

## MO 25: X-ray Spectroscopy

Time: Thursday 14:30–16:30

Location: HS XVI

## Invited Talk

MO 25.1 Thu 14:30 HS XVI

**In good neighborhood: Suppression of radiation damage to X-ray-ionized molecules by intermolecular decay** — ●ANDREAS HANS<sup>1</sup>, DANA BLOSS<sup>1</sup>, MADHUSREE ROY CHOWDHURY<sup>1</sup>, CATMARN KÜSTNER-WETEKAM<sup>1</sup>, FLORIAN TRINTER<sup>2</sup>, ALEXANDER KULEFF<sup>3</sup>, LORENZ S. CEDERBAUM<sup>3</sup>, and ARNO EHRESMANN<sup>1</sup> — <sup>1</sup>Universität Kassel, Kassel, Germany — <sup>2</sup>Fritz-Haber-Institut, Berlin, Germany — <sup>3</sup>Universität Heidelberg, Heidelberg, Germany

The exploration of the interaction of ionizing radiation with matter is the basis of many application-related questions. In isolated small organic molecules, the deposition of energy by X-rays usually triggers complete or partial disintegration. In the transition to realistic scenarios, it is crucial how the behavior of molecules changes when they have neighbors, like in an aqueous environment. Intermolecular decays can release large amounts of energy efficiently and directly into the environment. We demonstrate that energy can already be efficiently dissipated by intermolecular Coulombic decay of electronic core vacancies. This leads to a decisive change in the dissociation dynamics of a molecule. While the dissipation of energy to the environment generally is protective for the molecule, the reverse effect can also occur, in which energy absorbed by the water leads to the ionization of a solvated molecule.

MO 25.2 Thu 15:00 HS XVI

**Enhanced Intermolecular Coulombic Decay in thiophene dimers** — ●DEEPTHY MARIA MOOTHERIL<sup>1</sup>, ANNA SKITNEVSKAYA<sup>2</sup>, XUEGUANG REN<sup>3</sup>, THOMAS PFEIFER<sup>1</sup>, and ALEXANDER DORN<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — <sup>2</sup>Irkutsk, Russia — <sup>3</sup>Xi'an Jiaotong University, Xi'an 710049, China

Inter-atomic/intermolecular Coulombic decay (ICD) is an important electronic relaxation mechanism after inner-valence ionization of atoms or molecules with weakly bound neighbours, which leads to low-energy electron emissions that can contribute to radiation damage in biological matter. In this work, we investigate ICD in thiophene dimers, five-membered aromatic ring containing sulfur, a third-row element, as a heteroatom, induced by electron collisions (68 eV). A comparison of the projectile energy loss spectra with theoretical single ionization spectra reveals that the ICD process originates from the C 2s<sup>-1</sup> inner-valence vacancy in thiophene dimers, which exhibits significant sulfur contributions. Notably, we observe that relaxation of states between the ICD and Auger thresholds results in a strong enhancement of ICD electrons below 4 eV, in contrast to other aromatic ring systems containing second-row atoms. Based on this 'ICD-only' decay contribution, we estimate a reduced relative ICD probability above the Auger threshold, where competing Auger channels become significant.

MO 25.3 Thu 15:15 HS XVI

**Resonant double core hole spectroscopy of ultrafast decay dynamics in Fe complexes** — ●JULIUS SCHWARZ<sup>1</sup>, MATZ NISSEN<sup>1</sup>, ALBERTO DE FANIS<sup>2</sup>, ALJOSCHA RÖRIG<sup>2</sup>, THOMAS BAUMANN<sup>2</sup>, SIMON DOLD<sup>2</sup>, TOMMASO MAZZA<sup>2</sup>, YEVHENIY OVCHARENKO<sup>2</sup>, SERGEY USENKO<sup>2</sup>, ANDREAS PRZYSTAWIK<sup>1,6</sup>, KAROLIN BAEV<sup>5</sup>, HAMPUS WIKMARK<sup>3</sup>, FLORIAN TRINTER<sup>4</sup>, TIM LAARMANN<sup>1,6</sup>, MARKUS ILCHEN<sup>1,2</sup>, NILS HUSE<sup>1</sup>, MICHAEL MEYER<sup>2</sup>, PHILIPPE VERNET<sup>3</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Universität Hamburg, Germany — <sup>2</sup>European XFEL, Hamburg, Germany — <sup>3</sup>Uppsala University, Sweden — <sup>4</sup>Fritz-Haber-Institut, Berlin, Germany — <sup>5</sup>DESY, Hamburg, Germany — <sup>6</sup>The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

Resonant double core hole (DCH) spectroscopy allows for the observation of ultrafast dynamic processes in small 3d-metal compounds in the gas phase with enhanced sensitivity. Using the intense X-Ray pulses of the European XFEL, electron and ion spectroscopy was used to reveal the signature of iron 2p<sup>2</sup> resonant DCH excitation in iron pentacarbonyl and ferrocene. Comparing the experimental results to theoretical calculations reconstructs single core hole (SCH) and DCH photon-matter interactions in the two targets. The DCH Auger-Meitner electron signals offer insight to the electron dynamics during the core hole lifetime and their dependence on the chemical environment. The product ions show evidence for DCH processes in multiply charged iron cations.

