MO 1: Ultrafast Structural Dynamics

Time: Monday 11:30–13:15 Location: P 105

Invited Talk MO 1.1 Mon 11:30 P 105

Unraveling the early-stage dynamics of ionized water dimer in energy and time — •Sebastian Trippel[1,2], Ivo Vinklárek[1], Michal Belina[3], Luisa Blum[1,2], Hubertus Bromberger[1], Petr Slavíček[2], and Jochen Küpper[1,2] — [1]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — [2]Department of Physics & Center for Ultrafast Imaging, Universität Hamburg — [3]Department of Physical Chemistry, University of Chemistry and Technology, Prague, the Czech Republic

Radiation chemistry in aqueous systems initiated by ionizing radiation is primarily governed by the ultrafast dynamics of water molecules. The prompt response of the aqueous environment involves the formation of hydrated electrons and proton transfer on femtosecond timescales [1]. We employed a disruptive-probing scheme [2] on a purified ensemble of water dimer to investigate the prompt dynamics after strong-field ionization [3]. Investigating the relation of the hydronium fragment kinetic-energy release with the observed timescales reveals a coupling between proton transfer and fragmentation. With the observation of water-dimer-cation stabilization, this provides new insight into the ultrafast post-ionization dynamics underpinning radiation chemistry in aqueous environments.

[1] Schnorr, Belina, et int (7 authors), Slavíček, Moshammer, *Sci. Adv.* **9**, eadg7864 (2023)

[2] Jochim, DeJesus, Dantus, *Rev. Sci. Instrum.* **93**, 033003 (2022)

[3] Vinklárek, Bromberger, Vadassery, Jin, Küpper, Trippel, *J. Phys. Chem* A **128**, 1593 (2024), arXiv:2308.08006 [physics.atm-clus]

MO 1.2 Mon 12:00 P 105

Influence of the Bridging Length on the Ultrafast Isomerization Dynamics of Bridged Azobenzenes in a Molecular Beam — •Pascal Pessier[1,2], Maria Hergert[1], Lukas Guhl[1], and Friedrich Temps[1] — [1]Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstraße 40, 24098 Kiel, Germany — [2]now at Institute of Physics, University of Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

Bridged azobenzenes have drawn considerable attention in the last decade due to their superior photochemical properties compared to conventional azobenzene (AB). Here, the ultrafast isomerization dynamics of two bridged azobenzenes, -C_2H_2-bridged diazocine (Dz) and -CH_2-bridged diazepine (Dzp), were investigated using time-resolved time-of-flight mass spectrometry, photoelectron imaging and photoionization-photofragmentation spectroscopy aided by quantum chemical calculations.

While Dz was found to isomerize in a concerted fashion ($\tau_1 < 38 \pm 1$ fs), Dzp unfolds first and consecutively isomerizes ($\tau_1 < 38 \pm 7$ fs, $\tau_2 = 680 \pm 96$ fs), linked to the increased ring strain by the shorter bridge. Further, the ultrafast unfolding motion (τ_1) enables additional adiabatic transitions close to the D_0 minimum with an unfolded structure rather than the FC region in the single-color photoelectron spectra. In the freshly prepared ion, this induced unfolding motion is then conserved as a highly excited butterfly vibration, observable as pronounced oscillation of parent ion yield.

MO 1.3 Mon 12:15 P 105

Interpolating Grid Potential Energy Surfaces with X-MACE — •Paul Idzko[1], Daniel Bitterlich[2], Julia Westermayr[2], and Daniel Keefer[1] — [1]Max-Planck-Institute for Polymer Research, Mainz, Germany — [2]Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry - Leipzig University, Leipzig, Germany

The dynamics of electronically excited molecules is most accurately calculated by solving the time dependent Schrödinger equation (TDSE) on a grid. This gives access to the full nuclear wavefunction. A major challenge is to ensure high accuracy of the underlying electronic potential energy surfaces (PES). After performing quantum chemistry calculations on a sparse grid, interpolation to a much finer grid - usable in the dynamics simulations - becomes necessary. This especially applies to Conical Intersections, which exhibit cusps that are hard to interpolate *via* mathematical methods. X-MACE was presented as a deep learning architecture built upon the popular MACE program suite, enabling the learning of several electronic states, as well as the nonadiabatic coupling elements between the states. Here, X-MACE will be used to interpolate between the geometries calculated with quantum chemistry in an active learning approach. We investigate the influence of the *chemical* interpolation with X-MACE in contrast to *mathematical* interpolation (e.g. splines, polynomials...) on the quantum dynamic simulations for the system of 2,5-dichlorofuran.

