon the photoionization process for outer and near-outer subshells. This is particularly true for *s*-subshells because they are so penetrating that their binding energies are greatly increased by relativistic effects. Thus, their wave functions are more compact and Cooper minima, that appear in the continuum nonrelativistically, move well down into the discrete region, thereby changing the cross section considerably. And, since their binding energies are altered by relativity much more than nearby *p*-, *d*- and *f*-subshells, this strongly affects the interchannel coupling, of importance since *s*-subshells are very strongly affected by interchannel coupling.

In addition, although confinement resonances [5, 6] in the photoionization of confined atoms are largely determined by the cage structure, their dependence upon the photoelectron energy results in the confinement resonances being altered considerable by the relativistic interaction owing primarily to the relativistic differences in threshold energies.

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Towards Complete Photoionization Experiments beyond the Dipole Approximation

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ABSTRACT

Recently, photoionization experiments with both linearly and circularly polarized, intense XUV radiation became feasible at the free-electron laser FERMI. This opens a way to perform a new type of complete photoionization experiment. It is known that photoelectron angular distributions (PADs) from unpolarized atoms are not enough to extract all complex photoionization amplitudes even within the dipole approximation [1]. To overcome this obstacle different methods of producing polarized targets have been applied, usually involving additional field(s). Here we propose the measurement of PADs in sequential two-photon double ionization (2PDI) to perform a complete photoionization experiment, which is new in three aspects: this is a complete experiment with positive ions, it is generalized for accounting the quadrupole amplitude, and, finally, it provides additional data to complete the photoionization experiment with neutral atoms.

We imply the two-step mechanism of the 2PDI with creation of an intermediate single-charged ion. The PADs in the second ionization step have been measured many times for noble gas atoms [2]; the non-dipole effects in these PADs have been reported recently in argon [3]. The important feature of the process is that the intermediate ion is either aligned or oriented depending on polarization of the VUV pulse. Therefore, no additional efforts are needed to produce the polarized ionic target.

We showed [4,5] that for noble gases, within the Cooper-Zare model, five independent asymmetry parameters characterize the PAD in the second-step ionization for each field polarization. Two of the parameters are expressed in terms of the dipole amplitudes, while three parameters originate from the interference between electric dipole and quadrupole amplitudes. At the same time the ionization of the ion is characterized by four amplitudes, two dipole and two quadrupole, and the absolute ratio of the dipole amplitudes of the first ionization step. Thus, the PADs in the second ionization step for linearly and circularly polarized field are enough to extract three ratios of the complex second-step amplitudes and the absolute ratio of the first-step dipole amplitudes, i.e. enabling the complete experiment in the second step. The latter ratio, combined with the PADs of the first ionization step, completes also the experiment for the first step. Further discussion with examples will be presented at the conference.

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Role of the Super Atom Molecular Orbital (SAMO) Electronic States in the Photoionization of Fullerenes

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ABSTRACT

The Super Atom Molecular Orbital (SAMO) are excited electronic states where a valence electron has been promoted to a diffuse atomic-like orbital. They differ from Rydberg states because of the significant electronic density localized inside and in the close vicinity of the carbon cage, which stabilizes them and increases their binding energies. The SAMO states have been observed for C_{60} adsorbed on a surface[1] and for gas phase fullerenes using angular-resolved photoelectron spectroscopy.[2,3] The excitation of the ground state to a SAMO state leads to an electron transfer from the cage to a nanometer size orbital, which is of particular interest for organic photovoltaics. The understanding of the photoexcitation and photoionization processes is therefore important. We investigated the effect of the pulse duration and laser intensity on the photoionization of the SAMO states in C_{60}. We also investigated the effect of doping a bare fullerene on the photoexcitation process.

