

MO 43 Ultrafast Processes

Zeit: Dienstag 16:30–18:45

Raum: HU 2091

MO 43.1 Di 16:30 HU 2091

Electron transfer faster than inertial solvation: a vibrational mode to promote photoinduced ET in triphenylmethane lactones — ●JERZY KARPIUK¹, STEFAN LOCHBRUNNER², and EBERHARD RIEDLE² — ¹Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland — ²LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

Investigations of the intramolecular electron transfer (ET) in condensed phase donor-acceptor (D-A) systems on a time scale shorter than diffusional solvation can provide substantial insight into the initial stages of the ET dynamics. Such ultrafast ET processes are promoted by high-frequency intramolecular vibrational modes and inertial solvation, and better understanding of the interplay between these two driving forces requires the exploration of D A systems capable of undergoing ET on a sub-100 fs time scale. A 50-fs photoinduced intramolecular ET in triaryl-methane lactones (LTAMs) [1] allowed us to enter the time scale shorter than that of inertial solvation dynamics and to explore the ET coupling to vibrational modes. Using fs pump-probe spectroscopy to study the photophysics of LTAMs as a function of solvent polarity and proticity, we demonstrate a dominant role of the C-O bond in the lactonic ring in ultrafast charge separation in LTAMs.

[1] T. Bizjak, J. Karpiuk, S. Lochbrunner and E. Riedle, *J. Phys. Chem. A* 108, 10763 (2004).

MO 43.2 Di 16:45 HU 2091

Ultrafast emission quenching due to charge transfer from the perylene bisimide chromophore to its substituent — ●PATRIZIA KROK¹, IDA Z. KOZMA¹, STEFAN LOCHBRUNNER¹, HEINZ LANGHALS², and EBERHARD RIEDLE¹ — ¹LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — ²Department Chemie, Organische Chemie, Ludwig-Maximilians-Universität München

Perylene dyes can exhibit a fluorescence quantum yield of 100% due to vanishing internal conversion and intersystem crossing. At the same time they are of great interest for designing ultrafast intramolecular energy and charge transfer systems [1,2]. Their functionality is controlled by the specific substituents and the environment. An amino group can act as an acceptor resulting in strong fluorescence suppression [3]. We measure with a femtosecond visible continuum the transient emission and absorption after excitation by 30 fs pulses at 490 nm to gain insight into the intramolecular transfer dynamics. We compare the emission decay of the amino substituted perylene chromophore on the picosecond time scale to the ns decay in the case of a nonquenching substituent. It can be explained by electron transfer from the HOMO of the amino group to the chromophore. The back transfer proceeds in about 10 ps and makes the whole reaction cycle highly efficient.

[1] H. Langhals, *Heterocycles* 40, 477 (1995). [2] H. Langhals and S. Saulich, *Chem. Eur. J.* 8, 5630 (2002). [3] G. J. Mohr et al., *Anal. Chem.* 72, 1084 (2000).

MO 43.3 Di 17:00 HU 2091

Radikationenspektren von Squarin- Chromophoren nach photoinduziertem Elektronentransfer — ●MARTEN PIANTEK, M. MUCKE, CH. SPITZ und R. MENZEL — Universität Potsdam, Institut für Physik, Lehrstuhl Photonik, Am Neuen Palais 10, 14469 Potsdam

Squarinfarbstoffe gelten, trotz scharfer und intensiver Absorptionsbanden im roten Bereich, als äußerst stabile Chromophore. Sie sind deshalb vielversprechende Kandidaten z.B. für Anwendungen in der Photovoltaik oder zur optischen Datenspeicherung.

Die spektralen Eigenschaften der Squarinfarbstoffe machen sie außerdem zu sehr interessanten Kandidaten für polaritätsgetriebene Elektronentransferketten mit der Fähigkeit zur photoinduzierten Ladungstrennung, wie sie z.B. auf der Basis eines im UV absorbierenden Farbstoffes schon realisiert wurden[1]. Die dazu notwendige Verknüpfung des Farbstoffes mit Akzeptor- bzw. Donormolekülen sowie der intermolekulare Ladungstransfer dieser Verbindungen ist bisher jedoch nur wenig untersucht worden.

