

## MO 4: Photochemistry

Time: Monday 14:00–15:45

Location: PA 1.150

MO 4.1 Mon 14:00 PA 1.150

**Impact of kilobar Pressures on Ultrafast Photoisomerization Dynamics of a Triazene and of a Thiocyanine System** — ●LENA GRIMMELSMANN<sup>1</sup>, VITOR SCHUABB<sup>2</sup>, BERITAN TEKIN<sup>1</sup>, ROLAND WINTER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Physikalische Chemie I, Technische Universität Dortmund, 44227 Dortmund

Mechanisms of *cis-trans* photoisomerization can remarkably differ, depending on the actual molecular system and its environment. Previous liquid-phase studies at 1 bar have shown that the triazene compound berenil isomerizes *via* a volume-conserving bicycle-pedal motion, whereas for the thiocyanine NK88 a rotation mechanism with two competing excited-state pathways occurs. For disclosing the associated dynamics, systematic variation of the viscosity of the environment can be highly beneficial. However, if this is done by employing different solvents, the polarity of the solute's surrounding is modified as well to a significant degree. An alternative for adjusting the viscosity is pressurizing the system, thus keeping polarity changes low. In this study, we apply femtosecond fluorescence upconversion to berenil and NK88 dissolved in 2-propanol or water under pressures of 1 to 1500 bar. For berenil, a negligible impact of the viscosity on the fluorescence dynamics is found, in agreement with the bicycle-pedal motion. By contrast, the two fluorescence lifetimes of NK88 exhibit a prolongation scaling linearly with the viscosity, and their relative amplitudes indicate a pressure-dependent branching ratio for the two accessible photoisomerization pathways.

MO 4.2 Mon 14:15 PA 1.150

**Quantum chemical studies of a hemithioindigo-based photo-driven molecular motor** — ●FLORIAN ROTT<sup>1</sup>, SVEN OESTERLING<sup>1</sup>, LUDWIG HUBER<sup>1</sup>, ROLAND WILCKEN<sup>2</sup>, HENRY DUBE<sup>1</sup>, EBERHARD RIEDLE<sup>2</sup>, and REGINA DE VIVIE-RIEDEL<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich — <sup>2</sup>Lehrstuhl für BioMolekulare Optik, LMU Munich

In recent years photodriven molecular motors drew increasing interest due to their ability to convert light energy into directional motion. A hemithioindigo-based photodriven molecular motor was recently synthesized by Dube and Coworkers [1]. This motor performs a full 360° rotation after excitation with visible light, showing unidirectionality at a very fast rate of potentially up to 1 KHz at 20°C. The full rotation is believed to be a four step process consisting of two light induced and two thermal steps. However until now, the mechanism accounting for this fast rotation is not completely understood. We present possible pathways for the light-induced steps based on excited state quantum chemical calculations at the CASSCF level of theory. The calculations are compared to newly available results from time-resolved pump-probe experiments.

[1] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat. Commun.* **6**, 8406 (2015).

MO 4.3 Mon 14:30 PA 1.150

**Ultrafast Photoinduced dynamics of Benzocyclobutenedione in Solution** — ●XIAONAN MA, HANS-CHRISTIAN SCHMITT, MICHAEL WENZEL, MARCO FLOCK, INGO FISCHER, ROLAND MITRIĆ, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Benzocyclobutenedione (BCBD) has an abundant photochemistry and has been studied since decades, but its sub-ns photochemical dynamics remained unknown. In this work, the ultrafast photophysics and photochemistry of BCBD dissolved in dichloromethane was investigated by transient IR and UV/Vis absorption spectroscopy. The initial UV-populated  $S_3(\pi\pi^*)$  state deactivates rapidly to the  $S_1(n\pi^*)$  state via internal conversion (IC) followed by sub-ps vibrational relaxation (VR). In parallel, the  $S_1(v > 0)$  state BCBD decarboxylates to benzocyclopropenone, which subsequently rearranges to cyclopentadienyldieneketene. Two extra reactions on the  $S_1(v = 0)$  state that compete with deactivation to  $S_0$  were identified by transient IR spectra combined with DFT/TDDFT calculations. Ring-opening in the  $S_1(v = 0)$  state produces vibrationally hot bisketene cools within 22 ps. This process competes with the intramolecular rearrangement to singlet oxacarbene and subsequent conversion into the triplet carbene via inter-

system crossing (ISC). A long time product identified in the transient UV/Vis spectra is probably due to dimerization of the carbene. Molecular dynamics (MD) simulations of the early-time photochemistry of BCBD successfully reproduce the formation of benzocyclopropenone and oxacarbene.

