

## MO 12: Photochemistry and Catalysis

Time: Wednesday 11:00–12:45

Location: PH/HS1

## Invited Talk

MO 12.1 Wed 11:00 PH/HS1

**Generating high-valent iron with light. Photochemical dynamics** — ●PETER VÖHRINGER — Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, 53115 Bonn, Germany

The most abundant oxidation states of iron are the ferrous and ferric states, +II and +III, respectively. High-valent iron compounds contain Fe centers at the extraordinary oxidation states, +IV, +V, and +VI. Such species are of paramount importance for the catalysis of a number of biochemically or technologically relevant molecular transformations. Particularly reactive are high-valent iron species that feature a terminal iron-nitrogen bond, so called nitridoiron compounds, and in which the metal is embedded in a fourfold-symmetrical coordination geometry like in heme proteins. Their isolation has not been accomplished to date, but very few non-heme model systems have been prepared by photochemical means and cryo-trapped in low-temperature solid matrices. Very recently, we have been able to temporally trap such elusive octahedral nitridoiron species even in room temperature liquid solution, i.e. under biochemically and technologically relevant conditions, and to even allow for a preliminary study of their reactivity. To this end, we conducted various time-resolved infrared spectroscopies in combination with laser flash photolysis on time scales ranging from a few seconds all the way down to a few hundred femtoseconds. We will review our current state of understanding of the molecular-level mechanisms that are involved in the photochemical route to high-valent iron species as seen through these time-resolved IR methods.

MO 12.2 Wed 11:30 PH/HS1

**Hydrogen Abstractions by Triplet Excited Pyrimidinones** — ●CHRISTIAN TORRES ZIEGENBEIN<sup>1</sup>, MATHIAS MICHEEL<sup>2</sup>, GERALD RYSECK<sup>1</sup>, and PETER GILCH<sup>1</sup> — <sup>1</sup>HHU Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany — <sup>2</sup>PHT-Jena, Albert-Einstein-Straße 9, 07745 Jena, Germany

Pyrimidinones are moieties of the (6-4) photolesions of DNA. Their lowest energy absorption peaks are located at longer wavelengths than those of DNA bases. Under solar irradiation this results in high excitation probabilities and can lead to secondary DNA photo lesions [1]. Pyrimidinones may exhibit high quantum yields for triplet excitation. For example 1-methy-2(1H)-pyrimidinone (1MP) features a yield of ~0.5 (50%) [2]. In how far this kind of excitation contributes to the secondary photochemistry of DNA is the topic of this presentation. By means of steady state and nanosecond spectroscopy photoreactions of 1MP and quenchers bearing a CH<sub>x</sub>-O- moieties have been studied. The experiments show that triplet excited 1 MP abstracts hydrogen atoms from these quenchers. In particular, it could also abstract hydrogen atoms from deoxyribose pointing to the biological relevance of the process.

[1] K. Haiser, B. P. Fingerhut, K. Heil, A. Glas, T. T. Herzog, B. M. Pilles, W. J. Schreier, W. Zinth, R. de Vivie-Riedle, T. Carell, *Angew Chem Int Edit* 2012, 51, 408-411.

[2] G. Ryseck, T. Schmierer, K. Haiser, W. Schreier, W. Zinth, P. Gilch, *ChemPhysChem* 2011, 12, 1880-1888.

MO 12.3 Wed 11:45 PH/HS1

**Time-Resolved Step-Scan FTIR Investigations on Multimetallic Transition Metal Complexes in Solution and in the Solid State** — ●MANUEL ZIMMER<sup>1</sup>, FABIAN RUPP<sup>1</sup>, DANIEL VOLZ<sup>2</sup>, WIM KLOPPER<sup>2</sup>, ROLF DILLER<sup>1</sup>, STEFAN BRÄSE<sup>2</sup>, FRANK BREHER<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>TU Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Karlsruhe Institute of Technology, 76131 Karlsruhe

Time-resolved (TR) infrared experiments enable the investigation of chemical reactions, photochemical/-physical processes and their kinetic traces. With the step-scan technique we are able to identify electronically excited states and excited state structures by comparison with theoretical results from quantum chemical calculations. Our focus lies on cooperative effects in multimetallic transition metal complexes with 2 to 4 metal centers. Here we present the first TR step-scan FTIR measurements on a trimetallic Pd complex which has been demonstrated to be a potential catalyst for coupling reactions. The complex was investigated in solution (DMSO-d<sub>6</sub>) in the absence of air. We could determine the emissive electronic state (<sup>3</sup>A) and the structural arrangement of the complex in the excited state by comparing

the excited state IR spectra with (TD-)DFT calculations. The excited state lifetime of the emissive state, which was previously obtained by fluorescence lifetime measurements is confirmed. Furthermore we present results on different dimetallic copper complexes (differing in their ligand systems) in a KBr matrix. We show the capabilities of step-scan measurements in a KBr matrix, a method that is extremely useful for complexes which cannot be investigated in solution.