The low-lying SAMO states of the spherically symmetric C_{60} are not optically active. They can only be accessed indirectly by vibronic coupling to optically active valence states. Exciting C_{60} with a weak ($<4\ 10^{12}$ W/cm^2) 120fs laser pulse leads to photoelectron spectra with sharp peaks corresponding to the photoionization of the *s*, *p* and *d* SAMO states.[2] SAMO states which exhibit a simple hydrogenoid density have short photoionization lifetimes (i.e. the time it takes to ionize the excited state population) in the femtosecond timescale while valence states have lifetimes in the picosecond timescale, which explains why the SAMO are the only electronic states to significantly ionize during the laser pulse.[4] When the pulse duration is lowered to 20fs and the field strength gradually increased to $3\ 10^{13}$ W/cm^2, there is a transition from the photoionization of the SAMO to the photoionization of the Rydberg states. Below $5\ 10^{12}$W/cm^2, the SAMO dominate the photoionization spectra while for higher field strengths, the Rydberg states ionization overcomes ionization from SAMOs.[5] The photoionization process of endohedral fullerenes such as $Ho_3N@C_{80}$ drastically differs from that of the spherical C_{60} fullerene due to the symmetry breaking induced by the inclusion of the Ho_3N dopant. The SAMO states become optically active and can be excited directly from the ground state[6] by the laser pulse unlike in C_{60}. The ion yield is therefore higher than in C_{60} for a same laser intensity because of resonance-enhanced multiphoton ionization of intermediate SAMO states that promptly ionize by absorption of an extra photon.

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Experimental and Theoretical High-energy Resolution X-ray Absorption Spectroscopy: Implications for the Investigation of the Entatic State[1]

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ABSTRACT

Copper containing enzymes are a prominent example for charge transfer based bio catalysts that enable electron transfer. Understanding complexes like these is of great interest for catalytic applications. A very important factor is the geometry which strongly depends on the oxidation state of the metal. Exact knowledge of involved mechanisms is essential for understanding these compounds. HERFD-XAS provides information about local geometry and the local spin state, by reflecting the details of the lowest unoccupied states[2]. We therefore studied Copper I/II complexes by means of HERFD-XAS spectroscopy. These experimental spectra were compared to TD-DFT calculated spectra to check for the viability of both methods in elucidating geometrical and electronic parameters. One pair of copper complexes with a hybrid guanidine-pyridine ligand (Figure 1, left) only differing in oxidation state, forming a so called entatic state, was of great interest and value due to its biomimetic properties[3]. Structures derived from gas phase optimization, crystal structure and relaxed crystal structure were used. In addition to that two extreme structures in tetrahedral and square planar geometry were studied to explore the potential of HERFD-XAS studies for such type of complexes. The experimental spectra of the Cu(I) and Cu(II) compound (Figure 1, right) show clearly distinguishable features in the edge and a clearly separated pre-peak for the copper(II) species.

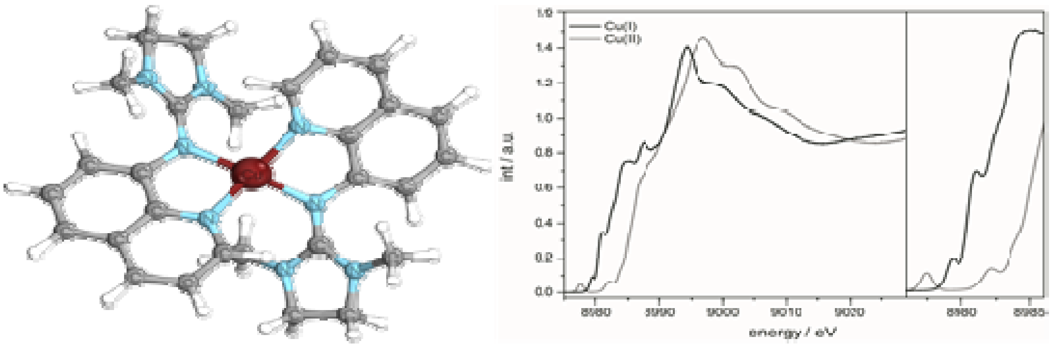

Figure 1: DMEGqu (N-(1,3-dimethylimidazolidin-2-ylidene)quinolin-8-amine) Cu complex (left) and experimental HERFD-XAS spectra of the Cu(I) (black) and Cu(II) (grey) compound with a zoom in on the pre-edge region

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Measurement of Angularly Resolved Spectral Phase for the Fano Resonance in Argon

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ABSTRACT

With the advent of attosecond technologies more than a decade ago, the electron dynamics for photoionization of atoms and molecules has become accessible with unprecedented resolution in the time domain. Measuring as well as controlling the physical parameters describing the interaction between photons and atoms and molecules have been in the forefront of recent research activities in attoscience. For example, the RABITT (reconstruction of attosecond beating by interference of two-photon transitions) protocol employing a train of attosecond pulses along with a weak infrared probe pulse has enabled the phase measurements of bound states in He atom [1] and autoionizing states in N_2 molecule [2]. Attosecond streaking in photoionization of Ne atoms has proved that the photoemission process is not instantaneous [3]. The RABITT scheme was also used to measure the relative photoionization time delay between the 3s and 3p orbitals in Ar atoms [4].

