

MO 12: Photochemistry I

Time: Wednesday 10:30–12:30

Location: F 142

Invited Talk

MO 12.1 We 10:30 F 142

Ultrafast photochemistry of fulgides: Tuning the ring-opening reaction by vibrational excess energy — ●SIMONE DRAXLER, THOMAS BRUST, MARKUS BRAUN, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, LMU München

Fulgides are molecular switches that can undergo reversible structural changes upon illumination. The ring-closure is a barrierless reaction on the sub-picosecond time-scale. The ring-opening reaction proceeds via two barriers in the excited state. Its dynamics and efficiency can be altered significantly by vibrational excess energy. It was found [1] that reaction times of the ring-opening decrease and quantum yields increase with rising temperature. The reaction also becomes more efficient by introducing optical excess energy [2]. These properties are used to guide the reaction path. Therefore we investigate the ring-opening reaction in a non-equilibrium state, where the closed form is generated in a preceding ring-closure reaction. We found, that the ring-opening reaction is accelerated when the delay time to the preceding reaction is decreased. In addition a more than threefold improvement of the reaction efficiency can be achieved. We conclude, that some picoseconds after ring-closure the intramolecular vibrational redistribution is not yet completed and that different groups of vibrational modes exist, with strongly different populations. Especially the modes promoting the ring-opening reaction are highly excited and promote the reaction before vibrational relaxation is completed on a time scale of about 5 ps.

[1] S. Draxler et al., Phys. Chem. Chem. Phys. (2009) 11, 5019

[2] T. Brust et al., J. Photochem. Photobiol. A (2009) 207, 209

MO 12.2 We 11:00 F 142

Ultrafast bidirectional switching of a spiropyran system — ●MARTIN KULLMANN, JOHANNES BUBACK, FLORIAN LANGHOJER, and TOBIAS BRIKNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Spiropyran, an example for a molecular switch, exists as a ring-open isomer (merocyanine) and as a ring-closed isomer (spiropyran) but only the ring-opening has been studied yet in detail. In this contribution we find ultrafast bidirectional switching for a dinitro substituted spiropyran (1',3'-dihydro-1',3',3'-trimethyl-6,8-dinitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] = 6,8-dinitro-BIPS).

We have carried out transient absorption experiments on 6,8-dinitro-BIPS in chloroform showing ultrafast photoreactions both for the ring-opening and the ring-closure direction. The ring-closure was observed with visible pump pulses (excitation to the S1 state of merocyanine) and probe pulses in the visible and the mid-infrared spectral range, indicating merocyanine bleach and spiropyran formation on a ps timescale. The ring opening reaction is also based on an ultrafast mechanism, as revealed by experiments using UV (266 nm) excitation and probing in the visible spectral range.

With the accumulated knowledge, two-color pump-repump-probe measurements were performed to induce ring-opening and the following reclosure showing a complete photocycle of the 6,8-dinitro-BIPS. This illustrates the possible application of spiropyrans as optical switches.

MO 12.3 We 11:15 F 142

The Triplet Spectrum of Xanthone Obtained via Time Resolved Infrared Spectroscopy — ●HALINA SARAH STRZALKA, ANDREAS DEEG, TOBIAS ERICH SCHRADER, PETER GILCH, and WOLFGANG ZINTH — Lehrstuhl für Biomolekulare Optik, LMU München

In order to extend the high sensitivity and the parallel detection of femtosecond infrared spectroscopy towards timescales of nano- and microseconds, we implemented electronic synchronization of the femtosecond system with a sub-nanosecond Nd-laser used for excitation. As a first application we present time-resolved IR-spectroscopy of Xanthone. Here the infrared spectrum of the triplet state was recorded in the nanosecond range. DFT-calculations are used for band assignment. The investigations clearly show the high potential of the presented experimental systems for the study of transient infrared spectroscopy from femtoseconds to microseconds.

MO 12.4 We 11:30 F 142

Increasing the efficiency of the ring-opening reaction of photochromic indolyfulgides by optical pre-excitation —

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Fulgides are interesting candidates for applications as molecular memories or switches [1]. Their reaction dynamics are on the same timescale as cooling dynamics, so the reaction starts from a thermal non-equilibrium [2]. Therefore multipulse experiments can give more insight into the properties of these molecules [3].

In this contribution the quantum efficiency of the ring-opening reaction upon pre-excitation is investigated in a multipulse experiment [4] for three indolyfulgides. The quantum efficiency grows by factor of up to 3.4, when the pre-excitation pulse immediately precedes the excitation process. The change in quantum efficiency after pre-excitation is discussed as a function of reaction time, steady-state quantum efficiency and energetic barriers in the excited electronic state. The observed differences can be explained by the molecular properties of the investigated indolyfulgides [5].

