MO 13: Photochemistry

Zeit: Montag 16:30–18:45 Raum: 6B

MO 13.1 Mo 16:30 6B

Beeinflussung der Ringöffnungsdynamik eines Indolylfulgids — •Florian Lederer[1], Simone Draxler[1], Thomas Brust[1], Stephan Malkmus[1], Jessica A. DiGirolamo[2], Watson J. Lees[2], Wolfgang Zinth[1] und Markus Braun[1] — [1]Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — [2]Department of Chemistry and Biochemistry, Florida International University

Unter den molekularen Schaltern fällt die Gruppe der Indolyl-Fulgide/Fulgimide durch ihre ausgeprägte Photochromie und die Stabilität ihrer Isomere auf. Die Absorptionsspektren der zyklisierten und zyklisierbaren Isomere, die durch photoinduzierten Ringschluss bzw. Ringöffnung ineinander überführt werden können, unterscheiden sich durch getrennte Banden im sichtbaren und ultravioletten Spektralbereich.

Durch Dauerstrich- und Femtosekunden-Pump-Probe-Spektroskopie wurden sowohl die Reaktionsausbeute als auch die Reaktionsdynamik der Ringöffnung untersucht. Sie lassen sich durch eine Vielzahl von Parametern beeinflussen: Während die Viskosität des Lösungsmittels keinen Effekt auf die Ausbeute hat, kann durch die Erhöhung des Dipolmoments die Ausbeute der Ringöffnungsreaktion deutlich reduziert werden. Die Auswirkungen einer Temperaturänderung weisen auf eine aktivierte Photoreaktion hin.

MO 13.2 Mo 16:45 6B

Photochemische Reaktionspfade nach Anregung in unterschiedliche elektronische Zustände: fluorierte Indolyl-Fulgide — •Simone Draxler[1], Stephan Malkmus[1], Thorben Cordes[1], Thomas Brust[1], Jessica A. DiGirolamo[2], Watson J. Lees[2], Wolfgang Zinth[1] und Markus Braun[1] — [1]LS für BioMolekulare Optik, LMU München — [2]Depmt. of Chem. and Biochem., FIU Miami, USA

Nach der Kasha-Regel beobachtet man Fluoreszenz im allgemeinen aus dem niedrigsten angeregten Zustand, unabhängig vom ursprünglich angeregten Zustand. Dies setzt eine ultraschnelle Relaxation vom S_n in den S_1 voraus. Auch für photochemische Prozesse wurde dieser Reaktionsweg aus dem S_1 in vielen Untersuchungen bestätigt, wenn auch Ausnahmen dazu auftreten (z.B. Azobenzol [1]). Als weitere Ausnahme von dieser Regel wird hier ein spezielles Fulgid vorgestellt.

Mittels transienter Absorptionsspektroskopie wurden die Reaktionspfade bei Anregung in den S_1 sowie S_2 des fluorierten Indolyl-Fulgids untersucht. Bei der Ringschlussreaktion wurde keine wesentliche Abweichung vom herkömmlichen Bild einer der Reaktion vorgeschalteten internen Konversion in den S_1 gefunden. Die UV-induzierte (S_2) Ringöffnungsreaktion hingegen weist einen anderen Reaktionspfad als die sichtbar induzierte (S_1) Reaktion auf. Dies spiegelt sich auch in der Vervierfachung der Quanteneffizienz wider (S_1: 7%; S_2: 28%).

[1] H. Satzger et al., J. Phys. Chem. A **108**, 6265, (2004)

MO 13.3 Mo 17:00 6B

Photodissociation of Uracil — •Michael Schneider[1], Christof Schon[1], Luis Rubio-Lago[2], Bastian Noller[1], Theofanis Kitsopoulos[2], and Ingo Fischer[1] — [1]Institut für Physikalische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FO.R.T.H.), P.O. Box 1527, 71110 Heraklion, Crete, Greece

We examined the photodissociation of uracil after UV excitation by H-atom photofragment Doppler spectroscopy and slice imaging. The kinetic energy distribution shows a behaviour typical for statistical dissociation. No anisotropy is observed in the angular distribution of the images. Thus the photodissociation is purely statistical and there is no evidence for the contribution of repulsive $\pi\sigma^*$-states as is the case in adenine.