In a recent study, both the amplitude and phase of an electron wave-packet, originated from the autoionizing Fano resonance in He atom have been measured using a spectrally resolved interferometric technique [5]. Previously, the variation of the spectral phase for the photoionization amplitude across the $3s^23p^6 \rightarrow 3s3p^64p$ autoionization transition in Ar atom was studied using a coherent extreme ultraviolet (XUV) comb of odd-order harmonics of a fundamental near-infrared (NIR) field [6]. The argon atom was ionized in the field of a two-color (XUV±NIR) radiation resulting in sideband photoelectrons having two contributions from the two adjacent harmonics [7]. The probability of the autoionization process shows the well-known Fano profile. In the present work, we have performed an angularly resolved study of the photoionization of the argon atom in the vicinity of the Fano resonance, using an identical interferometric setup. Photoelectron angular distributions for the Fano resonance were measured using a velocity map imaging (VMI) spectrometer in order to obtain a more complete picture about the dispersion dynamics of the scattered photoelectron. The oscillation in sideband amplitude as a function of the pump-probe delay was used to study the angular dependence of the spectral phase close to the Fano resonance. Details will be presented.

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Excited State Proton Transfer in Aqueous 2-mercaptopyridine Studied with RIXS

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ABSTRACT

Excited State Proton Transfer (ESPT) is a fundamental and ubiquitous process of importance for energy transfer and photo-stability in e.g. biological systems[1-2].

We study[3] ESPT in the model system 2-Mercaptopyridine, in aqueous solution, with nitrogen N1s Resonant Inelastic X-ray Scattering (RIXS) to investigate drivers, pathways and timescales.

By combining high level quantum chemical calculations with static and time-resolved measurements we are able to disentangle optically and X-ray induced dynamics which favors defragmentation along different coordinates. This demonstrates the strength of the combined modeling, and indicates how deformation of chemical bonds with varied photon energies could allow for selective control of molecular structures.

We identify a fingerprint for the deprotonation of the nitrogen site and benchmark the process to take place at femtosecond timescale, demonstrating RIXS as a viable probe for ESPT studies.

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Molecular Double Core Hole Spectroscopy: The Role of Electronic and Nuclear Dynamics

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ABSTRACT

The unprecedented radiation intensity of x-ray free electron lasers (XFELs) offers the possibility to create double core hole (DCH) states with a single laser pulse via sequential one photon absorption [1]. This x-ray two-photon process opens the way to a highly sensitive spectroscopy known as x-ray two-photon photoelectron spectroscopy (XTPPS).

The theoretical description of XTPPS is challenging owing to the competition between photon absorption and electronic relaxation by Auger decay which occur at similar femtosecond timescales. In case of molecular targets, nuclear dynamics, which takes place in this timescale, complicates further the analysis. Previous studies are limited to classical rate-equation models for describing the time evolution in the different ionization channels [1,2].

In this work, we present a novel methodology and the numerical tools to investigate DCH states through sequential one x-ray photon absorption and their Auger decay using a quantum treatment for both electronic and nuclear degrees of freedom. Our model takes into account for the first time these competitive processes and includes explicitly the laser pulse. The influence of the nuclear dynamics on core photoionization induced by a femtosecond laser pulse is assessed. The impact of the laser pulse width on the photoelectron spectrum energy broadening is investigated. Furthermore, we show that an active control over DCH states formation may be achieved through the laser pulse characteristics by studying the evolution of vibrationally resolved photoelectron spectra of DCH states of carbon monoxide (CO) with the pulse parameters.

