

MO 10: XUV-spectroscopy

Time: Wednesday 10:30–12:15

Location: MO-H6

MO 10.1 Wed 10:30 MO-H6

Attosecond pump-probe coincidence spectroscopy of small molecules at 100 kHz — ●MIKHAIL OSOLODKOV, TOBIAS WITTING, FEDERICO J. FURCH, FELIX SCHELL, CLAUS PETER SCHULZ, and MARC J. J. VRAKING — Max Born Institute, Berlin, Germany

It is advantageous to perform attosecond photoionization experiments in molecules with coincidence detection, since it allows resolving particular photoionization channels, such as dissociative channels. Here we report on experiments done at a beamline combining a table top high order harmonic generation (HHG) based extreme ultraviolet (XUV) laser pulse source operating at 100 kHz [1] with a reaction microscope [2], being recently commissioned. A noncollinear optical parametric chirped pulse amplification system (NOPCPA) operating at 800 nm central wavelength [3] serves as a driver. Both XUV attosecond pulse trains (APTs) [1], as well as isolated attosecond pulses (IAPs) are available for attosecond pump-probe experiments with a near infrared (NIR) probe. Employing the coincidence capabilities, the photoionization dynamics corresponding to the predissociative C state of the molecular nitrogen ion was studied state selectively using the RABBIT (reconstruction of attosecond beating by interference of two-photon transitions) technique with short XUV APTs and approximately 7 fs FWHM NIR pulses.

- [1] M. Osolodkov et al., *J. Phys. B: At. Mol. Opt. Phys.* (2020)
- [2] Sascha Birkner, PhD thesis, Freien Universität Berlin (2015)
- [3] Federico J. Furch et al., *Optics Letters* (2017)

MO 10.2 Wed 10:45 MO-H6

Experimental control of quantum-mechanical entanglement in an attosecond pump-probe experiment — ●LISAMARIE KOLL¹, LAURA MAIKOWSKI¹, LORENZ DRESCHER^{1,2}, TOBIAS WITTING¹, and MARC J.J. VRAKING¹ — ¹Max Born Institute, Berlin, Germany — ²Department of Chemistry, University of California, Berkeley, California 94720, USA

The photoionization of atoms or molecules creates a bipartite quantum system consisting of a photoelectron and an ion. In many experiments the observability of a physical quantity of interest relies on the coherence between the ionic or electronic parts of the wave function. However, this coherence can be limited by entanglement [1]. We show the control of entanglement by tuning the delay of two phase-locked XUV pulses in the dissociative ionization of hydrogen molecules [2]. Our experiments show the changing degree of vibrational coherence due to entanglement between the ionic and photoelectronic part of the quantum system.

- [1] M. J.J. Vrakking, "Control of Attosecond Entanglement and Coherence", *Physical Review Letters* 126, 113203 (2021)
- [2] L.-M. Koll et al., "Experimental control of quantum-mechanical entanglement in an attosecond pump-probe experiment", *Physical Review Letters* (in press) (or: arXiv:2108.11772 (2021))

MO 10.3 Wed 11:00 MO-H6

Observing the electronic coherence in uracil via simulated XUV spectra — ●LENA BÄUML¹, FLORIAN ROTT¹, THOMAS SCHNAPPINGER², and REGINA DE VIVIE-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Department of Physics, Stockholm University, Sweden

The nucleobase uracil exhibits a high photostability due to its ultrafast relaxation process mediated by a S_1/S_2 conical intersection (CoIn) seam. Here especially the interplay between nuclear and electron dynamics becomes prominent. Applying our NEMol Ansatz^[1,2] for coupled electron and nuclear dynamics on the quantum level, we were able to observe a seemingly long-lived electronic coherence for the CoIn-mediated relaxation process in uracil. We will discuss the origin of this longevity and will propose a possible experiment to observe this coherence. Our method of choice is the time-dependent transient XUV/X-ray absorption spectroscopy, since this method is sensitive to the fast changes in electronic structure. Therefore we calculated the transient XUV spectra for the O, N, and C edges based on the complete wavepacket relaxation dynamics after laser excitation. The calculations were performed at the restricted active space perturbation theory (RASPT2) level of theory as outlined by Rott et al.^[3]

- [1] T. Schnappinger et al., *J. Chem. Phys.*, **154**, 134306 (2021).

- [2] L. Bäuml et al., *Front. Phys.*, **9**, 246 (2021).

- [3] F. Rott et al., *Structural Dynamics*, **8**, 034104 (2021).

MO 10.4 Wed 11:15 MO-H6

X-ray absorption spectroscopy of the hydronium cation

— ●JULIUS SCHWARZ¹, FRIDTJOF KIELGAST¹, IVAN BAEV¹, SIMON REINWARDT¹, FLORIAN TRINTER², STEPHAN KLUMPP³, SADIYA BARI^{3,4}, ALEXANDER PERRY-SASSMANSHAUSEN⁵, TICIA BUHR⁵, STEFAN SCHIPPERS⁵, ALFRED MÜLLER⁵, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Germany — ²Goethe-Universität Frankfurt am Main, Frankfurt am Main, Germany — ³Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ⁴Rijksuniversiteit Groningen, Groningen, The Netherlands — ⁵Justus-Liebig-Universität Gießen, Gießen, Germany

Facilitated by the hydrogen-bond network of water, protons in liquid water are diffused at a rapid rate, with several possible explanations invoking the hydronium cation H_3O^+ . Among the many ways of gaining knowledge about H_3O^+ , the method of soft X-ray absorption spectroscopy has been established as a valuable analysis tool for ionic molecules and clusters [1].

