MO 21: Femtosecond Spectroscopy II

Zeit: Dienstag 10:30–12:30 Raum: 6D

Fachvortrag MO 21.1 Di 10:30 6D

Ab initio simulations of linear and nonlinear infrared spectroscopy — •Jens Dreyer — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany

Vibrational excitations play a central role for the ultrafast nonequilibrium dynamics of intra- and intermolecular hydrogen bonds. The stretching vibration of hydrogen-bonded O-H and N-H groups undergoes pronounced changes of frequency and vibrational line shape upon hydrogen bonding and frequently displays subpicosecond population lifetimes, which are much shorter than the corresponding lifetimes of free O-H/N-H groups. Relaxation via fingerprint mode overtone and combination bands mediated by Fermi resonance coupling as well a decay into low-frequency hydrogen bond modes have been invoked to explain such short lifetimes.

It will be shown how density functional theory calculations of anharmonic couplings in hydrogen bonds are used to address the linear and nonlinear vibrational spectroscopy of hydrogen bonds [1]. We predict and analyze multidimensional signatures of hydrogen bond coupling mechanisms by ab initio simulations of 2D IR spectra. The particular case of acetic acid dimers will be presented [2]. We address the lifetime shortening of 7-azaindole N-H stretching excitations in going from the monomer to the dimer as well as the mechanisms underlying the complex substructure of the N-H stretching infrared absorption band.

[1] J. Dreyer J. Chem. Phys. 2005, 122, 184306 ; [2] J. Dreyer Int. J. Quantum Chem. 2005, 104, 782.

MO 21.2 Di 11:00 6D

Ultrafast dynamics of vibrational N-H stretching excitations in the 7-azaindole dimer — •Jason R. Dwyer, Jens Dreyer, Erik T. J. Nibbering, and Thomas Elsaesser — Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany

The ultrafast vibrational response of hydrogen bonds in the 7-azaindole dimer, a model compound for DNA base pairing, is studied in infrared pump-probe experiments. We observe a ˜ 100 fs relaxation of the v = 1 state of the N-H stretching oscillators via anharmonically coupled over- and combination tones of fingerprint modes. In the monomer with a larger energy mismatch between the v = 1 state and over-/combination tones, a much longer lifetime of 10 ps is found. Femtosecond N-H stretching excitation induces coherent underdamped motions of the dimer, dominated by the anharmonically coupled 110 cm-1 stretching mode of the hydrogen bonds.

MO 21.3 Di 11:15 6D

Femtosecond vibrational sum frequency generation in the fingerprint region — •Sylvie Roke — MPI for Metals Research, Heisenbergstrasse 3, 70569 Stuttgart, Germany

Second-order nonlinear optical techniques are well established tools to study interfaces. Infrared visible Sum Frequency Generation (SFG) is an extremely valuable tool, since it combines the surface specificity with the ability to probe vibrational degrees of freedom. When using femtosecond lasers one can access both structure and dynamics of the interface.

Such studies have been limited, however, by the availability of femtosecond infrared laser sources. Therefore, most femtosecond SFG studies (as well as most other femtosecond tecniques that employ infrared radiation) have been performed in the frequency region of 4000-1000 cm^{-1}.

The fingerprint region (1000-500 cm^{-1}) is a very interesting one since this region contains typically vibrational modes that are specific to the 3D-structure of molecules, and is very sensitive to molecular interactions. This has remained unexplored. Therefore, we report a table-top femtosecond Ti:Sa laser that produces high power laser pulses, which are converted into tunable infrared radiation. The system produces infrared pulses with a tuning range from 4000-500 cm^{-1} and a power of 110-11 mW. We also show it is possible to probe surface vibrational modes in the fingerprint region, with a femtosecond SFG experiment.

MO 21.4 Di 11:30 6D

Towards Femtosecond Stimulated Raman Microscopy (FSRM) — •Evelyn Plötz, Stefan Laimgruber, Stefan Berner, and Peter Gilch — Institut für BioMolekulare Optik, Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Since the invention of microscopy diverse techniques to enhance the contrast of biological samples have been developed. In that respect, techniques relying on vibrational spectroscopy are very promising since the provide a contrast mechanism based on the chemical composition (chemical contrast). Because IR microscopy suffers from a low spatial resolution and (conventional) Raman microscopy from the low signal levels, non-linear Raman spectroscopy was applied for microscopy. Today the most important implementation is based on Coherent Anti-Stokes Raman Scattering (CARS) [1].

We here present a potential alternative to CARS microscopy, Femtosecond Stimulated Raman Microscopy (FSRM). In FSRM a femtosecond white light and narrow bandwidth laser pulse are focused onto the sample by a microscope objective. Stimulated Raman interaction superpose the Raman signature of the focal spot with the white light spectrum. By raster scanning the sample a FSRM micrograph can be recorded. Merits and pitfalls of FSRM in comparison with CARS microscopy will be discussed.

