

MO 13: Ultrafast Dynamics II

Time: Wednesday 11:00–13:00

Location: HS XVI

MO 13.1 Wed 11:00 HS XVI

Photo-induced structural dynamics of thymine with ultrafast electron diffraction — ●XIAOJUN WANG¹, JACKSON LEDERER², DENNIS MAYER¹, FABIANO LEVER¹, PEDRO NUNES², YUSONG LIU³, SURJENDU BHATTACHARYYA³, NIKHIL PACHISIA², XINXIN CHENG³, TIANZHE XU³, STEPHEN WEATHERSBY³, RANDY LEMONS³, PATRICK KRAMER³, PHILIPP LENZEN³, MING-FU LIN³, KIRK LARSEN³, FUHAO JI³, ROBERT ENGLAND³, CHRISTINA HAMPTON³, BRIAN KAUFMAN³, ALICE GREEN³, ALEXANDER REID³, TODD MARTINEZ^{3,4}, THOMAS WOLF³, MARTIN CENTURION², and MARKUS GUEHR^{1,5} — ¹Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, USA — ³SLAC National Accelerator Laboratory, Menlo Park, USA — ⁴Department of Chemistry, Stanford University, Stanford, USA — ⁵Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany

The photoprotection mechanism of thymine involves complex relaxation dynamics, where energy from photoexcitation is converted into vibrational energy through radiationless transitions. Previous studies have indicated that isolated thymine molecules undergo $^1\pi\pi^* \rightarrow ^1n\pi^*$ internal conversion within 100 femtoseconds (fs), followed by the intersystem crossing from $^1n\pi^*$ to the triplet state within 10 picoseconds (ps). However, the nuclear dynamics accompanying the transitions have not been experimentally resolved. Here we present a direct observation of the ultrafast nuclear motions using ultrafast electron diffraction, on the fs timescale and sub-Ångstrom resolution.

MO 13.2 Wed 11:15 HS XVI

Ultrafast electron diffraction imaging of wavelength-dependent trans-to-cis isomerization in azobenzene — SURJENDU BHATTACHARYYA¹, MING-FU LIN¹, THOMAS J. A. WOLF¹, ALICE E. GREEN¹, YUSONG LIU¹, XINXIN CHENG¹, PHILIPP LENZEN¹, XIAOZHE SHEN¹, ●KASRA AMINI², FERNANDO RODRIGUEZ DIAZ², FABIANO LEVER³, XIAOJUN WANG³, MARKUS GUEHR³, MIKE MINITTI¹, JOEL ENGLAND¹, and ALEXANDER H. REID¹ — ¹SLAC National Accelerator Laboratory, Menlo Park, CA, USA — ²Max-Born-Institut, Max-Born-Straße 2A, 12489, Berlin, Germany — ³Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

Molecular photoswitches, exemplified by azobenzene (AB), represent a key class of molecules displaying optical switching and structural rearrangement around a double bond - a process that is fundamental to human vision. Ab initio calculations predict that optical excitation of trans-AB to its second excited state at 297-nm undergoes trans-to-cis isomerization with a quantum yield of 12% within a 350-fs timescale. However, experimental investigations into the photochemistry and nuclear dynamics of gas-phase AB remain limited. Here, we present an ultrafast electron diffraction (UED) study of trans-to-cis isomerization in AB between 267-nm and 330-nm using the MeV-UED instrument at SLAC. We show that the onset of isomerization is wavelength-dependent, and we measure the first direct observation of the transient cis isomer which is formed within the predicted 350-fs timescale.

MO 13.3 Wed 11:30 HS XVI

Semiclassical simulations of laser-induced electron diffraction — ●ÁLVARO FERNÁNDEZ^{1,2}, ANDREY YACHMENEV^{1,3}, and JOCHEN KÜPPER^{1,2,3} — ¹Deutsches Elektronen-Synchrotron, DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Center for Ultrafast Imaging, Universität Hamburg

Laser-induced electron diffraction (LIED) [1] is a tabletop imaging technique capable of measuring photoelectron probability densities, which allow for determining nuclear positions with sub-bondlength and femtosecond precision. In LIED, electrons have much lower energies than those of standard electron diffraction and are significantly perturbed by interactions with the parent ion during rescattering. Consequently, retrieving molecular structures from LIED requires accurate theoretical simulations of the complex photoelectron dynamics.