MO 4.4 Mon 14:45 PA 1.150

**Fluorescence studies on photosensitizers based on thermally activated delayed fluorescence (TADF) dyes** — ●AYLA PÄPCKE<sup>1</sup>, HENRIK JUNGE<sup>2</sup>, STEFAN LOCHBRUNNER<sup>1</sup>, MATTHIAS BELLER<sup>2</sup>, and SHU-PING LUO<sup>3</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Albert-Einstein-Straße 23, 18059 Rostock — <sup>2</sup>Leibniz-Institut für Katalyse an der Universität Rostock e.V. — <sup>3</sup>State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology

As a result of the increasing scarcity of fossil fuels renewable energy fuels generated with the help of solar energy become a focus in current research. Photosensitizers responsible for the absorption of sun light play here a key role. In water reduction systems thermally activated delayed fluorescence (TADF) dyes can be used as efficient organic sensitizers. After an absorption event the water reduction catalyst (WRC) has to remove an electron from the excited singlet state of the TADF dye. The WRC acts as a mediator transferring the electron to protons in the water generating free hydrogen in a final step. Applying time resolved and stationary fluorescence measurements to the TADF dyes in the presence and absence of the WRC we investigate, if the proposed reaction scheme is indeed operational, and characterize the efficiency of the photo induced electron transfer steps.

MO 4.5 Mon 15:00 PA 1.150

**The Femtochemistry of the Ferrioxalate Actinometer** — ●STEFFEN STRAUB, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, 53177 Bonn, Germany

The ferrioxalate actinometer is an aqueous solution of the complex anion, potassium trisoxalatoferat(III), which is frequently used in preparative photochemistry to determine the internal radiant flux of photoreactors. Actinometers are needed to quantify the quantum yield and hence, the total efficiency of a photochemical reaction of interest. In the presence of light, ferrioxalate is reduced to ferrous oxalate and a neutral carbon dioxide together with a free oxalate anion is released from the complex. Despite having served as the "gold Standard" of liquid-phase actinometry for many years, the primary processes of ferrioxalate are entirely unknown. Previous femtosecond (fs) UV-pump/Vis-probe experiments and most recent ultrafast x-ray absorption spectroscopy have yielded ambiguous and partly contradictory results. Here, we report on fs-UV-pump mid-infrared probe spectroscopy, which is able to provide unique structural-dynamical information about the complex following its initial ultrafast optical excitation. The fs-spectra demonstrate that a hot CO<sub>2</sub> molecule is expelled from coordination sphere of the ferric center within 500 fs to generate a penta-coordinated ferrous species that bears an intriguing carbon dioxide radical anion ligand. A subsequent structural isomerization on a 10 ps-time scale and the loss of the CO<sub>2</sub><sup>-</sup> moiety yields the final ferrous product of the actinometer.

MO 4.6 Mon 15:15 PA 1.150

**Time-Resolved step-scan FTIR investigation of transition metal containing complexes** — ●PATRICK DI MARTINO-FUMO<sup>1</sup>, MANUEL ZIMMER<sup>1</sup>, SVEN OTTO<sup>2</sup>, HANNA WAGNER<sup>3</sup>, FRANK BREHER<sup>3</sup>, WIM KLOPPER<sup>4</sup>, KATJA HEINZE<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern, Germany — <sup>2</sup>Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University, Germany — <sup>3</sup>Inorganic Chemistry, KIT, Germany — <sup>4</sup>Physical and Theoretical Chemistry, KIT, Germany

In this contribution, the time-resolved step-scan FTIR technique is used for investigations of transition metal-complexes in their electronically excited states with lifetimes in the microsecond regime. The vibrational frequencies obtained from this technique compared with theoretical predictions allow a structural assignment of the excited states. In addition, the influence of temperature can be investigated due the possibility to cool down a solid sample to at least 20 K, which

e.g. results in an increase of lifetimes and an exclusive population of the lowest excited state. The chosen molecular systems include a mononuclear  $\text{Cr}^{3+}$ -complex with dipyrindinium ligands. This complex has a very high luminescence quantum yield and two energetically similar doublet states. Additionally, investigations on a catalytically active multinuclear complex with two ruthenium and three copper ions including tris(3-pyridin-2-yl)pyrazole ligands is presented. By comparison of calculated (DFT) and experimental spectra a significant geometry change between the electronic ground state (singlet) and the excited triplet state can be identified.

MO 4.7 Mon 15:30 PA 1.150

**Spectroscopic Investigation of Fe(II)-Complexes on the fs-Time Scale** — •ALEKSEJ FRIEDRICH<sup>1</sup>, PETER ZIMMER<sup>2</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics, Uni-

versity of Rostock — <sup>2</sup>Department Chemie, Universität Paderborn

Iron-complexes are interesting for photocatalytic applications, because they could act as photosensitizers and replace noble metals. A problem of such Fe-complexes is a short lifetime of the metal-to-ligand charge transfer state (MLCT). One promising way to extend the lifetime is to use ligands in the complex with N-heterocyclic carbene (NHC) moieties.

To get insight into the impact of the NHC ligands on the photophysics of the complexes ultrafast transient absorption measurements are performed. We see a nice correlation between the number of NHC sites and the lifetime of the MLCT state. Fe(II)-complexes with a low NHC number (2) relax from the MLCT state to the lowest metal-centered state within 100 fs while four NHC sites result in a MLCT lifetime of 8 ps.[1]

[1] P. Zimmer et al., *Inorg. Chem.*, accepted.