

## MO 21: Photochemistry

Time: Friday 10:30–12:30

Location: BEBEL HS213

MO 21.1 Fri 10:30 BEBEL HS213

**The Photodissociation Dynamics of Fulvenallene, C<sub>7</sub>H<sub>6</sub>, Investigated by Velocity Map Imaging** — ●JENS GIEGERICH and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland Süd, Würzburg

Fulvenallene is the most stable C<sub>7</sub>H<sub>6</sub> isomer and is assumed to be an intermediate in the combustion of toluene. C<sub>7</sub>H<sub>6</sub> has been observed in toluene rich flames and theoretical studies predict it to be the major decomposition product of the benzyl radical. It appears that fulvenallene is an important intermediate in oxidation and pyrolysis processes, which are relevant to the combustion of aromatic hydrocarbons and to the formation of PAH.

Fulvenallene was generated from phthalide as a precursor, which decomposes to the reactive intermediate in a vacuum jet flash pyrolysis source. The molecules were excited at around 247 nm. At this wavelength region the excited molecule dissociates to the fulvenallenyl radical C<sub>7</sub>H<sub>5</sub> + H. The H-atom dissociation products were ionized in a [1+1] REMPI process via the 1s-2p transition. The ionized H-atoms are recorded on a Velocity Map Imaging Detector. The observed translational energy distribution peaks around 0.06 eV. The expectation value for translational energy release lies at around 0.21 eV which accords to ~ 14% of the excess energy. The ionized H-atoms show an isotropic angular distribution, typical for statistical reactions. In addition time-delay scans were carried out. The time-delay scans show a rate with a time constant on the order of 150 ns and are in good agreement with RRKM predictions.

MO 21.2 Fri 10:45 BEBEL HS213

**Solvent Dependence of Excited-State Proton Transfer from Pyranine-derived Photoacids** — ●CHRISTIAN SPIES<sup>1</sup>, BJÖRN FINKLER<sup>1</sup>, DINA PINES<sup>2</sup>, EHUD PINES<sup>2</sup>, DAN HUPPERT<sup>3</sup>, and GREGOR JUNG<sup>1</sup> — <sup>1</sup>Biophysical Chemistry, Saarland University, Saarbrücken, Germany — <sup>2</sup>Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel — <sup>3</sup>Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Israel

The transfer of a proton to a base is one of the most fundamental chemical reactions. Especially, photoexcitation of aromatic alcohols, leading to an enhanced acidity, served as paradigm for this kind of reaction. One of the most widely used photoacids is hydroxypyrene-3-sulfonate (HPTS) and its even more acidic sulfonamide derivative (HPTA). Recently, we synthesized a new series of strong photoacids based on HPTS and HPTA, with high photostability and pK<sub>a</sub>\* values ranging from -0.7 to -4. In this contribution we study the solvent dependence of these photoacids. A differential solvatochromism approach enables us to identify a charge transfer as the most distinct feature for the strong solvatochromism and photoacidity of these molecules. The excited-state proton transfer rate (kPT) of these photoacids is measured in more detail by time-resolved spectroscopy. Different solvents in which proton transfer takes place such as water, methanol and ethanol are investigated. The results are quantitatively explained by adiabatic and non-adiabatic proton transfer formalism and analyzed in terms of Marcus free energy correlations.

MO 21.3 Fri 11:00 BEBEL HS213

**Self-Assembly and Size-Dependent Optical Properties of Perylene Bisimide Dye Aggregates** — ●FRANZISKA FENNEL<sup>1</sup>, STEFFEN WOLTER<sup>1</sup>, ZENGQI XIE<sup>2</sup>, PER-ARNO PLÖTZ<sup>1</sup>, OLIVER KÜHN<sup>1</sup>, FRANK WÜRTHNER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock — <sup>2</sup>Institut für Organische Chemie und Center for Nanosystem Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