MO 1.4 Mon 12:30 P 105

Resolving Reactive vs. Non-reactive Pathways in Ultrafast Photodissociation via Pulse Engineering — •Ilia Kichev, Vesna Erić, and Daniel Keefer — Max-Planck Institute for Polymer Research, Ackermannweg 10, 56128 Mainz, Germany

Ultrafast spectroscopy experiments use coherent laser sources to probe dynamics and chemical reactivity in molecular systems. Ultrafast photodissociation dynamics in substituted furan remain contentious, with experiments attributing primary reactivity to competing pathways: reactive ring (**RO**) opening and non-reactive ring puckering (**RP**). Both pathways encounter regions with conical intersections (**CoIns**), which further complicates the task to spectroscopically untangle them. The main hurdle is the fact that the chosen spectroscopic observables from both pathways are intertwined and difficult to separate. Here, we deploy Quantum Optimal Control Theory (**QOCT**) Pulse Engineering to isolate spectroscopic signals from both pathways. First, we tailor in silico optimal laser pulses that selectively drive the system toward one of the desired pathways. Then, the signal is spectrally examined to identify critical frequency/amplitude motifs governing pathway selectivity. This will lead to further understanding in the specifics of the reaction, enabling improved experiments and a deeper understanding of the dynamics of similar systems.

MO 1.5 Mon 12:45 P 105

Light-induced wave packet dynamics in sulfur dioxide molecules — •Sanduni Sandeepani Kudagama[1,2], Artem Rudenko[1], and Huynh Van Sa Lam[1] — [1]Kansas State University, Manhattan, KS, USA — [2]EuXFEL, Schenefeld, Germany

With the development of femtosecond lasers and modern imaging techniques, time-resolves studies of ultrafast light-induced dynamics have become an increasingly important topic in molecular physics and photochemistry. To capture ultrafast molecular dynamics in time domain, femtosecond lasers are often used in a pump-probe scheme. In this study, an intense near-infrared (800 nm) or visible (400 nm) pump pulse was used to trigger wave packet dynamics in neutral and singly charged sulfur dioxide, which were then probed by a second, more intense NIR pulse that further ionized and/or dissociate the molecule. The information on the time evolution of the created molecular wave packets were studied employing momentum-resolved ion spectroscopy and channel-selective Fourier analysis on the delay-dependent yield of several singly, doubly, and triply charged final states of the molecule. All channels were dominated by the ionic ground-state bending vibration, whereas the neutral ground-state bending vibration appeared only with the 800 nm pump as a weak signature in several channels. We incorporated inverse Fast Fourier Transform to reveal the initial direction of the wave packet motion in both ionic and neutral ground states. For either pump pulse used, clear signatures of rotational dynamics were observed. Our study also reveals many important quantum mechanical phenomena such as wave packet dephasing and revivals.

MO 1.6 Mon 13:00 P 105

Antisymmetric vibrations in the excited state dynamics of quadrupolar dyes — Somayeh Souri[1], Katrin Winte[1], Daniel Lünemann[1], Daniel Timmer[1], Elena Mena-Osteritz[2], Sergei Tretiak[3], Christoph Lienau[1], and •Antonietta De Sio[1] — [1]Universität Oldenburg — [2]Universität Ulm — [3]Los Alamos National Laboratory

Non-equilibrium dynamics following photoexcitation in molecular materials arise from a complex interplay of electronic and vibrational motion, with antisymmetric vibrations playing a key role in ultrafast nonadiabatic dynamics, such as at conical intersections. Their direct spectroscopic identification is, however, challenging, since these modes are often Raman inactive and only weakly affect optical transitions. Here, we show experimental signatures of vibronic coupling to antisymmetric modes in the ultrafast symmetry-breaking dynamics of a quasi-quadrupolar dye[1,2] using two-dimensional electronic spectroscopy (2DES). The sub-50-fs 2DES maps reveal an asymmetric

peak pattern with characteristic low-energy cross-peaks. We show that these peaks arise from stimulated emission from a double-minimum excited state potential energy surface induced by vibronic coupling to a ~1430 cm-1 antisymmetric mode[2]. Phenomenological essential state model simulations support the results. Our findings show that 2DES with sub-cycle vibrational resolution is a powerful method for identifying antisymmetric modes in the excited state dynamics prior to intramolecular vibrational relaxation and solvation.

[1] Winte et al, Nature Chemistry 17, 1742 (2025); [2] Souri et al, submitted (2025)