Ein Nachweis der Ladungstrennung ist durch den direkten Vergleich des Absorptionsspektrums des angeregten Farbstoffmoleküls mit den transienten Spektren der durch den photoinduzierten Ladungstransfer entstandenen Radikationen möglich.

Wir präsentieren den spektroskopischen Nachweis der Ladungstren-

nung an mehreren Squarin-Akzeptor/Donor-Kombinationen.

[1] C. Tedeschi et al., *J. Am. Chem. Soc.*, Vol. 126/10 (2004), pp 3218-3227

MO 43.4 Di 17:15 HU 2091

Photoinduzierter Elektronentransfer in Schichtsystemen mit Polaritätsgradient — ●MELANIE MUCKE¹, M. PIANTEK¹, CH. SPITZ¹, D. VON SEGGERN¹, R. MENZEL¹ und H. MÖHWALD² — ¹Universität Potsdam, Institut für Physik, Am Neuen Palais 10, 14469 Potsdam — ²Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Am Mühlberg 2, 14476 Golm

Ein und derselbe Chromophor kann sowohl als Elektronendonator als auch als -akzeptor wirken, sofern die Polarität seiner Umgebung stark variiert. Die Funktion als Akzeptor, z.B., kann durch ein Absenken der Energiezustände mittels Solvatation erreicht werden.

Wir haben durch Nutzung der Layer-by-Layer-Technik Polyelektrolytkapseln aufbauen können, die - über die gesamte Schichtdicke von wenigen Nanometern betrachtet - einen hohen Polaritätsgradienten aufweisen. Mit dieser Präparationsmethode kann eine geeignete Überlappung der Wellenfunktionen der Farbstoffmoleküle erreicht werden. Unter Verwendung von Pyren als Modellchromophor ist es uns zunächst gelungen, einen polaritätsgetriebenen Elektronentransfer laserspektroskopisch nachzuweisen. Um das Schichtsystem für mögliche Anwendungen vorzubereiten, ist der Wechsel vom Pyren (Absorption im UV) zum Squarin (Absorption im VIS) geplant und bereits begonnen.

MO 43.5 Di 17:30 HU 2091

Photochemie in superflüssigen Heliumtropfen: Ultraschneller intramolekularer Protonentransfer und die Wirkung polarer Lösungsmittel am Beispiel des 3-Hydroxyflavons — ●ALKWIN SLENCZKA und R. LEHNIG — Institut für Physikalische und Theoretische Chemie, Uni Regensburg,

Schnelle intramolekulare Prozesse in Molekülen werden in Pump-Probe Experimenten mit fs-Laserpulsen in Echtzeit beobachtet. Beispiel hierfür ist der ESIPT Prozess im 3-Hydroxyflavon. In der Frequenzdomäne entsprechen Lebensdauern von fs einigen cm^{-1} , die spektral leicht aufzulösen sind. Die Emissionsspektren des 3-Hydroxyflavons in superflüssigen Heliumtropfen zeigen einzelne Schwingungsübergänge. Aus einer Linienformanalyse können wir Lebensdauern und damit die Zeitkonstante des Protonenrücktransfers (BPT) ablesen. Darüber hinaus ermöglicht die superflüssige Matrix den Einfluß polarer Lösungsmittel auf den ESIPT im molekularen Maßstab zu untersuchen.

MO 43.6 Di 17:45 HU 2091

Energy transport and excited state dynamics of dyes in matrices — ●MARTIN SCHLOSSER and STEFAN LOCHBRUNNER — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

Supramolecular structures of interacting molecules are promising candidates for electronic nanodevices and functional materials. In such systems energy and charge transport are governed by the excited state dynamics of the participating compounds and the interaction between neighboring molecules. We investigate the interplay between excited state dynamics and transport properties by looking at the energy migration between Perylene Orange and Perylene Red dye molecules incorporated at high concentrations in thin layers of PMMA. The photoinduced dynamics is characterized by broadband pump-probe spectroscopy with 100 fs time resolution and compared to the dynamics at low concentrations in solution. The excited state absorption is disentangled from stimulated emission and bleaching contributions by its dependence on the polarization. To identify the mechanisms responsible for the observed dynamics the decay of the anisotropy and the dependence on the excitation energy density (fluence) is investigated.

