

MO 14 Ultrafast IR and Raman Probe and Control

Zeit: Montag 16:30–18:30

Raum: H12

MO 14.1 Mo 16:30 H12

Bulk ice at room temperature — ●MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Technische Universität München, Physik-Department E11, James-Franck-Straße, 85748 Garching

The complex three-dimensional hydrogen-bonded network of water molecules gives rise to unusual solid and liquid properties and strongly affects the melting behaviour of ice. Here we present the first experimental evidence for ultrafast superheating of bulk ice using an ultrafast temperature-jump technique with subpicosecond pulses for excitation and probing in the mid-infrared. The hydroxilic stretching vibrations (OH or OD) of isotopically mixed ice are used for energy deposition and for the fast and sensitive spectral probing of local temperature and H-bonding environment.

Measurements performed for a HDO:D₂O specimen with initial temperature of 270 K (close to the melting point of 274.8 K) provide evidence for substantial superheating of the ice lattice up to 301±2 K that persists over the monitored time interval of 250 ps without melting [1, 2]. For higher pumping levels evidence for ultrafast melting of bulk ice is obtained [1].

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller und A. Laubereau, *Nature* (2006), in press.

[2] H. Iglev, M. Schmeisser, A. Thaller und A. Laubereau, *subm.*

MO 14.2 Mo 16:45 H12

Ultrafast vibrational relaxation of the O–H bending mode in liquid H₂O — ●SATOSHI ASHIHARA, NILS HUSE, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

The mechanisms of vibrational energy transfer in liquid water are essential for the understanding of its physical and chemical properties. The dynamics of the O–H stretching vibrations in water have been intensively studied in recent years but much less is known about the dynamics of the O–H bending mode. This mode is highly relevant for the geometry of the intermolecular hydrogen bonds and for the relaxation of O–H stretching excitations. Here we study the population relaxation of the O–H bending mode in pure liquid H₂O in mid-infrared pump-probe experiments with 100 fs time resolution [1]. After resonant excitation of the $\nu = 0$ to 1 bending transition, a $\nu = 1$ lifetime of 170 fs is measured. This short lifetime is determined by the anharmonic couplings to the fluctuating liquid environment forming an extended hydrogen bond network. The population relaxation is followed by slower spectral diffusion and energy redistribution processes within 1-2 ps. Femtosecond excitation also induces ultrafast nonlinear changes of the broad librational absorption occurring at frequencies below the $\nu = 0$ to 1 bending transition.

[1] N. Huse, S. Ashihara, E.T.J. Nibbering, T. Elsaesser, *Chem. Phys. Lett.* **404** (2005) 389.

MO 14.3 Mo 17:00 H12

A picosecond thermometer and pressure gauge for H-bonded systems — ●MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Technische Universität München, Physik-Department E11, James-Franck-Straße, 85748 Garching

A spectroscopic method for sensitive temperature and pressure measurements in hydrogen-bonded materials on a picosecond timescale is demonstrated [1, 2]. The method is verified for an isotopic mixture of ice at 200 K and ambient pressure using the OH- and OD-stretching vibrations for ultrafast heating of the sample. The same vibration modes are known to be sensitive probes for H-bonding and represent suitable tools to distinguish local ice or water components with a time resolution of a few picoseconds.

We calibrate our picosecond thermometer taking into account the isochoric character of the ultrafast temperature rise in the sample, i.e. the simultaneous pressure increase because of the slow volume expansion (on the nanosecond timescale). We observe a temperature rise up to 20±2 K with a simultaneous pressure increase up to 26±4 MPa. Including the pressure-induced spectral changes in the data analysis we were able to extract the temporal evolution of the temperature and pressure changes in the sample. Our investigation shows that the use of a temperature scale is meaningful for ice as early as 25 ps after energy deposition [2].

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller und A. Laubereau, *Nature* (2006), in press.

[2] H. Iglev, M. Schmeisser, A. Thaller und A. Laubereau, *subm.*

MO 14.4 Mo 17:15 H12

Liquid phase interactions studied with time resolved hyper-Rayleigh scattering — ●TIAGO BUCKUP¹, MARCUS MOTZKUS¹, RICARDO CORREIA², JÚLIO SCHOFFEN², and SILVIO CUNHA² — ¹Physikalische Chemie, Phillips Universität Marburg, 35043 Marburg, Germany — ²Instituto de Física, UFRGS, Porto Alegre, Brazil

The liquid phase is well-known for its local order, where orientation and position correlations between molecules only prevail for several nanometers and where the corresponding interactions happen at different timescales. Due to the difficulties of studying the superposition of many-body interactions in the liquid phase, there is a high demand for new techniques which provide additional information about these complex interactions. This work introduces the concept of time resolved hyper-Rayleigh scattering with femtosecond resolution (TRHRS). TRHRS is based on the generation of elastic incoherent second harmonic radiation, a process related to the first molecular hyperpolarizability β . The obtained relaxation behavior for two model liquids (carbon tetrachloride and acetonitrile) agrees consistently with those obtained from spectral domain techniques. TRHRS opens the possibility not just to detect the long wings hardly seen in scattering spectra, but also to investigate the interactions in biological systems with high spatial and temporal resolution and to act as a new probe for orientation control experiments.

