MO 24: Femtosecond Spectroscopy III

Zeit: Dienstag 14:30–16:15 Raum: 6C

MO 24.1 Di 14:30 6C

Transient states and kinetics in the photochromic reaction of spironaphtoxazine — •Uwe Megerle, Uli Schmidhammer, Stefan Lochbrunner, and Eberhard Riedle — Lehrstuhl für BioMolekulare Optik, LMU München

We investigated the primary photoproducts of the photochromic molecular switch spironaphtoxazine (SNO) dissolved in DMSO. The experiments were performed by UV-excitation (345 nm) transient absorption spectroscopy with a time resolution of about 100 fs. The broad spectrum of the probe-continuum (350-750 nm) allowed observing the spectral characteristics of all intermediate states. By measuring kinetic curves at numerous wavelengths we determined precise rate constants for the different steps of the photoreaction. This was supported by examining the time dependence of the absorption shift as well as the temporal increase of the transition dipole moment. The relatively high viscosity and slow relaxation times of DMSO decelerate the isomerisation step in the ring opening reaction compared to other solvents and therefore facilitate the assignment of the observed decay times. Thus the sequence of processes on both potential energy surfaces becomes much clearer than in cyclohexane and acetonitrile solutions that were investigated for comparison and can be directly compared to recent calculations [1].

[1] F. Maurel, J. Aubard, P. Millie, J.P. Dognon, M. Rajzmann, R. Guglielmetti and A. Samat, J. Phys. Chem. **110** (2006), 4759.

MO 24.2 Di 14:45 6C

Dual Fluorescence in the Photochemical ZE Isomerization of Hemistilbene/Hemithioindigo-Molecules (HTI) — •Thorben Cordes[1], Nadja Regner[1], Björn Heinz[1], Tobias Schrader[1], Christian Hoppmann[2], Karola Rück-Braun[2], and Wolfgang Zinth[1] — [1]LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [2]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

Photoinduced isomerizations are intensively studied reactions due to their importance in chemistry and biology. Systems containing conjugated double bonds (e.g. stilbene, hexatriene) are used as model systems for Rhodopsin or Carotinoids to investigate ultrafast photoreactions and to understand them in detail. A combination of a hemistilbene part with the half of a thioindigo-dye brings up a new class of photochromic compounds. It could be shown, that these HTI-molecules are suitable to act as ultrafast light trigger in chromopeptides[1]. In this context these photoinduced reactions have been studied with pump-probe spectroscopy in the visible. To obtain a clear insight in the photochemical pathway the transient absorption data is complemented with time-resolved fluorescence and IR measurements. By combination of these techniques the photochemical pathway of the ZE isomerization is revealed.

[1] T. Cordes et. al. Chem. Phys. Lett. 428 (2006) 167-173

MO 24.3 Di 15:00 6C

Einfluss von Substitution und Umgebungsvariablen auf die photoinduzierte Isomerisierung von Hemistilben/Hemitioindigo-Molekülen — •Markus Lipp[1], Thorben Cordes[1], Torsten Schadendorf[2], Karola Rück-Braun[2] und Wolfgang Zinth[1] — [1]LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [2]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin

Hemistilbene/Hemithioindigo-Moleküle zeigen interessante photochrome Eigenschaften. Durch Licht im sichtbaren/UV Spektralbereich kann ultraschnell (ps - ns) zwischen zwei isomeren Zuständen (Z/E) geschaltet werden. Reaktionsgeschwindigkeit sowie Reaktions- und Fluoreszenzquantenausbeute hängen stark von der Substitution des Hemistilbenteils ab. Allgemein läuft die ZE Reaktion langsamer als die EZ Richtung ab, weiterhin ist ein Einfluss von Umgebungsvariablen wie Lösungsmittel und Temperatur auf alle genannten Parameter beobachtbar. Die qualitative Beschreibung dieses Verhalten durch Barrieren auf der Potentialfläche des angeregten Zustandes werden durch temperaturabhängige Messungen untermauert. Die Beobachtungen werden in ein Modell für die photochemische Umwandlung der beiden isomeren Zustände eingebracht und stützen das entwickelte Modell.