We present the implementation and results of semiclassical simulations of LIED [2]. In our model, the ionisation step is computed quantum-mechanically using the MO-ADK or Dyson formalisms. Subsequent photoelectron propagation and rescattering are treated classically, modelling the electrostatic potential of the parent ion using chosen quantum-chemical method. To obtain accurate results, billions

of different electron trajectories are simulated. The approach is implemented as a Python package, and its computational performance and accuracy are validated in simulations of OCS and indole-water molecules.

- [1] Karamatskos, E. T., *et al.*, *J. Chem. Phys.*, **150**, 24 (2019)
 [2] Wiese, J., *et al.*, *Phys. Rev. Research*, **3**, 013089, (2021)

MO 13.4 Wed 11:45 HS XVI

Towards Ultrafast Molecular Dynamics in Chiral Molecules in a Micro-solvated Environment — ●LILIANA M. RAMOS MORENO¹, DEEPAK K. PANDEY¹, SAGNIK DAS¹, CLAUS-PETER SCHULZ², HENDRIKE BRAUN-KNIE¹, and JOCHEN MIKOSCH¹ — ¹Institut für Physik, Universität Kassel, Kassel, Germany — ²Max Born Institute (MBI), Berlin, Germany

The environment surrounding a molecule, its solvent, affects the molecular properties and reaction dynamics. Solution in water is of particular relevance in biology and chemistry. Water is also of great fundamental interest as the “universal solvent”, with the ability to dissolve more substances than most other liquids. We follow a bottom-up approach to investigate solution effects with femtosecond laser spectroscopy step-by-step, by adding water molecules one at a time to a small molecule in the gas phase. The clusters are produced in a temperature-variable molecular beam source[1]. The experiments are performed in a Photoelectron Photoion Coincidence (PEPICO) spectrometer. It consists of a magnetic bottle for photoelectrons and a Wiley-McLaren spectrometer for photoions, allowing us to retrieve time-of-flight spectra, in coincidence. We will present our experimental setup and the progress of an experiment where we study the time-dependent Circular Dichroism (CD) in 3-methyl cyclopentanone (3-MCP). The temperature-variable source allows us to change the conformer composition of 3-MCP and test a hypothesis established in recent work[2]. [1]Müller et al., *JPCA* **118**, 8517 (2014) [2]Das et al., Control of circular dichroism in ion yield of 3-methyl cyclopentanone with femtosecond laser pulses(submitted).

MO 13.5 Wed 12:00 HS XVI

Dynamics of pyrrole-water studied by Coulomb-explosion imaging — ●SEBASTIAN TRIPPEL^{1,2} and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Physics, Universität Hamburg

Microsolvated biomolecules are promising model systems for studying the corresponding light-induced dynamics of molecules in solution [1]. Due to the still manageable complexity of the small clusters in the gas phase, atomic, molecular, and optical physics methods can be used to analyze and characterize their dynamics. Here, we will present our findings on the dynamics of ionized pyrrole-water [2]. Furthermore, we will discuss the creation of highly charged carbon atoms observed for the microsolvated clusters.

- [1] L. He, *et int.* (8 authors), J. Küpper, *J. Phys. Chem. Lett.* **14**, 10499 (2023)
 [1] M. Johny, *et int.* (6 authors), J. Küpper, *Phys. Chem. Chem. Phys.* **26**, 13118 (2024)

MO 13.6 Wed 12:15 HS XVI

Unraveling the dynamics of ionized water dimer in a highly-purified molecular beam — ●IVO S. VINKLÁREK¹, HUBERTUS BROMBERGER¹, LUISA BLUM^{1,2}, SEBASTIAN TRIPPEL¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Department of Physics, Universität Hamburg, Hamburg, DE — ³Center for Ultrafast Imaging, Universität Hamburg, Hamburg, DE

Radiation chemistry in biochemical systems is primarily driven by the ultrafast dynamics of water molecules after absorption of ionizing radiation. The initial water response to the ionization involves ultrafast hydrogen-bond-mediated proton transfer (PT), which was recently probed in the prototypical water-dimer cation (H₂O)₂⁺ [1], and subsequent fragmentation into highly reactant ions and radicals.

