

## MO 5: Ultrafast Dynamics I

Time: Tuesday 11:00–13:00

Location: HS XVI

MO 5.1 Tue 11:00 HS XVI

**Ultrafast Excited State Dynamics of the Nitrene Formation in Bis-Carbene-Ni/Pd/Pt-Azides** — ●MARKUS BAUER<sup>1</sup>, FREDERIK SCHERZ<sup>2</sup>, LUIS IGNACIO DOMENIANNI<sup>1</sup>, ANNA PAVUN<sup>3</sup>, BIPRAJIT SARKAR<sup>4</sup>, STEFAN HOHLOCH<sup>3</sup>, VERA KREWALD<sup>2</sup>, and PETER VÖHRINGER<sup>1</sup> — <sup>1</sup>Clausius Institut für physikalische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Deutschland — <sup>2</sup>Fachbereich Chemie, Technische Universität Darmstadt, Deutschland — <sup>3</sup>Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Österreich — <sup>4</sup>Fachbereich Biologie, Chemie, Pharmazie, Freie Universität Berlin, Deutschland

Nitrenes are highly reactive subvalent nitrogen species that are often used as intermediates in many organic and pharmaceutical syntheses.

We investigated the UV-induced photochemistry of three square-planar metal-azides coordinated by a tridentate ligand possessing two carbene and one amido donor (Metal=Ni, Pd, Pt). Utilizing femtosecond UV-pump-mIR-probe and UV-pump-Vis-probe spectroscopy, we were able to record the primary photochemical processes following the UV-excitation, which differ significantly depending on the metal center. Furthermore, we succeeded in identifying the key intermediates preceding nitrene formation using quantum chemical calculations.

The nickel-based complex undergoes almost exclusively ground-state recovery (GSR) and seems to remain on the singlet surface, while both the palladium, as well as the platinum species exhibit complex, but distinct intersystem crossing dynamics. Additionally, the quantum yield increases significantly with the mass of the metal center.

MO 5.2 Tue 11:15 HS XVI

**Excited-state wavepacket dynamics of the photoredox catalyst Ti<sup>IV</sup>(Cp)<sub>2</sub>(NCS)<sub>2</sub>** — ●JONAS SCHMIDT, LUIS IGNACIO DOMENIANNI, and PETER VÖHRINGER — Clausius-Institut für Physikalische und Theoretische Chemie, Bonn, Deutschland

Recently, we reported the observation of the entry events of Ti(Cp)<sub>2</sub>(NCS)<sub>2</sub> into a photo-catalytic cycle in real-time. Using time-resolved mid-infrared spectroscopy, we identified the intermediate states involved and tracked the reductive quenching reaction of the active catalyst with a sacrificial amine electron donor over broad timescales, spanning from picoseconds to hundreds of microseconds.

Here, we report on the very early dynamics of the electronic relaxation of the locally excited singlet state, S<sub>3</sub>. To this end, we employed ultra-fast near-UV-pump/white-light-probe spectroscopy with a time resolution of a few tens of femtoseconds. We could observe a prompt, structureless transient absorption ranging from 600 to 900 nm. On timescales below two picoseconds, the absorption exhibits coherent oscillations with a frequency of 140 cm<sup>-1</sup>. An analysis of probe-wavelength dependence of their phase and amplitude provides evidence that they are due to vibrational wavepacket dynamics in the energetically lowest singlet excited state, S<sub>1</sub>, of the complex. TDDFT suggests that the initial S<sub>3</sub>-to-S<sub>1</sub> internal conversion creates a coherent superposition in the Cp-Ti-Cp bending vibration of S<sub>1</sub>.

We are currently in the process of conducting complementary experiments on the fully methylated complex Ti(Cp)<sup>\*</sup><sub>2</sub>(NCS)<sub>2</sub> to verify this assignment.

MO 5.3 Tue 11:30 HS XVI

**Ultrafast Light-Induced Dynamics of Competing Reaction Pathways in Molecular Rings** — ●VESNA ERIC<sup>1</sup>, FRANCESCO MONTORSI<sup>1,2</sup>, SIMONA DJUMAYSKA<sup>1</sup>, and DANIEL KEEFER<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>University of Bologna, Bologna, Italy

Conical intersections mediate ultrafast light-induced processes in molecular systems. Due to the strong coupling of electronic and nuclear degrees of freedom, conical intersections open channels for fast energy transfer between excited states. Recent theoretical studies reveal the potential of stimulated X-ray Raman spectroscopy to provide distinct spectral signals of the passage through conical intersections, which previously remained elusive. Here, we extend this concept towards spectrally distinguishing competing conical intersection-mediated pathways. We employ computational modelling to investigate the photochemistry of 2,5-dichlorofuran molecules exhibiting competing reaction pathways, ring puckering and opening, as typically observed in molecular ring structures. Our simulation protocol includes

multireference (CASPT2) electronic structure calculations, quantum dynamics, and evaluation of stimulated X-ray Raman signals. Finally, we discuss the possibility of the spectral separation between the competing conical intersections by tuning the X-ray probe pulse to the pre-edge of the Carbon, Nitrogen and Oxygen transitions.

