

## MO 10: Collisions and Reactions

Time: Wednesday 11:00–13:30

Location: f142

MO 10.1 Wed 11:00 f142

**Electron emission asymmetry in multiphoton dissociation of H<sub>2</sub>** — ●PATRICK FROSS, DENHI MARTINEZ, NICOLAS CAMUS, THOMAS PFEIFER, and ROBERT MOSHAMMER — Max-Planck-Institut für Kernphysik, Heidelberg, Germany

When a diatomic molecule dissociates the released electron can either propagate along the neutral or the ionized atom. Depending on the dissociation pathways the electron is preferentially emitted in the direction of one or the other. This so-called electron localization asymmetry can be measured and gives information on the underlying dissociation pathways. We present results from multiphoton-dissociation of molecular hydrogen using single 35fs pulses with a central wavelength of 400nm ( $I=1 \cdot 10^{14}$  W/cm<sup>2</sup>) and a reaction microscope to image ions and electrons in coincidence. We report and explain the characteristic electron localization asymmetry behavior observed for the dissociation of H<sub>2</sub> depending on the nuclear electron correlation. To our knowledge these results are the first of their kind in the regime of multiphoton-ionization.

MO 10.2 Wed 11:15 f142

**XUV-photoinduced addition reactions from ethene measured with a radio frequency ion trap** — ●SIMON REINWARDT<sup>1</sup>, IVAN BAEV<sup>1</sup>, JULIUS SCHWARZ<sup>1</sup>, FRIDTJOF KIELGAST<sup>1</sup>, KAROLIN MERTENS<sup>1</sup>, FLORIAN TRINTER<sup>2,3</sup>, and MICHAEL MARTINS<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Hamburg, Germany — <sup>2</sup>FS-PETRA-S, DESY, Hamburg, Germany — <sup>3</sup>Molecular Physics, Fritz-Haber-Institut, Berlin, Germany

The interstellar formation of larger hydrocarbons is not fully clarified yet. There are different models in which the larger hydrocarbons are formed by dehydrogenation and fragmentation as well as isomerization of hydrocarbons [1]. In conventional experiments the formation of larger hydrocarbon systems is investigated by their fragmentation via X-rays. In contrast to that, the reverse path of generating larger hydrocarbons by XUV-induced addition reactions is realized here. An ideally suited setup for such experiments is the ion trap of the photon ion spectrometer (PIPE) [2] at the soft X-ray beamline P04 of the synchrotron PETRA III in Hamburg. For these experiments ethene (C<sub>2</sub>H<sub>4</sub>) was used as starting molecule. Consequently, photoactivation was achieved by the absorption of XUV-photons in the carbon K-edge region (~ 290 eV). In this way it was possible to find reaction products such as C<sub>6</sub>H<sub>x</sub><sup>+</sup> and C<sub>5</sub>H<sub>x</sub><sup>+</sup>, which were generated from a double collision.

[1] O. Berné and A. G. G. M. Tielens, *PNAS* **109**, 401 (2012).

[2] S. Schippers et al., *J. Phys. B: At. Mol. Opt. Phys.* **47**, 115602 (2014).

MO 10.3 Wed 11:30 f142

**Excited state proton transfer in solvated molecules studied by XUV time-resolved photoelectron spectroscopy** — ●EVGENII IKONNIKOV, JOHAN HUMMERT, and OLEG KORNILOV — Max-Born-Institute, Berlin

Photoelectron pump-probe time resolved spectroscopy is a powerful tool for studies of relaxation dynamics of electronically excited states. There are many pump-probe techniques developed for the gas phase but very few implementations for liquids. However, biological molecules in natural conditions, which often interact with their environment and, due to protic and polar nature of water solvent, besides intramolecular relaxation process there are additional processes possible such as proton transfer and solvent rearrangement upon photoexcitation. In this project we study ultrafast relaxation of molecules dissolved in water. We combine visible pump/XUV probe time-resolved photoelectron spectroscopy and the microliquid jet technique with high efficiency time-of-flight electron detector based on the "magnetic bottle" design. This experimental setup allows us to measure ground state energy of dissolved molecules with concentrations down to 500 μM and follow relaxation dynamics of excited states for samples with molecular concentrations down to 2 mM. We investigate relaxation of molecules exhibiting excited state proton transfer in solvents with different pH values.

MO 10.4 Wed 11:45 f142

**X-ray-induced ignition of a helium nanoplasma** — ●CRISTIAN

MEDINA<sup>1</sup>, DOMINIK SCHOMAS<sup>1</sup>, MARKUS DEBATIN<sup>1</sup>, LTAIF LTAIF<sup>2</sup>, ROBERT MOSHAMMER<sup>3</sup>, THOMAS PFEIFER<sup>3</sup>, FRANK STIENKEMEIER<sup>1</sup>, and MARCEL MUDRICH<sup>2</sup> — <sup>1</sup>Albert-Ludwigs-Universität, Freiburg — <sup>2</sup>Aarhus University, Aarhus — <sup>3</sup>Max-Planck-Institut für Kernphysik, Heidelberg