MO 13.4 Mo 17:15 6B

Intersystem Crossing Driven by Vibronic Spin-Orbit Coupling: A Case Study on Psoralen — •Jörg Tatchen, Martin Kleinschmidt, and Christel Marian — Institute of Theoretical Chemistry, Heinrich-Heine University, Universitätsstraße 1, D-40225 Düsseldorf

Psoralens are used in combination with UVA radiation in the treatment of several skin diseases. In order to understand the mechanisms behind the therapeutical action and undesired side effects, insight into the photophysics of psoralens is highly desirable. By means of quantum chemical methods, we investigate the mechanisms of singlet-triplet ($S \rightsquigarrow T$) intersystem crossing (ISC) in photoexcited psoralen.

Our results [1,2,3] show that the dominant channel of $S \rightsquigarrow T$ ISC for psoralen is $S_1\,(\pi \rightarrow \pi^*) \rightsquigarrow T_1(\pi \rightarrow \pi^*)$ even though the corresponding spin-orbit matrix element (SOME) $\langle S_1|\mathcal{H}_{\mathrm{SO}}|T_1\rangle$ at the planar S_1 state equilibrium geometry is negligible. Efficient $S_1 \rightsquigarrow T_1$ ISC takes place due to vibronic spin-orbit coupling which is included by a Herzberg-Teller type expansion of the coupling SOMEs. In addition, a conical intersection between the S_1 and T_1 state potential energy surfaces near the S_1 minimum geometry brings about favorable Franck-Condon factors for the $S_1 \rightsquigarrow T_1$ ISC.

References

[1] Tatchen, J.; Kleinschmidt, M.; Marian, C. M.: *J. Photochem. Photobiol. A*, 167, 201-212 (2004).

[2] Tatchen, J.; Marian, C. M.: *Chem. Phys. Phys. Chem.* , 8, 2133-2144 (2006).

MO 13.5 Mo 17:30 6B

Femtosecond Experiments on the Photochemistry of Organic N-Oxides — •Nadja Regner, Thorben Cordes, Tobias Schrader, and Peter Gilch — Lehrstuhl für BioMolekulare Optik, Department für Physik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

The photo-rearrangement of organic N-oxides is a useful synthetic tool to synthesize chemicals which are difficult to access by other methods. Therefore, a large variety of N-oxides have been tested for photoreactivity and in most cases these tests turned out positive [1]. In contrast to this wealth of empirical information our knowledge of the mechanisms of these reactions is poor. In particular, no spectroscopic experiments with a suitable time resolution have yet been published. We here report on a combined femtosecond UV/Vis and IR study on the rearrangement of an N-oxide (2-benzoyl-3-phenylquinoxaline-1,4-dioxide). This rearrangement results in large structural changes which involve several elementary steps occurring with time constants of a few picoseconds to beyond nanoseconds. Based on the femtosesecond IR signatures reactions associated with these times constants are suggested.

[1] A. Albini and M. Alpegiani Chem. Rev. 84 (1984) 43

MO 13.6 Mo 17:45 6B

Precursor molecules for organic synthesis: A model system for initial dissociation dynamics of diphenylmethylchloride — •Benjamin Fingerhut, Dorothee Geppert, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Our investigations focus on the laser induced dissociation dynamics of diphenylmethylchloride and its derivatives which occur on a femtosecond timescale. An understanding of the initial fragmentation pathways gives insight into the formation of carbo-cations in solution, key intermediates in organic synthesis.

For an accurate description of the excitation and the dissociation process at least three electronic states have to be taken into account by quantum chemical methods. A π^*-σ^*-charge-transfer connects the Franck-Condon region with a repulsive potential, followed by non-radiative relaxation into the competing reaction channels. The branching ratio between the bound and the repulsive fragmentation pathway is facilitated by at least one conical intersection and defined by appropriate non-adiabatic-coupling-matrix-elements.

We present a model system, based on our ab-initio data which is suitable to describe the multidimensional dissociation process in a reduced reactive coordinate subspace. Herein we are able to follow the dissociation dynamics via multiple conical intersections after femtosecond laser excitation.