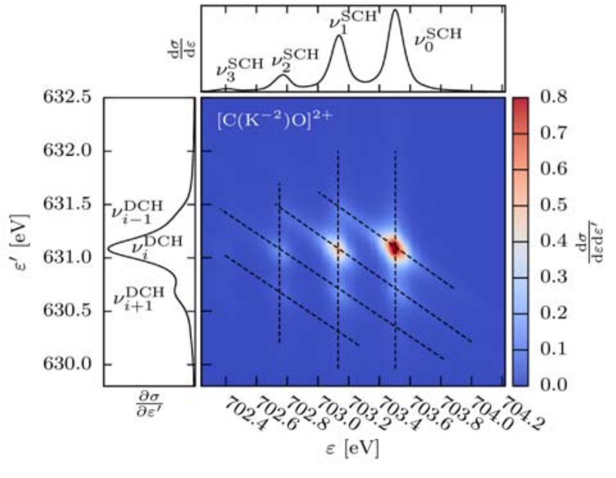

Fig. : Photoelectron-photoelectron spectrum of the single-site DCH state of carbon of the CO molecule.

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Probing Molecular Processes in Collagen Peptidic Models with Ionizing Radiation

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ABSTRACT

Collagen is the most abundant protein in the human body. Cartilage and tendons owe their special mechanical properties to the fibrous collagen structure. These strong fibrils are aggregates of a sub-unit consisting of three collagen proteins wound around each other in a triple helix. The response of this protein to ionizing radiation has never been studied, despite its fundamental importance. Recently, we probed the effect of UV, VUV and soft X-ray photon absorption on an isolated peptidic sequence of type 1 collagen, as well as a model of the collagen triple helix, by coupling tandem mass spectrometers to an OPO laser and a synchrotron beamline. For UV photon energy below the ionization threshold, photoabsorption is found to induce electronic excitation followed by peptidic backbone cleavage. Increasing the photon energy around the ionization threshold, a smooth transition from excitation to ionization occurs, and we observe inter- followed by intra-molecular fragmentation. The latter is strongly reduced for the triple-helix model compared to the isolated peptide. This is consistent with conversion of the photon energy into molecular ro-vibrational energy. Peptide side-chain losses are found to be due to radical-mediated mechanisms. Besides, our results show that proline hydroxylation, a typical post-translational modification of collagen, induces strong H_2O loss from the peptides studied.

We want to push further our work on collagen by irradiating the model peptides with heavy ions, by using a unique home-built experimental apparatus recently developed in Caen. In this set-up, molecular ions are produced by an electrospray ionization source, mass-over-charge selected, and accumulated in a Paul trap, before being extracted, and they finally cross the ion beam. Products of the interaction are analyzed by a time-of-flight mass spectrometer. Very recently, we validated our set-up by irradiating the leucine-enkephalin peptide with He^+ ions at 7 keV: our results are the same as those obtained with the Paultje set-up at the University of Groningen [1]. The next step will be to compare results for collagen peptides to those obtained with photons, and look for ion-induced specific molecular processes such as deprotonation [2].

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RIXS on $Ba_3M_{2-x}Ir_{1+x}O_9$

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ABSTRACT

Spin-orbit entangled j=1/2 Mott insulators set the stage for fascinating novel quantum states of matter [1] based on frustrated bond-directional Kitaev exchange interactions J_K (different spin components couple along different bonds). On a honeycomb lattice, the Kitaev terms may yield a Kitaev-type spin liquid with the long-sought Majorana fermion excitations, while the triangular lattice is expected to show a Z_2-vortex crystal phase even for Heisenberg coupling $J >> J_K$ [2]. It is an important issue to understand how to realize a pure j=1/2 state in candidate materials such as the $5d^5$ iridates with Ir^{4+} ions in an octahedral crystal field, in which deviations from octahedral symmetry give rise to a mixing of j=1/2 and j=3/2 states

RIXS at the Ir *L* edge is an ideal tool to determine the j=1/2 character by measuring the crystal-field splitting caused by the distortion. Previous data on different iridates [3-6] indicate that the spin-orbit exciton (excitation from j=1/2 to 3/2) is mixed with interband excitations and show an additional unexplained peak, questioning the validity of a simple analysis. To understand the nature of the excitations, it is instructive to compare compounds with different Ir lattices and environments.

The hexagonal compounds $Ba_3M_{2-x}Ir_{1+x}O_9$ show stacks of single layers and bilayers in which the metal ions form a triangular lattice. In the ideal case, $Ba_3TiIr_2O_9$ shows bilayers of triangular Ir-O planes separated by Ti-O planes, but Ti^{4+} and Ir^{4+} show significant site disorder. The triangular lattice is particularly interesting because it shows both, geometric frustration and Kitaev-type exchange frustration. We discuss the j=1/2 character and the role of disorder.