MO 12.4 Wed 12:00 PH/HS1

**Light-Driven Electron and Energy Transfer in a Photocatalytic Model System** — ●ALEKSEJ FRIEDRICH<sup>1</sup>, ESTEBAN MEJÍA<sup>2</sup>, SHU-PING LUO<sup>2</sup>, HENRIK JUNGE<sup>2</sup>, MATTHIAS BELLER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Rostock, 18051 Rostock, Germany — <sup>2</sup>Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

A promising route to provide environmentally friendly energy is the generation of solar fuels by photocatalysis. We investigate a hydrogen evolving homogeneous photocatalytic model system consisting of a non-noble metal-photosensitizer (PS), an iron-catalyst, and triethylamine (TEA) as a sacrificial reductant.[1,2] So far little is known, about the fundamental reaction steps and possible loss channels. Here we study the intermolecular electron and energy transfer by time resolved luminescence and transient absorption spectroscopy on the nanosecond timescale. It is found that 20 vol% of the sacrificial reductant reduces the luminescence lifetime of the copper-PS in acetonitrile moderately from 280 ns to 210 ns. Contrary, the iron-catalyst quenches the lifetime more efficiently to 110 ns. Long living products of the quenching events are observed by the transient absorption measurements. To identify the products and to determine the transfer yield control experiments with the strong electron acceptor methyl viologen are performed. By comparison the electron transfer efficiency from the PS to the catalyst is determined to 4%.

Literature: [1] S. Luo et al., *Angew. Chem.* **125**, 437-441 (2012). [2] E. Mejia et al., *Chem. Eur. J.* **19**, 15972-15978 (2013).

MO 12.5 Wed 12:15 PH/HS1

**Ultrafast Time-Resolved Spectroscopy of New Reversible Photoswitchable Diarylethene Derivates** — ●TIAGO BUCKUP<sup>1</sup>, SVEN MEHLHOSE<sup>1</sup>, CHRISTOPHER SARTER<sup>2</sup>, ANDRES JÄSCHKE<sup>2</sup>, HANS-ROBERT VOLPP<sup>1</sup>, and MARCUS MOTZKUS<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg. — <sup>2</sup>Institut für Pharmazie und Molekulare Biotechnologie, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Diarylethenes (DE) are an important class of compounds with promising applications due to their photochromatic behavior. Recently, photoswitchable DEs were combined with the structural features and molecular recognition properties of nucleic acids to design new photochromic nucleosides [1]. In this work, we investigate the ultrafast dynamics of the ring-opening photo-reaction of several DE derivatives with ultrashort excitation (<20 fs) in transient absorption. We observe a very fast excited state ballistic deactivation of the Franck Condon region towards the conical intersection (CI) within the first 300 fs. The ring-opening reaction takes place within 1.6-5.5 ps, depending on the DE derivative. The branching ratio at the CI can be estimated by the incomplete recovery of the bleach signal of the closed-form absorption between 450-500 nm. The quantum yield for the ring-opening photo-reaction of such DE derivatives is significantly enhanced (over 70% efficiencies) by specific thiophene substitutions. A global target analysis (GTA) of transient absorption data further depicts a simple kinetic model starting with a sequential reaction followed by a branching reaction at the CI. [1] Singer, et al, *JACS* 132 (2010) 8372.

MO 12.6 Wed 12:30 PH/HS1

**Alkali effect on bimetallic hydroamination catalysts the gas-phase** — ●JOHANNES LANG, PATRICK DI MARTINO-FUMO, MERVE CAYIR, WERNER R. THIEL, and GERON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany

Electrospray ionization (ESI) in combination with tandem mass spectrometry is an established tool to investigate transition metal complexes[1] as well as alkali ion adducts[2] under isolated conditions in the gasphase. We investigated bimetallic hydroamination catalysts

via ESI-MS of their alkali adducts in a Paul type ion trap. Using a multi-methods approach we characterized the structural changes of the catalysts upon coordination of the alkali ion as well as gradual changes of the structure and fragmentation behavior. We record Infrared Multiple Photon Dissociation (IRMPD) spectra and conduct density functional theory (B3LYP/cc pVDZ, RSC ECP) calculations. Collision Induced Dissociation (CID) studies reveal a gradual change of the fragmentation behavior in dependence of the alkali ion size. This

is well understood under consideration of calculated binding energies. The alkali ion size plays a crucial role in the stabilization of the fragments, which leads to a change of the fragmentation behavior.

1. Nosenko, Y., et al., *Physical Chemistry Chemical Physics*, 2013, 15(21): p. 8171-8178.

2. Citir, M., et al., *The Journal of Physical Chemistry A*, 2012, 116(6): p. 1532-1541.