Molecular self-assembly is widely applied to create functional nanostructures. However, in many cases a quantitative description of the assembly processes is missing. In the presented work, the self-assembly of a perylene bisimide dye and the associated changes in the photophysical properties are investigated [1]. We find a remarkable behavior of the fluorescence yield upon aggregation, which first decreases and then increases again. The findings point to the presence of three different species during the assembly process, namely monomers, dimers with H-type and aggregates with J-type characteristics. An aggregation model is developed, which describes quantitatively the assembly process and the concentration dependence of the photophysical prop-

erties. The basic concept is that with increasing concentration first energetically favored dimers are formed which are not suitable for the association of further monomers due to their geometry. Larger aggregates are formed via a second dimeric species, which exhibits a different structure than the energetically favored dimer. This mechanism should also be responsible for the aggregation behavior of many other compounds. [1] Fennel F. et. al. *J. Am. Chem. Soc.*, **2013**, 135 (50),18722

MO 21.4 Fri 11:15 BEBEL HS213

**Electron and Energy Transfer Processes in Homogeneous Photocatalytic Systems** — ●ANTJE NEUBAUER<sup>1</sup>, SERGEY I. BOKAREV<sup>2</sup>, GILBERT GRELL<sup>2</sup>, ALEKSEJ FRIEDRICH<sup>1</sup>, PATRICK SCHWARZBACH<sup>1</sup>, DAVID SCHALLENBERG<sup>3</sup>, WOLFRAM W. SEIDEL<sup>3</sup>, HENRIK JUNGE<sup>4</sup>, MATTHIAS BELLER<sup>4</sup>, OLIVER KÜHN<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock — <sup>2</sup>Institut für Physik, Universität Rostock — <sup>3</sup>Institut für Chemie, Universität Rostock — <sup>4</sup>Leibniz-Institut für Katalyse Rostock

Photocatalytic water splitting for hydrogen generation has recently gained high scientific attention. However, there are only a few studies that focus on mechanistic insight on a molecular level.

Here we investigate homogeneous photocatalytic systems for water reduction based on Iridium(III)-photosensitizers (IrPS) with the aim to clarify the mechanisms of the individual reaction pathways relevant for photocatalysis. By employing time-resolved photoluminescence spectroscopy as well as time-dependent density functional theory calculations we address the following reaction steps: i) electron transfer from a sacrificial donor to the excited IrPS, and ii) excited state quenching of IrPS by an iron catalyst.

In addition to the unbound multi-component system, we study the intramolecular processes of a dinuclear Iridium-Nickel-complex with a novel phenanthroline-5,6-dithiolate bridging ligand. Such complexes have the potential of fast electron or energy transfer as essential reaction step in photophysical applications. For both systems, the role of electron and energy transfer processes is highlighted.

MO 21.5 Fri 11:30 BEBEL HS213

**Proton Transfer in Aqueous Solutions** — ●ISAAK UNGER<sup>1</sup>, STEPHAN THÜRMER<sup>2</sup>, and BERND WINTER<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie — <sup>2</sup>Center for Frontier Science, Chiba University, Japan

Synchrotron radiation has been used to core-excite several hydrogen-bonded species (Ammonia, Glycine) in aqueous solution using a liquid microjet as a sample. In contrast to gaseous samples, Auger decay is not the sole possible deexcitation channel in aqueous solutions. In the intermolecular Coulombic decay, the released energy upon a recombination of a valence electron with a core hole is transferred to a neighboring molecule releasing an electron. Auger electron spectroscopy of different aqueous solutions and their deuterated equivalents show a considerable influence of the proton mass on the decay probability of such delocalized deexcitation processes. We propose a model of proton transfer assisted decay to explain the different decay behaviour of deuterated species in hydrogen-bonded systems.