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High Energy Resolution X-ray Absorption and Emission Spectroscopy for the Investigation of Spin Crossover Processes

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ABSTRACT

Spin crossover (SCO) is an example of potential molecular bistability, in which the high-spin (HS) and low-spin (LS) states are interconvertible by physical perturbation, such as temperature.[1] Since its first discovery the phenomenon has attracted much attention from chemists and physicists, because it offers an important application of ligand field theory. But despite the tremendous insights that have been gained into the underlying electronic principles responsible for the occurrence and the specific behavior of spin transition processes, the study of SCO complexes is still a highly attractive research field due to their high potential for electronic devices.[2] Most characterizations are based on either determining the structural changes (XRD, XAS) or the changes of the spin state (Mößbauer, SQUID). For further understanding of the molecular mechanism of SCO processes the simultaneous measurement of structural and spin state changes is desirable.

X-ray emission based methods offer new possibilities to record both parameters (quasi simultaneously) in one experiment by means of HERFD-XAS, $K\beta_{1,3}$-XES and EXAFS. While $K\beta_{1,3}$-XES and HERFD-XAS provide information about the metal spin state, more exactly, about the effective number of unpaired 3d electrons[3], EXAFS allows to access the local structure around the metal center. Since hard X-rays are used, all three techniques can be carried out under nearly every experimental conditions.

We therefore studied selected mono- and dinuclear iron-based spin crossover compounds by temperature dependent HERFD-XAS, Kβ1,3-XES and EXAFS to receive information about the structural and electronic changes occurring during the spin transition process. The transition behavior of the quasi octahedral compound [Fe(L-N4Bz2)(NCS)2][4] (Fig.1), which shows an gradual spin transition from low spin to high spin, is examined and the experimental basics, data analysis approach and results are presented with this contribution.

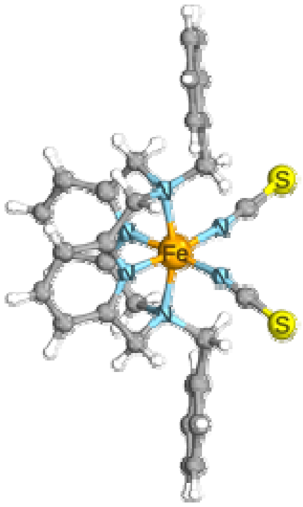

Figure 1: Structure of $[Fe(L\text{-}N_4Bz_2)(NCS)_2]$

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VUV Photo-ionization of Planetary Aerosols Investigated by Imaging Angle-resolved Photoemission

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ABSTRACT

Titan, the largest moon of Saturn, has a dense atmosphere whose upper layers are mainly composed of methane (CH_4) and molecular nitrogen (N_2). Their photochemistry leads to the formation of aerosols at very high altitudes (>800 km)[1]. Once these aerosols are formed and through their descent towards the surface, they will still interact with persistent UV/VUV radiations, at different energies, that can reach lower atmospheric layers. This interaction has some impact, for example on the radiative transfer or on the ionization yield of the atmospheric compounds.

Models are a good way to study those processes, but the lack of data on the refractive index or the absolute absorption/ionization cross sections of the aerosols can be an obstacle.

In order to shed some light and quantify those processes, we ionize analogs of aerosols (tholins) produced with the PAMPRE experiment (LATMOS) on the SAPHIRS platform of the DESIRS VUV beamline (synchrotron SOLEIL), equipped with an aerodynamic lens. The aerosols are injected directly under vacuum as isolated free nanoparticles[2]. The generated photoelectrons are then collected with a Velocity Map Imaging detector and their energetic and angular signatures are analyzed by ARPES (Angle-Resolved PhotoElectron Spectroscopy).

Both the nanoparticles size distribution and the incident wavelength determine the parameters governing the photoemission process (intra-particles electron mean free path, photon penetration depth) as revealed by the angular distribution of the photoelectron showing in same cases a marked forward/backward asymmetry with respect to the photon axis[3,4]. Those parameters may provide us with information on the optical behavior of the aerosols, and how they contribute to the global albedo (ie reflectivity) of Titan atmosphere. In addition we can extract the ionization threshold energy together with the absolute absorption cross sections of the aerosols, from which altitude dependent photodynamics can be unraveled. Such information is important since the corresponding formed slow electrons may be involved in the formation of anions via dissociative electron attachment for instance.

