

MO 34: Photochemistry

Time: Friday 10:30–13:00

Location: TOE 317

MO 34.1 Fri 10:30 TOE 317

Ring-closure and isomerization capabilities of spiropyran-derived merocyanine isomers — ●JOHANNES BUBACK¹, MARTIN KULLMANN¹, PATRICK NUERNBERGER¹, RALF SCHMIDT², FRANK WÜRTHNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We report the photochemistry of two ring-open isomers, namely TTC and TTT, of a bidirectional photoswitchable spiropyran, 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6,8-dinitro BIPS). Both isomers are capable of ring closure after excitation with visible fs laser pulses, as disclosed by pump-wavelength-dependent transient absorption experiments in the visible spectral range. The main isomer TTC has its maximum absorption at 560 nm, whereas the minor isomer TTT is red shifted (600 nm). The excited-state lifetimes differ strongly ($\tau = 902$ ps for TTT and $\tau = 94$ ps for TTC), nevertheless the quantum efficiencies for ring closure (40% for TTC and 35% for TTT) and isomerization (1–2% for TTC and 1–2% for TTT) are comparable. With regard to the bidirectional photoswitching capabilities, 6,8-dinitro BIPS is the first molecular switch based on a 6 π -electrocyclic reaction where both ring-open isomers are capable of ring closure.

MO 34.2 Fri 10:45 TOE 317

Control of the dissociation of diphenylallyl derivatives — ●MICHAEL MIKHAILOV¹, IGOR PUGLIESI¹, KONSTANTIN TROSHIN², HERBERT MAYR², and EBERHARD RIEDLE¹ — ¹LS BioMolekulare Optik, LMU München — ²AK Mayr, Dept. Chemie, LMU München

We study the photodissociation of the model system (E)-1,3-diphenylallyl acetate (H-H-OAc) using broadband fs spectroscopy. After UV excitation H-H-OAc undergoes simultaneous homolysis and heterolysis to form (1,3-diphenylallyl)• and (1,3-diphenylallyl)⁺. The formation of the same products is also observed for two asymmetrically substituted isomers of the model compound: (E)-1-(3,5-difluorophenyl)-3-p-tolylallyl acetate (Me-mFF-OAc), where the methyl electron-donating substituent is attached to the styrene part and the electron-withdrawing fluorine substituents to the toluene part, and (E)-3-(3,5-difluorophenyl)-1-p-tolylallyl acetate (mFF-Me-OAc), where the substitution is reversed. While the bond cleavage is similar to H-H-OAc, the reaction rates are significantly different: 24.2 ps and 96.3 ps for the cation and radical rise and decay times of Me-mFF-OAc, and 190 ps and about 9 ns for the cation and radical rise and decay times of mFF-Me-OAc. The observed difference can be explained by the fact, that attaching the electron donating methyl substituent to the styrene part stabilizes the cation and radical of Me-mFF-OAc, whereas destabilization of the styrene part takes place for mFF-Me-OAc due to the electron withdrawing fluorines. Thus, a control over the photoinduced bond cleavage rates can be achieved by the substituent change.

MO 34.3 Fri 11:00 TOE 317

Ultrafast photochemical bond cleavage of diphenylmethylphosphonium cations — ●SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN SAILER², BENJAMIN PHILLIP FINGERHUT¹, EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstraße 11, D-81377 München, Germany — ²Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, D-80538 München, Germany

Diphenylmethylphosphonium cations (DPM-PR₃⁺) are known as one of the most effective precursors for photo-produced benzhydryl cations, which are cationic key intermediates in S_N1 reactions. With a combined theoretical and experimental investigation we elucidate the mechanism of the initial ultrafast bond cleavage process of DPM-PPH₃⁺. The calculations are performed for a model system with only two phenyl rings. It is designed to preserve the main properties of the full system, still allowing the use of highly correlated quantum chemical methods. The mechanism of the optical excitation and subsequent charge exchange which finally leads to bond cleavage of the C-P bond will be discussed.

Ultrafast broadband transient absorption measurements of DPM-PPH₃⁺ and DPM-PMPh₂⁺ show similar dynamics, supporting an iden-

tical mechanism. This legitimates the transfer of the theoretical results of the model system to DPM-PPH₃⁺. The rise of the cation signal after 10–20 ps indicates the expected bond cleavage. The theoretically predicted initial radical formation on the sub-picosecond timescale is not confirmed yet due to the overlay of several transient signals.

