Thirteenth International Conference on Time-Resolved Vibrational Spectroscopy

Freising, Germany

May 19-25, 2007

Book of Abstracts

Thirteenth International Conference on Time-Resolved Vibrational Spectroscopy

Bildungszentrum Kardinal-Döpfner-Haus
Domberg 27
D-85354 Freising
Germany

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Introduction

The thirteenth meeting in a long-standing series of "Time-Resolved Vibrational Spectroscopy" (TRVS) conferences will be held May 19th to 25th at the Kardinal Döpfner Haus in Freising organized by the two Munich Universities, Ludwig-Maximilians-Universität and Technische Universität München. This international gathering will continue the illustrious tradition of the original 1982 meeting that took place in Lake Placid, NY. The series of meetings was initiated by leading, world-renowned experts in the field of ultrafast laser spectroscopy, and is still guided by its founder, Prof. George Atkinson (University of Arizona and Science and Technology Advisor to the Secretary of State). In its current format, the conference promotes the traditional areas of time resolved vibrational spectroscopies including infrared, Raman and related laser methods for emerging technology areas. The scientific program addresses basic science, energy related research and advancing novel commercial applications. Since monitoring time-dependent phenomena in molecular systems is becoming the focus of many developing research programs in academia, government and industry, the conference focuses on molecular dynamics topics for a wide attendance base.

This meeting on Time Resolved Vibrational Spectroscopy will promote science that is at the heart of the physical sciences, including chemistry, biophysics, biology, and material science. Vibrational spectra are molecule and bond-specific. Thus, time-resolved vibrational studies provide detailed structural and kinetic information about primary dynamical processes on the picometer length scale. From this perspective, the goal of achieving a complete understanding of complex chemical and physical processes at the molecular level is well served by fostering a venue for recent progress in experimental and theoretical vibrational studies in condensed phase and interfacial environments.

Our current meeting program is presented below. The present meeting features world-renowned plenary and invited speakers chosen to attract graduate students, postdoctoral researchers and starting investigators interested in using infrared, Raman and related vibrational spectroscopies in their careers. In parallel to experimental research there will be highlights of related theoretical investigations. It is hoped that the topical sessions will enable contributors and participants engaged in modern applications of vibrational spectroscopy to "cross-fertilize". The venue of TRVS XIII will certainly pave the way for exciting future

scientific developments and collaborations in an expanding and active field. Poster sessions will also allow to present science in open discussion formats.

The Time-Resolved Vibrational Spectroscopy Conferences provide a unique opportunity to assemble a critical number of the leading researchers from academia, industry and government from all over the world. It is recognized as the “leading venue” for researchers to discuss their findings every two years. We hope to attract new people interested in diversifying their work to incorporate related but differing specializations, along with attracting a significant numbers of students and young researchers who would bring new points of view to most exciting and demanding current problems.

We all wish you an interesting and fruitful conference and a splendid time in the Munich area.

Munich, May 2007

Alfred Laubereau, Wolfgang Zinth, Peter Gilch, Karl-Heinz Mantel and Hristo Iglev

Conference Organizers

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Book of Abstracts: Simone Draxler, Ludwig-Maximilians-Universität München

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of the International Organizing Committee
TRVS XIII – 2006

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					Banquet-Dinner		

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Saturday Afternoon

Opening Session

Transient 2D-IR spectroscopy

P. Hamm

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The importance of structural dynamics of biomacromolecules in solution phase is widely appreciated. 2D-IR spectroscopy is a novel spectroscopic tool that uniquely combines ultrafast time resolution with appreciable structure resolution power. In analogy to 2D-NMR spectroscopy, the connectivity of various vibrational states can be related to local contacts of molecular groups, which is the basic principle of structure determination in both cases. All fundamental NMR experiments (COSY, NOESY, and EXSY) have been demonstrated in the IR range in the meanwhile. By nature of the close analogy, the biggest competitor of 2D-IR spectroscopy will be 2D-NMR spectroscopy. That puts the bar high! Both methods are, in principle, capable to resolve certain functional groups in a molecule, work (mostly) in the solution phase and aim to elucidate structure as well as dynamics of solution phase systems.

It has often been argued that the big potential of 2D-IR spectroscopy, as compared to 2D-NMR spectroscopy, is the by many orders of magnitudes higher intrinsic time resolution of the former. However, one must be very careful in specifying what exactly is meant with 'time resolution'. Fig. 1a shows the time regimes that can be covered by various variants of NMR spectroscopy, which do in fact include the ultrafast picosecond and even sub-picosecond range. For example, the orientational diffusion time of bulk water has been deduced already in the mid-70's by NMR spectroscopy, revealing a value that agrees well with IR results some 20 years later. The way how the ultrafast time regime is accessed by the intrinsically very slow NMR spectroscopy is indirect through relaxation methods (T1, T2, NOE, residual dipolar couplings in Fig. 1). The important difference between IR and NMR spectroscopy is the time range that can be accessed in 'real time', which would be exchange spectroscopy (EXSY) and pump-probe spectroscopy in Fig. 1.

Clearly the biggest potential of IR spectroscopy, as compared to NMR spectroscopy, lies in the almost unlimited time range accessible to non-equilibrium pump-probe experiments. This is why we made a strategic decision some time ago to explore and develop exactly this capability of 2D-IR spectroscopy: Measuring snap-shot structures of fast evolving molecular systems by means of transient 2D-IR spectroscopy. This is where the dynamic aspect of NMR spectroscopy almost completely fails. In this overview talk, I will discuss variants of transient 2D-IR spectroscopy as well as applications in biology and chemistry

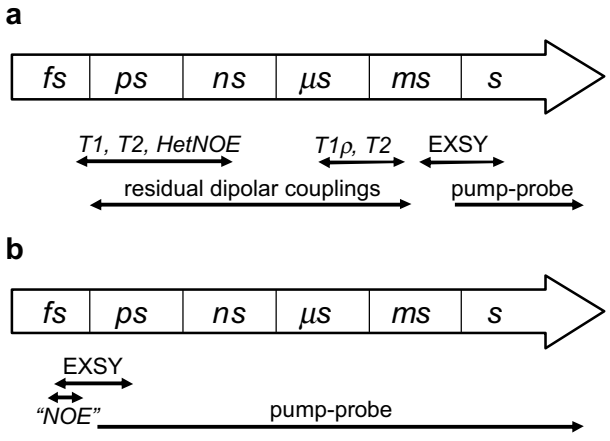

Fig 1. Time arrow from femtoseconds to seconds together with time regimes that can be covered by various techniques of (a) 2D-NMR and (b) 2D-IR spectroscopy.

Persistent Oscillations of a Molecular Wheel observed by Femtosecond Vibrational Spectroscopy

Sergey Yeremenko[1], Pavol Bodis[1,2], Wybren Jan Buma[2], Jose Berna-Canovas[3], David A. Leigh[3] and Sander Woutersen[1,2]

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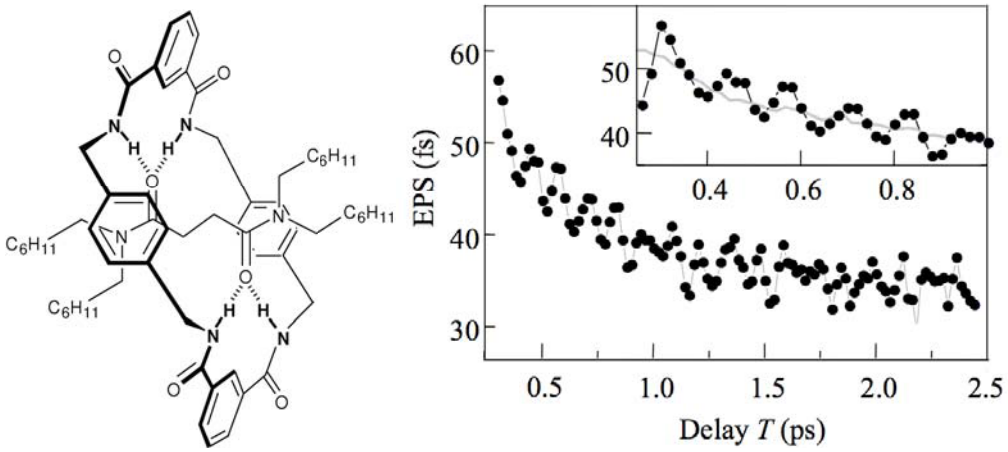
Rotaxanes and catenanes—molecules in which the components are mechanically linked but not connected by covalent bonds—are currently used as building blocks for artificial molecular machinery. Although it is tempting to regard such multi-component assemblies as "molecular meccano",[1] many aspects of classical mechanics become meaningless at this level of miniaturization, since viscous forces and Brownian motion will strongly influence the mechanical behavior.

We have investigated the motions of a rotaxane 'molecular wheel' (see figure) using femtosecond vibrational spectroscopy. The instantaneous length of the NH···O hydrogen bonds connecting the 'rim' and 'axle' determines the frequency of the NH-stretch mode. As the fluctuations of these hydrogen bonds are governed by the structural dynamics of the rim and the axle, the dynamics of the NH-stretch mode reflect the global motions of the nano-wheel. To investigate the NH-stretch dynamics we use the 3-pulse photon-echo peak shift technique, which gives direct access to the correlation function of the frequency fluctuations.[2] We find that the dynamics of the rotaxane involve Brownian motion of the constituent components with respect to each other, as well as oscillatory motions. These oscillations involve an overall distortion of the structure (they are not observed in substructures of the rotaxane, see inset), and persist for several periods. Such underdamped oscillatory motion implies that the rotaxane system has a certain degree of stiffness, and behaves more like a macroscopic wheel than might be expected at first sight. This suggests that a 'meccano' picture of rotaxane- and catenane-based molecular devices is not entirely unrealistic.



Left: Chemical structure of the investigated rotaxane. Right: NH-stretch photon-echo peak shift (EPS) as a function of waiting time *T*. The inset shows a close-up at short *T*. The grey curve in the inset is the EPS observed in a pyrrole:DMA complex containing the same NH···OC hydrogen-bond motif as the rotaxane. The absence of oscillations in this substructure implies that the oscillatory motions involve the rim part of the rotaxane, and require overall structural integrity of the nano-wheel.

References:

[1] J. F. Stoddart, *Pure and Applied Chem*. **77**, 1089 (2005).

[2] M. Cho, J. Y. Yu, T. H. Joo, Y. Nagasawa, S. A. Passino, and G. R. Fleming, *J. Phys. Chem.* **100**, 11944 (1996).

