MO 23 Femtosecond Spectroscopy

Zeit: Samstag 14:00–16:00 Raum: HU 2091

MO 23.1 Sa 14:00 HU 2091

Untersuchung der Triplettbildung in Farbstoff/ Halbleitersystemen — •Martin O. Lenz und Josef Wachtveitl — Universität Frankfurt, Institut für Physikalische und Theoretische Chemie, Marie-Curie-Str. 11, 60439 Frankfurt/ Main

Photosensibilisierte Halbleiter spielen eine zentrale Rolle bei neuartigen Solarzellen wie z.B. der Grätzel-Zelle. Um den Elektronen-Transfer bei dieser Art von Solarzellen besser verstehen zu können und diese weiter zu optimieren, werden verschiedene Farbstoffe mit unterschiedlichen elektronischen Kopplungsstärken untersucht und im Hinblick auf die Dynamik der Elektronen-Injektion charakterisiert, u.a. auch Merocyanine. Für diese Moleküle ist bekannt, dass es nach Photoanregung zur Bildung eines langlebigen Triplett-Zustandes kommen kann.

Mittels zeitaufgelöster breitbandiger UV-VIS-Femtosekunden-Absorptionsspektroskopie haben wir sowohl die Dynamik purer Merocyanine nach Photanregung als auch die Dynamik des Elektronen-Transfers verschiedener Merocyanin-Halbleiter-Systeme untersucht. Dabei wurde neben der Elektronen-Injektion und der Entstehung des Kations beobachtet, dass die Effizienz und die Rate der Bildung des Triplett-Zustandes durch Kopplung an Halbleiter-Kolloide beeinflusst werden kann. Für gekoppelte reaktive Systeme (Merocyanin/TiO_2) kommt es zu keiner Besetzung dieses Zustandes, im Falle von gekoppelten nicht-reaktiven Systemen (Merocyanin/ZrO_2) ist die Besetzung des Tripletts im Vergleich zu reinen Farbstoffsystemen verlangsamt. Diese Beobachtungen sollen im Hinblick auf mögliche Konsequenzen für eine weitere Entwicklung von Farbstoff/Halbleitersystemen diskutiert werden.

MO 23.2 Sa 14:15 HU 2091

Femtosecond pump-repump-probe spectroscopy of the solvated electron in methanol: The role of H-bonds — •Andy Thaller, Robert Laenen, and Alfred Laubereau — Technische Universitaet Muenchen, Physik-Department E11, James-Franck-Strasse, D-85748 Garching

We present a detailed investigation of the solvated electron in methanol. The electrons are generated via two photon absorption of the third harmonic (4.5 eV, 100 fs) of a regenerative amplified Ti:Sapphire laser. Part of the original pulse at 820 nm is used to selectively re-excite the electrons at a certain time after generation (preparation time). The induced ΔOD of the sample due to generation or re-excitation is obtained polarization-resolved using probe pulses ranging from 450 nm to 2.4 μm.

In a global analysis a kinetic model is fitted to our data. This yields temporal and spectral information used to interpret the nature of the involved transient species. With this approach we reach a detailed microscopic model that emphasizes the important role H-bonds in the solvation shell play in electron solvation dynamics.

MO 23.3 Sa 14:30 HU 2091

Photoionisation dynamics of longchained alcohols and alkanes — •Martin K. Fischer, Andy Thaller, and Alfred Laubereau — Technische Universität München, Physik-Department E11, James-Franck-Strasse, D-85748 Garching

The photoionization process of the longchained molecules dodecane and decanol is compared to study the effect of hydrogen bonding in electron trapping process. The relaxation dynamics are investigated after two photon excitation at 9.2 eV (pump 270 nm) in a large spectral range from 450 nm to 5.2 μm.

The transient absorption spectra measured in decanol show two separate absorption bands: The well known absorption band of an electron in a solvation shell of O-H-groups and a notable absorption band in the near IR at around 0.6 eV not reported previously. To identify this feature as a new kind of trap, investigations in a comparable alkane are conducted. In fact, in dodecane an absorption with the same dynamics and very similar spectral features can be observed. As a result the absorption can be clearly assigned to a solvated electron localized in a shell of C-H-groups.

A comparison of the results on decanol with dodekane and methanol is presented. Clear evidence is provided for the existence of two different electron traps in decanol formed on the one hand by O-H-groups of the alcohol as in methanol and, on the other hand by C-H-groups of the alkylic part as in dodecane.

MO 23.4 Sa 14:45 HU 2091

A compact laser flash photolysis technique compatible with ultrafast pump-probe setups — •Stefan Roth[1], Uli Schmidhammer[1], Alexander Tishkov[2], Eberhard Riedle[1], and Herbert Mayr[2] — [1]LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — [2]Department Chemie, Organische Chemie, Ludwig-Maxilimians-Universität München

Photoinduced chemical reaction cycles can display time scales from few femtoseconds to milliseconds. We can readily monitor the femtosecond and picosecond regime with state of the art light pulses. Laser Flash Photolysis classically provides an effective method up to the ns timescale. The recent development of pulsed diode lasers and high power light emitting diodes (LEDs) open the route to a miniaturized laser flash photolysis system that is fully compatible with the femtosecond setup.

Instead of a high power lamp laser diodes or LEDs at various wavelengths in the visible and NIR are used as monitoring beam. These small sized semiconductor devices are positioned in an ultrafast pump-probe setup substituting the femtosecond white light or single wavelength probe. The sample is excited in both setups with fully tunable femtosecond pulses.