MO 34.4 Fri 11:15 TOE 317

Theoretical study of charge-transfer processes in [Ir(ppy)₂(bpy)]⁺ based systems for photocatalytic water splitting — ●OLGA BOKAREVA, SERGEY BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock, Deutschland

The general scheme of the homogeneous water splitting solar cell consists of separated water oxidation and water reduction half reactions employing sacrificial reagents that donate or accept electrons in the catalytic system. However, the homogenous systems are usually less active due to the complexity of the multielectron processes of water reduction. In present work, we aimed at clarifying the primary steps of charge-transfer reaction and discussing the ways to increase the efficiency of the overall process. We focused on the theoretical investigation of the iridium photosensitizer [Ir(ppy)₂(bpy)]⁺ (ppy = phenyl pyridine and bpy = bipyridine) in the ground and lowest excited electronic states of metal-to-ligand and ligand-centred character.

To investigate the possible ways to increase the efficiency of the charge-transfer process we performed the theoretical study of the possible binding of photosensitizer with the small metal clusters Ag_n (n = 2–20) and influence on the structure of the excited electronic states and electronic spectra.

The results obtained can be further used for quantum dynamics simulation of the charge-transfer processes of both solvated and adsorbed photosensitizer as well as for guidance in the interpretation of ultra-fast spectroscopic experiments on surface-deposited metal clusters.

MO 34.5 Fri 11:30 TOE 317

Time-resolved Spectroscopy of [Ir(ppy)₂(bpy)]⁺ within a Photocatalytic System — ●ANTJE NEUBAUER¹, ALEKSEJ FRIEDRICH¹, FELIX GÄRTNER², HENRIK JUNGE², MATTHIAS BELLER², and STEFAN LOCHBRUNNER¹ — ¹Universität Rostock, Universitätsplatz 3, 18051 Rostock — ²Leibniz-Institut für Katalyse Rostock, Albert-Einstein-Str. 29a, 18059 Rostock

Iridium (III)-complexes have recently regained high attention especially in the field of organic light-emitting diodes and as photosensitizers in homogeneous water-reducing systems. For the latter application typically a photo-sensitizer is used to absorb light, and to transfer subsequently electrons to a catalyst, which actually reduces the water to generate molecular hydrogen. Often a sacrificial reductant (SR) serves as an electron source in order to avoid oxygen evolution. However, the notion about the involved processes in those complex systems is quite vague and only little is known about the responsible mechanisms and the factors determining the efficiency.

We present here mechanistic studies of a heteroleptic Ir(III)-complex in different solutions within the framework of an iron-based photocatalytic water-reducing system,^[1] and by means of time-resolved photoluminescence and femtosecond transient absorption spectroscopy. The results elucidate the impact of the solvent mixture for the investigated photo-catalytic system.

[1] F. Gärtner *et al.*, *Angew. Chem.* **2009**, *121*, 10147.

MO 34.6 Fri 11:45 TOE 317

Temperature dependent generation and relaxation behavior of photoswitchable [Ru(bpy)₂(OSO)]⁺ — ●SEBASTIAN EICKE, ANNIKA KRUSE, VOLKER DIECKMANN, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany

Ruthenium sulfoxide [Ru(bpy)₂(OSO)]⁺ (OSO: 2-methylsulfinylbenzoate) offers a light-induced linkage isomerization located at the SO-ligand resulting in pronounced changes of characteristic optical properties. This molecule dissolved in propylene carbonate was studied in respect to its photochromism and kinetics of the generation and relaxation of the light-induced metastable isomers. The kinetics were determined by temperature and exposure dependent pump-probe technique and show in each case a temperature dependency on the charac-

teristic time constants following Arrhenius law. The generation kinetics reveal two ways the linkage isomerization can take place. Whereas one exhibits an activation energy $E_{A,1} \approx 0.1$ eV, the second one only appears for $T > 25$ °C with a temperature independent behavior. The relaxation kinetics disclose two activation energies $E_{A,2} = 0.76$ eV and $E_{A,2} = 1.00$ eV which can be assigned to the two metastable isomers $MS_{1,2}$. An efficient and fast light-induced conversion and long lifetimes of the two metastable isomers in the range of 10^3 s at room temperature allow for application of this molecule in a multiplicity of devices like ultra-fast optical switches or optical molecular data storage.