Ultrafast Bidirectional Isomerization of a New Class of Biomimetic Photoswitches

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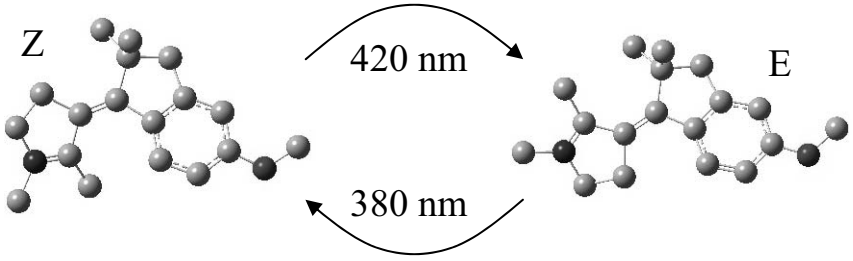
We present high level ab initio calculations and transient infrared measurements of the ultrafast isomerization of a new class of biomimetic photoswitches, which were designed to mimic various aspects of the photoisomerization of rhodopsin[1]. The switches can be selectively prepared in the Z and the E form and isomerize with high quantum efficiency upon excitation by light near 400 nm.

Combined ab initio quantum mechanics/molecular mechanics excited state minimum energy path calculations (CASPT2//CASSCF/AMBER) in methanol indicate a barrierless access to the S_1/S_0 conical intersection from the Frank-Condon region in the S_1 excited state. The initial reaction coordinate is characterized by C=C bond stretching followed by torsional motion about the isomerizing bond.

Analysis of the C=C stretch band region in femtosecond UV-IR pump-probe measurements has allowed us to separate the signal due to the ultrafast return of the molecules to the electronic ground state from contributions due to thermal excitation of low frequency modes and solvation. The data shows that the molecules isomerize in less than 1 picosecond, in line with a fluorescence decay time of a few 100 femtoseconds. The quantum yield of E→Z isomerization is found to be 20% in methanol solution. Nearly 90% of the molecules can be converted to the thermally unstable E-form by continuous irradiation at 454 nm. The E→Z reaction could thus be studied separately and was found to proceed on the same timescale as the E→Z isomerization, however, with an even larger quantum yield of 35%.

The high efficiency, high polarity and simple isomerization mechanism of these molecules should make them a promising alternative to the widely used azobenzene-based photoswitches, for example for the triggering of conformational dynamics in peptides[2, 3].



Z and E isomers of the investigated photoswitch. Isomerization about the C=C bond linking the two 5-membered rings upon S_1-excitation near 400 nm takes place in less than a picosecond in both directions.

[1] Lumento, F.; Zanirato, V.; Fusi, S.; Busi, E.; Latterini, L.; Elisei, F.; Sinicropi, A.; Andruniów, T.; Ferré, N.; Basosi, R.; Olivucci, M., *Angew. Chem. Int. Ed.* **2007,** 46, 414-420.

[2] Bredenbeck, J.; Helbing, J.; Kumita, J. R.; Woolley, G. A.; Hamm, P., *Proc. Natl. Acad. Sci. U.S.A.* **2005,** 102, 2379-2384.

[3] Andruniów, T.; Fantacci, S.; Angelis, F. D.; Ferré, N.; Olivucci, M., *Angew. Chem. Int. Ed.* **2005,** 44, 6077-6081.

Sunday Morning Session

Biology I

Single and dual frequency 2D IR of the coupling of water to proteins and ions

Y. S. Kim,F. Kuo, D. Vorobayev and R. M. Hochstrasser

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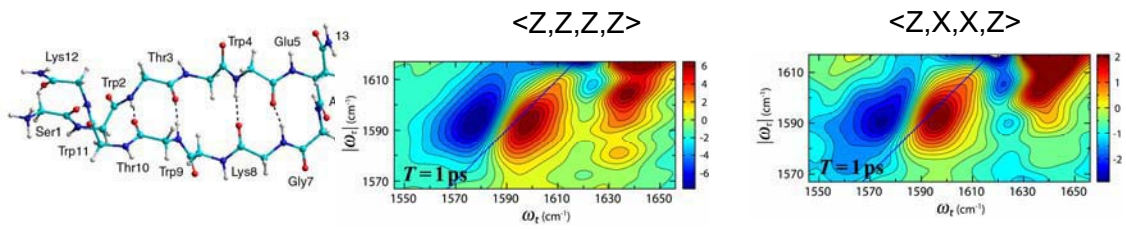
The structures and dynamics of the solvent association to peptides, representing a range of secondary structures and ions in a variety of environments including water, micelles and lipid bilayers, are studied using 2D IR with one and two center frequencies (one at the mode of interest the other at water vibrations). The observations of population exchange allow specific structures of water to be visualized at a residue level for some peptides such as the beta-hairpin models. The 2D IR measurements are made residue specific by means of isotopomers.The interactions between peptide groups is sensed by electrostatic anharmonic coupling and also by incoherent energy transport over significant distances in polypeptides and demonstrably between tertiary related structures localized in model membranes. The results provide the extent to which peptide amide-I transitions are localized and how this condition influences the cross peaks in 2D IR.

One example we have studied in detail is the ^{13}C-^{18}O isotopomer of TypZip2, a 14 residue hairpin model peptide (see Figure). The amide-I mode of the isotopomer shown in the Figure is well separated from the peptide main transitions and its dynamics in response to local water motions can be seen clearly. The 2D IR spectral results as a function of the population times are consistent with there being a few identifiable water configurations around the carbonyl and that these are exchanging on the 1-2 ps time scale. Experiments of this type are permitting the study of the detailed dynamics of water molecules near the surfaces of peptides and ions exposing what may be widely occurring at protein water interfaces.

The cross peaks in 2D IR of the isotopomers have been found to be strongly dependent on the population time because of energy transport between the system transitions. We can show that the coherent responses are quite different when the coupled states involve significant solvent motions compared with when they are approximate eigenstates of a solute Hamiltonian. The existence of underlying structure on the diagonal peak is evidenced by the cross peaks near $\omega_\tau = 1630$ cm-1. Time permitting, recent results on molecular ions will be discussed. (This research is supported by NIH grants GM12592 and RR03148)



Dynamics of TrypZip2 Glycine-7 transition showing water structure interchange and energy transport. The main bands of the peptide are not on-scale; only their cross peaks with the Gly7 are shown.

Ultrafast Dynamics of Model Molecular Photoswitches in Liquid and Solid Phase

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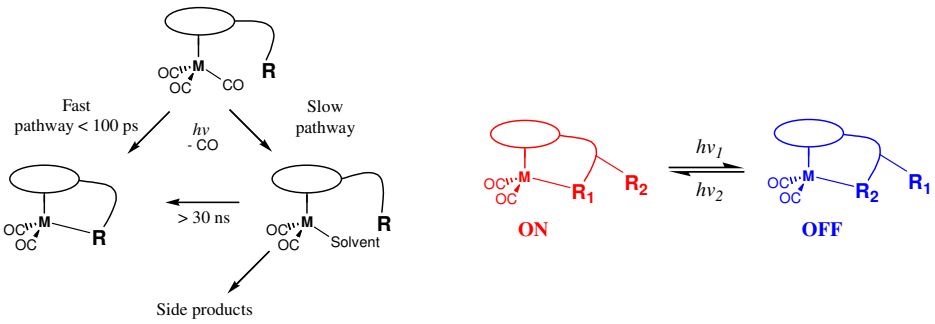
There is great interest in developing high speed reversible molecular photoswitches for photonic devices. Fast rates, high quantum yields, and low fatigue are desirable features. The current challenge for the application of these novel molecules is that their desirable properties can be hindered by cage processes such as recombination and solvation. For example, recombination ultimately slows down a reaction since it lowers the quantum yield and thereby requires additional excitation to complete the reaction. Solvation prolongs the lifetime of transient species and provides more opportunities for side reactions and hence fatigue in molecular devices. These processes are known to occur on the sub-picosecond timescale and so it is prudent to design the system to have an ultrafast response, attain near unity quantum yield, and control the reaction mechanism which is driven by transient molecular structures and reaction environment. To reach these goals, we synthetically manipulate the molecular structures and use picosecond time-resolved infrared spectroscopy to directly measure their physicochemical responses. We have synthesized and demonstrated model molecular photoswitches capable of chelation (ring formation of metal-multidentate ligand complexes) to the exclusion of ultrafast solvent coordination and cage recombination in solution. In this presentation, the chelation dynamics of organomanganese complexes in various reaction environments (**in solution and in solid films**) will be discussed as well as how ultrafast chelation has been utilized as a mechanistic platform for designing reversible molecular photoswitches.



Left : controlling the reaction pathways by changing the structure of the chelatable ligand, the metal center, and reaction environment. **Right :** molecular photoswitches based on ultrafast reversible non-competing chelation. Strong IR absorption of the M-CO group allows direct measurement of the physicochemical changes using picosecond time-resolved infrared spectroscopy.

Methods of Time-Resolved IR Spectroscopy for the Study of Photobiological Systems from Nanoseconds to Milliseconds

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Albert-Ludwigs-Universität, Freiburg, Germany

Infrared difference spectra of photobiological systems are characterized by small absorbance changes against a large background absorption caused by the protein. Furthermore, the time-scales of the reaction usually extend from femtoseconds to milliseconds. In the first part the different methods of time-resolved IR spectroscopy covering the time range from nanoseconds to milliseconds will be shortly reviewed and typical applications will be shown. Because of the small absorbance changes in the range of 10^{-4} to $5*10^{-3}$ signal averaging and/or spectrum averaging are required. Therefore, most of these methods required samples exhibiting reversible photoreactions or reactions which can be reliably driven back by light. Since many systems in biology and photochemistry exhibit irreversible reactions, the extension of methods for the study of such photoreactions was urgently needed. The critical parameter is the amount of material needed to cover a large spectral range, often extending from 1800 to 800 cm^{-1}. The most promising methods appear to be the step-scan method with micro-illuminator and movable sample, and the pump-probe technique using laser-derived pulses with electronic delay. First data on the photoreaction of the visual pigment rhodopsin using the step-scan technique will be shown.

