

MO 1: Photochemistry

Time: Monday 14:30–16:30

Location: N 6

Invited Talk

MO 1.1 Mon 14:30 N 6

Dynamic Solvent Effects Treated with a Quantum/Classical TDSCF Approach — ●MARTIN PESCHEL, JULIUS ZAULECK, FLORIAN ROTT, and REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-University, Munich, Germany

The simulation of quantum dynamics on potential energy surfaces is a powerful tool to examine chemical reactions. The course of these reactions might be substantially altered in solution. A coupled quantum dynamics/molecular dynamics approach (cQD/MD) is presented to introduce solvent effects into the simulations. It treats the solvent by classical molecular dynamics and couples this classical system to the quantum solvated molecule in a time-dependent self-consistent fashion. We discuss the solvent-induced changes in wavepacket coherence and dispersion of the quantum system. As an example, the photodissociation of ICN in liquid argon is considered in detail with an outlook on more complex systems.

MO 1.2 Mon 15:00 N 6

Photocleavage of coumarin dimers studied by uv ultrafast transient absorption spectroscopy — ●MAN JIANG¹, NICHOLAS PAUL¹, NIKOLAI BIENIEK², TIAGO BUCKUP¹, NORBERT HAMPP², and MARCUS MOTZKUS¹ — ¹Institute of Physical Chemistry, Im Neuenheimer Feld 229, University of Heidelberg, D-69120 Heidelberg — ²Department of Chemistry, Hans-Meerwein-Str. 4, University of Marburg, D-35032 Marburg

The photoinduced cleavage of a coumarin dimer into its two monomers is a promising mechanism for laser controlled medical applications. In order to understand the underlying dynamics of the cleavage reaction in details and develop strategies for an increase of the reaction efficiency, UV transient absorption spectroscopy was applied to three unsubstituted coumarin dimer isomers, the anti-head-to-head dimer, the syn-head-to-head dimer and the syn-head-to-tail dimer. The experiments performed under 280 nm pumping and broadband (300–650 nm) probing reveal that the cleavage reaction of coumarin dimers occurs via non-radiative short-lived singlet states. Two branched kinetic models were developed, which describe the formation of monomers and relaxation dynamics of dimers, from which we were able to explore the precise time-scale of coumarin monomers formation and the quantum yields of the dimer splitting. The anti-hh dimer shows the highest cleavage efficiency with a value of about 20 %. The differences of cleavage efficiency for three dimer isomers are interpreted in terms of different steric hindrances of substitution groups attached to the cyclobutane ring and charge delocalization on the intermediate state.

MO 1.3 Mon 15:15 N 6

Spectroscopic Investigation of a Cr-Complex on the fs-Time Scale — ●ALEKSEJ FRIEDRICH¹, SVEN OTTO², CHRISTOPH FÖRSTER², CHRISTOPH KREITNER², KATJA HEINZE², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, Germany — ²Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University of Mainz, Germany

Ultrafast spectroscopy is performed on the metal complex [Cr(ddpd)₂][BF₄]₃ (ddpd: N,N'-dimethyl-N,N'-dipyridine-2-ylpyridine-2,6-diamine). The compound is an interesting candidate for NIR OLEDs, fiber-optic telecommunication applications, night-vision readable displays, oxygen sensing, and in vivo imaging. The molecule is water soluble and exhibits strong and extremely long living photo luminescence around 775 nm [1]. While the ground state is a quartet state the emitting state is a doublet. The intermolecular processes after excitation are not fully understood. We carried out fs-transient-absorption and streak-camera measurements to investigate these processes. We found a fast population of the lowest emitting doublet state within 6 ps and a luminescence lifetime of 840 μs. No indication for stimulated emission was observed. This indicates that the intersystem crossing between the quartet and doublet manifold occurs within our time resolution of 100 fs and the 6 ps dynamics is due to relaxation within the doublet manifold.

[1] S. Otto et al., *Angew. Chem. Int. Ed.*, 54, 11572 (2015).

MO 1.4 Mon 15:30 N 6

The Photodissociation of the ortho- & para-Xylyl Radical, C₈H₉, Investigated by Velocity Map Imaging — ●KAI PACH-

NER and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Deutschland

Xylyl radicals can be found as intermediates in combustion processes. Their parent molecules, the xylenes, are used as additives in fuels to increase antiknock properties. The thermal decomposition of the xylyl radicals has been explored recently by Hemberger et al. in a synchrotron experiment [1]. Based on these studies, we investigated the photodissociation of the ortho- & para-xylyl radical using velocity map imaging. Xylyl radicals were formed via flash pyrolysis in a pulsed molecular beam using 2-/4-methylphenethyl nitrite as a precursor. Irradiation of the xylyl radical with UV light around 310 nm leads to the formation of the corresponding xylenes for both radicals, or benzocyclobutene for the ortho-xylyl radical respectively, by hydrogen atom loss. Generated hydrogen fragments are then ionized in a [1+1']-REMPI process via the 1s-2p transition and detected on a velocity map imaging detector. The translational energy distribution of the hydrogen fragments as well as their angular distribution and rate constants for the hydrogen atom loss indicate a statistical dissociation in the ground state or an indirect dissociation in the excited state.