Helium Nanoplasmas are usually created by intense near-infrared laser pulses. After tunnel-ionization of the cluster or some dopant atoms, the cluster fully avalanche-ionizes as the electrons are driven back and forth through the cluster by the laser field. Here, we demonstrate a different scheme for igniting the nanoplasma on helium nanodroplets doped with heavy rare gas atoms. An ultrashort x-ray pulse (FLASH-1 at DESY, Hamburg) first inner-shell ionizes the dopant cluster, followed by Auger decay and charge-transfer ionization of the helium shell. A second near-infrared pulse then drives the nanoplasma at variable delay with respect to the x-ray pulse. The yields of electrons and helium ions are recorded for different dopant species (Ar, Kr, Xe), helium droplet sizes, and laser pulse intensities.

MO 10.5 Wed 12:00 f142

**Z → E and E → Z Photoisomerization Dynamics of an Oxygen-Heterodiazocine upon S<sub>1</sub>(nπ\*) Photoexcitation** — ●DENNIS BANK<sup>1</sup>, BIRTHE BEHR<sup>1</sup>, FALK RENTH<sup>1</sup>, MELANIE HAMMERICH<sup>2</sup>, RAINER HERGES<sup>2</sup>, and FRIEDRICH TEMPS<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany — <sup>2</sup>Institute of Organic Chemistry, Christian-Albrechts-University Kiel, Germany

Heterodiazocines are a novel class of azobenzene-related photochromic molecules with an intramolecular bridge consisting a CH<sub>2</sub>-heteroatom linker group between their phenyl rings. This bridge initiates a steric tension that results in superior photophysical properties. We investigated the very efficient photo-induced isomerization ( $\Phi_{Z \rightarrow E} = 0.7$  and  $\Phi_{E \rightarrow Z} = 0.55$ ) dynamics of 12*H*-dibenzo[b,f][1,4,5] oxadiazocine (ODz) by a combination of femtosecond time-resolved electronic absorption spectroscopy and ab initio quantum chemical calculations. After photoexcitation of the thermodynamically stable *Z*<sub>boat</sub> isomer at  $\lambda_{\text{pump}} = 387$  nm the populated S<sub>1</sub>(nπ\*) state deactivates within  $\tau \leq 150$  fs. The subsequent complex ground-state dynamics of the *Z*<sub>boat</sub> → *E*<sub>twist</sub> isomerization proceeds via formation of the vibrationally hot intermediate *E*<sub>chair</sub> species with  $\tau = 3$  ps and crossing of an energy barrier of *E* = 0.55 eV within  $\tau = 15$  ps. In contrast, the *E*<sub>twist</sub> → *Z*<sub>boat</sub> photoisomerization upon excitation at  $\lambda_{\text{pump}} = 530$  nm is completed after only  $\tau = 230$  fs followed by vibrational cooling in the ground state with  $\tau = 20$  ps.

MO 10.6 Wed 12:15 f142

**Consecutive photoinduced electron transfer: The mechanism of the photocatalyst rhodamine-6G.** — ●FABIAN BRANDL, SEBASTIAN BERGWINKL, CARINA ALLACHER, and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Universitätsstrasse 31, 93053 Regensburg, Germany.

The dye Rhodamine-6G (R6G) acts as photocatalyst via photoinduced electron transfer by forming the R6G radical (reduction potential ca. -0.90 V) after excitation with green light. König et al. proposed a strategy, termed consecutive photoinduced electron transfer (conPET), that adds the energy of two photons for a photoreduction, using a photogenerated radical as an intermediate [1]. Subsequently it has been reported that photoexcitation of the R6G radical at 420 nm splits aryl bromides, suggesting a conPET process [2]. Here we present a study of the mechanism of the formation and photoreactions of the R6G radical by using transient spectroscopy (femtoseconds to minutes) and quantum chemical calculations. We conclude that one photon of 540 nm light produces two R6G radicals. The photoexcited radical decays in ca. 350 fs, either relaxing to the ground state or releasing an electron to the solvent, which returns on a timescale of nanoseconds. Unless the substrate is already attached to the radical, it is reduced by solvated electrons. Vibrational cooling of hot R6G and hot R6G radical occurs within 10ps.

[1] B. König et al. *Science*. 2014, 346, 725-728.

[2] B. König et al. *Chem Commun*. 2016, 52, 8695-8698.

MO 10.7 Wed 12:30 f142

**Velocity map imaging of chlorine from photodissociation with**

a **[1+1]-REMPI scheme** — ●CHRISTIAN MATTHAEI, DEB PRATIM MUKHOPADHYAY, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Velocity map imaging (VMI) is a well-established method for studying the photodissociation dynamics of molecules [1]. When studying chlorine fragments, a [2+1] resonance-enhanced multiphoton ionization (REMPI) scheme is usually employed, requiring a laser with a wavelength of around 235 nm. Since many molecules and radicals also absorb light of this wavelength, the dissociation is generally performed with the same laser. The major disadvantages of these one-colour experiments are that a clean study of the molecules of interest is not always feasible and the dissociation wavelength cannot be changed.

