

MO 16: Ultrafast Dynamics I

Time: Wednesday 14:30–16:30

Location: HS 3044

MO 16.1 Wed 14:30 HS 3044

Imaging thermal-energy chemical dynamics of solvated (bio)molecular complex system — ●MUKHTAR SINGH^{1,2,3}, MATTHEW SCOTT ROBINSON^{1,2,3}, HUBERTUS BROMBERGER^{1,2}, 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

We present the imaging of ultrafast thermal-energy-induced chemical dynamics of a micro-solvated (bio) molecular complex probed with a time-dependent strong field ionization, and ion mass spectroscopy [1]. We produce a pure gas-phase indole-water sample using a combination of a cold molecular beam and the electrostatic deflector [2]. By employing a mid-IR pump to excite a single vibrational mode [3], the resulting thermal-energy chemical dynamics between the indole and water moieties were investigated. The dissociation of the micro-solvated system was monitored using strong-field multi-photon ionization by 1.3 μm wavelength light from a femtosecond pulsed laser, tracking the time-dependent ion signals of the indole-water cluster as well as the individual indole and water ionic products.

- [1] J Onvlee, *et al.*, *Nat Commun.* **13**, 7462 (2022)
 [2] S. Trippel, *et al.*, *Rev. Sci. Instrum.* **89**, 096110 (2018)
 [3] M.S. Robinson, *et al.*, *Phys. Chem. Chem. Phys.* (2023)

MO 16.2 Wed 14:45 HS 3044

Probing ultrafast nonadiabatic dynamics of NO₂ with time-resolved X-ray absorption spectroscopy at N K-edge — ●LORENZO RESTAINO¹, ZHUAN-YANG ZHANG², MICHAEL COATES¹, MICHAEL ODELIUS¹, MARKUS KOWALEWSKI¹, ERIK T. J. NIBBERING², and ARNAUD ROUZÉ² — ¹Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden — ²Max-Born-Institute, Max-Born-Str. 2A, 12489 Berlin, Germany

Time-resolved X-ray absorption spectroscopy (tr-XAS) is a chemically sensitive method well-suited for investigating the intricate behavior of electronically excited molecules. We employed tr-XAS to explore the ultrafast nonadiabatic processes occurring at the conical intersection (CI) between the electronic ground and first excited state of nitrogen dioxide. Despite the success of the experimental tr-XAS spectrum in revealing photodissociation, its capacity to capture the CI dynamics was hindered by the restricted temporal resolution of the 60 fs UV pump pulse. To overcome this constraint, we performed high-level quantum dynamics simulations with a shorter pump pulse, allowing us to access the complex nonadiabatic relaxation events. In our study, an 8-fs UV pump pulse at 400 nm excited the system from the ground state, followed by a 1-fs Gaussian probe pulse at the nitrogen K-edge to probe the core-hole states. By using this temporally resolved pump, we were able to map the system's passage through the conical intersection, identified through a spectral signature indicative of wave packet bifurcation. Consequently, we achieved a detailed tracing of the NO+O dissociation process.

MO 16.3 Wed 15:00 HS 3044

Investigating the Ultrafast Molecular Relaxation of 4-Thiouracil Using Time-Resolved X-Ray Photoelectron Spectroscopy — ●DENNIS MAYER¹, DAVID PICCONI², MATTEO BONANOMI^{3,4}, MILTCHO DANAILOV⁵, ALEXANDER DEMIDOVICH⁵, MICHELE DEVETTA⁴, MICHELE DI FRAIA⁵, DAVIDE FACCIALA⁴, RAIMUND FEIFEL⁶, CESARE GRAZIOLI⁷, FABIANO LEVER¹, NITSH PAL⁸, VASILIS PETROPOULOS³, KEVIN PRINCE⁵, OKSANA PLEKAN⁵, RICHARD SQUIBB⁶, CATERINA VOZZI⁴, GIULIO CERULLO^{3,4}, and MARKUS GÜHR^{1,9} — ¹DESY, Hamburg, Germany — ²University of Groningen, The Netherlands — ³Politecnico di Milano, Italy — ⁴CNR-IFN, Milan, Italy — ⁵Elettra-Sincrotrone Trieste, Italy — ⁶University of Gothenburg, Sweden — ⁷CNR-IOM, Trieste, Italy — ⁸Heriot-Watt University, Edinburgh, UK — ⁹University of Hamburg, Germany