Femtosecond infrared spectroscopy of the anesthetic gas nitrous oxide in lipid-membranes

Logan Chieffo[1,3], Jason J. Amsden[2,3], Jeffrey Shattuck[1,3], M. K. Hong[2,3], Lawrence Ziegler[1,3], Shyamsunder Erramilli[2,3,4]

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More than 150 years after the discovery of anesthesia, the molecular mechanism of anesthetic action remains an unsolved problem. Recently we measured the vibrational energy relaxation lifetime of the fundamental antisymmetric stretching mode ν_3 centered at 2218 cm^{-1} of the anesthetic gas nitrous oxide ($^{14}N_2{}^{16}O$) dissolved in octanol and olive oil, both model systems in use today for assessment of anesthetic potency[1]. We report here the first studies of the vibrational energy relaxation of nitrous oxide in a lipid-water model membrane system. The relaxation of N_2O in the fully hydrated phospholipid system 1,2-Dimyristoyl-*sn*-Glycero-3-Phosphocholine (DMPC)-water has a characteristic time τ_r of 65 ps at room temperature, with interesting evidence of energy exchange with water. The results are to be compared with our earlier pump-probe studies using olive oil and octanol (τ_r = 52 ± 1 ps). The lifetimes suggest that energy relaxation of the anesthetic is determined primarily by the hydrophobic nature of the molecular environment. We have also measured the relaxation time of N_2O dissolved in bulk water, where we observe τ_r to be 10 ps. Measurement of the relaxation of nitrous oxide associated with interlamellar water in fully hydrated DMPC, which forms a lamellar liquid crystalline L_α phase at room temperature, shows that the environment of nitrous oxide in interlamellar water is similar to that in the bulk water phase. Nitrous oxide is a good model system for probing anesthetic-solvent interactions using femtosecond nonlinear infrared spectroscopy. The potential of femtosecond 1D- and 2D-IR spectroscopy on nitrous oxide in lipid membranes for studying the molecular mechanism of anesthetic action is unique and may help to unravel the molecular mechanism of anesthetic action.

Support is gratefully acknowledged from the US National Science Foundation and the Department of Defense.

[1]Chieffo, L.; Amsden, J. J.; Shattuck, J.; Hong, M. K.; Ziegler, L.; Erramilli, S. *Biophysical Reviews and Letters* **2006**, 1, 309-316.

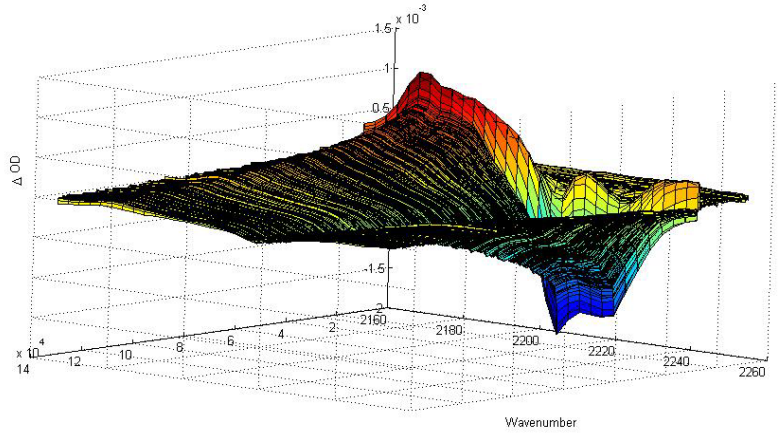

Figure 1. Infrared pump-probe spectra of the fundamental antisymmetric stretching mode of nitrous oxide in fully hydrated DMPC-water using an MCT array detector.

Infrared two-color dynamic hole burning in hydrated phospholipid membranes

V. V. Volkov[1], *D. J. Palmer*[1], *R. Righini*[1]

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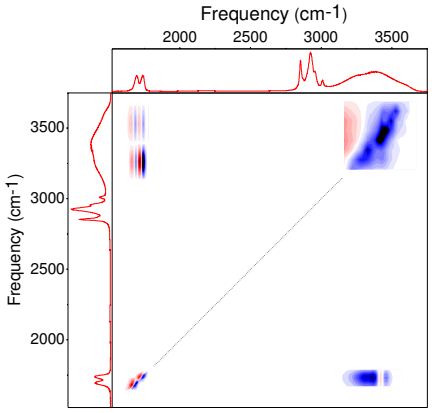
Two-color two dimensional infrared spectroscopy is used to probe the structural and dynamical correlations of water and carbonyl groups at the polar interface of a phospholipid bilayer.

The diagonal resonances in the 1700 and 3400 cm^{-1} regions, probed in a hole-burning experiment, allow us to disentangle the homogeneous and inhomogeneous contributions to the linebroadening of the CO and H_2O stretching modes. In particular, the heterogeneity of the water local structure is pointed out.

Two color broadband pump-probe experiments are performed by tuning the excitation and probe pulses in the two separate spectral regions corresponding to carbonyl and water stretching vibrations. The off-diagonal spectra provide information on the hydration of the CO groups and on the energy relaxation in weakly hydrated phospholipid membranes.



Full two-dimensional infrared spectrum (at zero delay time) of a hydrated bilayer

Direct observation of ligand transfer in cytochrome c oxidase using mid-infrared chirped-pulse upconversion

Johanne Treuffet, Kevin J. Kubarych, Jean-Christophe Lambry, Eric Pilet, Jean-Louis Martin, Marten H. Vos, Manuel Joffre, Antigoni Alexandrou*

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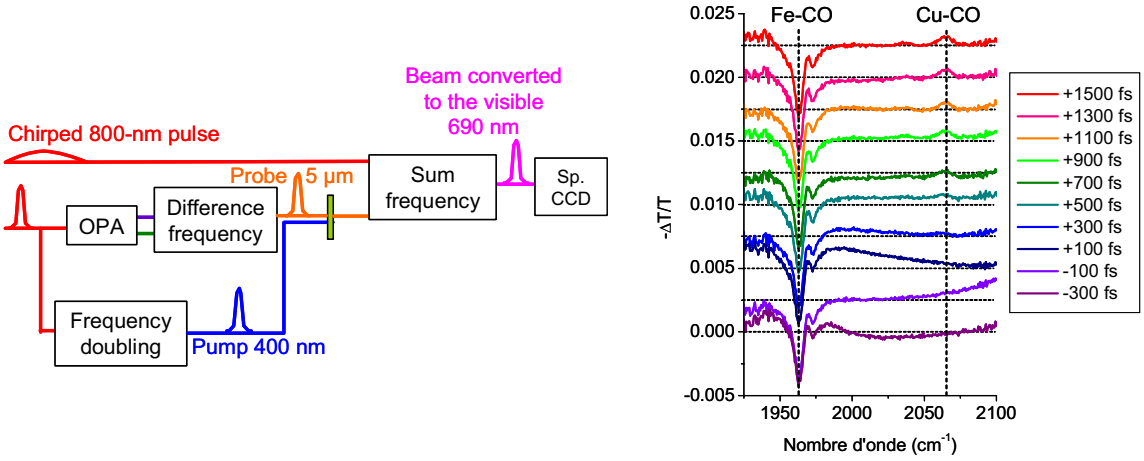
Cytochrome *c* oxidase (CcO) is the key enzyme of the respiratory chain that reduces oxygen to water and couples the energy of this reaction to the pumping of four protons across the membrane. The active site includes the Fe atom of a heme molecule and a close-lying (~5 Å) Cu atom. A doorstep role for ligands on their way into and out of the active site has also been attributed to Cu. Indeed, it has been shown that CO binds to Cu after photodissociation from the Fe on its way out of the protein. The ultrafast sub-ps dynamics of this process, however, has been observed either indirectly using experiments in the visible sensitive to the heme electronic transitions[1] or with picosecond time resolution.[2] Apart from implications for the functioning of CcO, this transfer process of a diatomic molecule between two well-identified binding sites can be seen as a model system for bond breaking and formation processes.

We here present spectrally resolved femtosecond visible pump – mid-infrared probe experiments which are directly sensitive to the CO ligand vibrational frequency indicative of the CO binding site (1963 and 2065 cm^{-1} for CO bound to Fe and Cu, respectively). The originality of our approach lies in the detection scheme of the mid-infrared probe by transposition to the visible domain *via* sum-frequency generation with a chirped 800-nm pulse.[3] This allows exploiting the advantages of CCD technology in terms of spectral resolution and signal-to-noise ratio for the spectrum measurement.

The differential transmission spectra show the arrival dynamics of CO to the Cu binding site. This dynamics can be best fit by an exponential with a characteristic time of 450 fs *displaced by 200 fs*. This behaviour indicates the contribution of a ballistic component to the transfer process and is in agreement with molecular dynamics simulations. Furthermore, the initial appearance of the Cu-CO vibrational peak at a lower frequency than the final value of 2065 cm^{-1} speaks for a ligand transfer process without formation of "free" CO.



Left: Scheme of the experimental setup (Sp.: spectrometer). Right: Differential transmission spectra for pump-probe delays between -300 and +1500 fs. The spectra have been displaced vertically for clarity.

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Sunday Afternoon Session

Water I

Ultrafast structural dynamics of liquid H_2O probed by vibrational excitations

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In the liquid phase, water molecules form a disordered network of intermolecular hydrogen bonds. This equilibrium structure fluctuates on femto- to picosecond time scales, involving multiple molecular rearrangements, the breaking and the reformation of hydrogen bonds. Most experimental probes of water structure such as neutron scattering, x-ray diffraction and x-ray absorption average over these fluctuations in space and time, thus giving limited insight into the elementary microscopic dynamics. In contrast, femtosecond vibrational spectroscopy provides direct information on transient local structure and allows to separate molecular interactions underlying structural fluctuations and changes[1,2]. Using both inter- and intramolecular vibrations as structural probes, we demonstrate a two-stage structural response of the hydrogen bond network to a disposal of vibrational excess energy: Vibrational energy is transferred from excited water molecules to intermolecular modes, resulting in a sub-100 fs nuclear rearrangement that leaves the local hydrogen bonds weakened but unbroken. Subsequent energy delocalization over many molecules occurs on a ~1 ps time scale and is connected with the breaking of hydrogen bonds, resulting in a macroscopically heated liquid.

In our experiments with a 100 fs time resolution, we measure transient infrared spectra of intermolecular librational modes and the intramolecular OH bending vibration, both being highly sensitive probes of water structure, after excitation of three different modes, (a) high-frequency librations, (b) the OH bending mode, and (c) the OH stretching mode[3]. Upon librational excitation at 1350 cm^{-1}, the librational L2 band with maximum absorption at 670 cm^{-1} displays a pronounced shift to lower frequency which builds up on a sub-100 fs time scale and is followed by a slower ~1 ps component. In contrast, the concomitant red-shift of OH bending absorption exclusively displays the ~1 ps component. The sub-100 fs librational red-shift is due to a weakening of local hydrogen bonds which remain unbroken on this ultrafast time scale. The slower ~1 ps kinetics of librational and OH bending absorption reflects the delocalization of excess energy in the hydrogen bond network connected with breaking of hydrogen bonds.

