MO 31 Ultrafast Photochemistry

Zeit: Montag 10:15–12:30 Raum: HU 2091

Hauptvortrag

MO 31.1 Mo 10:15 HU 2091

Nuclear wavepacket motion in ultrafast chemical reactions in solution — •Tahei Tahara, Satoshi Takeuchi, and Kunihiko Ishii — Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako 351-0198, Japan

Thanks to the improvement of ultrashort-pulse lasers, we are now able to directly observe nuclear wavepacket motion of excited-state polyatomic molecules in solution. We chose cis-stilbene, diphenylcyclopropenone and 10-hydroxybenzoquinoline that undergo prototypical ultrafast photochemical reactions (isomerization, dissociation and proton transfer, respectively), and carried out ultraviolet-visible two-color pump-probe experiments with time-resolution of 30 - 70 fs. In each system, we successfully observed the nuclear wavepacket motion of the excited state. We discuss the assignment of the motions observed and their relevance to the reaction coordinate [1,2].

1. K. Ishii, S. Takeuchi and T. Tahara, Chem. Phys. Lett., 398, 400 (2004).
2. S. Takeuchi and T. Tahara, J. Chem. Phys., 120, 4768 (2004).

MO 31.2 Mo 10:45 HU 2091

Ionization and Fragmentation of C60 Fullerenes Exposed to Intense Laser Radiation with a Pulse Duration down to 9 fs — •I. Shchatsinin, G. Stibenz, G. Steinmeyer, T. Laarmann, C.P. Schulz, and I.V. Hertel — Max-Born-Institut, Max-Born-Str. 2a, D-12489 Berlin, Germany

Fullerenes are interesting model systems for studying the dynamics of ionisation and energy coupling in large but finite systems with many degrees of freedom. We have investigated the photo excitation and ionisation of C_{60} fullerenes with intense fs laser radiation. Ultrashort pulses with a duration of about 9 fs and an intensity up to 5×10^{14} W/cm^2 have been focused on the molecular beam. From a detailed analysis of the resulting time-of-flight mass spectra as a function of important laser parameters, i.e. pulse duration and intensity, a deep insight into the ionisation and fragmentation processes can be obtained. The derived saturation intensities for C_{60}^{+}, C_{60}^{2+} and C_{60}^{3+} will be discussed in the light of different theoretical models.

MO 31.3 Mo 11:00 HU 2091

Excited-State Decay of Ethyl and Propargyl Radical, investigated by Femtosecond Time-Resolved Photoionization — •Matthias Zierhut[1], Bastian Noller[1], Ingo Fischer[1], and Thomas Schultz[2] — [1]Institute of Physical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg — [2]Max-Born-Institute, Max-Born-Straße 2a, D-10247 Berlin

The excited state decay of the hydrocarbon radicals ethyl, C_2H_5, and propargyl, C_3H_3, was investigated by femtosecond time-resolved photoionisation. Radicals were generated by flash pyrolysis of n-propyl nitrite and propargyl bromide, respectively. It is shown that the $2^2A'$ (3s) Rydberg state of ethyl around 250 nm decays with a time constant of 20 fs. No residual signal was observed at longer delay times. For the 3 $^2B_1$ state of propargyl a somewhat slower decay with a time constant between 40 and 60 fs was determined.

MO 31.4 Mo 11:15 HU 2091

Analyse von Wellenpaketsbewegungen in Oxazin 1 im Frequenz- und Zeitraum — •Markus Braun, Regina Dürr, Constanze Sobotta, Stephan Malkmus, Horst Pulvermacher und Wolfgang Zinth — Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München

Der Laserfarbstoff Oxazin 1 zeigt ausgeprägte Schwingungs-Wellenpakete nach optischer Anregung mit ultrakurzen Lichtimpulsen (15 fs). Diese Wellenpakete lassen sich über Pump-Probe Spektroskopie als oszillatorische Komponente auf dem transienten Absorptionssignal nachweisen. Um die Beeinflussung benachbarter Moden bei der Auswertung der Fourier-transformierten Spektren zu berücksichtigen, wird ein entsprechender Auswerte-Algorithmus vorgestellt, der die Phase und Interferenz benachbarter Moden beachtet.

Über Experimente mit gechirpten Anregungsimpulsen wird eine Zuordnung der Wellenpakete zu Grundzustand und angeregtem Zustand vorgenommen.

MO 31.5 Mo 11:30 HU 2091

Solvent Dependent Photoacidity State of Pyranine as Monitored with Transient Mid-Infrared Spectroscopy — •Omar F. Mohammed[1], Jens Dreyer[1], Ben-Zion Magnes[2], Ehud Pines[2], and Erik T. J. Nibbering[1] — [1]Max Born Institut, Max Born Strasse 2A, D-12489 Berlin, Germany — [2]Ben Gurion Univeristy of the Negev, Beer-Sheva 84125, Israel

Photoacids are well known molecular systems used to optically trigger proton transfer reaction dynamics. Understanding the nature of photoacidity, i.e. the property of enhanced acidity in electronic excited states, is thus of fundamental importance. We investigate with femtosecond mid-infrared spectroscopy the vibrational mode characteristics of the electronic states involved in pyranine (HPTS), and its methoxy derivative (MPTS). We compare the observed vibrational band patterns of MPTS and of HPTS after electronic excitation in the solvents deuterated dimethylsulfoxide and H2O/D2O, from which we conclude that for MPTS and HPTS photoacid the first excited singlet state reached within our time resolution (150 fs) appears to have charge transfer (CT) properties in water. In contrast, in aprotic dimethylsulfoxide the photoacid appears to be in a less-polar electronic excited state. We compare our results with existing models for photoacidity. For the fingerprint vibrations we do not observe dynamics on a time scale of a few picoseconds, and with our results obtained on the O-H stretching vibration we argue that the dynamical behaviour observed in previous UV/vis pump-probe studies is likely to be related to solvation dynamics.

