

## MO 28: Photochemistry

Time: Friday 11:00–12:30

Location: F 102

## Invited Talk

MO 28.1 Fri 11:00 F 102

**Combined IR/IR/UV spectroscopy to analyze structures and proton transfer reactions in different electronic states** — ●MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Photochemically induced reactions like proton transfer reactions or proton wires are of great interest due to their importance in chemical and biological processes. Mass selective molecular beam investigations combined with isomer selective double, triple and quadruple resonance combined IR/UV spectroscopic techniques are very powerful tools to analyze the photochemically induced reactions. In comparison with (TD)-DFT calculations direct structural information on the electronic ground and electronically excited states of isolated molecules and clusters are obtained. The applications to different chromone and flavonoid based photoreactive species are presented including the first IR/IR application to an isolated proton wire in the gas phase (the doubly hydrated 3-hydroxyflavone molecule). In general the IR/IR/UV techniques (including the new introduced IR/UV/IR/UV method) applied on isolated species offer the possibility to yield isomer selection and structural assignments in electronic ground and also excited states of reactive systems especially in the case of overlapping isomers with the same electronic excitation energies. The great potential of IR/IR double resonance techniques is described.

MO 28.2 Fri 11:30 F 102

**The Photodissociation Dynamics of the Ethyl Radical, C<sub>2</sub>H<sub>5</sub>, Investigated by Velocity Map Imaging** — ●JENS GIEGERICH, KATHRIN H. FISCHER, MICHAEL STEINBAUER, and INGO FISCHER — University of Würzburg, Institute for Physical and Theoretical Chemistry, Am Hubland Süd, 97074 Würzburg, Germany

Ethyl radicals were generated from n-propyl nitrite as a precursor, which decomposes to the desired radical in a vacuum jet flash pyrolysis source. The radicals were excited to the  $\tilde{A} 2A^* (3s)$  Rydberg state around 250 nm. At this wavelength region the energetically most favorable reaction channel is the dissociation to C<sub>2</sub>H<sub>4</sub> (ethane) + H. The H-atom dissociation products were ionized in a [1+1\*] REMPI process via the 1s-2p transition and recorded on a Velocity Map Imaging Detector. The observed translational energy distribution is bimodal. A contribution of slow H-atoms with an isotropic angular distribution, typical for statistical dissociation reactions, peaks at low translational energies. A fast H-atom channel with an anisotropic angular distribution, typical for a direct dissociation process, peaks at around 1.8 eV. Time-delay scans with varying extraction voltages were carried out in addition to the Velocity Map Imaging experiments. These scans indicate the presence of two rates for the formation of H-atoms. One rate with a sub-nanosecond time constant is connected with H-atoms with large translational energy. The second rate with a time constant on the order of 100 ns is connected with H-atoms formed with low translational energy.

MO 28.3 Fri 11:45 F 102

**Time resolved studies on 9-fluorenon in the gas phase** — ●THIEMO GERBICH, JÖRG HERTERICH, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

The fast dynamics of isolated 9-fluorenon were observed by picosecond

time resolved photoionization spectroscopy. Laser pulses with wavelengths from 260 to 320 nm were used for molecule excitation. For several excited states we found a biexponential decay. The results were compared to former studies in the femtosecond region and to experiments in the liquid phase.

MO 28.4 Fri 12:00 F 102

**Luminescence Quenching of non-Noble Metal-Photosensitizers in a Photocatalytic Model System** — ●ALEKSEJ FRIEDRICH<sup>1</sup>, PATRICK SCHWARZBACH<sup>1</sup>, STEFANIE TSCHIERLEI<sup>1</sup>, ESTEBAN MEJIA<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, Germany — <sup>2</sup>Leibniz-Institut für Katalyse Rostock, Germany

The efficient hydrogen generation by photocatalytic water splitting is a challenge in the field of renewable energy. In the last years several homogeneous systems have been investigated. Disadvantage of most of them is the application of rare metals like ruthenium or iridium. In this contribution, we study an active, photocatalytic model system consisting of a non-noble metal-photosensitizer (PS), an iron-catalyst, and triethylamine (TEA) as a sacrificial reductant [1]. Here, we focus on the energy and electron transfer reaction steps of the PS after optical excitation and compare the behavior of different copper sensitizers.

Luminescence quenching by TEA and the catalyst is studied by steady-state and time-resolved luminescence measurements. The measured luminescence lifetimes of the PSs vary between 70 ns and 50  $\mu$ s. We see a correlation between the turn over number and the lifetime indicating that good PSs exhibit a minimum lifetime of about 3  $\mu$ s. Quenching by the iron-catalyst is found to be efficient reducing the PS lifetime to the range of 80 ns to 500 ns. Contrary, quenching of the sacrificial reductant TEA is inefficient indicating that the oxidative pathway dominates.

[1] S.-P. Luo *et al.*, *Angew. Chem.* **2012**, *accepted*.

MO 28.5 Fri 12:15 F 102

**An organic photochromic triad acting as optical gate** — ●MARTTI PÄRS<sup>1</sup>, MICHAEL GRADMANN<sup>1</sup>, REGINA SCHMIDT<sup>1</sup>, KATJA GRÄF<sup>2</sup>, PETER BAUER<sup>2</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We demonstrate optical modulation experiments with an organic photoswitchable triad. The triad consists of a photochromic unit (dithienylcyclopentene, DCP) that can be interconverted between two bistable (open and closed) forms by light, and two highly efficient fluorophores (perylenebisimide, PBI). [1] Fluorescence microscopy reveals that the DCP features a highly efficient photoreaction which can be probed via the fluorescence change of the PBI unit. Conversion the DCP unit by visible and UV radiation, results in a reversible strong modulation of the fluorescence intensity of the PBI. Hence the DCP unit acts as a gate (triggered by a few photons), that controls the flow of many fluorescence photons from the PBI unit. We will present a model that describes the experimental observations, such as the fluorescence modulation contrast ratio, the reaction rates and the reaction quantum yields as a function of radiation intensities.

[1] M. Pärs, C.C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat, J. Köhler, *Angew. Chem. Int. Ed.* **2011**, *50*, 11405-11408