A similar behavior occurs after OH bending and stretching excitation with, however, the energy transfer rates being determined by the lifetimes of the intramolecular modes[4,5]. In particular, relaxation of the OH stretching vibration occurs predominantly via the OH bending mode with a two-step transfer of excess energy to intermolecular modes. Our results demonstrate the key role of librational motions for both the loss of local structural correlations and ultrafast energy dissipation.

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Femtosecond mid-infrared spectroscopy on liquid-to-supercritical water: Vibrational energy relaxation versus spectral diffusion

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Liquid water exhibits an intriguing hydrogen bond (H-bonds) network, which is structurally and dynamically highly random in nature. Breakage and formation of H-bonds continuously interconvert local H-bonded structures on a variety of time scales and result in spectral diffusion within the intramolecular vibrational resonances of the liquid. To disentangle the two fundamental vibrational dynamics, i.e. vibrational energy relaxation (VER) on one hand and vibrational spectral diffusion (VSD) on the other, we performed fs-mid-IR pump-probe spectroscopy on the OH-stretching mode of HOD in D_2O over wide ranges of pressure and temperature corresponding to the liquid and the supercritical phase of the solution.

Except for sufficiently low temperatures, i.e. $T < 130°C$, the excited state transient absorption and the ground-state bleach of the OH-stretch decay strictly single-exponentially with identical time constants (see Figure 1). Transient differential transmission spectra reveal a characteristic isosbestic wavelength separating excited-state absorption from ground state bleach. Our surprising experimental results complement previous fs-mid-IR pump-probe[1] and 2D-IR studies[2], which were preformed on the same system under atmospheric pressure only.

We correlate our experimentally determined VER rate constants with the pressure and temperature dependent dielectric constant, $\varepsilon(T,p)$, of fluid D_2O (see Figure 2). Recent molecular dynamics simulations suggest that $\varepsilon(T,p)$ can be taken as a measure of the average H-bond connectivity within the random D_2O network[3]. Based on such a correlation, we show that the nature of the apparent pump-probe decays changes as the temperature of the liquid is lowered. In the high-temperature limit, spectral diffusion is so fast that our pump pulses are unable to photo-select any local H-bonded structures. The apparent VER rate constant can then be understood as an "ensemble-averaged" quantity. In contrast, for sufficiently low temperatures, i.e. $T < 130°C$, VER and VSD occur on similar time scales, yet the apparent decays are biased to slower relaxing OH-oscillators that are only weakly connected to the random D_2O network.

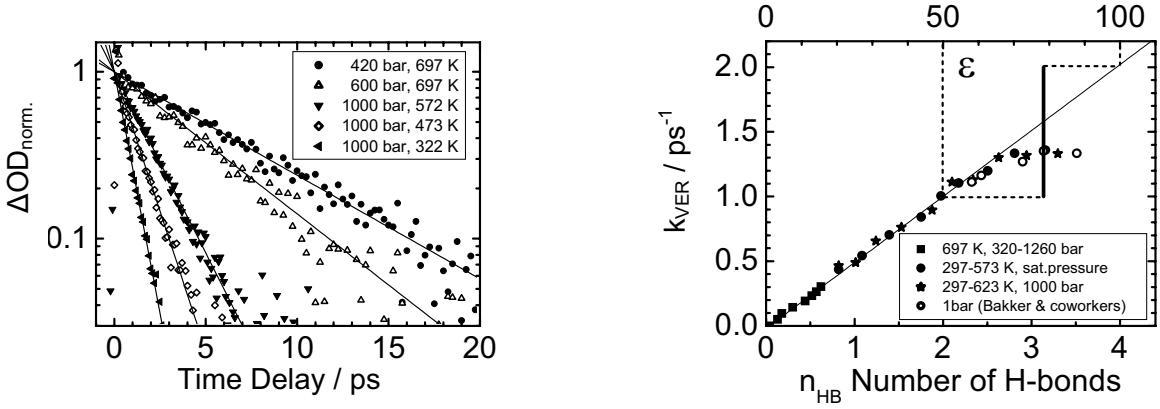

Fig. 1. Left panel: Normalized transient absorption signals of HOD in D_2O. Right panel: OH-stretch relaxation rate constant of HOD versus the dielectric constant of D_2O (top axis) and the average number of hydrogen bonds per HOD molecule as derived from MD simulations [3].

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Correlation 2D IR spectroscopy on monomeric water molecules

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One of the most intriguing aspects regarding the sub-ps dynamics of the OH stretching band in liquid water is the extremely fast depolarization. Several groups have shown that the anisotropy decays with a time constant of about 0.1 ps[1,2] which is viewed to be related to the strong coupling of neighboring water molecules. However, a similar behavior of anisotropy was recently observed in a pump-probe study on the OH stretching mode of monomeric H_2O molecules in acetonitrile[3]. These results suggest that the loss of the orientational memory in bulk water can be caused by both *intermolecular* energy transfer and *intramolecular* anharmonic couplings. In order to distinguish between these two routes, it is essential to comprehend the ultrafast dynamics of isolated water molecules, where the intermolecular interactions are switched off. Two-dimensional (2D) femtosecond correlation spectroscopy is the best suited technique which provides information on the mode coupling as well as additional insights into the ultrafast dynamics[4].

Figure 1 shows typical experimental and simulated 2D spectra of the OH stretching modes of H_2O in acetonitrile. Our results reveal a very fast (0.2 ± 0.1 ps) energy transfer between the asymmetric (ω_a) and symmetric (ω_s) stretching modes and allow mapping the relevant transitions. A total number of 16 transitions compose the signal, 8 of them occurring directly after excitation and 8 following the intramolecular energy transfer. The anisotropy decay observed in pump-probe appears to be related to interplay between these transitions. The theoretical 2D spectra calculated from a Hamiltonian trajectory by numerical integration of the Schrödinger equation, allow the precise assignment of the main experimental features[5].

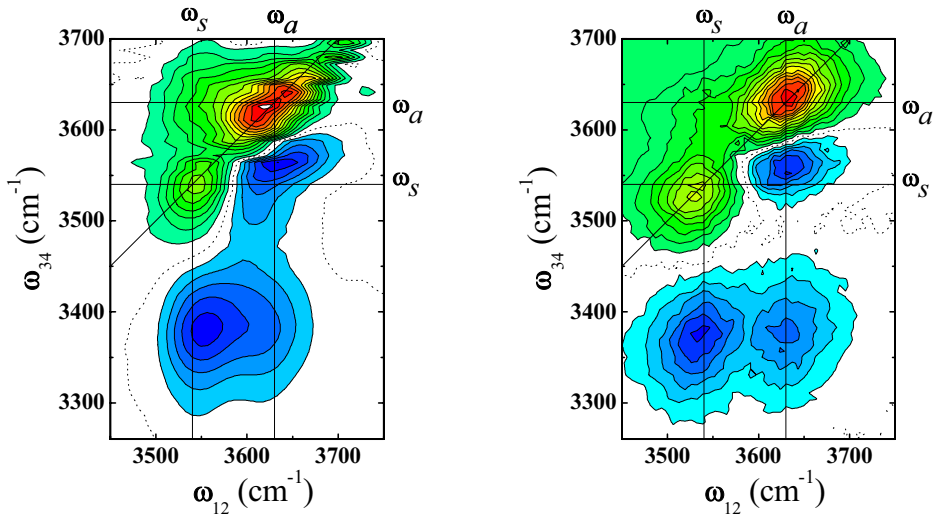

Fig.1. Experimental (left) and calculated (right) two-dimensional correlation spectra for 0.1 ps waiting time. The maximum (red) and minimum (blue) of the signal are separated by twenty one equally spaced levels. The dotted line corresponds to zero amplitude.

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Solvent dependence of OH stretch and bend vibrational relaxation of monomeric water molecules in liquid solution

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The vibrational dynamics of isolated water molecules dissolved in several nonpolar organic liquids have been studied using an IR pump-probe experiment with ≈ 2 ps time resolution. Analyzing transient, time- and spectrally resolved data in both the OH bending and the OH stretching region, the relaxation pathways of single water molecules were disentangled comprehensively[1], proving that the vibrational energy of H_2O molecules is relaxing following the scheme OH-stretch → OH bend overtone → OH bend → ground state, as indicated in Fig. 1.

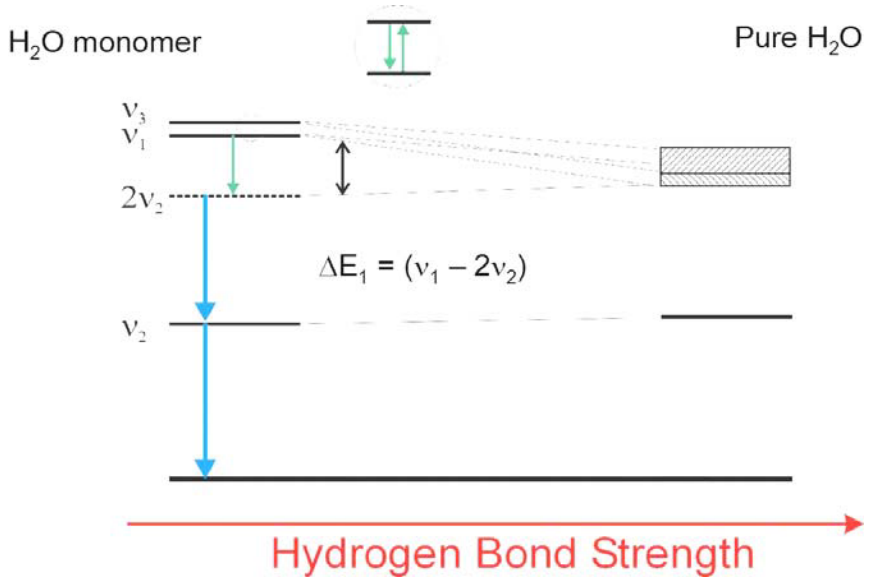

Figure 1: Schematic view of H_2O relaxation pathways. The anharmonic shift of the energy levels with increasing hydrogen bond strength increases the OH stretch relaxation rate, whereas the OH bend lifetime does not follow this correlation.

In a previous work we have shown that the OH stretch relaxation is accelerated monotonically upon increase of the solute-solvent interaction[2]. In contrast, OH bending relaxation shows an individual behavior for various solvent-solute combinations indicating that this last, intermolecular relaxation step[3] thermalizing the excess vibrational energy is depending on the individual resonance structure (accepting modes) of the solvent molecule.

In the presentation, an overview of results obtained in various solvents will be given.

