

MO 6: Metal Complexes

Time: Monday 14:00–16:00

Location: S HS 001 Biologie

Invited Talk MO 6.1 Mon 14:00 S HS 001 Biologie
Investigation of structures and electronic states of transition metal containing complexes via transient FTIR spectroscopy— PATRICK DI MARTINO-FUMO¹, PIT BODEN¹, JASMIN BUSCH², SVEN OTTO³, KATJA HEINZE³, STEFAN BRÄSE², and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern, Germany — ²Organic Chemistry, KIT, Germany — ³Inorganic Chemistry and Analytical Chemistry, JGU Mainz, Germany

In order to analyze structures, electronic properties and lifetimes of transition metal complexes in their electronically excited states transient step-scan FTIR spectroscopy in the nanosecond and microsecond regime turns out to be a very efficient tool. We combine transient FTIR-spectroscopy with powerful tunable ns laser systems from the IR to the UV at different repetition rates which are used for specific electronic excitations. For investigation of temperature dependent effects samples can be cooled down to about 10 K. Furthermore different samples (solution, pellets, films) offer the possibility to analyze *e.g.* the influence of environment, aggregation state or electronic properties. The presented molecular systems include a series of bi- and tetranuclear Cu(I)-complexes relevant for the development of Iridium free OLEDs. Additionally Cr³⁺-containing complexes are mentioned which are efficient NIR emitters. Here newly developed double resonance techniques are presented, which are applied to specifically influence the relative population of two energetically similar electronically excited states.

MO 6.2 Mon 14:30 S HS 001 Biologie

Iron complexes as photosensitizers for hydrogen production— BJÖRN ALTENBURGER¹, AYLA PÄPCKE¹, ALEKSEJ FRIEDRICH¹, STEFAN LOCHBRUNNER¹, PHILIPP DIERKS², PETER ZIMMER², and MATTHIAS BAUER² — ¹Institute of Physics, University of Rostock — ²Department of Chemistry, University of Paderborn

Iron is a promising candidate to replace rare transition metals in photosensitizer complexes used for light harvesting and photocatalytic applications. Even though its electronic properties are a severe obstacle to obtain a long living metal-to-ligand charge transfer (MLCT) state, the availability and environmental aspects make it worthwhile to investigate these complexes. In our research the focus is on Fe(II) complexes with N-heterocyclic carbene ligands which result in an enhanced ligand field. Our investigations using ultrafast transient absorption spectroscopy show that the lifetime of the MLCT state can be increased to several picoseconds utilizing these ligands [1]. Modifying them by adding electron withdrawing groups can prolong the lifetime even further. Recently, along this route developed iron complexes show even fluorescence. Pump-probe measurements are combined with time resolved fluorescence spectroscopy to identify the relaxation pathways and to determine the lifetime of the involved states.

[1] P. Zimmer et al., *Inorg. Chem.* 2018, 57, 360-373

MO 6.3 Mon 14:45 S HS 001 Biologie

Optimally-tuned long-range corrected density functional for modeling excited states of spin-crossover iron complexes

— OLGA BOKAREVA, SERGEY BOKAREV, and OLIVER KÜHN — Institute of Physics, Rostock University, Albert Einstein Straße 23-24, 18059 Rostock

Transition metal complexes play an essential role as photosensitizers, photoemitters, and dyes. Although notable progress has been achieved with iridium(III) and ruthenium (III) complexes, the substitution of noble metals with earth-abundant and biocompatible elements is highly desirable from the viewpoint of overall costs and ecological impact. Iron compounds and especially spin-crossover complexes represent a convenient alternative but before going to real applications, profound mechanistic studies of excited state structure and dynamics, as well as the influence of chemical "tuning" on excited state order, should be performed. To this end, high-level theoretical studies are required to complement experiments.

In this work, we have applied optimally-tuned long-range corrected density functional theory for the modeling of ground- and excited state properties of a series of iron (III) spin-crossover complexes. The choice of the method is dictated by the objective to describe accurately long-range metal-to-ligand charge-transfer (MLCT) states which are of crucial importance for creating long-living excited states involved in fur-

ther photocatalytic reactions. The character of singlet and triplet excited states is carefully analyzed and shown to be very sensitive to the applied computational scheme.