Recent experiments on 4-thiouracil observed different time constants for the UV-induced relaxation into its triplet state that go beyond the difference between experiments in the gas and solution phase [1,2]. Utilizing the element- and site-selectivity of x-rays, we studied the relaxation process 4-thiouracil using gas-phase time-resolved x-ray photoelectron spectroscopy (XPS) at the free-electron laser FERMI. Lifetimes of the chemical shifts at the S 2p edge support previous gas-

phase experiments [1]. In comparison to its isomer 2-thiouracil [3], the molecule shows an additional excited-state spectral feature.

- [1] Chem. Phys. 515, 572 (2018); [2] J. Am. Chem. Soc. 140, 16087-16093 (2018); [3] Nat. Comm. 13, 198 (2022)

MO 16.4 Wed 15:15 HS 3044

Investigating the ultrafast dynamics of photoexcited azobenzene with an x-ray free electron laser — ●FABIANO LEVER¹, DENNIS MAYER¹, ATIA TUL NOOR¹, GESA GOETZKE¹, JULIUS SCHWARZ², MICHAEL MARTINS², REBECCA INGLE³, STEFAN DUESTERER¹, STEFFEN PALUTKE¹, TARAN DEXTER CYRUS DRIVER⁴, ULRIKE FRUEHLING¹, and MARKUS GÜHR¹ — ¹DESY, Hamburg, DE — ²Hamburg Universität, DE — ³UCL, London, UK — ⁴SLAC, Menlo Park, USA

Ultraviolet excitation triggers a light-induced isomerization reaction in the molecular switch azobenzene, changing its geometry from the trans ground state into the cis isomer. This work presents results from an ultrafast UV pump / soft x-ray probe experiment at the Free-Electron Laser FLASH. The electronic state dynamics of photoexcited azobenzene is probed with time-resolved x-ray absorption and photoelectron spectroscopy. In both observables, we measure dynamical features on a sub-picosecond scale. Comparing the experimental results to theoretical calculations for both datasets, we identify the ultrafast relaxation of the initially photoexcited S₂ ($\pi\pi^*$) to lower states.

MO 16.5 Wed 15:30 HS 3044

Capturing ultrafast dynamics of bio-relevant molecules combining few-femtosecond UV pulses with electropray ionization — ●SERGEY RYABCHUK^{1,2}, AARATHI NAIR¹, JOSINA HAHNE^{1,2}, LAURA PILLE³, JULIETTE LEROUX^{3,4}, NICOLAS VELASQUEZ⁵, BART OOSTENRIJK¹, ERIK P. MÅNSSON⁶, LUCAS SCHWOB³, VINCENT WANIE⁶, SADIA BARI⁷, and FRANCESCA CALEGARI^{1,2,6} — ¹The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany — ²Universität Hamburg, Hamburg, Germany — ³DESY, Hamburg, Germany — ⁴Université de Caen Normandie, Caen, France — ⁵Sorbonne Université, Paris, France — ⁶CFEL, Hamburg, Germany — ⁷University of Groningen, Groningen, The Netherlands

Ultraviolet (UV) light exposure induces various important chemical and biological processes in nature [1]. Electropray ionization (ESI) technique [2] allows to bring intact large and fragile bio-relevant molecules into the gas phase which is not feasible by other conventional methods. Time-resolved experiments have been recently developed to study the dynamics of such molecules following UV excitation by combining ESI devices with sources of ultrashort laser pulses [3]. However, the time resolution of these studies was limited by 80 fs UV pulses.

The present study involves the merging of an ESI source and an all-vacuum beamline, delivering few-fs UV pulses with few-cycle NIR pulses in a pump-probe scheme. This sophisticated experimental setup allows us to track the UV-induced dynamics and non-adiabatic processes in complex systems such as cobalt protoporphyrin IX and deprotonated nucleotides with an unprecedented temporal resolution.