[1] Hemberger et al., *J. Phys. Chem. A*, 2014, 118, 3593 - 3604.

MO 1.5 Mon 15:45 N 6

Dynamical studies on the photodissociation of diphenylmethyl bromide — ●FRANZISKA SCHÜPPEL, MATTHIAS K. ROOS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carboradicals and -cations are key intermediates for many chemical reactions. They may be generated by UV-laser excitation of carbohalide compounds such as diphenylmethyl bromide. Here, a local $\pi - \pi^*$ excitation occurs, followed by the C-Br bond cleavage leading to radical or ion pairs within a femtosecond timescale.

We use both, quantum dynamical and semiclassical on-the-fly dynamical methods to simulate the reaction. In both approaches we employ an ONIOM two-layer method with CASSCF as high level method. In the quantum dynamics we take the solvent environment into account using the Dynamic Continuum ansatz [1] developed in our group.

We verify for both simulations the decisive role of two consecutive conical intersections for the product splitting, like we recently showed [2] for chlorine as leaving group. Nonetheless, we report remarkable differences compared to the chlorine case and we especially discuss the role of the pyramidalization of the central carbon atom. We evaluate product ratio and delay times for both approaches and compare them with experimental results.

[1] S. Thallmair et al., *J. Phys. Chem. Lett.* **5** (2014), 3480–3485.

[2] S. Thallmair et al., *Struct. Dyn.* **3** (2016), 043205.

MO 1.6 Mon 16:00 N 6

Time-Resolved Step-Scan FTIR Investigations on Dinuclear Cu(I)-NHETPHOS-complexes — ●MANUEL ZIMMER¹, FABIAN DIETRICH¹, FLORIAN BÄPPLER¹, MANUELA WALLECH², DANIEL VOLZ³, STEFAN BRÄSE², ROLF DILLER¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, 67663 Kaiserslautern — ²Karlsruhe Institute of Technology, 76131 Karlsruhe — ³CYNORA GmbH, 76646 Bruchsal

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. Here we present the first TR step-scan FTIR measurements on dinuclear Cu(I)-NHETPHOS-complexes in solid state (KBr matrix and thin film). These complexes, which are developed for emitter material in OLEDs, are a very promising substitute for currently used Ir-complexes. Time-resolved IR spectra of electronically excited states have been obtained by step-scan FTIR measurements and in addition, wavelength and temperature dependent measurements as well as femtosecond transient absorption and reflectivity measurements have been performed to gain detailed information about the excited state processes and deactivation mechanisms. The temperature dependent measurements down to 20 K provided valuable information to confirm the postulated thermally activated delayed fluorescence (TADF) mechanism at room temperature (RT). The interpretation of measured spectra succeeded in combina-

tion with quantum chemical calculations (DFT and TD-DFT).

MO 1.7 Mon 16:15 N 6

New Insights into the Photodissociation of Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide — ●STEFFEN STRAUB, CARA TABEA LOHRMANN, JÖRG LINDNER, and PETER VÖHRINGER — Rheinische Friedrich-Wilhelms-Universität Bonn

Benzoylphosphine oxides are widely known as industrial photoinitiators in photochemical curing processes. In the recent past, their photochemistry and photophysics have been studied, for example by Picosecond Pump Probe Spectroscopy. These efforts suggested a C-P-bond breakage taking place on a time scale of hundred picoseconds and being facilitated by an S_1 - T_1 intersystem crossing.

Here, we unravel the primary processes of the photoinitiator

Bisphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (BTPO) in great detail, using femtosecond UV-pump IR-probe spectroscopy. All experiments were carried out using pump pulses of 100 fs duration, centered at a wavelength of $\lambda = 380$ nm.

We found that the formation of the benzoyl radical occurs in a delayed fashion and cannot be fit to first order growth kinetics, as was assumed previously. A careful analysis of the spectro-temporal evolution in the mid-infrared region yields accurate time constants of 20 ps and 120 ps for the initial S_1 - T_1 intersystem crossing and the ensuing α -cleavage with radical pair formation, respectively. Moreover, we were able to identify the C=C-stretching mode of the benzoyl radical in liquid solution, which has been accomplished previously only in the gaseous phase or through complex cryogenic matrix isolation techniques.