MO 6.4 Mon 15:00 S HS 001 Biologie

Singlet Oxygen Reactivity with Carbonate Solvents Used for Li-ion Battery Electrolytes — MATTHIAS K. ROOS¹, ANNA T. S. FREIBERG², JOHANNES WANDT², HUBERT A. GASTEIGER², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, Ludwig-Maximilians-Universität München, München — ²Lehrstuhl für Technische Elektrochemie, Technische Universität München, Garching

Increasing the energy density of modern Li-ion batteries is essential for their future widespread use in the automotive sector. To achieve this goal, new cathode active materials are required, for which mixed transition metal layered oxides are promising candidates. However, for high state of charge, the release of singlet oxygen was observed from these cathode materials, resulting in drastically reduced battery lifetimes. In this joint experimental and theoretical work, we investigate the reactivity of the commonly used battery electrolytes ethylene carbonate (EC) and dimethyl carbonate (DMC) towards singlet oxygen [1]. Employing Rose Bengal to photochemically generate singlet oxygen in the bare electrolyte solutions, gaseous products are detected and quantified by on-line mass spectrometry. With quantum chemical and on-the-fly dynamical calculations a two-step reaction cascade is proposed, leading to the same products as found in the experiment. The uncommon reaction of an alkane with singlet oxygen in the first step constitutes the key element, activating the molecules for their further decay. The reaction mechanism is verified by colorimetric product detection in solution.

[1] *J. Phys. Chem. A* **122** (2018), 8828–8839.

MO 6.5 Mon 15:15 S HS 001 Biologie

Ultrafast processes in a luminescent mononuclear Cu(I) complex in liquid and solid phase — MERTEN GRUPE¹, FLORIAN BÄPPLER¹, MAXIMILIAN THEISS¹, FABIAN DIETRICH², STEFAN BRÄSE³, MARKUS GERHARDS², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Dept. of Org. Chem., KIT, 76131 Karlsruhe

The primary photo induced processes in the OLED-usable mononuclear, heteroleptic Cu(I) complex ([DPEPhos]Cu[PyrTet]^[1]) were investigated in various solvents and solid state samples via femtosecond (fs) time resolved UV/Vis and fs time resolved mid-IR transient absorption spectroscopy (TA). Vibrational dynamics by mid-IR fs-TA are best described by a tri-exponential fit with $\tau_1 \approx 0.85$ ps, $\tau_2 \approx 5$ ps, $\tau_3 \approx 37$ ps. The UV/Vis data exhibit basically the same dynamics, however, dependent on the solvent a tri- or tetra-exponential fit is required. UV/Vis TA in solid phase leads to a tetra-exponential fit ($\tau_1 \approx 0.5$ ps, $\tau_2 \approx 2.6$ ps, $\tau_3 \approx 20$ ps, $\tau_4 \approx 200$ ps) as well, interestingly, with spectral dynamics significantly differing from that in solution. Based on our results we suggest that flattening distortion and/or a ligand twist (TD-DFT) occur on the time scale of τ_2 in solution and that, in contrast to literature on another mononuclear Cu(I) complex^[2], ISC (τ_3) is not necessarily associated with a spectral blue shift.

[1] Bergmann et al. *Chem. Commun.*, 2013, 49 6501[2] Iwamura et al. *Acc. Chem. Res.* 2015, 48 782

MO 6.6 Mon 15:30 S HS 001 Biologie

Time-resolved spectroscopy of the charge separation in Zn(III)-Au(III)-porphyrin dyads — AYLA PÄPCKE¹, SEBASTIAN PREISS², KATJA HEINZE², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23, 18059 Rostock — ²Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, 55128 Mainz

To convert sunlight into chemical energy photoinduced energy transfer and electron transfer processes within the photosynthetic components are essential. Bioinspired systems contain porphyrins to mimic the role of chlorophyll in natural photosynthesis. Porphyrins are desired photosensitizers because of the easy functionalization, the strong absorption in the visible region, the often high fluorescence yield and the easy tunable redox properties [1].

Recently, gold(III) porphyrin cations have been used as electron

acceptors in photosynthetic charge-separation [2]. Applying ultrafast transient absorption and time resolved photoluminescence spectroscopy we investigated the photoinduced electron transfer process of Zn(III)-Au(III)-porphyrin dyads and the dynamics of the formation of the Au(II) species.

[1] P. K. Poddutoori, *et al.*, *Phys. Chem. Chem. Phys.* **17**, 26346-26358 (2015)

[2] S. Preiß, *et al.*, *Nat. Chem.* **9**, 1249-1255 (2017)

MO 6.7 Mon 15:45 S HS 001 Biologie

Soft x-ray beam damage of a solid transition-metal complex — •JAN LUDWIG¹, MARKUS KUBIN², ROLF MITZNER², CHRIS-

TIAN WENIGER², ALEXANDER FÖHLISCH², JAN KERN³, VITAL YACHANDRA³, JUNKO YANO³, and PHILIPPE WERNET² — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Germany — ²Helmholtz-Zentrum Berlin, Berlin, Germany — ³Lawrence Berkeley National Laboratory, Berkeley, USA

Soft x-rays are widely used for L-edge spectroscopy on transition-metal compounds, but also cause beam damage due to photoreduction. Here we determine the acceptable threshold of x-ray dose tolerable for L-edge absorption spectroscopy of a Mn(III) compound and discuss the underlying mechanisms. The results are important for acquiring damage-free L-edge spectra of transition-metal compounds in general.