MO 21.6 Fri 11:45 BEBEL HS213

**Structural investigations on the jet-cooled neutral and ionic 7-hydroxy-4-methylcoumarin dimer and its hydrates by combined IR/UV spectroscopy** — ANKE STAMM, ●KIRSTEN SCHWING, and MARKUS GERHARDS — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

The photochemistry of solvated 7-hydroxy-4-methylcoumarin (7H4MC), e.g. known as one of the first industrially applied optical brighteners, was intensively investigated in the past e.g. comprising absorption spectroscopy, fluorescence measurements leading to quantum yields and life times or phosphorescence and triplet-triplet spectra. In this context the influence of solvents on the photochemical behavior was one of the main interests. From aqueous solution it is additionally known that the coumarin dyes show a tendency for self-aggregation. However, no detailed experimental analysis of the intrinsic structural properties of 7H4MC was performed so far. Thus we applied mass-, (isomer-) and state-selective combined double and triple resonance IR/UV methods for 7-hydroxy-4-methylcoumarin. IR

spectra of the neutral and ionic dimer ( $S_0$ ,  $D_0$  states) of 7H4MC as well as its mono- and dihydrate could be obtained. A comparison with calculated IR spectra for possible DFT-optimized isomers of a species allowed structural assignments. The presented measurements on 7H4MC are the first gas phase investigations on a neutral and ionic dimer of a coumarin derivative. The tendency of coumarin dyes for self-aggregation observed in aqueous solution is now investigated in detail on isolated species which can be successively hydrated.

MO 21.7 Fri 12:00 BEBEL HS213

**Quantumchemical studies on the decay of photoexcited 4,4'-Dihydroxythioindigo and its methylated counterpart** — ●SVEN OESTERLING<sup>1</sup>, MARC DITTMANN<sup>2</sup>, FRANZISKA F. GRAUPNER<sup>3</sup>, BENJAMIN MAERZ<sup>3</sup>, WOLFGANG ZINTH<sup>3</sup>, MARTIN ENGELHARD<sup>2</sup>, WOLFGANG LÜTTKE<sup>4</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>LMU München, Dept. Chemie, München, Germany — <sup>2</sup>MPI für Molekulare Physiologie, Dortmund, Germany — <sup>3</sup>LMU München, Fakultät für Physik, München, Germany — <sup>4</sup>GAU Göttingen, Fakultät für Chemie, Göttingen, Germany

The Thioindigo derivatives 4,4'-Dihydroxythioindigo (DHTI) and 4,4'-Dimethoxythioindigo (DMTI) show different behaviour after photoexcitation. Both exhibit strong fluorescence, but the lifetime of the excited state of DHTI (50 ps) is roughly 200 times shorter than the one of DMTI (11 ns). Contrary to DHTI, in DMTI a *cis-trans*-isomerization around the central double bond can be observed, which stems from a deactivation pathway, known for thioindigo itself, too.

Our quantumchemical calculations on CASSCF/PT2 level of theory

reveal a different route to reach the ground state for DHTI, mediated through an excited state intramolecular proton transfer (ESIPT). Although the corresponding conical intersection lies below the Franck-Condon energy in DMTI, too, this path is obstructed for DMTI, where, instead of a proton, a methylation had to be transferred.

Marc Dittmann et al., *Angew. Ch. Int. Ed.* **2013**, 52, 1-5

MO 21.8 Fri 12:15 BEBEL HS213

**A coherent-control study of 6-nitro BIPS** — ●CRISTINA CONSANI, STEFAN RUETZEL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present a coherent-control study on the isomerizing merocyanine dye 6-nitro BIPS in liquid environment. This molecule has been extensively studied in our group by means of ultrafast transient absorption and two-dimensional (2D) electronic spectroscopy, unraveling the details of the photo-induced isomerization. Two-dimensional spectroscopy represents an example of how extended photochemical information can be retrieved by employing a modulated electric field as excitation pulse. Coherent control techniques are a natural extension of this concept. In our approach, the results of 2D spectroscopy are used as input for the control study. We investigate how systematic variation of the excitation field within restricted parametrization spaces can be used to address specific molecular processes, thus completing and extending the information obtained by third-order spectroscopies.