We will present here the experiments performed, at different VUV energies, on Titan's aerosol analogs with the ARPES method and show how the first results can have implications regarding Titan's atmosphere overall optical characteristics.

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Hard-X-ray-induced Multistep Ultrafast Dissociation: Multistep Core-hole-clock Approach

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ABSTRACT

Creation of deep core holes with very short (≤1 fs) lifetimes triggers a chain of relaxation events leading to extensive nuclear dynamics on just a few-femtosecond timescale. For example, multistep ultrafast dissociation (MUST UFD) is observed for HCl following Cl $1s\rightarrow\sigma^*$ excitation.[1] Intermediate states with one or multiple holes in the shallower core electron shells are generated in the course of the decay cascades of the initially created deep-core-hole states.

In the HCl molecule, the leading relaxation decays of the Cl $1s^{-1}\sigma^*$ state are Auger KLL (76%), KLM (13%) and radiative KL (10%) channels.[2] KLL and KL cascades create intermediate Cl $2p^{-2}\sigma^*$ and $2p^{-1}\sigma^*$ states, respectively. The latter one can be created by direct soft X-ray absorption.[2] It is known to undergo ultrafast dissociation (UFD) within the Cl $2p^{-1}$ lifetime of ~8 fs.[2] The lifetime of the double-core-hole states is more than twice shorter than that of the corresponding single core-hole states.[3] The repulsive character and large gradients of the potential energy surfaces of these intermediates enable ultrafast fragmentation after the absorption of a hard x-ray photon within only a few of femtoseconds before the Auger decay takes place.

As a result atomic-like Auger electrons with different kinetic energies can be emitted at different times corresponding to different steps of the cascade. Therefore, a single Auger electron spectrum provides information on system dynamics occurring at different time intervals. MUST UFD can be used as an alternative approach to a conventional pump-probe experiment, where several probes are available at time delays defined by nature – intrinsic lifetime of the intermediate states in the decay cascades.

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Rescattering Electron Spectroscopy and Geometric Structure Retrieval on C_2H_4 Molecules

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ABSTRACT

A growing number of studies have been carried out to establish new experimental techniques to map a structural change of gas phase molecules in a femtosecond time scale. Rescattering electron spectroscopy in intense laser fields is one of the methods for such a purpose. After a proposal of a method to extract differential cross sections (DCSs) for electron-ion elastic scattering from the rescattering photoelectron spectra [1, 2], a few number of studies have been reported on structure retrieval of linear [3, 4] or planar [5] molecules. In this study, we measured angle-resolved rescattring electron spectra of C_2H_4 molecules and compared the results with theoretical calculations employing ePolyScat of a scattering calculation package toward the structure retrieval.

The output of a Ti:Sapphire laser (800 nm, 100 fs, 1.5 mJ, 1 kHz) was injected to an optical parametric amplifier to convert the wavelength to 1650 nm. The laser was introduced in a high vacuum chamber through a half waveplate and focused on C_2H_4 molecules. Emitted electrons were detected with a field-free time-of-flight spectrometer, as rotating the polarization of the laser to get a two-dimensional momentum distribution of the electrons.

Fig. 1 gives a DCS extracted from an experimental result for a recollision momentum of 2.5 a.u. (σ_M), which shows a similar trend with an theoretical atomic DCS (σ_A), or the incoherent sum of DCSs of all the atoms in the molecule. In Fig. 2, molecular contrast factors (MCFs) defined as $(\sigma_M\text{-}\sigma_A)/\sigma_A$ are depicted as a function of momentum transfer. A clear oscillatory structure reflecting molecular geometry can be seen, showing good agreement with a theoretical one.

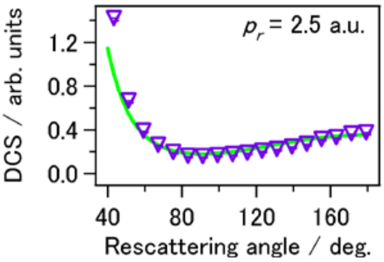

Fig. 1 Experimental DCS (violet) and theoretical atomic DCS (green).