MO 16.6 Wed 15:45 HS 3044

Excited state dynamics of BN-9,10-naphthalene: The impact of replacing CC by BN — ●FLORIANE STURM, MICHAEL BÜHLER, CHRISTOPH STAPPER, JOHANNES SCHNEIDER, HOLGER HELTEN, INGO FISCHER, and MERLE RÖHR — Julius-Maximilians-Universität Würzburg

Substituting CC by BN units is an excellent means to modify the optoelectronic properties of PAHs.¹⁻³ In our research, the excited state spectroscopy and dynamics of BN-9,10-naphthalene were studied by picosecond time-resolved photoionization in a supersonic jet. A REMPI spectrum reveals the S₁ origin at 33841 cm⁻¹, which is in very good agreement with theory. Several vibrational bands were resolved and assigned by comparison with computations. A [1+1] photoelectron spectrum via the S₁ origin yielded an adiabatic ionization energy of 8.27 eV. Selected vibrational bands were investigated by pump-probe photoionization. While the origin as well as several low-lying vibronic states exhibit lifetimes in the ns-range, a monoexponential decay is observed at higher excitation energies, ranging from 400 ps, at +1710 cm⁻¹ to 13 ps at +3360 cm⁻¹. Based on quantum chemical calculations, the deactivation is attributed to a conical intersection to the

ground state. In order to access it, an energy barrier has to be passed, which requires sufficient excess energy.

[1] M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.*, **87**, 8-29 (2009).

[2] H. L. van de Wouw, R. S. Klausen, *J. Org. Chem.*, **84**, 1117-1125 (2019).

[3] Z. Liu, T. B. Marder, *Angew. Chem. Int. Ed.*, **47**, 242-244 (2008).

MO 16.7 Wed 16:00 HS 3044

Non-adiabatic electronic relaxation of tetracene studied by time-resolved photoelectron spectroscopy — ●SEBASTIAN HARTWEG¹, AUDREY SCOGNAMIGLIO¹, KARIN S. THALMANN¹, NICOLAS RENDLER¹, AARON NGAI¹, LUKAS BRUDER¹, PEDRO B. COTO², MICHAEL THOSS¹, and FRANK STIENKEMEIER¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Materials Physics Center, Spanish National Research Council, Donostia-San Sebastian, Spain

Polycyclic aromatic hydrocarbons are assumed to be important sources of carbon in the interstellar medium. Additionally, some of these species, especially the acenes consisting of linearly-fused benzene units, are promising candidates for organic semiconductor applications. These applications motivate the fundamental study of the ultrafast excitation dynamics of the acenes and their aggregates to provide a fundamental understanding of the underlying processes and energetics.

I will present a femtosecond time-resolved photoelectron spectroscopy study of tetracene molecules supported by high-level ab initio calculations, revealing the ultrafast non-adiabatic dynamics following the excitation to a bright state in the UV range. The stepwise relaxation via an intermediate dark state to a low lying electronic excited state is accompanied by nuclear motion imprinted in the photoelectron

spectra by the time-dependent Franck-Condon factors of the delayed photoionization step.

MO 16.8 Wed 16:15 HS 3044

Residue Size Dependency of the Geminate Recombination Dynamics of the Biologically Relevant Disulfide Moiety after UV-cleavage investigated by TRXAS — ●JESSICA HARICH — Institute of Nanostructure and Solid State Physics, University of Hamburg and Center for Free-Electron Laser Science, Germany

The tertiary structure of proteins is stabilized by disulfide bonds formed from two spatially adjacent L-cysteiny residues. These disulfide bridges are prone to UV radiation damage with potentially adverse effects. We employ time resolved X-ray absorption spectroscopy (TRXAS) to observe the UV photochemistry of the natural amino acid dimer L-cystine and the tripeptide Glutathione disulfide in aqueous solution to understand the photochemistry under physiological conditions. Furthermore, we have first exciting insights into the UV-photochemistry of the disulfide bridges within the protein hen egg white Lysozyme.

We find that upon UV irradiation, aliphatic disulfides immediately undergo S-S bond cleavage, leading to the formation of two identical thiyl radicals, followed by fast geminate recombination indicating a very effective recombination process for thiyl radicals to the ground state. This process is only possible in condensed phases and its speed increases with chain length. Our results show that L-cystine already captures the essence of the ultrafast photochemistry of the disulfide bridge, but that the size of the residue adjacent to the disulfide bonds has a strong influence on the immediate recombination dynamics of the photoproducts.