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Mode-Selective O-H Stretching Relaxation and Energy Redistribution in a Hydrogen Bond Studied by Ultrafast Vibrational Spectroscopy

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Vibrational excitations play a central role in the ultrafast nonequilibrium dynamics of intra- and intermolecular hydrogen bonds. However, experimental evidence for relaxation pathways has remained very limited and – in most cases – the overall relaxation scenario is not understood.

Here we present an experimental study of the relaxation of the O-H stretching mode and subsequent intramolecular vibrational energy redistribution (IVR) in the medium strong intramolecular O-H...N hydrogen bond of the prototype system (2'-hydroxy-5'-methyl-phenyl)benzotriazole (Tinuvin P) dissolved in C_2Cl_4.[1] We apply two-color infrared-pump/infrared probe and picosecond infrared-pump/anti-Stokes resonance Raman probe spectroscopy. These studies are combined with theoretical calculations of vibrational energy transfer rates based on a Fermi golden rule (FGR) approach.

A population decay time of the O-H stretching vibration of 200±20 fs was determined by femtosecond infrared spectroscopy. Picosecond Raman experiments were carried out in a wide spectral range between 300 and 1700 cm^{-1} (i) for measuring population lifetimes of several vibrational modes after resonant infrared excitation and (ii) for monitoring rise and decay of mode populations induced by IVR after exciting in the high-frequency O-H stretching band.

After pumping the O-H stretching vibration we observe selective excitation of distinct modes. The fastest rise times, i.e. rise times close to the population decay time of the O-H stretching mode, are observed for modes exhibiting pronounced in-plane O-H bending contributions (δOH). Modes with much smaller δOH contributions have substantial slower rise times and become considerably less excited. Thermal equilibrium between the modes is achieved after 5-10 ps.

The similarity of rise times of a few distinct modes with the decay time of the O-H stretching vibration indicates that these primary accepting modes are populated mainly by IVR from the directly excited O-H stretching vibration. Population numbers derived from transient anti-Stokes Raman intensities suggest that about 40 % of the initial O-H stretching population decays through the mode with the largest δOH contribution, whereas only about half of this fraction is transferred through two additional modes, both showing considerable δOH contributions as well. These 3 modes accept a total of about 70-80 % of the initial O-H stretching population. The remaining population is distributed over several other modes, among them infrared active vibrations.

Our combined ultrafast infrared/Raman study demonstrates that the hydrogen-bonded OH stretching mode in Tinuvin relaxes through a few major channels that all involve combination and overtone bands of modes with considerable δOH character. In particular, the mode with the largest δOH contribution plays a prominent role for primary IVR processes. This highlights the important role of energy transfer from stretching to bending motions in hydrogen bonds. Our theoretical calculations account for these experimental findings.

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Observation of ice-like water around hydrophobic groups

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Water plays an essential role in maintaining the structure and function of biological macromolecules, such as proteins and nucleic acids. The stability of a protein conformation is governed by a complex interplay of both (direct) water-protein interactions and (indirect) hydrophobic interactions. The origin of the hydrophobic interactions can be found in the way hydrophobic groups are solvated by water. It has long been suspected that a rigid, ice-like shell of water molecules is formed around hydrophobic groups, which, being entropically unfavorable, leads to the association of these groups in water. Experimental evidence for the existence of an ice-like solvation shell, however, is indirect (e.g. heat capacity measurements) because of the inherent difficulty in separating the response of bulk and solvation shell water .

We use mid-infrared pump-probe spectroscopy to directly probe the orientational dynamics of water molecules in the solvation shells of hydrophobic groups. For this purpose we have studied solutions of different osmolytes in water. Osmolytes are small organic molecules that are known to affect the stability of proteins. In addition they contain hydrophobic groups and are highly soluble in water. Among the studied osmolytes are urea and tetramethylurea, both strong protein denaturants and trimethylamine-N-oxide (TMAO), a strong stabilizing osmolyte.

Our results show that in an osmolyte solution the water is partitioned into two-fractions: water molecules that show bulk-like dynamics and water molecules that are strongly immobilized. The orientational dynamics of the bulk-like water fraction turn out to be different for stabilizing and destabilizing osmolytes. For the destabilizing osmolytes urea and tetramethylurea the reorientation time constant is indistinguishable from that of pure water (2.5 ps), whereas for the stabilizing osmolyte trimethylamine-N-oxide (TMAO) remarkably faster dynamics are observed (1.5 ps).

The immobilized water fraction scales linearly with the osmolyte concentration. Moreover, the number of immobilized water molecules per osmolyte molecule is directly related to the hydrophobic nature of the osmolyte: approximately three water OH groups are immobilized for every methyl group contained in the osmolyte molecule. This unambiguously proves the existence of an ice-like solvation shell around hydrophobic groups.

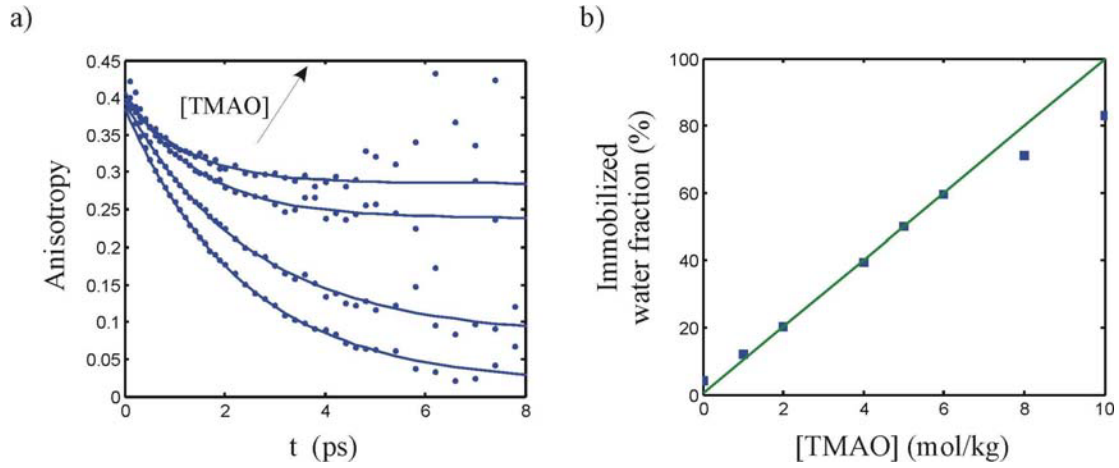

Figure 1: a) Anistropy decay of HDO molecules in aqueous trimethylamine-N-oxide (TMAO) solutions of varying concentrations. b) Fraction of immobilized water molecules as a function of TMAO concentration.

Melting of bulk ice on the picosecond timescale

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The structural changes of ice that undergoes melting are governed by the properties of the hydrogen-bonded network of the water molecules. The relaxation dynamics of the H-bonded groups include many elementary steps in the femtosecond and picosecond time domain. Obviously, the microscopic understanding of ice-water phase transition requires investigations of the process on ultrashort timescales.

We have performed an experimental study on the bulk melting of HDO:D_2O ice using a recently developed ultrafast temperature jump technique[1]. The OH-stretching vibration is applied for rapid energy deposition and heating of the ice lattice. The same mode is known as a fast and sensitive probe of local temperature and structure.

In our recent study on isotopically mixed ice we demonstrated that shock laser heating of bulk ice can avoid the common surface melting, leading to substantial superheating of the ice lattice[2]. For larger energy deposition ultrafast melting of bulk ice was observed for the first time[3]. For this process a time constant of 33 ps was determined, while the consumed energy amounts agree with the latent heat of melting (see Figs. 1A and B). Experimental evidence for the spectral properties of the molten species in HDO:D_2O ice is presented in Fig. 1C. The agreement with the well-known band-shape of liquid HDO:D_2O at 275 K (dashed line) is noteworthy. It is concluded that liquid water is formed within 15 ps.

Further details of the kinetics of bulk melting of ice will be presented and the mechanism of the melting process discussed.

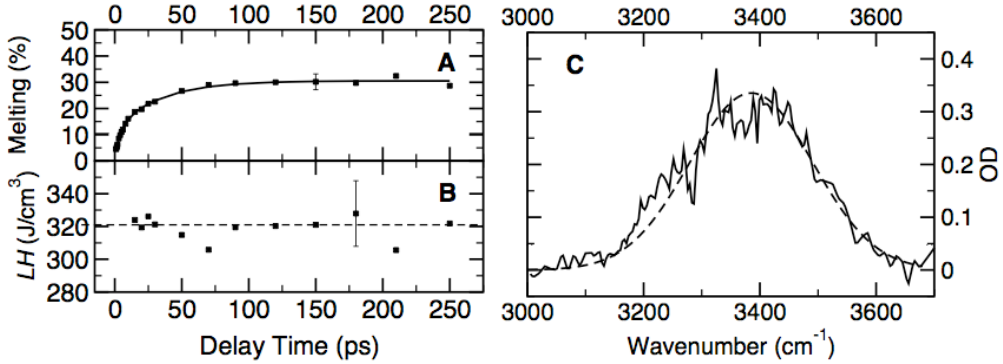

Figure 1. (**A**) Temporal evolution of the amount of molten liquid. (**B**) Transient latent heat *LH* consumed by the melting process compared to the steady-state value of 321 J/cm3 (dashed line). (**C**) Transient absorption spectrum of the molten component measured 15 ps after IR excitation of HDO:D2O ice (solid line). The steady-state spectrum of liquid HDO:D2O at 275 K is shown for comparison (dashed curve).

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Monday Morning Session

Biology II

Proton Transfer in Biological Systems Studied With Infrared Spectroscopy

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The fundamental chemical processes of proton and hydride transfers are biologically essential, and enzymes are very efficient catalysts for these reactions. The roles of protein dynamics and conformational changes in enzyme catalysis are highly debated, as are the role of specific amino acids and functional water molecules in so-called proton-wires.
In my talk I will present results on the light-driven chlorophyll biosynthetic enzyme NADPH:protochlorophyllide oxidoreductase (POR) which indicate that after binding of the substrates, a conformational change of the enzyme complex takes place that leads to coupled proton and hydride transfer taking place with a very high rate and efficiency.

In the second part of my talk I will discuss results from femtosecond visible pump/midIR probe experiments on Green Fluorescent Protein. The color of the fluorescent light emitted by GFP depends on a light-induced proton transfer reaction occurring in a 'proton-wire' that is formed by the chromophore, a water molecule (W22), S205 and E222. Our results yield new and surprising insights into the order of the proton transfer steps over the wire.

Events in the Photocycle of Proteorhodopsin: an Infrared Study

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Proteorhodopsin (PR) is the first eubacterial member of the type I retinal binding protein family[1]. Upon excitation the protein undergoes a photocycle with a series of distinguishable intermediates similar to that of bacteriorhodopsin (BR)[1,2,3]. It is suggested that PR functions as a light-driven ion-pump with variable vectoriality[3]. As for BR it is believed also for PR that the control of the deprotonation and reprotonation steps during the photocycle is important for the overall pumping activity of the protein.