MO 13.7 Mo 18:00 6B

Singlet Oxygen generation from Aromatic Endoperoxides — •Alexandra Lauer[1], Inés Corral[2], Leticia González[2], Henk Fidder[1], and Karsten Heyne[1] — [1]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin — [2]Freie Universität Berlin, Fachbereich Chemie, Takustrasse 3, 14195 Berlin

Aromatic endoperoxides are claimed to exhibit homolytic cleavage

from the lowest electronic excited state, while higher electronic states lead to singlet oxygen generation. However, this lowest electronic state has never been located, and recent semi-empirical calculations even denied the existence of this state. In our contribution state-of-the-art ab initio calculations are combined with steady-state absorption and fluorescence experiments, and polarization-resolved femtosecond UV-pump/IR-probe spectroscopy, to resolve this issue. We observe the disputed S1 state of APO that leads to homolytic O-O cleavage, at 33700 cm^{-1}, in excellent agreement with our ab initio calculations. Femtosecond polarization resolved UV/IR experiments confirm that the absorption transition dipole at 36800 cm^{-1} is indeed polarized parallel to the oxygen bridge, thereby verifying the theoretical assignment of this band to the S0→S4 transition. A mechanism for $^1O_2$ generation from APO is presented, based on the ab initio calculations, that indicates how excitation to the S2 ($\pi_{CC} \rightarrow \pi^*_{CC}$) or S4 ($\pi^*_{OO} \rightarrow \pi^*_{CC}$) state leads to non-adiabatic population of the Sx ($\pi^*_{OO} \rightarrow \sigma^*_{CO}$) state, which plays a decisive role in the $^1O_2$ generation.

MO 13.8 Mo 18:15 6B

H-transfer reaction in 2-aminopyridine dimer studied by fs pump-probe spectroscopy — •Elena Samoylova[1], Yuliya Rulyk[1], Dirk Nolting[1], Hans-Hermann Ritze[1], Wolfgang Radloff[1], Ingolf Volker Hertel[2], and Thomas Schultz[1] — [1]Max Born Institute, Max-Born Str.2A, Berlin, Germany — [2]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, Berlin, Germany

H-bonded intermolecular interactions play a very important role in the biophysics of DNA, determining its structure and dynamics. For the electronically excited states, theory predicted a very fast deactivation mechanism involving H-transfer along the N-H coordinate in DNA base pairs. This mechanism can quench highly reactive excited states and provide the necessary photostability against photoinduced damage for the genetic information. We studied the H-transfer mechanism in 2-aminopyridine dimer, a model system for H-bound Watson-Crick DNA base pairs. Using time-resolved ion and electron spectroscopy we identified a fast deactivation pathway of the excited state (life time is 69 ps at 274 nm). Higher vibrational excitation at 250 nm lead to a slight increase of the life time to 75 ps, and we observed an additional ultrafast (less then 50 fs) deactivation channel. The ultrafast contribution can be explained by the initial wave packet motion along N-H stretching mode carrying part of the population over the H-transfer barrier. The remaining population is caught in the local minimum and decays on the ps time scale.

MO 13.9 Mo 18:30 6B

Photochemistry inside superfluid helium nano droplets — •Alkwin Slenczka, Alexander Vdovin, and Bernhard Dick — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Superfluid helium nano droplets serve as the most gentle cryogenic matrix for creating isolated and cold molecules [1]. High resolution electronic spectroscopy is sensitive for the investigation of the very weak perturbation of the helium droplet on the embedded molecule. Fluorescence excitation spectra, dispersed emission spectra and pump-probe-spectra show details of the salvation of molecules in helium droplets which were attributed to relaxation processes of the first solvation layer around the dopant [2]. Photochemistry such as ESIPT, tautomerization by proton transfer and charge transfer are highly sensitve on intermolecular perturbations. We have studied such processes in superfluid helium droplets. The comparison with the respective gas phase experiments and quantum chemical calculations reveals further details on the photochemistry as well as on the perturbation by the superfluid helium droplet.

[1] F. Stienkemeier, K. K. Lehmann, J. Phys. B: Mol. Opt. Phys. 39(2006) R127-R166.

[2] R. Lehnig, and A. Slenczka, J. Chem. Phys. 123, (2005).; Chem. Phys. Chem. 5, (2004) 1013-1019; J. Chem. Phys. 120, (2004), 5064-5066; J. Chem. Phys. 118, (2003) 8256-8260.