MO 34.7 Fri 12:00 TOE 317

Photochemistry of 3-hydroxyflavone and its water clusters inside superfluid helium nanodroplets — ●TOBIAS PREMKE and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

3-hydroxyflavone is a prototype system for excited state intramolecular proton transfer (ESIPT), which was identified by a Stokes shift in the emission of 8000 cm^{-1} [1]. Besides numerous other studies, the bare molecule and its water cluster have been investigated in helium droplets [2] as well as in the gas phase [3]. New data will be presented on the investigation of ESIPT in helium droplets for the deuterated isomer of the bare molecule and of the water complex. The spectra of the deuterated molecule confirm that the transfer of the proton or deuterium is not influenced by a barrier. Neither complexation with H₂O nor with D₂O could hinder the ESIP/DT. The spectra of the water complex revealed significant amounts of backprotonation of D₂O prior to pick up by the droplet. While the spectra provide evidence for only a single configuration of the water complex an experimental indication for a particular complex configuration is still missing.

[1] P.K. Sengupta and M. Kasha, Chem. Phys. Lett. 68, 382 (1979).
[2] R. Lehnig, D. Pentlechner, A. Vdovin, B. Dick, and A. Slenczka, J. Chem. Phys. 131, 194307 (2009) [3] N.P. Ernsting, and B. Dick, Chem. Phys. 136, 181 (1989). A. Mühlpfordt et al., Chem. Phys. 181, 447 (1994). A. Ito et al., J. Chem. Phys. 96, 7474 (1992). K. Bartl et al., J. Chem. Phys. 129, 234306 (2008). K. Bartl et al., Phys. Chem. Chem. Phys. 11, 1173 (2009).

MO 34.8 Fri 12:15 TOE 317

Photoionization of Reactive Intermediates — ●MICHAEL STEINBAUER¹, PATRICK HEMBERGER¹, INGO FISCHER¹, and ANDRAS BÖDI² — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Molecular Dynamics Group, Paul-Scherrer-Institut, 5232 Villigen, Switzerland

Our group examines the dynamic of reactive intermediates in the gas phase. These radicals play an important role in the formation of soot in combustion processes, polycyclic aromatic hydrocarbons (PAHs) or in the chemistry of Earth's atmosphere. Ionization energies (IE) can be used as a kind of fingerprint for identification in flames if the latter is known in advance. Dissociative Photoionization (DPI) can be used to determine binding energies in the radicals instead.

Synchrotron radiation as a tunable light source along with Threshold Photoelectron Photoion Coincidence (TPEPICO) spectroscopy can be used for this purpose. As example the threshold photoelectron spectra of the transient species bromomethyl radical CH₂Br and the fulvenallenylradical C₇H₅ are presented in this talk. For the second very little is known, thus the IE can be used for detection in flames for example. For CH₂Br the DPI was examined and a breakdown diagram could be recorded. Out of a thermocycle the C-Br binding energy could be determined.

MO 34.9 Fri 12:30 TOE 317

Precise and rapid detection of optical activity for femtosecond spectroscopy — ●ANDREAS STEINBACHER, JOHANNES BUBACK, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We introduce polarimetry, *i.e.* the detection of optical rotation of light polarization, in a configuration that is suitable for femtosecond spectroscopy. The polarimeter is based on the common-path optical heterodyne interferometry method and provides fast and highly sensitive detection of rotating power. Femtosecond pump and polarimeter probe beams are integrated into a recently developed accumulative technique that further enhances sensitivity with respect to single-pulse methods. The high speed of the polarimeter affords optical rotation detection during the pump-pulse illumination period of a few seconds. We illustrate the concept on the photodissociation of the chiral enantiomers of methyl *p*-tolyl sulfoxide. The sensitivity of rotatory detection, *i.e.* the minimum rotation angle that can be measured, is determined experimentally including all noise sources to be 0.10 milli-degrees for a measurement time of only one second and an interaction length of 250 μm .

MO 34.10 Fri 12:45 TOE 317

A new technique: Quadruple-resonance-spectroscopy for isomer selection in an electronically excited state — ●MARTIN WEILER, KRISTINA BARTL, ANDREAS FUNK, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrodinger-Strasse 52, 67663 Kaiserslautern

Photochemical reactions are of great interest due to their importance in chemical and biological processes. For the first time we have been able to observe a proton wire reaction in an isolated system, the 3-hydroxyflavone(H₂O)₂ cluster, by applying combined IR/UV spectroscopy. The IR spectra in the electronic ground and excited state seem to indicate the existence of two isomers but due to overlapping UV spectra, an UV(excitation)/IR/UV(ionization) scheme yields no isomer selectivity in a molecular beam experiment. Here we show that the new IR/UV/IR/UV quadruple-resonance-spectroscopy (with a preselecting IR excitation) solves this problem. According to this new method two different species can unambiguously be assigned in accordance to DFT calculations. The technique offers the possibility to yield isomer selection and structural assignments in excited states of reactive systems which can also be relevant in biological environments.