To demonstrate the versatile options of the system, we investigate the photoinduced chemistry of benzhydryl cations with the nitrite ion. The photodissociation takes some 100 fs while the combination is detected with 500 ps (for diode lasers) to few nanosecond resolution. In this way the full reaction cycle can be monitored with identical excitation conditions.

MO 23.5 Sa 15:00 HU 2091

Direct measurement of the group velocity mismatch and derivation of the refractive index dispersion for solvents in the ultraviolet — •Ida Z. Kozma, Patrizia Krok, and Eberhard Riedle — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

In order to predict the group velocity mismatch (GVM) between interacting pulses the wavelength dependence of the refractive index of the medium must be known. The GVM is crucial for the temporal resolution that can be obtained in an ultrafast experiment. Data are hardly available in the literature and their accurate measurement remains a challenge especially in the UV. A new method for use in the UV was developed for the direct measurement of the GVM. It is based on a standard pump probe arrangement with a sample of considerable thickness, making the precise determination of the GVM possible. From the measured wavelength dependence of the GVM the refractive index dispersion can be determined. To illustrate the accuracy of the method we measured the GVM of water because its refractive index dispersion is well documented in the literature. Our experimental results show a good agreement with reported data. The GVM was measured and dispersion formulae were derived in the 230 to 640 nm spectral range for eleven solvents, supplying data useful for the most common spectroscopic situations.

MO 23.6 Sa 15:15 HU 2091

Position Sensitive Detection of Fragmentation of Fullerenes after Femtosecond Laser Irradiation — •C.P. Schulz[1], M. Boyle[1], T. Laarmann[1], K. Hansen[2], E.E.B. Campbell[2], and I.V. Hertel[1] — [1]Max-Born-Institut, Max-Born-Str. 2a, D-12489 Berlin, Germany — [2]Dept. of Experimental Physics, Göteborg University and Chalmers University of Technology, SE-41296 Göteborg, Sweden

The fragmentation of fullerenes after photo excitation is interesting because of the competition between the strong binding energy (10 eV for a C_2 loss) and the relatively low ionization energy of 7.6 eV. The photofragmentation of fullerenes after nanosecond pulses has been found to proceed through statistical mechanisms and is characterized by sequential C_2 loss. Here, we study the fragmentation of fullerenes after femtosecond laser irradiation with a time-of-flight spectrometer and a position sensitive detector (RoentDek). Using statistical models, we are able to extract an initial internal temperature, as well as derive a general formula to predict the velocity distribution of the fragment ions as a function of the number of C_2 units lost. The good agreement of the measured velocity distributions indicates that the fragmentation of fullerenes after femtosecond laser irradiation is statistical in nature.

MO 23.7 Sa 15:30 HU 2091

A New Spectroscopic Method: Frequency-Selective Spectroscopy using Shaped Femtosecond Laser Pulses

— •Jakow Konradi, Ajay K. Singh, and Arnulf Materny — International University Bremen, School of Engineering and Science, Campus Ring 1, 28759 Bremen (e-mail: a.materny@iu-bremen.de)

The use of femtosecond lasers limits the spectral resolution considerably. Fourier-transform limited pulses of a length of 100 fs have a spectral width of approximately 150 cm^{-1}. Therefore, ultrashort pulses are exclusively used for spectroscopy in the time domain. Recently, we have demonstrated that a change of the chirp of femtosecond laser pulses has a striking influence on the spectrum arising from the light-matter interaction. In our contribution we will present our latest results on frequency-selective spectroscopy with spectrally broad ultrashort pulses. Using nonlinear four-wave mixing spectroscopic techniques like CARS (coherent anti-Stokes Raman scattering), we excite several vibrational modes in a molecule at the same time. These modes usually contribute to the spectrum resulting in a poorly resolved counterpart of the spectrum obtained using narrow band lasers. This changes completely if the phase shape of the laser pulse is varied. Applying a computer-controlled pulse shaper we are able to optimize the specific spectral lines. For the optimization we use as feedback the spectrum detected by a polychromator in a learning evolutionary algorithm that step by step improves the phase of one of the exciting femtosecond laser pulses. With this method we are able to filter out week lines and/or suppress lines that normally dominate the spectrum due to their large intensity.

MO 23.8 Sa 15:45 HU 2091

Manipulation photochemischer Prozesse durch intensive Femtosekunden-Laserpulse: Aufbau und erste Ergebnisse

— •Hans Georg Breunig und Karl-Michael Weitzel — Philipps-Universität Marburg, Institut für Physikalische Chemie

Wir stellen einen Aufbau zur Untersuchung ultrakurzer photochemischer Prozesse in Molekülionen vor. Der Aufbau besteht aus einem Femtosekunden-Lasersystem, das in zwei Strahlen Pulse unterschiedlicher Wellenlängen bereitstellt. Die Wellenlänge beider Strahlen lässt sich unabhängig voneinander im UV- bis zum IR-Bereich einstellen. Die Pulsdauern liegen im Bereich von 50 fs. Der Nachweis der Molekülionen erfolgt durch ein Flugzeitmassenspektrometer.

Erste experimentelle Ergebnisse zur Ionisation und Dissoziation von DCl durch intensive, nicht-resonante Laserpulse werden vorgestellt. Die Ergebnisse zeigen, dass die Ausbeute der Dissoziation, die zur Bildung von Cl^+ und D^+ führt, experimentell durch die Intensität der Pulse kontrolliert werden kann. Insbesondere ergibt sich mit zunehmender Intensität ein signifikanter Anstieg des Verhältnisses der D^+- und Cl^+-Ionenausbeute.