MO 5.4 Tue 11:45 HS XVI

**Investigating Competing Photochemical Pathways in Furan-based systems via Surface Hopping and Ultrafast Electron Diffraction simulations** — ●SIMONA DJUMAYSKA, FRANCESCO MONTORSI, VESNA ERIC, and DANIEL KEEFER — Max Planck Institute for Polymer research, Mainz, Germany

Photochemical reactions at conical intersections (CIs) play a crucial role in determining the photoproducts of excited-state dynamics in molecular systems. Such is the case for systems like furan and its derivatives, which exhibit complex nonadiabatic dynamics influenced by these intersections. The photochemistry of furan involves two main competing pathways: ring-opening and ring-puckering. In this work, we used surface-hopping (SH) dynamics based on high-level CASPT2 calculations of the electronic structure to study these photochemical reactions. This approach allows us to simulate the motion of nuclei as they undergo non-adiabatic transitions between electronic states at CIs. To better interpret these results and connect them to experiments, we calculate ultrafast electron diffraction (UED) signals. We demonstrate how UED signals can differentiate between the ring-opening and ring-puckering motions. This study shows that combining SH dynamics with UED simulations is a useful way to investigate and distinguish photochemical processes in molecules like furan. Our simulations further help to predict and interpret cutting-edge UED experiments geared towards unraveling the interplay between nuclear motion and electronic transitions in excited states.

MO 5.5 Tue 12:00 HS XVI

**Investigating the Ultrafast Molecular Relaxation of 4-Thiouracil Using Time-Resolved X-Ray Photoelectron Spectroscopy** — ●DENNIS MAYER<sup>1</sup>, DAVID PICCONI<sup>2</sup>, MATTEO BONANOMI<sup>3,4</sup>, MILTCHO DANAILOV<sup>5</sup>, ALEXANDER DEMIDOVICH<sup>5</sup>, MICHELE DEVETTA<sup>4</sup>, MICHELE DI FRAIA<sup>5</sup>, DAVIDE FACCIALA<sup>4</sup>, RAIMUND FEIFEL<sup>6</sup>, CESARE GRAZIOLI<sup>7</sup>, FABIANO LEVER<sup>1</sup>, NITSH PAL<sup>8</sup>, VASILIS PETROPOULOS<sup>3</sup>, KEVIN PRINCE<sup>5</sup>, OKSANA PLEKAN<sup>5</sup>, RICHARD SQUIBB<sup>6</sup>, CATERINA VOZZI<sup>4</sup>, GIULIO CERULLO<sup>3,4</sup>, and MARKUS GÜHR<sup>1,9</sup> — <sup>1</sup>DESY, Hamburg, Germany — <sup>2</sup>Heinrich-Heine University, Düsseldorf, Germany — <sup>3</sup>Politecnico di Milano, Italy — <sup>4</sup>CNR-IFN, Milan, Italy — <sup>5</sup>Elettra-Sincrotrone Trieste, Italy — <sup>6</sup>University of Gothenburg, Sweden — <sup>7</sup>CNR-IOM, Trieste, Italy — <sup>8</sup>Heriot-Watt University, Edinburgh, UK — <sup>9</sup>University 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 5.6 Tue 12:15 HS XVI

**Excited state dynamics of 4a,4b-Azaboraphenanthene** — ●JONAS FACKELMAYER, MICHAEL BÜHLER, MICHAEL MÜLLER, JAN-NIK MARKERT, and INGO FISCHER — Julius-Maximilians Universität, Würzburg, Deutschland

With growing interest in renewable energy generation, efficiently harnessing solar power has emerged as a major focus of both research and industry. The efficiency of organic solar cells might be increased significantly utilizing the photophysical process of singlet fission, a process in which a single excited singlet state splits into two triplet states therefore increasing the number of charge carriers generated from a single photon. Among the molecules that exhibit this process, polycyclic aromatic hydrocarbons (PAHs) are particularly noteworthy, as

their optoelectronic properties can be tailored through the substitution of carbon units with boron and nitrogen.

