

MO 6: Femtosecond Spectroscopy 1

Time: Tuesday 10:30–12:15

Location: BEBEL HS213

Invited Talk

MO 6.1 Tue 10:30 BEBEL HS213

Time-resolved absorption studies of photoinitiator molecules in solution — ●ANDREAS-NEIL UNTERREINER¹, HANNA A. ERNST¹, THOMAS J. A. WOLF¹, DOMINIK VOLL², ELENA FRICK², and CHRISTOPHER BARNER-KOWOLLIK² — ¹Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany — ²Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

Understanding early-time dynamics of photo-induced polymerization can be important for successful high-tech applications. This also implies the development of search criteria for molecules showing e.g. efficient triplet radical initiation processes. In this context, it is important to accurately determine the efficiency for both radical formation after photo-excitation and polymerization of formed radicals. In this contribution, focus is given on the elucidation of the first steps particularly with regard to radical formation by reporting new results of type-I (radical formation after α -cleavage) photoinitiators. It will be shown that ultrafast intersystem crossing (ISC) on a picosecond timescale is one crucial process towards adequately describing polymerization efficiency although the relevant timescales (ISC and radical polymerization) differ by many orders of magnitude. In combination with time-dependent density functional theory (TD-DFT) calculations and pulsed laser polymerization with subsequent electrospray ionization mass spectrometry (PLP-ESI-MS) for post-mortem analysis of the polymerization products, one can obtain a more detailed picture of the relevant pathways of some recently published photoinitiator molecules.

MO 6.2 Tue 11:00 BEBEL HS213

A comparative study on chirped-pulse upconversion and direct multichannel MCT detection — ●JOHANNES KNORR, PHILIPP RUDOLF, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present a comparative study on two spectroscopic techniques employed to detect ultrafast absorption changes in the mid-infrared spectral range, namely direct multichannel detection via HgCdTe (MCT) photodiode arrays and the newly established technique of chirped-pulse upconversion (CPU) [1,2]. Whereas both methods are meanwhile individually used in a routine manner, we directly juxtapose their applicability in femtosecond pump-probe experiments based on 1 kHz shot-to-shot data acquisition [3]. Additionally, different phase-matching conditions in the CPU scheme for a given mid-infrared spectrum are examined, thereby simultaneously detecting signals which are separated by more than 200 cm^{-1} .

[1] K. J. Kubarych et al., *Opt. Lett.* 2005, 30, 1228-1230[2] K. F. Lee et al., *Opt. Express* 2009, 17, 18738-18744[3] J. Knorr et al., *Opt. Express* 2013, 21, 30693-30706

MO 6.3 Tue 11:15 BEBEL HS213

Ultrafast dynamics of asymmetric trihalides – Which bond breaks? — ●SEBASTIAN SCHOTT, ANJA HASENKOPF, FLORIAN KANAL, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Trihalides are very successful model systems for ultrafast time-resolved spectroscopy. These molecules allow detailed theoretical treatments, due to their small size, while providing pronounced dynamic observables. Especially triiodide I_3^- has been studied extensively with ultrafast spectroscopy in solution, e.g. by Ruhman [1] and Vöhringer [2]. The special feature of the asymmetric trihalides IBrCl^- , I_2Br^- , I_2Cl^- and Br_2Cl^- , compared to the well-known symmetric triiodide, is the existence of two distinguishable chemical bonds. Therefore, the existence of two different diatomic fragments after photodissociation (e.g. $\text{IBrCl} + h\nu \rightarrow \text{IBr} + \text{Cl}$ or $\text{ICl} + \text{Br}$) is in principle possible. We use transient absorption spectroscopy with supercontinuum white-light probe pulses to investigate possible reaction paths with the aim to elucidate which parameters may have an impact on the outcome of the photoinduced dynamics. Especially, pronounced wave packet oscillations, observed during the first 3 ps, are promising for the identification of the newly formed products.