MO 24.4 Di 15:15 6C

Zeitaufgelöste akkumulative Spektroskopie einer Photoreaktion — •Florian Langhojer[1], Frank Dimler[1], Gregor Jung[2] und Tobias Brixner[1] — [1]Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Bei bisher üblichen Techniken für femtosekundenaufgelöste Experimente werden gleiche Ausgangsbedingungen für jeden neuen Laserimpuls hergestellt, indem jede Wechselwirkung mit einem neuen Probenvolumen stattfindet. Wir präsentieren das Konzept und Anwendungen der akkumulativen Detektion von Photoprodukten. Ein solcher Aufbau erlaubt die Wechselwirkung vieler identischer Laserpulse bzw. Pulsfolgen mit einem kleinen Flüssigkeitsvolumen. Nach einer gewissen Zeit werden die akkumulierten, stabilen Photoprodukte detektiert. So können auch Photoreaktionen mit geringen Produktausbeuten beobachtet werden, deren Messsignal für konventionelle Spektroskopie zu gering wäre. Das Probenvolumen wird dann automatisiert ausgetauscht und das Experiment kann mit anderen Laserimpulsen bzw. unterschiedlichen Pump-Probe-Verzögerungszeiten wiederholt werden.

Der Akkumulationsprozess wird quantitativ betrachtet. Die Methode wurde auf die Photokonversion des Grün Fluoreszierenden Proteins (GFP) angewandt. Nach der Anregung mit einem Laserimpuls um 400 nm kann durch Absorption eines 800 nm Photons eine Photoreaktion mit stabilem Produkt erfolgen. Wir haben die Zeitabhängigkeit dieser Reaktion untersucht.

MO 24.5 Di 15:30 6C

Early excited state dynamics of β carotene near a conical intersection detected by Pump – Degenerate Four Wave Mixing (Pump – DFWM) — •Jürgen Hauer, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

The early femtosecond dynamics on the electronically excited states of carotenoids play a crucial role in photosynthetic light harvesting. For understanding the evolution of β carotene near the conical intersection between its first two excited states, it is necessary to study the interplay between electronic and nuclear dynamics. We use a time domain method (Pump – DFWM [1]) yielding both time resolved excited state molecular Raman modes and information on the development of the involved electronic states.

Degenerate Four Wave Mixing (DFWM) has already proven to be a versatile tool for studying and controlling vibrational dynamics on β carotene's ground state. [2]. Introducing an additional pump pulse preceding the DFWM – sequence, allows studying excited state vibrations. The technique delivers a time resolution only limited by the duration of the employed ultrashort pulses (sub 20 fs) and a spectral resolution better than $20\ \mathrm{cm}^{-1}$.

Since the DFWM - signal shows a decay time constant depending on the electronic state under investigation, the experiment also yields results on population dynamics near the conical intersection.

[1] Hornung et al., Chemical Physics Letters 402 (2005) 283–288

[2] Hauer et. al., Chemical Physics Letters 421 (2006) 523–528

MO 24.6 Di 15:45 6C

Model studies of laser induced femtosecond dynamics in the excited states of β-carotene — •Judith Voll, Benjamin Fingerhut, and Regina de Vivie-Riedle — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Based on data from coherent control experiments performed on β-carotene in the group of M. Motzkus we present a model for the theoretical description of the laser induced quantum dynamics. After excitation by a femtosecond pulse from the electronic ground state into the S_2 state the system relaxes via conical intersections and is then detected in the S_1 state by transient raman spectroscopy.

To specify the kinetic hamiltonian, the raman modes involved, their force constants and the relative position of the interacting potentials were extracted from ab initio calculations. With this model the mechanism of internal conversion is studied, incorporating vibrational cooling in the S_1 state. The influence of the topology of the electronic states as well as the position of the S_2 - S_1 conical intersection on the dynamics are examined. These results are used to investigate the controllability of the transfer rate by modulated laser pulses.

MO 24.7 Di 16:00 6C

Femtosecond Optical and Vibrational Spectroscopy: Evidence for Vibronic Coupling — •Alexander Weigel, Alexander Dobryakov, and Luis Perez Lustres — Humboldt Universität zu Berlin, Fachbereich Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Flavin derivatives serve as antenna pigments in blue light photoreceptors. To gain insight into primary activation steps the dynamics of riboflavin in solution was examined by ultrafast transient absorption spectroscopy. After vibrationless S_1 excitation at 490 nm the signal rises on the timescale of solvation dynamics and decays in agreement with the fluorescence lifetime. The transient spectra shape exhibits a significant solvent dependence. In aprotic DMSO environment stimulated emission and ground state bleach are of similar intensity, whereas in protic aqueous solution the stimulated emission band is diminished already at time zero indicating strong coupling to nearby dark states.

Excitation with 5000 cm^{-1} excess of energy evidences vibronic coupling in DMSO as well. Most strikingly, the transient spectrum evolves non-exponentially and shows strong oscillation with a frequency of 95 cm^{-1}. The quantum dynamics could be modelled by assuming a degenerate two state system with complete population of the S_1 state at time zero while damping occurs through intramolecular vibrational redistribution of S_1.

The results were further supported by femtosecond stimulated Raman experiments.