We report the use of a flowing afterglow ion source to record the soft X-ray absorption spectrum of the hydronium H_3O^+ cation at the O 1s edge using the photon ion spectrometer (PIPE) at the synchrotron lightsource PETRA III in Hamburg [2]. H_2O^+ cations have been analyzed for comparison. The spectra show significant shifts in resonance energies and widths compared to neutral H_2O and relative to each other.

- [1] Martins et al., *J. Phys. Chem. Lett.*, **12** 5 (2021), 1390–1395
- [2] S. Schippers et al., *X-Ray Spectrometry*, **49** 11 (2020)

MO 10.5 Wed 11:30 MO-H6

Revealing ultrafast proton transfer dynamics in ionized aqueous urea solution through time-resolved x-ray absorption spectra and *ab initio* simulations — ●YASHOJ SHAKYA^{1,2},

LUDGER INHESTER¹, ZHONG YIN³, YI-PING CHANG⁴, TADAS BALČIUNAS⁴, JEAN-PIERRE WOLF⁴, HANS JAKOB WÖRNER³, and ROBIN SANTRA^{1,2,5} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, Germany — ³Laboratory for Physical Chemistry, ETH Zürich, Zürich, Switzerland — ⁴GAP-Biophotonics, Université de Genève, Geneva, Switzerland — ⁵Hamburg Centre for Ultrafast Imaging, Hamburg, Germany

Probing the early dynamics of chemical systems following ionization is essential for our understanding of radiation damage. Time-resolved x-ray absorption spectroscopy (TRXAS) on a femtosecond timescale can provide crucial insights into the ultrafast processes occurring upon ionization due to its element-specificity. However, to get a clear interpretation of the dynamical features in the spectra, one often has to rely on theoretical simulations.

In this theoretical study, we investigate the response of urea in 10M aqueous solution to ionizing radiation and how it can be probed via TRXAS. We are able to interpret the temporal variation in the carbon K -edge resonance signal as an effect of proton transfer between two hydrogen bonded ureas through our *ab initio* simulations. Our results are in good agreement with recent pump-probe experiments on 10 M aqueous urea solution.

MO 10.6 Wed 11:45 MO-H6

Ultrafast photoisomerization studied by time-resolved photoelectron spectroscopy — CAMILO GRANADOS¹, EVGENII TITOV²,

JOHAN HUMMERT¹, EVGENII IKONNIKOV¹, STEFAN HAACKE³, ROLAND MITRIC⁴, and ●OLEG KORNILOV¹ — ¹Max Born Institute, Berlin — ²Department of Chemistry, University of Potsdam — ³Institut de physique et de chimie des Matériaux, Strasbourg — ⁴Institute of Physical and Theoretical Chemistry, University of Würzburg

Ultrafast photoinduced isomerization is a fundamental process governing molecular dynamics both in biologically relevant chromophores and in functional materials. It is widely accepted that the isomerization efficiency is governed by the dynamics through conical intersections. However, the influence of the complex environments hosting the chromophores on the dynamics through the conical intersection is not fully understood. XUV time-resolved photoelectron spectroscopy (TRPES),

are promising in delivering detectable signals from the regions of conical intersection. TRPES of molecular chromophores requires application of photoemission methods to the liquid phase samples (molecular solutions). By combining an ultrafast tunable XUV source with a microliquid jet sample we demonstrated liquid phase TRPES of organic molecules. In this contribution we will report on the recent results applying this method to the prototypical molecules, Methyl Orange and Metanil Yellow[2]. The experimental results are complemented by high-level TDDFT surface hopping calculations to reveal electronic state involved in ultrafast isomerization of the molecules. We will further show preliminary results for several bio-mimetic chromophores.

MO 10.7 Wed 12:00 MO-H6

Molecular environments in the time-domain — •CHRISTIAN SCHRÖDER, MAXIMILIAN POLLANKA, PASCAL SCIGALLA, MICHAEL MITTERMAIR, ANDREAS DUENSING, MARTIN WANCKEL, and REINHARD KIENBERGER — Chair for laser and X-ray physics E11, Technische Universität München, Germany

We report on photoemission timing measurements performed on small

iodine-substituted organic molecules in the gas phase. The iodine atom's $4d$ photoemission serves as an intra-molecular timing reference which is clocked against the accurately known He1s photoemission.

Using the iodine atom as an intra-molecular reference is motivated by the presence of a giant resonance in the $I4d \rightarrow \epsilon f$ photoemission channel which is expected to be largely unaffected by its chemical environment. Therefore, in proximity to the resonance, any difference in the observable photoemission delay between different molecules is expected to a consequence of the differences in molecular environment experienced by the leaving photoelectron wavepacket during its propagation through the molecular potential landscape.

We complement our findings with scattering calculations in order to gain deeper insight into the relationship between the observable photoemission time and molecular geometry, the photoelectron angular distribution and the role of the molecule's orientation during the experiment, thereby paving the road towards establishing photoemission timing experiments as an efficient and accurate means to study molecular environments.