In our most recent study we investigated the excited states dynamics of 4a,4b-azaboraphenanthrene by picosecond time-resolved photoionization in a supersonic jet. A resonance-enhanced multi photon ionization (REMPI) spectrum reveals the  $S_1$  origin at around  $22880\text{ cm}^{-1}$  and shows many vibronic bands. Time-resolved time-of-flight and photoelectron imaging experiments with pump wavelengths between 401 and 437 nm and probe wavelengths of 351 and 263,5 nm yield time constants between 20 and 35 ps. The experiments are accompanied by computational studies to gain further insights into the involved vibrational modes and deactivation mechanisms.

MO 5.7 Tue 12:30 HS XVI

**Ultrafast photoisomerization dynamics of protonated azobenzene in an ion trap** — ●MARCEL J. P. SCHMITT<sup>1</sup>, GEREON NIEDNER-SCHATTEBURG<sup>1</sup>, SABINE BECKER<sup>1</sup>, CAROLIN MÜLLER<sup>2</sup>, and CHRISTOPH RIEHN<sup>1</sup> — <sup>1</sup>Department of Chemistry, RPTU Kaiserslautern — <sup>2</sup>Computer Chemistry Center, FAU Erlangen-Nürnberg, Erlangen

The  $E/Z$  photoswitchability of azobenzenes is widely used in biological, medicinal,[1] and optical applications as molecular machines[2] and reversible photoswitchable metallocycles.[3] Less is known about the photophysics and deactivation processes of simple protonated azobenzene compound. Here, we report transient photodissociation action spectra of isolated azonium monocations that reveal ultrafast dynamics of the  $E$  isomers. Multiexponential electronic decays in the sub-ps and ps time regimes occur with faster decay rates as for neutral azobenzene. Superimposed, there is a rapidly damped wave packet dynamics of 0.4 ps oscillations that indicate torsional modes of isomerization. These findings find support by nonadiabatic dynamics simulations (CASSCF) that decipher deactivation pathways.

[1] M. Medved', M. Di Donato, W. J. Buma, A. D. Laurent, L.

Lameijer, T. Hrivnák, I. Romanov, S. Tran, B. L. Feringa, W. Szymanski, G. A. Woolley, *J. Am. Chem. Soc.* 2023, 145, 19894. [2] S. Megow, H.-L. Fitschen, F. Tuzcek, *F. Temps, J. Phys. Chem. Lett.* 2019, 10, 6048. [3] R. I. Petrikat, J. Hornbogen, M. J. P. Schmitt, E. Resmann, C. Wiedemann, N. I. Dilmen, H. Schneider, A. M. Pick, C. Riehn, R. Diller, S. Becker, *Chem. Eur. J.* 2024, 30, e202400205.

MO 5.8 Tue 12:45 HS XVI

**Probing UV-induced dynamics of phenanthridine with time-resolved X-ray absorption and X-ray photoelectron spectroscopy** — ●DOROTHEE SCHAFFNER<sup>1</sup>, CONSTANT SCHOUDER<sup>2</sup>, KIRA DIEMER<sup>1</sup>, XINCHENG MIAO<sup>1</sup>, EMIL KARAEV<sup>1</sup>, DENNIS MAYER<sup>3</sup>, ANDREY SCOGNAMIGLIO<sup>2</sup>, ANDRE AL HADDAD<sup>4</sup>, ANTOINE SARRACINI<sup>4</sup>, GREGOR KNOPP<sup>4</sup>, LOU BARREAU<sup>2</sup>, LIONEL POISSON<sup>2</sup>, PATRICK HEMBERGER<sup>4</sup>, KIRSTEN SCHNORR<sup>4</sup>, ROLAND MITRIC<sup>1</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>University of Würzburg, Germany — <sup>2</sup>ISMO, Paris-Saclay University, France — <sup>3</sup>DESY, Hamburg, Germany — <sup>4</sup>PSI, Villigen, Switzerland

Modifying polycyclic aromatic hydrocarbons (PAHs) by replacing a carbon by a nitrogen atom introduces  $n\pi^*$  states into the molecules, in addition to existing  $\pi\pi^*$  states. This leads to an alteration in optoelectronic properties making nitrogen-containing PAHs (PANHs) promising candidates e.g. for organic photovoltaic devices. In this experiment we investigated the excited state dynamics of the PANH phenanthridine after UV excitation into the S3 state ( $\pi\pi^*$  character). Using the Maloja endstation at SwissFEL, time-resolved X-ray absorption and photoelectron spectra were recorded near the N1s edge that are particularly sensitive towards  $n\pi^*$  states. Significant shifts are observed in the time-resolved spectra and time constants for the deactivation process were derived. Spectral features of the excited states and time constants are compared to theoretical results from surface hopping dynamics simulations combined with TDDFT calculations.