[1] J.-X. Cheng, X.S. Xie, J. Phys. Chem. B 108 (2004) 827

MO 21.5 Di 11:45 6D

Mode-Selective Excitation with Tailored Femtosecond Laser Pulses under Electronically Resonant and Nonresonant Excitation Conditions: The Role of Phase and Amplitude Modulation — •Jakow Konradi[1], Atila Gaál[2], Abraham Scaria[1], Vinu Namboodiri[1], and Arnulf Materny[1] — [1]International University Bremen (Jacobs University Bremen as of spring 2007), Germany — [2]International Laser Center, Bratislava, Slovak Republic

Coherent anti-Stokes Raman scattering (CARS) spectroscopy with femtosecond laser pulses is a powerful tool for the investigation of vibrational dynamics on an ultrashort time scale. However, the gain of temporal resolution entails a poor spectral resolution due to the inherent spectral width of the femtosecond excitation pulses. Recently, we have demonstrated that the nonlinear four-wave mixing signal extremely sensitively depends on the “chirp” of the exciting and probing pulses. The application of a self-learning loop approach for the optimal shaping of the femtosecond laser pulses allows for a relative (and absolute) enhancement or suppression of selected vibrational modes. Here, the ratio of signal intensities of different Raman lines observed in the CARS spectrum served as feedback signal for an evolutionary algorithm finding the best setting for the pulse shaper. While in our first experiments solely a modulation of the phases of the spectral pulse components was applied, in our present contribution we will discuss results obtained from an optimization varying phase as well as amplitudes. The optimization of the CARS spectra was performed both under electronically resonant and nonresonant excitation conditions.

MO 21.6 Di 12:00 6D

Symmetrieabhängige Solvatation bei Donor-substituierten Triarylboranen — •Uwe Megerle[1], Stefan Lochbrunner[1], Eberhard Riedle[1], Rainer Stahl[2] und Christoph Lambert[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Institut für Organische Chemie, Universität Würzburg

Donor-substituierte Triarylborane (TABs) zeigen eine ausgeprägte Solvatochromie aufgrund der starken Veränderung und Umkehr des Dipolmoments bei Zustandswechseln. Bei dem eigentlich hochsymmetrischen dreifach Carbazol-substituierten TAB muss zusätzlich ein umgebungsinduzierter Symmetriebruch vorliegen [1]. Die Solvatation von TABs mit einem und drei Carbazol-Subchromophoren wurde anhand der Rotverschiebung der Emission in einem fs-Anrege-Abfrage-Experiment untersucht. Das dreiarmige TAB wird in dem vergleichsweise stark viskosen Benzonitril langsamer (8 ps) und in dem niedrig viskosen Chloroform schneller (1 ps) solvatisiert als das einarmige (jeweils 4-5 ps). Wir vermuten, dass sich je nach Viskosität das Dipolmoment im elektronisch angeregten symmetrischen TAB drehen kann. Bei hoher Viskosität bleibt der Symmetriebruch des Grundzustands erhalten und die Lösungsmitteldipole müssen sich entsprechend dem umgekehrten Dipolmoment des angeregten Zustands ausrichten. Bei niedriger Viskosität kann dagegen der Symmetriebruch aufgehoben werden und ein Anregungstransfer zwischen den Subchromophoren und eine schnellere Absenkung des angeregten Zustands stattfinden. Messungen des Anisotropiezerfalls unterstützen dieses Modell.

[1] R. Stahl et al., Chem. Eur. J. **12** (2006), 2358.

MO 21.7 Di 12:15 6D

Excited State Reaction Pathways of a Photo-induced Pericyclic Ring Opening and Closure — •Björn Heinz[1], Stephan Malkmus[1], Stefan Laimgruber[1], Steffen Dietrich[2], Christine Schulz[2], Karola Rück-Braun[2], Markus Braun[1], Wolfgang Zinth[1], and Peter Gilch[1] — [1]Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany — [2]Institut für Chemie, Technische Universität Berlin, Str. d. 17. Juni, D-10623 Berlin, Germany

Many chemical reactions involving cyclic transition states obey the Woodward-Hoffmann rules. They make predictions on the occurrence and the stereochemistry of such reactions and can be applied for either direction of a chemical reaction – for instance a cyclisation and a cycloreversion. This suggests that both directions follow the same reaction path on the potential energy surface. For a photochemical cyclisation/cycloreversion of a fulgimide we present experimental evidence that this is not the case. We have recorded femtosecond fluorescence data for either direction and have observed pronounced temporal and spectral differences: The cyclisation proceeds with a characteristic time of $\sim$ 400 fs whereas the cycloreversion is about six times slower. Further, the transient fluorescence spectra of the photo-excited isomers significantly differ thoughout the reaction. We discuss the possible involvement of other excited states and a two-dimensional model to account for our observations.