Our detailed study utilizing purified molecular beams of (H₂O)₂⁺ [2] revealed that (H₂O)₂⁺ can either stabilize or undergo fragmentation along more than ten distinct pathways. While theoretical studies have explored the rates and dynamics of some of these reactions, experimental evidence is completely lacking. To address this, we employed

a disruptive-probing scheme [3] that allows us to track early PT dynamics and the populations of ionic products, thus directly yielding effective reaction-rate constants. These findings provide crucial insights into ionizing processes in both the atmosphere and living organisms.

- [1] Schnorr, K. *et al.*, *Sci. Adv.* 9, eadg7864 (2023)
- [2] Vinklársek, I.S. *et al.*, *J. Phys. Chem. A* 128, 1593 (2024),
- [3] Jochim, B. *et al.*, *Rev. Sci. Instrum.* 93, 033003 (2022)

MO 13.7 Wed 12:30 HS XVI

Understanding fragmentation dynamics of difluorodiodomethane — •NIDIN VADASSERY^{1,3}, SEBASTIAN TRIPPEL^{1,2,4}, and JOCHEN KÜPPER^{1,2,3,4} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Center for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany — ³Department of Chemistry, Universität Hamburg, Hamburg, Germany — ⁴Department of Physics, Universität Hamburg, Hamburg, Germany

Unimolecular photo-fragmentation is crucial in environmental chemical reactions like ozone depletion and aerosol formation [1]. Photodissociation of polyhalohydrocarbons significantly contributes to these climate-impacting processes. Difluorodiodomethane (CF₂I₂) exhibits unconventional dynamics near dissociative energies [2]. We present experimental results exploring CF₂I₂ dissociation dynamics using near-infrared laser pulses. A pure CF₂I₂ sample was produced using an electrostatic deflector, revealing metastable states and quantum-state-specific dynamics during photo-fragmentation [3]. We also outline a time-resolved x-ray diffraction approach and present computational

results of diffraction simulations for laser-aligned gas-phase CF₂I₂.

- [1] J. C. G. Martin, *et al.*, *J. Am. Chem. Soc.* **144**, 9240 (2022)
- [2] P. Z. El-Khoury, *et al.*, *J. Chem. Phys.* **132**, 124501 (2010)
- [3] I. S. Vinklársek, *et int.* (3 authors), J. Küpper, S. Trippel, *J. Phys. Chem. A* **128**, 1593(2024) *arXiv:2308.08006* [physics].

MO 13.8 Wed 12:45 HS XVI

Single and Double Ionization of Pyridine and Pyridine-water Complexes — •SITANATH MONDAL¹, BRENDAN WOUTERLOOD¹, MYRIAM DRISSI², GUSTAVO A. GARCIA², LAURENT NAHON², FRANK STIENKEMEIER¹, and SEBASTIAN HARTWEG¹ — ¹Institute of Physics, Albert-Ludwigs-Universität Freiburg, Germany — ²Desirs Beamline, Synchrotron Soleil, St. Aubin, France

Cell and gene damage caused by slow electrons created by secondary processes after interaction with ionizing radiation is an important field of research. Photoelectron studies of biomolecule-water complexes in the gas phase can give us insight about some of the fundamental processes producing low energy secondary electrons and inducing fragmentation of cationic products. I will present a photoelectron photoion coincidence study of pyridine, pyridine clusters, and pyridine-water complexes considering single and double ionization processes. Our data provides insight on the single and double ionization energies of these systems and reveals differences in the dissociation pathways of pyridine in different environments. The ion-ion coincidence spectroscopy allows us to distinguish between different local double ionization and non-local double ionization mechanisms like intermolecular Coulombic Decay.