MO 31.6 Mo 11:45 HU 2091

Femtosecond dynamics of an aqueous fluoride CTTS system — •Hristo Iglev and Alfred Laubereau — Physik-Department E11, Technische Universität München, James-Franck-Straße, 85748 Garching

We report on the ultrafast electron photodetachment of concentrated aqueous electrolyte solutions at room temperature. The relaxation dynamics after two-photon excitation at 310 nm of the fluoride anion is studied by polarization-resolved pump-probe absorption spectroscopy in the VIS and NIR with 100 fs temporal resolution. Evidence is found for internal conversion within the CTTS manifold on a time scale of 380 fs proceeding to an intermediate level assigned to the lowest charge transfer state in a non-equilibrated solvation layer. The subsequent rearrangement of the water molecules around the new charge distribution acompanies the separation of the excess electron from the parent atom. Different to previous studies on other halides, an evidence is obtained that the quantum yield of the process is reduced by several ten percent by internal conversion to the fluoride ground level. Our results are consistent with the physical picture that a solvated electron:halogen atom pair is formed. The electron detachment to the final solvated electron competes with direct geminate recombination, so that approximately 23

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Photon-echo and transient grating measurements with tunable 8 fs pulses from a NOPA — •Peter Baum[1], Jaroslaw Sperling[2], Franz Milota[2], Harald F. Kauffmann[2], and Eberhard Riedle[1] — [1]LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — [2]Institut für Physikalische Chemie, Universität Wien

The dynamics of solvation crucially determines many chemical and physical processes in the condensed phase. Time-resolved photon-echo and transient grating experiments on molecular solutes provide concise information about the electronic phase decay and the spreading of population gratings due to solute-solvent interactions. Such third-order nonlinear time domain probes of solvation yield access to the frequency fluctuation correlation function and thus allow to extract static and dynamics components from linear absorption spectra.

To match the pulse spectrum to the sample absorption and to resolve the fastest time scales, extremely short and widely tunable visble pulses are needed. We present successful photon echo and transient grating experiments with 8 to 20 fs pulses from a 1 kHz NOPA. A crucial point in photon-echo experiments is the elimination of satellite pulses. We use ZAP-SPIDER [1] to fully characterize and optimize the pulse shape and obtain Fourier-limited pulses.

Results on several spectrally and chemically distinct two-level model dyes are discussed. The dynamics in polar solvents reflect the rigidity and the degree of conformational freedom. Larger molecules seem to become more independent of the bath, in particular if the solvent is less polar. The data is further compared to that obtained from a soluble conjugated polymer, where the nonlinear response reflects a distribution of conformational subunits.

[1] P. Baum, S. Lochbrunner, and E. Riedle, Opt. Lett. 29, 210 (2004)

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Attosecond quantum dynamics of bond breaking studied by neutron-proton scattering — •C. Aris C.-Dreismann[1] and Tyno Abdul-Redah[2] — [1]Inst. f. Chemie, Stranski Lab., TU Berlin, D-10623 Berlin — [2]ISIS Facility, R.A.L., Oxfordshire, OX11 0QX, U.K.

Compton scattering of neutrons from protons takes place in the attosecond time range. Due to the large energy and momentum transfers applied in these experiments, the chemical H-X bonds (X: O, C, N, etc.) are broken. Several experiments on liquid and solid samples containing protons show a striking shortfall in the intensity of epithermal neutrons scattered by the protons [1,2]. E.g., neutrons colliding with water for just attoseconds will see a ratio of H to O of roughly 1.5 to 1, instead of 2 to 1 [1,2]; accordingly, the measured ratio of H to C in benzene is roughly 4 to 6, instead of 6 to 6. Recently this effect has been confirmed using electron-proton Compton scattering (ECS) from a solid polymer [1b,2]. Recall that electrons and neutrons interact with protons via fundamentally different forces – electromagnetic and strong. Theoretical considerations support the presence of attosecond quantum entanglement in the dynamics of the protons and the surrounding electrons. Current NCS experiments on liquid hydrogen (H_2, D_2, and HD; T = 20 K) demonstrate that spin-entanglement between two protons play no role in this effect. Our results indicate hitherto unknown features of sub-femtosecond dynamics of chemical bonds.

[1] (a) C. A. Chatzidimitriou-Dreismann et al., *Phys. Rev. Lett.* **79**, 2839 (1997); and (b) *Phys. Rev. Lett.* **91**, 057403 (2003). [2] Cf.: *Physics Today*, p. 9, Sept. 2003; *Physik in unserer Zeit* **35**(4), 174 (2004).