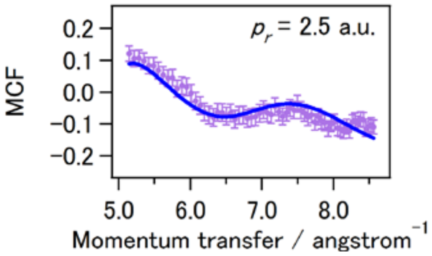

Fig. 2 Experimental MCF (violet) and theoretical MCF with ePolyScat (blue).

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Time-resolved Observation of XFEL Induced Dynamics in CH_2I_2 Molecule

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ABSTRACT

X-ray free-electron lasers (XFELs) opened the way to the investigation of unexplored optical phenomena in the x-ray spectral region. At SACLA, in Japan, we have initiated a program to study the interaction of XFEL pulses with isolated molecules containing heavy atoms such as iodine [1-3].

In this study, we performed time-resolved ion yield measurements for diiodomethane (CH_2I_2) molecules using an intense 5.5-keV XFEL pulse generated by SACLA as a pump, and an 800-nm NIR laser pulse as a probe. The molecule is multiply ionized via cycles of 2*p* inner-shell photoionization of the iodine atom and the subsequent Auger cascades, and then explodes violently due to Coulomb repulsive forces. Measuring the yields of fragment ions as a function of the NIR laser arrival delay, we tried to decipher the interplay between electron and molecular dynamics induced by XFEL irradiation.

The resulting yield of each fragment ion shows a different temporal structure. We succeeded in extracting information on the dynamics associated with the electronic decay processes from the experimental data.

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Nanoplasma Produced by a Femtosecond Hard-X-ray Laser Pulse in Xenon Clusters

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ABSTRACT

Understanding ultrafast reactions induced by X-ray Free Electron Laser (XFEL) pulses is of fundamental interest, as well as of crucial importance for the use of XFEL pulses for structure studies. Recently, it was reported that a nanoplasma is formed when an atomic cluster is irradiated by an XFEL pulse in the hard X-ray regime [1]. We present the first femtosecond time-resolved study on nanoplasma formation from an atomic cluster irradiated by an XFEL pulse.

In the present study, Xe clusters with an estimated average size of 5000 atoms were irradiated by XFEL pulses (5.5 keV, 10 fs FWHM) at SACLA. A NIR-probe laser (800 nm, 32 fs FWHM) was used for further ionizing the excited xenon atoms created in the early stages of the nanoplasma formation. The Xe^{1+} yield (the dominant ion fragment) was measured as a function of the time delay between the XFEL-pump and the NIR-probe pulses. We used an arrival timing monitor [2] for measuring the temporal jitters between the XFEL and NIR pulses on a shot-to-shot basis and improved the time-resolution of the XFEL-pump–NIR-probe experiment down to a few tens of femtoseconds.

The results revealed an ultrafast population (~12 fs) and depopulation (~310 fs) of excited states of the Xe atoms in the cluster during the nanoplasma formation. The measured time-constants suggest that electron collisions and interatomic relaxation processes [3] are among the primary mechanisms for nanoplasma formation upon irradiation with intense hard X-rays.

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Sequence-specific Ionization Potentials of Oligonucleotides Correlated with VUV-induced DNA Strand Breaks

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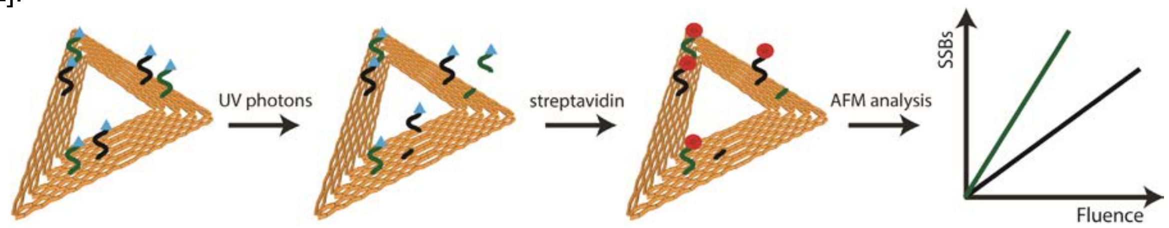
ABSTRACT