[1] S. Malkmus et al., Adv. Funct. Mater. (2007) 17, 3657

[2] T. Brust et al., J. Photochem. Photobiol. A (2009) 207, 209

[3] S. Draxler et al., Phys. Chem. Chem. Phys. (2009) 11, 5019

[4] S. Draxler et al., Opt. Commun. (2009), doi:10.1016/j.optcom.2009.10.105

[5] T. Brust et al., Chem. Phys. Lett. (2009) 477, 298

MO 12.5 We 11:45 F 142

Absolute photodetachment cross-section for anions of astro-physical relevance — ●THORSTEN BEST¹, RICO OTTO¹, SEBASTIAN TRIPPEL¹, MARTIN STEI¹, PETR HLAVENKA¹, ERIK VIGREN², WOLF GEPPERT², and ROLAND WESTER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Molecular Physics Division, Stockholm University, S106 91 Stockholm, Sweden

The discovery of several molecular anions in interstellar clouds has been a surprise for interstellar astrophysics. Among the molecules of interest, hydrated carbon chains (C_nH⁻) play an important role [1,2]. By trapping and buffer gas cooling of these molecular anions in a 22pole radio-frequency trap, we are able to simulate interstellar conditions in our laboratory [3]. In particular, using a recently developed tomographic method [4], we have determined absolute values for the photodetachment cross-section of these molecules. We thereby hope to help answering the question to which extent photodetachment determines the lifetime of molecular anions in photon-dominated regions and more general cosmic environments.

[1] M.C. McCarthy et al., Ap. J., **652**, 141 [2] J. Cernicharo et al., Astronomy and Astrophysics, **467**, 37 (2007) [3] R. Wester, J. Phys. B **42**, 154001 (2009) [4] P. Hlavenka et al., J. Chem. Phys. **130**, 061105 (2009)

MO 12.6 We 12:00 F 142

Time-resolved nuclear motion of core-excited iodine molecules — ●MARIA KRIKUNOVA¹, THEOPHILOS MALTEZPOULOS¹, PHILIPP WESSELS¹, MORITZ SCHLIE¹, ARMIN AZIMA¹, NIKOLAY KABACHNIK², MAREK WIELAND¹, and MARKUS DRESCHER¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Institute of Nuclear Physics, Moscow State University, 119991 Moscow, Russia

The core-ionisation in molecules followed by a complex sequence of multi-electron relaxation processes is intimately associated with the cleavage of chemical bonds. Depending on the final molecular ionic state and the core-hole lifetime the dissociation is controlled by several competing processes i.a. Coulomb repulsion, indirect pre-dissociation or fast dissociation preceding electronic relaxation. Utilizing a XUV / optical laser pump-probe technique the complex interplay between dissociative channels was studied in molecular iodine in real time. The kinetic energy release of ionic fragments was measured following excitation with XUV pulses from the Free-Electron-LASer in Hamburg (FLASH). A methodological challenge is connected with the timing jitter of the order of a few hundred fs between XUV- and laser pulses. A tagging technique was developed and applied recently for delay measurement in a simultaneously operated experiment. Applying this technique to the current study the change in the dissociation mechanism manifested by the time-dependent loss in the kinetic energy of I³⁺ ion

fragments can be resolved.

MO 12.7 We 12:15 F 142

Beyond the van der Lugt/Oosterhoff Model: When the Conical Intersection Seam and the Excited State Minimum Energy Path Do Not Cross — •PATRICK KÖLLE¹, ARTUR NENOV¹, MICHAEL ROBB², and REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-Universität München, Germany — ²Imperial College London, UK

The photoinduced ring opening reaction of cyclohexadiene is a textbook example for electrocyclic reactions. It was one of the first systems used to elucidate the fundamental role of conical intersections (CoIns) in ultrafast photochemical processes. In this paper we report the complete "minimum energy path" (MEP) in the CoIn space reaching from

the closed to the open ring side. The seam was calculated using an analytic approach in which the intersection space in the vicinity of a CoIn is described to second order[1]. The topography of the seam was investigated, revealing minimum energy and transition state structures. In addition the energy profile of the seam was rationalized using valence bond theory. The geometrical changes along the seam have been related to the motions along the excited state MEP in a conceptual model highlighting the quasi parallel orientation of the seam and the IRC-MEP[2]. Our model shows, that even though the van der Lugt and Oosterhoff concept predicts the formation of an avoided crossing along the excited state IRC-MEP, it provides an incomplete description of the decay process to the ground state.

[1] F.Sicilia et al., *J. Chem. Theor. and Comp.* 4, 257 (2008). [2] A. Nenov, P. Kölle et al., *J. Org. Chem.*, DOI: 10.1021/jo902111r