[1] U. Banin, A. Waldman, S. Ruhman, *J. Chem. Phys.* 1992, 96, 2416[2] T. Kühne, P. Vöhringer, *J. Chem. Phys.* 1996, 105, 10788

MO 6.4 Tue 11:30 BEBEL HS213

Ultrafast UV-induced photoisomerization of intramolecularly H-bonded β -diketones — ●PRAMOD KUMAR VERMA, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The chelated enol form (H-bonded) of β -diketones usually exhibits strong absorption bands in the UV region originating from the dipole-allowed $\pi\pi^*$ transitions ($S_2 \leftarrow S_0$). The photochemistry following the $\pi\pi^*$ transitions can lead to multiple pathways (isomerization, tautomerization, fragmentation) and is highly sensitive to the environment of the molecule. In the gas phase, the dominant pathway is fragmentation with the loss of an OH radical. In contrast, when β -diketones in solution are subjected to UV irradiation, isomerization is the main channel while no fluorescence is detected. The absence of fluorescence suggests the presence of very efficient non-radiative processes from the lowest excited singlet state. The aim of the present study is to understand the relaxation processes of simple β -diketones after excitation to the S_2 state in solution phase. Thus, the excited-state dynamics of β -diketones have been investigated using femtosecond transient absorption with broadband UV white-light detection. Our results confirm that the formation of the non-chelated conformers on electronic excitation of the chelated form occurs on an ultrafast time scale through a dark state. We propose a model that qualitatively explains the microscopic photochemical pathways based on all the experimental and theoretical data currently available.

MO 6.5 Tue 11:45 BEBEL HS213

IR-Vis Two-Photon Fluorescence Spectroscopy on Oxacine1 — ●FRANK FRIEDRISZIK and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

We present an infrared-excitation Raman-probe setup in the femtosecond-regime and demonstrate its potential by two photon absorption and time-resolved fluorescence measurements on a dye. A regenerative Ti:sapphire amplifier system generating ultrashort laser pulses at 800 nm serves as primary light source. One part of its output is spectrally narrowed by laser line filters and will be used as Raman-probe. Another part of the pump light is converted to infrared radiation by an optical parametric amplifier and a non-collinear difference frequency mixing stage. The time resolution of the setup is better than 700 fs as it was measured by sum frequency mixing of the IR and Raman-probe pulses.

In a first test experiment the fluorescence of the dye Oxacine1 is excited by two-photon absorption of the IR and probe light. The observed fluorescence dynamics with respect to the time delay between the IR and the probe pulse is discussed in the framework of vibrational redistribution processes.

MO 6.6 Tue 12:00 BEBEL HS213

S_2 to S_1 Relaxation Dynamics in Perylene Bisimide Aggregates and Monomers — ●STEFFEN WOLTER¹, FRANZISKA FENNEL¹, MARCO SCHRÖTER¹, FRANK WÜRTNER², OLIVER KÜHN¹, and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock — ²Institut für Organische Chemie und Center for Nanosystem Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

In this contribution, the relaxation dynamics from the electronic S_2 state to the S_1 state of monomeric and aggregated perylene bisimide dyes are investigated by femtosecond pump-probe spectroscopy. The considered perylene bisimides are known for forming long J-aggregate chains at ambient conditions in which exciton migration and annihilation can occur. During the annihilation process, a transient population and fast relaxation of highly excited states is assumed. Therefore, the relaxation pathways of these highly excited states have to be investigated to understand the annihilation process itself.

To this end, ultrafast transient absorption measurements with excitation of the S_2 and the S_1 state are performed and compared to each other. After optical population of the S_2 state a delayed onset of the stimulated emission from the S_1 state is observed for the aggregate as well as for the monomer. This effect is induced by the S_2 to S_1 decay, which happens on an ultrafast time scale of less than 500 fs. The impact of aggregation on the S_2 to S_1 relaxation is discussed and

the results are compared to theoretical predictions [1].

[1] Schröter M., Kühn O. *J. Phys. Chem. A* **117**, 7580 (2013)