Here, we present a technique for first dissociating molecules with one dye laser and then ionizing chlorine with a second dye laser via a novel [1+1]-REMPI scheme. For the ionization the output of a dye-laser is tripled in a noble gas-filled cell, generating 118 nm light in order to directly promote the electron into the excited state. Following ionization, the chlorine atoms are then detected via time-of-flight mass spectrometry and VMI. First measurements on test systems are shown.

Literature:

[1] M. N. R. Ashfold et al., *Phys. Chem. Chem. Phys.* 2006, 8, 26-53

MO 10.8 Wed 12:45 f142

**Photochemical and spectroscopic investigation of highly soluble fluorinated TADF copper complexes** — ●SOPHIE STEIGER<sup>1</sup>, PIT BODEN<sup>1</sup>, PATRICK DI MARTINO-FUMO<sup>1</sup>, JASMIN BUSCH<sup>2</sup>, DANIEL ZINK<sup>2</sup>, FLORIAN REHAK<sup>3</sup>, STEFAN BRÄSE<sup>2</sup>, WIM KLOPPER<sup>3</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern, Germany — <sup>2</sup>Organic Chemistry, KIT, Germany — <sup>3</sup>Physical and Theoretical Chemistry, KIT, Germany

This contribution presents the investigation of fluorinated copper complexes capable for TADF (Thermally Activated Delayed Fluorescence) analyzed by time-resolved FTIR and emission (luminescence) spectroscopy. The highly soluble fluorinated complexes show good (photo)chemical stability in common solvents. With the help of emission spectroscopy, the stability was investigated and the energetic position of the excited states and their lifetime were determined. Furthermore, the TADF capability of the complexes in solids was investigated using temperature-dependent, time-resolved FTIR and emission spectroscopy. The measured spectra are compared and interpreted with (TD)DFT calculations, observing a clear TADF process at room temperature for all structures. A strong lifetime extension and a distinct redshift of the emission band around 20K confirm phosphorescence at low temperatures in contrast to the TADF process observed at room temperature.

MO 10.9 Wed 13:00 f142

**Switching between proton vacancy and excess proton transfer using a bifunctional photoacid with the help of a third reaction partner** — ●MARIUS-ANDREI CODESCU, OLEG KORNILOV, and ERIK T.J. NIBBERING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, 12489 Berlin, DE

Proton exchange between an acid and a base in protic solvents may in general occur along two different pathways. Recent results obtained on the bifunctional photoacid 7-hydroxyquinoline (7HQ) in water-methanol mixtures has been concluded to take place via a methoxide/hydroxide transport mechanism between the proton-donating OH group and the proton-accepting quinoline group on a timescale of tens to hundreds of picoseconds [Ekimova et al., *J. Am. Chem. Soc.* 141, 14581 (2019)]. Here, we show that by using cesium formate (Cs+HCOO-) as a third reaction partner, it is possible to steer the reaction dynamics in such a fashion that the excess proton transfer pathway takes over as a dominant reaction mechanism. We follow the reaction kinetics by probing IR-active marker modes of different charged states of 7HQ, and of formic acid, in methanol solution using femtosecond UV-pump IR-probe spectroscopy. A dedicated analysis of the transient IR spectra results in a consistent and quantitative picture of the reaction mechanism for the 7HQ-formate reaction pairs, where the formate acts as an essential component in facilitating a full excess proton transport pathway from the proton-donating OH group to the proton-accepting quinoline group of 7HQ, before the regular proton vacancy (methoxide) transfer pathway can come in full effect.

MO 10.10 Wed 13:15 f142

**Femtosecond-resolved study of x-ray induced fragmentation of buckyballs** — ●ZOLTAN JUREK<sup>1</sup>, NORA BERRAH<sup>2</sup>, ALVARO SANCHEZ-GONZALEZ<sup>3</sup>, SANG-KIL SON<sup>1</sup>, and ROBIN SANTRA<sup>1,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany — <sup>2</sup>Physics Department, University of Connecticut, Storrs, CT, USA — <sup>3</sup>Department of Physics, Imperial College London, London, UK — <sup>4</sup>Department of Physics, Universität Hamburg, Hamburg, Germany

In this talk we report on a joint experimental-theoretical time resolved study of the dynamics of gas phase C<sub>60</sub> molecules exposed to ultrashort intense X-ray Free Electron Laser (XFEL) pulses [1]. In the experiment two consecutive x-ray pulses were applied: the first (pump) pulse initiated the time evolution by multiply ionizing the molecule, while the second one (probe pulse) altered the system by further ionization, creating pump-probe delay dependent spectroscopy signals. Our theoretical simulations reveal exciting details of the complex fragmentation, such as the release of neutral atomic fragments. Moreover, the simulations also connect delay times appearing in the observed pump-probe data directly to real timescales of the dynamics initiated by a single pulse. Our study is an important step in the understanding of XFEL-matter interaction, crucial for high intensity XFEL applications.

[1] N. Berrah et al, *Nat. Phys.* (2019) doi:10.1038/s41567-019-0665-7