

## MO 8: XUV and X-ray Excitation and Spectroscopy

Time: Monday 16:15–17:45

Location: S HS 001 Biologie

MO 8.1 Mon 16:15 S HS 001 Biologie

**Time domain measurement of the ultrafast electronic decay of core excited HCl molecules by THz streaking**— ●KATHARINA WENIG<sup>1</sup>, MAREK WIELAND<sup>1</sup>, SOPHIE WALTHER<sup>1</sup>, ARNE BAUMANN<sup>1</sup>, ANASTASIOS DIMITRIOU<sup>1</sup>, MARK PRANDOLINI<sup>1</sup>, OLIVER SCHEPP<sup>1</sup>, IVETTE BERMÚDEZ MACIAS<sup>1</sup>, MALTE SUMFLETH<sup>1</sup>, NIKOLA STOJANOVIC<sup>2</sup>, STEFAN DÜSTERER<sup>2</sup>, JULIANE RÖNTSCH-SCHULENBURG<sup>2</sup>, MARKUS DRESCHER<sup>1</sup>, and ULRIKE FRÜHLING<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Deutschland — <sup>2</sup>Deutsches Elektron-Synchrotron DESY, Hamburg, Deutschland

After excitation of 2p core electrons to the antibonding  $\sigma^*$  orbital the HCl molecules dissociate and the electronic excitation relaxes via an Auger decay. We have measured the ultrafast electronic decay of HCl molecules in the time domain.

In the experiment we addressed the 2p core electrons with 40 fs (FWHM) soft x-ray pulses from the free-electron laser in Hamburg (FLASH). Superimposing the pump pulse with intense THz light electrons emitted from the molecules are accelerated (streaked) by the THz electric field. Thereby, the resulting momentum change of the electron depends on the THz phase at the instant of ionization. We were able to measure the phase shift between the photo- and Auger electrons in the THz streak spectrograms and determine the Auger decay constant of the HCl molecule. In order to verify the resolution of our experiment the MNN Auger decay of Krypton atoms was investigated as well. The accuracy of the extracted value is on the order of two femtoseconds and therefore much below the duration of the exciting pump pulse.

MO 8.2 Mon 16:30 S HS 001 Biologie

**Delayed relaxation of highly excited cationic states in naphthalene**— GEERT REITSMA<sup>1</sup>, JOHAN HUMMERT<sup>1</sup>, JUDITH DURA<sup>1</sup>, VINCENT LORIENT<sup>2</sup>, MARC J. J. VRACKING<sup>1</sup>, FRANCK LÉPINE<sup>2</sup>, and ●OLEG KORNILOV<sup>1</sup> — <sup>1</sup>Max Born Institute, Berlin, Germany — <sup>2</sup>Institut Lumière Matière, Université Lyon 1, CNRS, France

The efficiency of energy transfer in ultrafast electronic relaxation of molecules depends strongly on the complex interplay between electronic and nuclear motion. Modern tools of time-resolved spectroscopy allow investigation of these processes in "real" time. In this study we report two-color pump-probe experiments that probe the relaxation dynamics of highly excited cationic states of naphthalene, a prototypical polycyclic aromatic hydrocarbon molecule. The cations are produced using wavelength-selected, ultrashort extreme ultraviolet pulses and probed by subsequent ionization with a moderately-strong NIR pulses. Surprisingly, the observed relaxation lifetimes increase with the cationic excitation energy. We postulate that the observed effect is the result of a quantum mechanical population trapping that leads to delayed relaxation of molecules in the regions with high density of excited states. Comparison with previous results on relaxation dynamics of larger polyaromatic hydrocarbons suggests that this may be a general phenomenon in relaxation of PAH molecules.

MO 8.3 Mon 16:45 S HS 001 Biologie

**Femtosecond dynamics in highly excited neutral CO<sub>2</sub>: an experimental and theoretical study**— ●THOMAS SCHNAPPINGER<sup>1</sup>, MATTEO LUCCHINI<sup>2</sup>, MARIO MURARI<sup>2</sup>, GIACINTO D. LUCARELLI<sup>2</sup>, LUCA POLETTI<sup>2</sup>, FABIO FRASSETTO<sup>2</sup>, MAURO NISOLI<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich, Germany — <sup>2</sup>Physics Department, Politecnico di Milan, Italy

The idea of this work is to combine an extreme UV (XUV) pulse and a few-femtosecond IR pulse in a pump-probe approach on carbon dioxide molecules. Here we want to present the first theoretical results obtained to interpret the experimental findings.

The dominant, almost constant, signal in the time dependent photoelectron spectrum arises from the direct ionization of the molecule just by the XUV pulse. A weaker oscillating signal with lower kinetic energy is also detected. The fastest observed period is around 28 fs.

Using high-level multi-reference methods (CASSCF and CASPT2) we are able to determine the electronic states of carbon dioxide in an energy range from 0 to 20 eV. Calculating the potential energy surfaces of various states it is possible to locate bound neutral states in the vicinity of the ionization threshold. The information of the static calculations in combination with the experimental results offers an interpretation of the weaker oscillating signal. The observed oscillation

can be attributed to the vibrational motion of the nuclear wave packet in highly excited states around 1 eV below the ionization threshold.