We studied the primary dynamics of PR via ultrashort vis-pump infrared-probe spectroscopy by monitoring the marker bands at about 1540 cm^{-1} and 1630 cm^{-1}. The band at 1540 cm^{-1} corresponds to a C=C stretching vibration of the chromophore, reflecting the π-electron delocalization in the polyene part. In the region of 1630 cm^{-1} the C=N stretching vibrations of the chromophore can be observed. This mode is sensitive to the environment of the Schiff base linkage between the chromophore and the lysine[4]. The time resolved vibrational spectra show the formation of the red shifted PR_K intermediate via a biphasic decay of the S_1 state, which is in agreement with vis-pump vis-probe measurements[5]. Further studies of the C-C-stretch region at about 1200 cm^{-1} will reveal more information about the chromophore configuration. Currently pH-dependent measurements on wild type and site specifically mutated PR[6] are being performed to learn more about the molecular mechanisms of the primary steps in the photocycle.

Low temperature difference spectroscopy at pH 9, 7, 5 and 4 was performed similar to protocols reported before for BR or PR[7,8]. Under alkaline conditions we observed three different intermediates being in equilibrium with each other. The first difference signal belongs to a K intermediate also observed in ultrafast spectroscopy. The evolution of several marker bands (1756 cm^{-1}, 1742 cm^{-1}, 1555 cm^{-1}, 1541 cm^{-1} and 1516 cm^{-1}) represents the conversion to M. With rising temperatures, the appearance of a signal at 1556 cm^{-1} is assigned to the formation of a later intermediate. Under acidic conditions the spectral characteristics of the same three intermediates could be identified with different temperature characteristics than for pH 9. In contrast to kinetic studies[3,9,10] the M intermediate could clearly be observed. The reason for this could be of thermodynamic nature. The appearance of a M intermediate at acidic conditions is a further indication of the vectoriality of PR.

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Primary charge separation in PS2 core from *Synechocystis*: a comparison of femtosecond visible/mid-IR pump-probe spectra of wild type and two P_{680} mutants.

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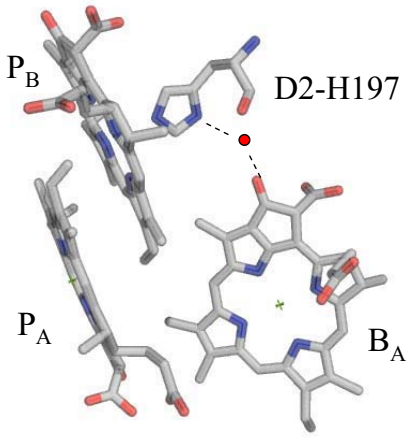
The process of primary charge separation in PS2 core from the photosynthetic bacterium *Synechocystis* PCC 6803 has been studied by femtosecond visible/Mid-IR pump probe spectroscopy upon excitation at 680 nm. It is now quite well accepted that the primary donor in PS2 core is not the special pair P_{680}, but the accessory chlorophyll B_A.[1] In order to identify spectral signatures of B_A, and to better clarify the process of primary charge separation, we have compared the femto-IR pump-probe spectra of the wild type PS2 core with those of two mutants, in which the histidine residue coordinated to P_B (D2-H197) has been changed to alanine or glutamine. Since the mutated histidine is indirectly H-bonded to the putative primary donor B_A through a water molecule, the mutation is expected both to perturb the vibrational properties of B_A, possibly by displacing the H-bonded water molecule, and to modify the electronic properties and the cation localization on P_{680}. The comparison of steady state light-induced FTIR difference spectra of the wild type and the D2-H197A mutant indeed showed that the modification of the coordinating ligand on P_B induces a charge redistribution on P_{680}^+. The femto-IR spectra of wild type and both the mutants showed differences in the region where the 9-keto carbonyls of P_{680} and of B_A are expected to absorb, allowing the identification of spectral signatures attributable to the perturbation of the H-bond on B_A.



Structural arrangement of P680 and the monomer Chl located on the D1 branch of PS2 cores, showing the mutated histidine coordinated to P_B

[1] M.L. Groot, N.P. Pawlowicz, L.J.G.W. van Wilderen, J. Breton, I.H.M. van Stokkum, R. van Grondelle, Proc. Natl. Acad. Sci. U.S.A., **2005**, 102, 13087-13092

Watching DNA Get "Sunburned"

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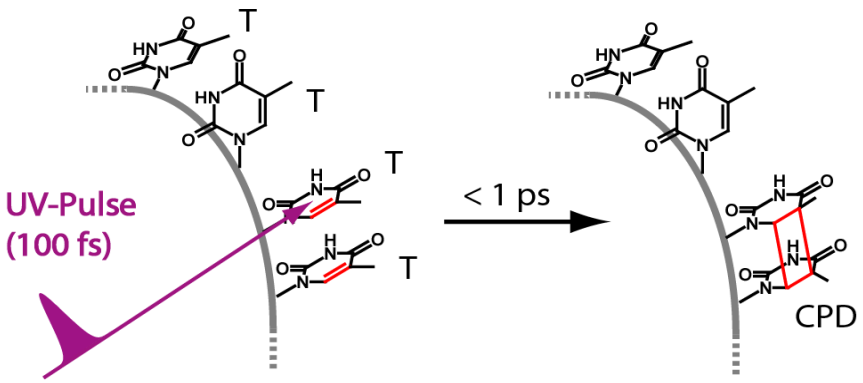
DNA, the carrier of genetic information, is constantly subject to internal and external hazards. One of the external hazards is the UV light to which one is exposed when sunbathing. UV light is absorbed by the DNA bases and can induce hazardous photoreactions. Among the various photoproducts the CPD (cyclobutane pyrimidine dimer) lesion is the most abundant. It can form if two thymine (T) bases are adjacent in a DNA strand. These combine in a [2+2] photoaddition to yield the CPD (see figure). The formation of this lesion has been reported more than forty years ago[1]; yet, its kinetics has only been resolved very recently[2].

We have employed femtosecond UV pump IR probe spectroscopy to time resolve the formation of the CPD lesion. These experiments have proven to be very challenging, since even under ideal conditions (in terms of the measurement, not in health terms) the quantum yield of the dimer formation amounts to only a few percent. Most of the photo-excited bases rapidly decay non-radiatively and this decay dominates the femtosecond IR spectra. Weak signatures of the CPD formation can easily be obscured. Our approach to detect the formation has been to record the femtosecond IR spectra of a single thymine base (TMP) and that of a DNA single strand containing 18 thymine bases (dT_{18}). Since TMP only features the signature of the rapid non-radiative decay, subtracting the TMP data from dT_{18} data isolates the signature of the dimer. In this difference representation three distinct IR bands appear between 1300 and 1500 cm^{-1}. A steady-state illumination experiment unequivocally assigns these bands to the CPD. These markers are already discernible one picosecond after UV excitation and virtually do not change thereafter. This proves that the photo-reactive state is the primarily excited singlet $\pi\pi^*$ and not longer lived secondary states (singlet $n\pi^*$ or triplet states). The short time scale of the reaction implies that the CPD lesion only occurs if the two thymines adopt a favorable relative conformation *prior* to photoexcitation (see Figure). In that sense the helical arrangement of the bases in duplex DNA has a protective effect – photo-reactive conformations are rare here.



Schematic of the formation of the CPD lesion. Only thymines with a suitable conformation (the lower two here) are reactive.

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Investigation of the Z → E Isomerization of a Hemistilbene/Hemithioindigo Based Peptide-Switch with Ultrafast Infrared Spectroscopy

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Photoinduced isomerizations are intensively studied reactions due to their importance in chemistry and biology[1]. Systems containing conjugated double bonds (e.g. stilbene, hexatriene) are used as model systems for Rhodopsin or Carotinoids to investigate ultrafast photoreactions. It could be shown, that the novel photochromic HTI-molecules are suitable to act as ultrafast light trigger in chromopeptides[2].

As a first characterization the molecular photoreaction Z→E (Fig.1, upper part) was investigated with pump-probe spectroscopy in the visible. Using this method, all states, which are involved in the reaction could be observed. A fast component (Fig.1. lower part: τ_1, 1 ps range) is assigned to the relaxation of the excited Franck-Condon species with subsequent re-arrangement of the solvent shell. The slower components (Fig.1. lower part: τ_2, 10 ps range; τ_3, 30 ps range) are motions of the molecule on the excited state potential surface and relaxation into the ground state of either educt or product. The assignment of the different states to specific molecular structures seems impossible, via visible spectroscopy, thus the progression of involved states (Fig.1. lower part, sequential vs. branched) is still unknown[2].

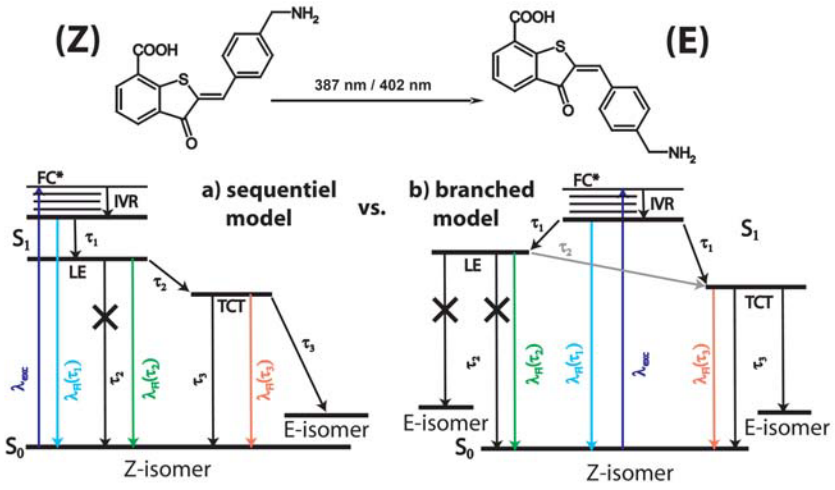

Figure 1 Schematical drawing of the photoreaction and possible state modells

The obtain a deeper insight transient fluorescence and infrared spectroscopy was applied to the system. Transient fluorescence allows to follow the dynamics of the excited state exclusively. Very important information can be obtained using time resolved infrared spectroscopy, because it is possible to reveal the timescale of product formation. The transient IR-data in the Carbonyl-region shows only two time constants (τ_1 and τ_3), this fact proscribes the transition from the excited state to the educt ground state within τ_2.