MO 25.4 Thu 15:30 HS XVI

**XUV Double-Ionisation of Micro-Solvated Bio-relevant Molecules** — ●BRENDAN WOUTERLOOD<sup>1</sup>, SITANATH MONDAL<sup>1</sup>, MYRIAM DRISSI<sup>2</sup>, MADHUSREE ROY-CHOWDHURY<sup>2</sup>, GUSTAVO GARCIA-MARCAS<sup>2</sup>, LAURENT NAHON<sup>2</sup>, FRANK STIENKEMEIER<sup>1</sup>, and SEBASTIAN HARTWEG<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Freiburg — <sup>2</sup>Synchrotron SOLEIL, St. Aubin, France

Studying the XUV-photoionisation of biomolecules, such as the nucleobase thymine and its precursor, pyridine, in the gas phase allows detailed insights into energetics and dynamics at the molecular level. As in-vivo biomolecular systems exist in the condensed phase, studying complexes of these molecules with water gives greater insight into decay channels that are available in biological systems, while still allowing the application of typical gas phase experimental approaches such as electron-ion coincidence spectroscopy. The electron-ion-ion coincidence detection of doubly-ionised molecules and complexes enables correlation of cationic states to certain fragmentation pathways. Above the double-ionisation potential, molecular fragmentation channels differ from single ionisation processes with intramolecular proton transfer reactions stabilising the cationic fragments. In these complexes different auto-ionisation processes, such as the non-local intermolecular Coulombic decay (ICD) and electron transfer mediated decay (ETMD), and local Auger-Meitner decay can thus be distinguished. These processes are important to the field of radiation chemistry since the production of low energy electrons can trigger reactions which damage biological material.

MO 25.5 Thu 15:45 HS XVI

**Influence of a single water molecule on the X-ray absorption spectra of gas-phase phosphotyrosine** — ●JULIETTE LEROUX<sup>1,2,3</sup>, JEAN-YVES CHESNEL<sup>1</sup>, LUCAS SCHWOB<sup>2</sup>, and SADIA BARI<sup>2,4</sup> — <sup>1</sup>CIMAP, University of Caen — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY — <sup>3</sup>University of Hamburg — <sup>4</sup>University of Groningen

The isolation of biomolecules in the gas phase removes all interactions with the solvent and enables stepwise control of these interactions by progressively increasing the number of bound water molecules, ultimately bridging the gap between isolated molecules and aqueous conditions. Already, a single water molecule can induce significant structural changes in the molecule, such as the location of the protonation site. Over the last thirty years, there have been efforts to develop experimental techniques to study hydrated species in the gas phase using an electrospray ionization source.

To study the effect of hydration on the structure of biomolecules, our technique of choice is near-edge X-ray absorption mass spectrometry (NEXAMS). NEXAMS provides a local probe into the atomic environment and is based on the electronic excitations of core electrons to unoccupied molecular orbitals, thus capturing the electronic and geometric structure of the system under investigation. In this context, we studied the influence of a single water molecule on the structure and radiation-induced fragmentation of protonated phosphotyrosine. In particular, I will discuss the results we obtained at the carbon and oxygen K-edges in comparison with density functional theory calculations to decipher the structure of singly hydrated phosphotyrosine.

MO 25.6 Thu 16:00 HS XVI

**Ultrafast molecular ion dynamics illuminated by soft X-ray spectroscopy** — ●SIMON REINWARDT<sup>1</sup>, ALEXANDER PERRY-SASSMANNSHAUSEN<sup>2</sup>, TICIA BUHR<sup>3</sup>, ALFRED MÜLLER<sup>2</sup>, STEFAN SCHIPPERS<sup>2</sup>, FLORIAN TRINTER<sup>4</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Universität Hamburg, Hamburg, Germany — <sup>2</sup>Justus-Liebig-Universität Gießen, Gießen, Germany — <sup>3</sup>Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — <sup>4</sup>Fritz-Haber-Institut, Berlin, Germany

Synchrotron radiation has turned out to be a very powerful tool to study molecular dynamics of small molecules [1]. Photoexcitation is an instructive technique that facilitates the investigation of ultrafast dissociation processes on a time scale similar to lifetime of Auger decay [2]. Using the photon-ion merged-beams technique, implemented at the Photon-Ion Spectrometer at PETRA III (DESY, Hamburg), we measured the kinetic energy release of molecular ions depending on the photon energy [3]. Thereby, the ultrafast dynamics of the photodissociation process of molecular ions NH<sup>+</sup> and OH<sup>+</sup> was revealed

particularly as a result of  $1s \rightarrow \pi^*$  and  $1s \rightarrow \sigma^*$  excitations.

- [1] J. D. Bozek and C. Miron, *J. Electron. Spectrosc. Relat. Phenom.* **204**, 269 (2015).
- [2] O. Travnikova *et al.*, *Phys. Rev. Lett.* **116**, 213001 (2016).
- [3] M. Martins *et al.*, *J. Phys. Chem. Lett.* **12**, 1390 (2021).

MO 25.7 Thu 16:15 HS XVI

**Novel Apparatus for Synchrotron X-ray Photoelectron Spectroscopy of Size-Selected Gas-Phase Clusters** — ●LOTAR KURTI, PHILLIP STÖCKS, FABIAN BÄR, LUKAS WEISE, and BERND V. ISSENDORFF — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany

A newly developed apparatus enables X-ray photoelectron spectroscopy on mass-selected cluster ions at synchrotrons for the first time. The system's centerpiece is a liquid nitrogen-cooled linear Paul trap, where stored cluster ions interact with synchrotron radiation. The emitted electrons are directed by a specially designed magnetic field into a Hemispherical Energy Analyzer, where photoelectron spectra are captured. Clusters are generated in a magnetron cluster source, mass-selected using a quadrupole mass spectrometer, and then introduced into the linear ion trap. This setup enables element-specific binding energy measurements of core levels, providing detailed insights into the chemical bonding of pure and mixed metal and semiconductor clusters. Additionally, we will present initial test spectra of emitted electrons recorded with the apparatus, demonstrating its ability to capture high-resolution photoelectron spectra and validating its potential for advancing studies in cluster ion chemistry and bonding.