MO 8.4 Mon 17:00 S HS 001 Biologie

**XUV-photoion spectra from neutral gases measured with a radio frequency ion trap**— ●SIMON REINWARDT<sup>1</sup>, IVAN BAEV<sup>1</sup>, KAROLIN MERTENS<sup>1</sup>, FLORIAN TRINTER<sup>2,3</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Hamburg, Germany — <sup>2</sup>FS-PE, DESY, Hamburg, Germany — <sup>3</sup>Molecular Physics, Fritz-Haber-Institut, Berlin, Germany

Photoion spectra of the neutral gases CO<sub>2</sub> and CH<sub>4</sub> were measured using a radio frequency ion trap at the soft X-ray beamline P04 of the synchrotron PETRA III at DESY in Hamburg. The used ion trap is part of the stationary Photon-Ion-Spectrometer (PIPE) [1]. In this experiment the neutral gas was photo ionized with monochromatized synchrotron light and the generated photoions were trapped in the radio frequency potential of the ion trap. In this way it was possible to measure a photoion NEXAFS spectrum at the carbon K-edge (290 eV) and for CO<sub>2</sub> also at the oxygen K-edge (535 eV).

Besides that we could show that the trapped ionized gas molecules are able to react with neutral gas to form larger molecular ions. At CO<sub>2</sub> we observed a small amount of CO<sub>3</sub><sup>+</sup> and at CH<sub>4</sub> we found products with up to two carbon atoms. Depending on the resonant excitation, it is possible to change the generated ion as well as the electronic state of the ion so that the subsequent reaction is influenced. In addition similar measurements could be performed on ethene. Possible channels for these photochemical reactions will be discussed.

[1] S. Schippers et al., J. Phys. B: At. Mol. Opt. Phys 47, 115602, 2014.

MO 8.5 Mon 17:15 S HS 001 Biologie

**Interrogating the Electronic Structure of Aqueous Diazines Using Non-Resonant and Resonant Soft X-ray Photoelectron Spectroscopy**— ●MD SABBIR AHSAN<sup>1,2</sup> and IAIN WILKINSON<sup>1</sup> — <sup>1</sup>Methods for Material Development, Helmholtz-Zentrum Berlin, Hahn Meitner platz 1, 14109 Berlin, Germany — <sup>2</sup>Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Diazines play important roles in determining the photophysicochemical properties of bio-molecules such as DNA and RNA. We will present the electronic structure study of aqueous (aq.) diazines using liquid-microjet-based x-ray photoelectron spectroscopy (XPS). Valence band (HOMO) and core level C 1s and N 1s BE's are red shifted in aq. solution in comparison to the gas-phase. Preliminary surface- and bulk-sensitive studies on pyrimidine highlight an increase of N 1s BE's in the bulk compared to at the vacuum/liquid interface, whereas the C 1s spectra show the opposite behavior. Pyrimidine shows the lowest N 1s BE among the diazines in the surface-sensitive measurements. Moreover, resonant photoelectron spectroscopy (RPES) scans over the diazine N K-edges were recorded to study local and non-local relaxation processes in aq. solution. A number of core-valence resonances were identified and were found to be blue shifted compared to isolated gas phase molecules. Our study highlights solvent-induced electronic structure perturbations which are expected to provide information about the intra and intermolecular energy and proton transfer processes occurring in aq. diazine solutions following x-ray excitation.

MO 8.6 Mon 17:30 S HS 001 Biologie

**Soft X-ray Absorption Spectroscopy of Aqueous Solutions Using a Table-Top Femtosecond Soft X-ray Source**

— ●CARLO KLEINE, MARIA EKIMOVA, GILDAS GOLDSZTEJN, SEBASTIAN RAABE, CHRISTIAN STRÜBER, JAN LUDWIG, SURESH YARLAGADDA, STEFAN EISEBITT, MARC VRACKING, THOMAS ELSAESSER, ERIK NIBBERING, and ARNAUD ROUZÉE — Max-Born-Institut

The advent of novel light sources like free electron lasers and high-harmonic generation (HHG) sources that offer the possibility to generate radiation in the soft X-ray wavelength range with femtosecond pulse durations has sparked widespread interest in the development of various forms of ultrafast, element-specific core-level spectroscopy. Here, we demonstrate the feasibility of soft X-ray absorption spectroscopy in the water window on organic molecules and inorganic salts in aqueous solution using a table-top laser-based approach. Using a high-order harmonic source that delivers femtosecond pulses of short

wavelength radiation in the photon energy range from 220 eV to 450 eV, we report static soft X-ray absorption measurements in transmission mode on a series of solvated compounds using flatjet technology. We monitor the absorption of the molecular samples between the carbon (280 eV) and nitrogen (400 eV) K-edges and compare our results

with previous measurements performed at the BESSYII facility. We discuss the roles of pulse stability and photon flux in the outcome of our experiments. Our experiment paves the way towards table-top femtosecond, solution phase soft X-ray absorption spectroscopy in the water window.