

## MO 13: Femtosecond Spectroscopy III

Time: Wednesday 14:30–15:45

Location: MO-H5

MO 13.1 Wed 14:30 MO-H5

**Ultrafast excited-state dynamics of new Fe(II) photosensitizers with linked organic chromophores** — ●MIGUEL ANDRE ARGÜELLO CORDERO<sup>1</sup>, AYLA KRUSE<sup>1</sup>, PHILIPP DIERKS<sup>2</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>University of Rostock, Germany — <sup>2</sup>University of Paderborn, Germany

Photocatalytic approaches for the generation of solar fuels are of rising interest, due to their potential as source for renewable energy. As one key component they contain typically metal-based photosensitizers (PS) to absorb sunlight. Because of the low costs and availability of iron, PS based on it are currently intensively investigated to replace their rare and noble metal-based analogues. When the PS absorb light a metal-to-ligand charge-transfer state is populated. Its lifetime should be in the ns region to perform chemical reactions. In this work we present newly synthesized Fe(II)-based PS with an organic chromophore linked to its ligand backbone. With this additional unit the complexes not only show a wider absorption range in the visible. After optical excitation emissive excited states with lifetimes of some ns seem to become populated. Comparison with the emission behaviour of the pure ligands lead to the assumption that the chromophore moiety undergoes electronic decoupling from the rest of the ligand, if the ligand is linked to the Fe(II) centre. This may lay a basis for the exploration of the reservoir effect, facilitating a populated state located on the linked chromophore. Here we present our results on ultrafast pump-probe absorption and time-resolved emission spectroscopy of these new PS and discuss them with respect to the electronic relaxation pathways.

MO 13.2 Wed 14:45 MO-H5

**Femtosecond-NeNePo Spectroscopy of Small Silver Clusters** — ●MAX GRELLMANN, JIAYE JIN, JÜRGEN JÄSCHKE, MARCEL JOREWITZ, and KNUT R. ASMIS — Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Vibrational spectroscopy on mass-selected neutral silver clusters is still difficult to be performed due to a lack of efficient methods to directly select a single mass for neutral species in the gas-phase and rare intense and tunable far infrared sources in the vibrational frequency range of metal-metal bonds.

Here, we present experimental results probing the wave packet dynamics on the electronic ground state potential energy surface of the neutral silver tetramer by using femtosecond pump-probe spectroscopy via three charge states, so-called NeNePo (negative-neutral-positive) spectroscopy. Silver clusters are produced in a liquid nitrogen cooled magnetron sputter source. Mass-selected silver tetramer anions are accumulated in a gas-filled ion trap, thermalized to 20 K and subsequently photodetached using an 800 nm ultrafast pump pulse. The wave packet dynamics are then probed using a second, photoionizing ultrafast 400 nm probe pulse. The so produced signal of silver tetramer cations (and its fragments) is monitored mass-selectively as a function of the laser pulses delay time, yielding a NeNePo spectrum. Frequency analysis by Fourier transform reveals evidence for the time-dependent excitation of all six vibrational modes and the time scale of intramolecular vibrational energy redistribution processes.

MO 13.3 Wed 15:00 MO-H5

**Time-resolved ultrafast spectroscopy of acene monomers and acene complexes in helium nanodroplets** — ●AUDREY SCOGNAMIGLIO, NICOLAS RENDLER, KATRIN DULITZ, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder Straße 3, 79104 Freiburg-im-Breisgau

The motivation to study acene molecules such as tetracene and pentacene originates from the recent interest in organic photovoltaics research (OPVs)[1]. Indeed, those molecules are known to produce multi-

ple charge carriers through singlet fission, thus enhancing the efficiency of such devices[2], [3]. On the one hand, we experimentally study acene monomers in the gas phase to get insights into their energy-level structure, and into the possible intramolecular relaxation dynamics and associated time scales. On the other hand, we use the helium nanodroplet matrix isolation technique to synthesize complexes of two or more molecules. So far, experimental studies are available only for crystalline or solution-based systems. We present here time-resolved two-colour pump-probe studies on acene monomers and acene complexes, investigated using photoelectron imaging and high-resolution ion-time-of-flight mass spectrometry over a large mass/charge range.

- [1] T. M. Clarke and J. R. Durrant, *Chem. Rev.*, vol. 110(11), 2010  
 [2] P. M. Zimmerman *et al.*, *J. Am. Chem. Soc.*, vol. 133(49), 2011  
 [3] P. M. Zimmerman *et al.*, *Nat. Chem.*, vol. 2(8), 2010

MO 13.4 Wed 15:15 MO-H5

**Coherent two-dimensional photoelectron spectroscopy** — ●DANIEL UHL, ULRICH BANGERT, LUKAS BRUDER, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Germany.

Coherent multidimensional spectroscopy (CMDS) is a powerful ultrafast spectroscopic technique which provides spectro-temporal information otherwise only accessible in disjunct experiments. Photoelectron spectroscopy, on the other hand, provides detailed information about the chemical composition and electronic states of the sample.

Here we present a combination of both methods in a single experiment [1]. This becomes feasible with the development of an efficient single-counting detection and multichannel software-based lock-in amplification [2]. The approach offers high temporal, spectral and kinetic energy resolution. It enables differential CMDS experiments with unprecedented selectivity and enhances the dynamic range of CMDS by up to two orders of magnitude. The presented concept opens up a new perspective for atomically-resolved CMDS experiments using X-ray photoelectron spectroscopy.

- [1] D. Uhl, U. Bangert, L. Bruder, and F. Stienkemeier, *Optica* 8, 1316-1324 (2021)

- [2] D. Uhl, L. Bruder, and F. Stienkemeier, *Review of Scientific Instruments* 92, 083101 (2021).

MO 13.5 Wed 15:30 MO-H5

**Simulating time-resolved X-ray absorption spectroscopy of pyrazine at the nitrogen K-edge with a full time-domain approach** — ●ANTONIA FREIBERT<sup>1,2</sup>, DAVID MENDIVE-TAPIA<sup>2</sup>, NILS HUSE<sup>1</sup>, and ORIOL VENDRELL<sup>2</sup> — <sup>1</sup>University of Hamburg, Hamburg, Germany — <sup>2</sup>Heidelberg University, Heidelberg, Germany

Ultrafast X-ray absorption spectroscopy offers elemental specificity and in principle access to the natural time evolution of valence excitations when studying electronic and structural configurations of molecules and materials. Due to the complex nature of probing structural dynamics on the femtosecond timescale, detailed theoretical studies are required to link the spectroscopic observables to the underlying dynamics and thereby access the high information content contained in this experimental method. A large influence of nuclear dynamics can be expected in nonlinear spectroscopy which requires a time-dependent framework that is able to describe non-adiabatic phenomena.

I will present time-resolved X-ray absorption spectroscopy simulations of pyrazine at the nitrogen K-edge including wavepacket dynamics in both the valence- and core-excited state manifolds. We discuss the validity of the widely used short-time (or Lorentzian) approximation which neglects the nuclear dynamics following the X-ray probe transition. We further demonstrate the impact of an explicit description of the external electric field and explicitly calculate the effect of an increasingly longer excitation pulse on the observed photo-triggered wavepacket dynamics.