Combing time resolved infrared spectroscopy with visible methods leads to a limitation of possible state models of the Z→E photoisomerisation of HTI-molecules. The IR-data significantly improves the formerly derived state model and makes it possible to assign the chemical and physical nature to the involved states which are namely Franck-Condon (FC*), locally excited (LE) and twisted charge transfer (TCT).

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Real-time monitoring of biological processes inside a living cell by functional CARS microspectroscopy

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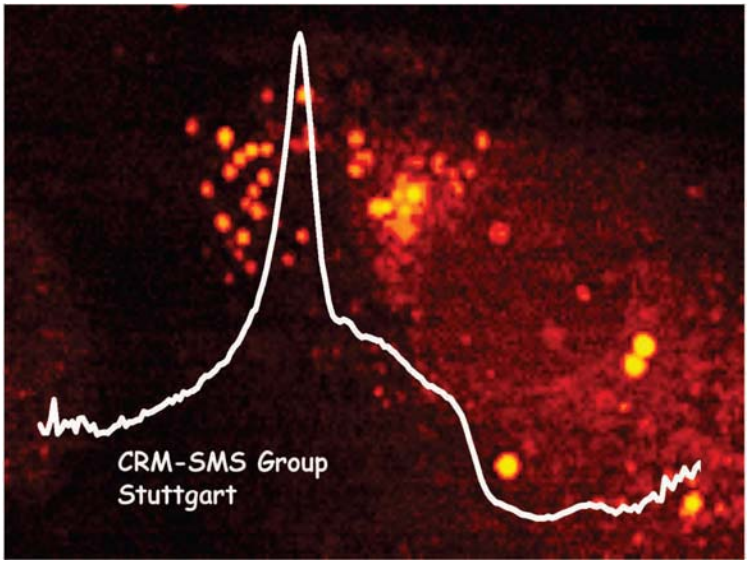
A series of recent advances have made coherent anti-Stokes Raman scattering (CARS) microscopy a powerful tool in the material and life sciences. It allows the noninvasive vibrational characterization of chemical species or biological components within a complex heterogeneous system, e.g. a living cell, with high detection sensitivity, high spatial resolution, and three-dimensional sectioning capability[1].

By going beyond vibrational imaging that has been the predominant realization of CARS microscopy to date, our efforts have been focused on the application of high-sensitivity multiplex CARS microspectroscopy, which offers the possibility for space- and frequency-resolved vibrational spectroscopy, thus providing access to the full wealth of the spectroscopic information content of macromolecular objects on the sub-micron length scale with typical data acquisition times below 100 ms. Combined with a detailed CARS spectral analysis, this vibrational microspectroscopy allows the noninvasive and quantitative chemical examination of slow dynamical processes inside a living cell occurring on time scales of seconds to hours. Here, we demonstrate the feasibility of monitoring the time evolution of the C-H stretching Raman response from individual intracellular lipid droplet organelles inside a living NIH3T3-L1 adipocyte cell. This *in vivo* study aims to address the chemical dynamics of lipolysis involved in lipid droplet metabolism that are currently not possible to address with conventional techniques in a non-destructive manner.



Noninvasive intracellular CARS imaging and microspectroscopy of individual lipid droplet organelles inside a living NIH 3T3-L1 fibroblast cell.

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Monday Afternoon Session

Theory

Relation between frequency and H bond length in heavy water

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The published work on H bond dynamics mainly refers to diluted solutions HDO/D_2O rather than to normal water[1]. The reasons for this choice are both theoretical and experimental. Mechanical isolation of the OH vibrator eliminating the resonant energy transfer makes it a better probe of the local H bond network, while the dilution in heavy water reduces the infrared absorption, which permits the use of thicker experimental cells. The isotopic substitution does not alter crucially the nature of the problem. The water dynamics is still the subject of intense theoretical [2] and experimental[3] studies. The length r of an OH…O group is statistically distributed over a large interval comprised between 2.7 and 3.2 A with a mean value r_0 = 2.86 A. Liquid water may thus be viewed as a mixture of hydrogen bonds of different length. Two important characteristics of hydrogen bonding must be mentioned. (i) The OH stretching vibrations are strongly affected by this interaction. The shorter the length r of the hydrogen bond, the strongest the H bond link and the lower is its frequency: the covalent OH bond energy is lent to the OH..O bond and reinforces the latter. A number of useful relationships between ω and r were published to express this correlation. The one adopted in our previous work is the relationship due to Mikenda[4]. (ii) Not only the OH vibrations, but also the HDO rotations are influenced noticeably by hydrogen bonding. This is due to steric forces that hinder the HDO rotations. As they are stronger in short than in long hydrogen bonds, rotations are slower in the first case than in the second. This effect was only recently discovered, but its existence is hardly to be contested.[5] In the present contribution, we want to revisit the relationship between the frequency of the OH vibrator and the distance OH..O from the theoretical point of view . Our theory is based on the observation that the geometry of a disordered system is a statistical notion. The structure of a macroscopic body may be defined by giving the positions of all atoms, but a virtually infinite amount of data would be required. The fact that the atoms are continuously moving complicates the situation further. A statistical definition of molecular geometry is thus preferable. The usual approach consists in introducing various atom-atom distribution functions, in particular the two-, three- or four-atom distribution functions. Although they do not define the structure of the body completely, they provide a picture of its local structure. This approach is well adapted to study the geometry of OH...O bonds in diluted HDO/D_2O solutions.

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Vibrational Energy Transfer through Molecular Chains

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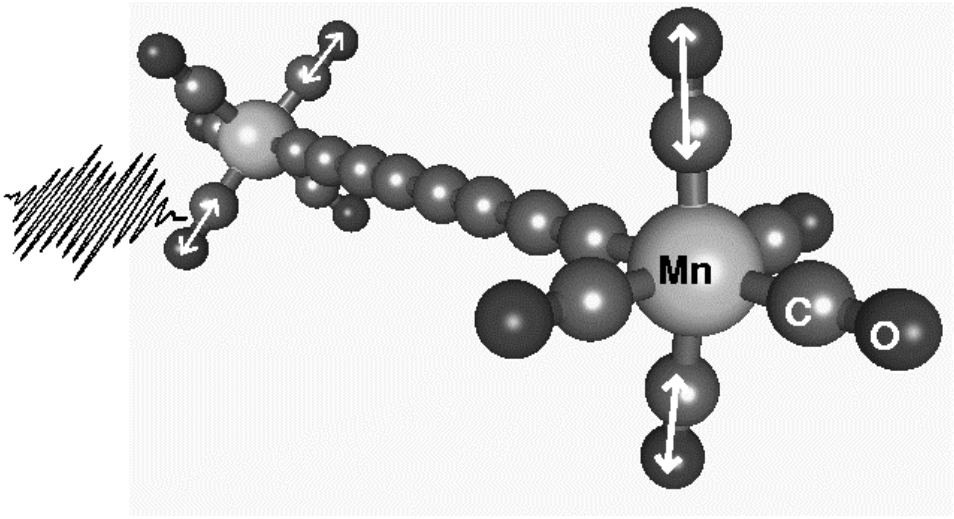
Molecular bridge systems as octatetrayne offer an innovative possibility to realize the scalability of our approach of molecular quantum computing with vibrational qubits[1] and to construct quantum networks. Within this concept the chain molecules represent the units, essential for the transfer of vibrational energy, which can be regarded as quantum information transfer between different end groups that represent the qubit sub units.

The selected linear molecular chain consists of C-C single and triple bonds and the corresponding model is constructed as a set of kinetically coupled oscillators. Their frequencies and coupling strength are obtained from quantum chemical calculations. For the quantum dynamical investigations we transfer the system into an eigenstate representation.

Especially, we focus on the dynamics and the mechanisms of intramolecular vibrational state transfer from one end group to the other, which is induced by specially shaped ultrashort laser pulses in the IR regime. The optimal laser fields for different end groups are calculated with Optimal Control Theory (OCT). Different quantum channels are detected from the analysis of the optimized laser pulses and the corresponding mechanisms. By introducing a spectral shape function in the OCT functional the population transport can be optimized through several distinct channels.

Furthermore, possible applications of the bridging molecules within the concept of vibrational quantum computing are given.



Vibrational energy transfer through molecular chains induced by specially shaped ultrashort laser pulses.

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Ultrafast Internal Conversion Processes for Excited Solvated Electrons for Clusters and the Bulk.

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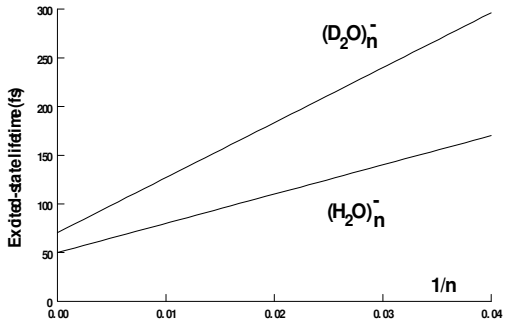
The nonadiabatic coupling is evaluated for electronically excited anionic clusters like $(H_2O)^-_n$, $(NH_3)^-_n$ and $(CH_3 - OH)^-_n$ as a function of the cluster size. The nonadiabatic coupling is represented in terms of a Förster-type transition dipole to transition dipole coupling and it is shown that a universal law for the lifetime can be derived which has the form (see figure) $\tau(n) = \tau(\infty)\left(1+\frac{\alpha}{n}\right)$ with the bulk value $\tau(\infty)$ and a value for $\alpha = 10.5\, a^3\rho$, where a represents the electronic radius for the equilibrium configuration within the excited p-like state and ρ is the density of the states.

For the bulk value $\tau(\infty)$ we find the rate of expression

$$\tau^{-1}(\infty) = \frac{8\pi}{9\hbar}\frac{\rho}{a^3}\frac{(\mu^v)^2(\mu^v)^2}{\sigma}\exp\left\{-\frac{(E-\lambda-\hbar\omega)^2}{2\sigma^2}\right\}$$

with the IR transition dipole μ^v of the dominant IR active mode ω, which is in the case of water the O-H- streching mode and in the case of NH_3 a bending mode. λ is the reorganization energy and σ^2 the mean square fluctuation.

All these parameters are evaluated by quantum calculations [1] and continuum models [2,3] Comparisons with various experiments by Laubereau et al[4]., Wiersma et al., [5] Neumarkt et al[6]., Vöhringer et al[7]., are discussed.