MO 14.5 Mo 17:30 H12

Small Bandwidth 400 nm Pulses for Femtosecond Stimulated Raman Spectroscopy — ●HILMAR SCHACHENMAYR, PETER GILCH, and STEFAN LAIMGRUBER — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Femtosecond Stimulated Raman Spectroscopy (FSRS) copes with several drawbacks of conventional time resolved Raman spectroscopy, as there are weak signal levels, strong fluorescence backgrounds, and an *instrumental* time bandwidth limit. Thereby, FSRS renders Raman techniques competitive with time resolved IR spectroscopy for monitoring fast molecular re-arrangements. In FSRS spectroscopy a femtosecond white light pulse and an intense laser pulse (Raman pump) cross in the sample. The white light spectrum gets modulated and the modulations can be transformed into the Raman spectrum of the sample. In most application a spectrally narrowed TiSa pulse at 800 nm serves as Raman pump. For many photo-active molecules absorbing in the UV a 400 nm Raman pump is advantageous due to substantial resonance enhancements. We here report on a set-up generating 400 nm pulses for FSRS. Two equally but oppositely in sign chirped 800 nm pulses are mixed in a non-linear crystal. This results in intense small bandwidth 400 nm pulses. With these pulses FSRS spectra with high signal levels and good spectral resolution can be obtained. Examples for their application will be given.

MO 14.6 Mo 17:45 H12

Ultrafast Dynamics of Molecules Exhibiting Double Minimum Potential — ●A.V. SCARIA, J. KONRADI, A.K. SINGH, and A. MATERNY — International University Bremen, Germany

Femtosecond time-resolved four-wave mixing (FWM) spectroscopy is a powerful technique for observing ultrafast molecular dynamics. Studies are carried out on molecules exhibiting double minimum potential structure in gas phase and in liquid phase using different FWM techniques. Of particular interest among them are *e.g.* molecules showing ring puckering vibrations (characteristic for cyclic molecules having -CH₂-, -O- or -S- groups). Ring puckering vibrations involve the bending motions of the group out of the plane of the ring. The potential energy curve for the vibration shows, therefore, two (nearly) identical minima corresponding to the ring being puckered upwards or downwards. Investigations are carried out on Trimethylene Sulfide (TMS) and Trimethylene Oxide (TMO) having barrier heights of 274 and 15 cm⁻¹, respectively. The time-resolved techniques applied are femtosecond degenerate four-wave mixing (DFWM) and coherent anti-Stokes Raman scattering (CARS). The observed dynamics of these vibrational modes obtained from gas and liquid phase will be presented and discussed in comparison with each other.

MO 14.7 Mo 18:00 H12

Kontrolle der Produktausbeuten der Photofragmentation von Deuteriumchlorid-Ionen (DCl^+): $\text{Cl} + \text{D}^+ \leftarrow \text{DCl}^+ \rightarrow \text{Cl}^+ + \text{D}$ —

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Wir untersuchen die Kontrolle der Photofragmentation von Deuteriumchlorid-Ionen (DCl^+) durch ultrakurze IR-Laserpulse in Experimenten und anhand der numerischen Lösung gekoppelter Schrödinger-Gleichungen. Die Berechnungen zeigen, dass das Ionen-Ausbeuteverhältnis von Cl^+ zu D^+ durch eine geeignete Wahl von Laserpulspartnern, insbesondere der Zentralwellenlänge, der Pulsdauer, der Intensität und dem Chirp manipuliert werden kann [1]. Die Untersuchung der zeitabhängigen Besetzungen zeigt phasensensitive, miteinander konkurrierende Anregungen innerhalb und zwischen elektronischen Zuständen.

Zusätzlich haben wir Ein- und Zweifarb-Experimente zur Dissoziation von DCl^+ -Ionen bei 800 nm [2] und im Bereich 3.5 μm bis 7.5 μm (2857 cm^{-1} bis 1333 cm^{-1}) durchgeführt. Insbesondere zeigen wir, dass das Verhältnis der Produktausbeute D^+/Cl^+ durch den Chirp der Laserpulse im mittleren IR-Bereich kontrolliert werden kann.

[1] M.V. Korolkov, K.-M. Weitzel, J. Chem. Phys. 123, 164308, (2005)

[2] H.G. Breunig, A. Lauer, K.-M. Weitzel, Proceedings of the Femtochemistry VII (2005)

MO 14.8 Mo 18:15 H12

Local control of molecular fragmentation: the role of orientation — •PHILIPP MARQUETAND¹, CHRISTOPH MEIER², and VOLKER ENGEL¹ — ¹Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg, Germany — ²Laboratoire Collisions, Agrégats et Réactivité, IRSAMC,*Université Paul Sabatier,*31062 Toulouse, France

Local control theory, where the instantaneous response of a system to an external field determines the control field, is employed for the purpose to induce molecular fragmentation processes via infrared (IR) excitation. In particular, the effects of the orientational motion are investigated and compared to the idealized case of a frozen rotation. It is shown that the rotational degree of freedom is crucial for the applicability of the employed local control algorithm. The addition of an additional static electric field which induces a molecular preorientation, offers an efficient way for the local control. In particular, with increasing static field strength, the fragmentation yield approaches unity so that the idealized rotation-less case is recovered. Numerical results are presented for the NaI molecule.