DNA is one of the most important biological molecules and its interaction with ionizing radiation is of ongoing interest as the mechanisms of energy deposition, deactivation and accordingly of DNA destruction are still mostly unclear. Since the photoionization threshold of biomolecules is around 10 eV, we use vacuum ultra violet light (VUV) in this energy range to induce single strand breaks (SSBs) in DNA oligonucleotides. This sequence-specific DNA damage is studied on the single-molecule level. Specifically designed oligonucleotides can be attached to DNA nanostructures and adsorbed on a VUV transparent substrate to be irradiated in an Argon filled chamber by a well-defined VUV beam. VUV induced bond dissociations can be visualized by Atomic Force Microscopy (AFM), quantified and plotted against the photon fluence of the irradiation experiment to determine a cross section for single strand breaks for a DNA sequence at a certain irradiation energy (see Fig. below) [1,2].



By means of gas phase VUV photo ionization mass spectrometry we want to investigate the detailed pathway of the photon-induced damage of the same DNA targets and under the same experimental conditions (photon energies and fluxes). Herein, the oligonucleotides will be isolated in an ion trap, thus allowing to determine their ionization thresholds. The experiment can be performed by coupling a linear ion trap, fitted with an electrospray ionization source (ESI), to the synchrotron beamline and applying tandem mass spectrometry [3].

The results of both experiments will be combined and will give new insights into the energy deactivation process in DNA by the impact of VUV photons. As one example DNA strands of different length that are containing only adenine as a nucleobase were investigated. Herein the ionization threshold increases with the number of nucleotides whereas the number of SSBs is decreasing with the size of the system.

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Mean Free Paths of Slow Electrons from Velocity Map Imaging of Aerosol Particles

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ABSTRACT

Electron mean free paths are important quantities for a number of physico-chemical phenomena ranging from aerosol physics and chemistry to radiation damage of biological tissues [1]. Angle-resolved photoemission data from size-selected aerosol particles combined with detailed electron scattering calculations represents a promising method for the determination of electron mean free paths in both solids and liquids. We vary both the size of the aerosol particles and the wavelength of the ionizing radiation and measure the kinetic energy and anisotropy of the resulting photoelectrons. These finite size effects depend sensitively on the mean free path and thus provide potentially more information than corresponding liquid jet, thin film, or bulk data.

By comparing experimental photoelectron velocity map images from aerosol particles with simulated ones [2], we are able to determine electron mean free paths in a given substance. We present the method and results where it was applied to determine mean free paths of low kinetic energy electrons (≤3 eV) in potassium chloride nanoparticles [3] and liquid water droplets [2]. The electron mean free paths reported for liquid water are a first of their kind at these electron kinetic energies and answer a longstanding question regarding their order of magnitude. Furthermore, new results on photoemission from size-selected, core-shell nanoparticles will be discussed. For the presented studies, experimental photoelectron images were recorded using either the VUV beamline of the Swiss Light Source or a table-top UV / VUV laser setup as photoionization source.

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Picosecond X-ray Tracking of Optically Driven Molecular Dynamics

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ABSTRACT

The Advanced Photon Source provides high-repetition-rate, ultrastable, widely tunable picosecond x-ray pulses where the assumption of linear, single-photon x-ray matter interactions is valid. Stability is key for laser-induced dynamics experiments where extraction of a small deviation from the ground state is required. Coupled with rapid advances in high-average-power, high-repetition-rate ultrafast optical laser technology, it is possible to synchronize and use every x-ray pulse in the APS storage ring to probe the evolution of transient species [1], either in a pump–probe or pump–probe-probe-probe… scheme – such that the average x-ray flux available is comparable to that at XFELs. In combination with x-ray microprobe techniques, high-repetition-rate ultrafast laser excitation sources, from the mid-IR to the UV, can saturate molecular transitions to ensure high excited-state fraction and uniform excitation over the x-ray probed region. A variety of light-induced processes have been tracked in a pump–probe fashion, e.g. strong-field ionization [2], adiabatic molecular alignment [3], spin-crossover [4], and ligand exchange, using simultaneous x-ray spectroscopies, (absorption, emission, resonant inelastic scattering and elastic scattering). Recent advances in detection methods [5] and x-ray beam characteristics promise several orders of magnitude increased sensitivity.

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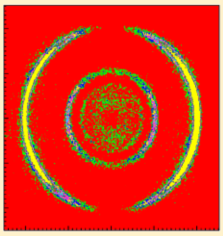
COMPANIES ADVERTISEMENTS

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