MO 43.7 Di 18:00 HU 2091

Anharmonic couplings underlying ultrafast vibrational dynamics of acetic acid dimers — ●N. HUSE¹, B. D. BRUNER², M. L. COWAN², J. DREYER¹, E. T. J. NIBBERING¹, R. J. D. MILLER², and T. ELSAESSER¹ — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany — ²Departments of Physics and Chemistry, University of Toronto, 80 St. George St., Toronto, ON, M5S 3H6 Canada

Hydrogen bonded systems display strong anharmonic couplings between different vibrations resulting in complex vibrational spectra and dynamics. We analyze the line shape of the O-H stretching band of cyclic acetic acid dimers in solution, an important model system with two O-H...O bonds. Two-dimensional (2D) heterodyne detected photon echo spectroscopy based on a new diffractive optic (DO) technique [1] and on spectral interferometry are used to record the 2D infrared spectra. Signal Phase stability is better than $\lambda/150$. We find pronounced Fermi resonances between the O-H stretching $v=1$ level and combination/overtone levels of O-H bending, C-O and C=O stretching modes and multi-level quantum beats in the coupled low-frequency modes. Fermi resonance couplings of 40 to 150 cm^{-1} are of similar strength as those of the low-frequency hydrogen bond stretching and in-plane deformation modes [2].

1. Cowan, J. P. Ogilvie and R. J. D. Miller, Chem. Phys. Lett. **386**, 184, 2004.
2. Heyne, N. Huse, J. Dreyer, E. T. J. Nibbering, T. Elsaesser and S. Mukamel, J. Chem. Phys. **121**, 902, 2004.

MO 43.8 Di 18:15 HU 2091

Ultrafast Infrared Spectroscopy of the Ring Opening Reaction of CN-Dihydroazulene — ●TOBIAS SCHRADER, ULI SCHMIDHAMMER, WOLFGANG SCHREIER, FLORIAN KOLLER, ARNE SIEG, and EBERHARD RIEDLE — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

Ultrafast molecular switches offer a large potential in the field of optoelectronics. A promising candidate is the photochromic compound 1,1-dicyano-2-(4-cyanophenyl)-1,8a-dihydroazulene (CN-DHA). Upon excitation with UV light it undergoes a ring opening reaction to its vinylheptafulvene (CN-VHF) isomer. We report on the first UV pump, mid IR probe experiments of the ultrafast reaction dynamics and compare it to existing UV pump, visible probe data [1]. The IR experiments were performed in acetonitrile- d_3 at probe wavelengths between 1400 cm^{-1} and 1570 cm^{-1} with a time resolution of 200 fs. We observe strong excited state absorption (ESA) that shows some variations at early times which are indicative of the previously concluded excited state ring opening [1]. The ESA decays with a time constant of 13 ps that corresponds to the return to the electronic ground state. Slower contributions to the signal are likely linked to the cis-trans isomerisation of VHF. The results are interpreted with the help of high level quantum chemical calculations.

[1] V. De Waele, M. Beutter, U. Schmidhammer, E. Riedle and J. Daub, Chem. Phys. Lett. 390 (2004) 328.

MO 43.9 Di 18:30 HU 2091

Photo-Rearrangement of *o*-Nitrobenzaldehyde Probed by Femtosecond Raman Spectroscopy — ●STEFAN LAIMGRUBER, WOLFGANG SCHREIER und PETER GILCH — Department für Physik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, D-80538 München, Germany

Aromatic nitro-compounds are known to photochemically abstract hydrogen atoms from adjacent hydrocarbon moieties. For *ortho*-substituted nitro-aromatics these abstractions proceed intra-molecularly and trigger secondary processes. Due to these processes aromatic nitro-compounds are used as, e.g., photo-labile protecting groups and as the leaving group in caged compounds. Here, we study a prototypical nitro-compound, *o*-nitrobenzaldehyde, which is photochemically transformed into *o*-nitrosobenzoic acid by a femtosecond stimulated Raman technique. This technique uses a white light continuum as the Stokes pulse in the stimulated Raman process. To our knowledge this is the first application of this technique for the investigation of photochemical processes. The transient Raman spectra obtained are compared with calculated spectra of possible intermediates and the mechanism of the reaction is discussed.