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Fifth-order nonlinear spectroscopy (3D-IR) to probe non-Gaussian stochastic processes

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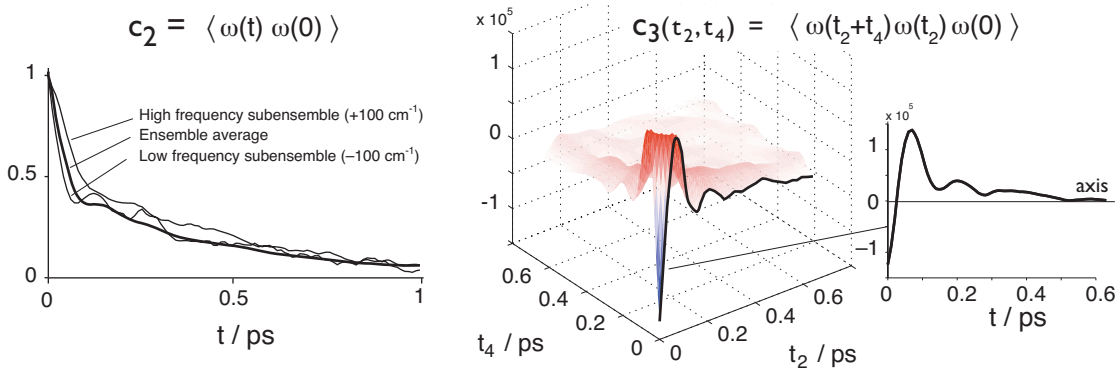
When the fluctuations of a stochastic process are Gaussian, then a 2-point correlation function completely characterizes the dynamics. Higher-order correlation functions are either zero (odd orders) or factor into 2-point correlation functions (even orders). For example, the fluctuations of the electronic transitions of a choromophore in solution are often Gaussian because it is coupled electrostatically to many molecules and the central limit theorem applies. The vibrational dynamics of an oscillator, however, and especially a hydrogen-bonded one, are governed by local interactions. The vibrator feels the hydrogen-bonding partner strongly, the first solvent shell weakly, and further solvent shells negligibly. To assume Gaussian statistics for a hydrogen-bonded OH stretch is clearly not valid, so there must be more to the dynamics than the 2-point frequency fluctuation correlation function.

Non-linear spectroscopies can be classified in terms of higher order frequency fluctuation correlation functions[1] – certain moments of the multidimensional spectra give the multipoint correlation functions. This classification is rigorous in the inhomogeneous limit, and remains approximately valid when motional narrowing is important. In this classification, 1D (linear) spectroscopies are sensitive only to the first and second moments of the frequency distribution $\langle\omega\rangle$ and $\langle\delta\omega^2\rangle$, where $\delta\omega$ is the deviation of the frequency from its average; third-order spectroscopies (e.g. 2D-IR and vibrational echo experiments) are sensitive to 2-point correlation functions $c_2 = \langle\delta\omega(t)\delta\omega(0)\rangle$; and fifth-order experiments (3D-IR) should be sensitive to 3-point correlation functions such as $c_3 = \langle\omega(t_2+t_4)\omega(t_2)\omega(0)\rangle$.

Langevin dynamics on model free-energy surfaces and molecular dynamics simulations of SPC water show the information content potentially available in these 3-point correlation functions. The Langevin trajectories show that processes with identical 2-point correlation functions may have distinguishable 3-point correlation functions, and the MD simulations show how the instantaneous dynamics of an OH vibrator depend on its local environment and can be measured in the dynamical skewness of the 3D spectrum.



2- and 3-point correlation functions from MD simulations of SPC water. The 3-point correlation function reverses sign (from negative to positive) because of the faster vibrational dephasing on the red side of the absorption line, indicating the faster dynamics in stronger hydrogen bonds.

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Mixed Frequency/Time Domain Coherent Multidimensional Vibrational Spectroscopy and Coherence Transfer Spectroscopy

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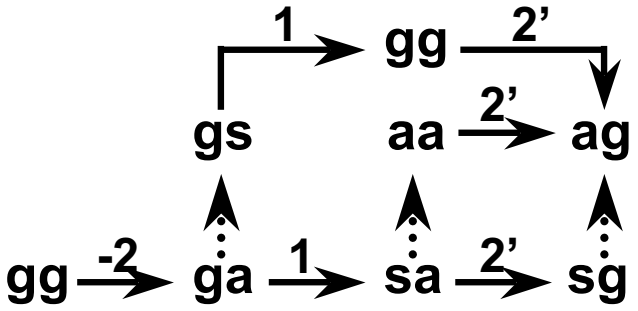
Coherent light creates quantum entanglements between the vibrational states that preserve the quantum mechanical phase information. The very large electric fields of focused electromagnetic fields entangle vibrational states so one can observe how the excitation of one state affects other states that are coupled to it by intra- or intermolecular interactions. These multiply entangled quantum states form the basis for a new family of coherent multidimensional spectroscopies that are analogous to multidimensional NMR but work with electronic and vibrational states. Often, these methods are based on time domain spectroscopy. In this talk, we will describe a mixed frequency/time domain approach that resolves the individual states involved in the coherent processes and allows one to follow the evolution of these entangled vibrational states to form new quantum entanglements by the process of coherence transfer. Coherence transfer is the coherent counterpart (i.e. it retains the quantum mechanical phase) of population relaxation and dephasing (T_1 and T_2 in NMR) and it is part of the Redfield relaxation tensor that is seldom probed because there have been no direct measurement methods to probe it. We show how the equivalent pathways for forming the entanglements interfere to create diffraction patterns analogous to the quantum mechanical 2 slit experiment. We also show how one can suppress the pathways that do not involve coherence transfer so the states undergoing transfer are isolated. Coherence transfer forms the basis for new coherent multidimensional spectroscopies where the output frequency is shifted so it can be spectrally distinguished from the excitation frequencies.



Example coherence transfer pathways for triply vibrationally enhanced four wave mixing where coherence transfer occurs between the symmetric and asymmetric vibrational states of a dicarbonyl and tricarbonyl metal chelates.

Vibrational dephasing in confined myoglobin

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Solvent confinement can influence both reactivity and structure of a solute. Confined water is ubiquitous in biological environments, in certain glasses, and in synthetic structures. Multidimensional infrared spectroscopy has the capacity to probe the effect of solvent confinement on the motions of a protein in solution. Infrared echo measurements on heme proteins in several glassy environments[1,2] have demonstrated that the vibrational dephasing of the CO ligand is sensitive to the degree of solvent confinement. We have calculated[3] frequency-resolved three-pulse vibrational echoes for the myoglobin mutant H64V in liquid water and in confined aqueous environments, to explore the extent to which protein dynamics are controlled by solvent relaxation. The H64V mutant lacks the distal histidine residue that interacts most strongly with the CO ligand in the wild type protein and hence models the interaction of the CO vibration with the rest of the protein and with the solvent in the wild type species. Our calculations employ a model in which the CO vibration is coupled to electrostatic forces generated by the protein and solvent, with the time-dependence of these forces determined from molecular dynamics simulations of H64V-CO in a solvent of discrete water molecules. When the protein in solvated by static water molecules or by a single mobile water layer surrounded by a static solvent, the CO vibration in H64V-CO dephases by interaction with rapid, harmonic protein motions. Slower protein motions present in liquid solution are not permitted by the solvent in these confined cases. By contrast, H64V solvated by two mobile water layers shows an echo signal similar to that for a liquid solvent, despite the restricted nature of the water dynamics. Translational and rotational dynamics of water molecules in this confined case are substantially hindered relative to motions in the first two water layers solvating the protein in liquid water, but these restricted solvent dynamics are sufficient to allow the protein to relax on the experimental time scale.

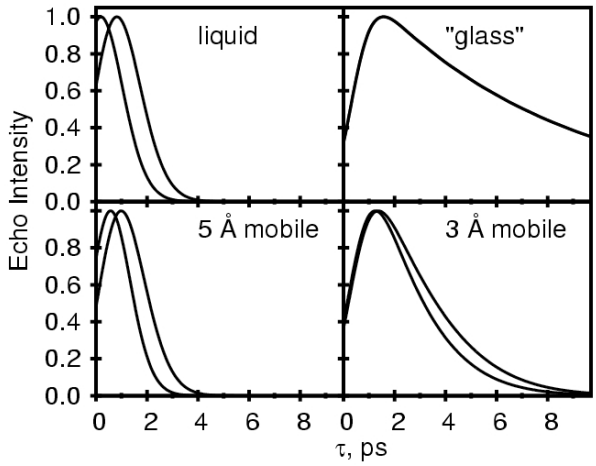

Figure. Three-pulse vibrational echo signal is calculated for the myoglobin mutant H64V for T_W=0 and 8 ps for a liquid water solvent, for a solvent of static water molecules and for solvation by either one or two mobile water layers. The first and second delay times are denoted respectively τ and T_W.

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Tuesday Morning Session

Chemistry

Structural change during ultrafast photoisomerization of *cis*-stilbene monitored through nuclear wavepacket motion

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Stilbene is a prototypical molecule showing photoisomerization. It is known that isomerization from the S_1 *cis* isomer proceeds within a few picoseconds in a nearly barrierless way, whereas isomerization from the S_1 *trans* takes about a hundred picoseconds in solution. We recently carried out pump-probe measurements of *cis*-stilbene with 40-fs time-resolution, and observed a wavepacket motion (~220 cm^{-1}) of the S_1 state[1]. The dephasing time of the motion was much shorter than the isomerization time, implying that the ~220 cm^{-1} motion is not directly correlated with the reaction coordinate. Its fast dephasing indicated a highly anharmonic nature of the potential energy surface (PES) of S_1 *cis*-stilbene. In this pump-probe experiment, we observed the nuclear wavepacket motion in the vicinity of the Franck-Condon region in the S_1 PES because the wavepacket motion was induced by $S_1 \leftarrow S_0$ photoexcitation.

To know more about reactive PES of *cis*-stilbene, we carried out TR-ISRS experiments[2]. In this experiment, the S_1 state is generated by the uv pump pulse, and the wavepacket motion is induced in the S_1 state by the impulsive Raman process at a certain delay time (ΔT). The resultant wavepacket motion is observed by the third pulse as the oscillation of the transient absorption intensiy. We observed the ~220-cm^{-1} motion also in this experiment. Interestingly, Fourier analysis showed that the frequency of the wavepacket motion significantly changes with the delay time: 239 cm^{-1} (ΔT=0.3 ps) $\rightarrow$ 224 cm^{-1} (1.2 ps) $\rightarrow$ 215 cm^{-1} (2 ps). The frequency of the wavepacket motion is determined by the curvature of the S_1 PES along the corresponding coordinate. Therefore, the temporal frequency shift indicates that the relevant curvature of the S_1 PES changes with time. We considered that it reflects a structural change occurring along another coordinate that is anharmonically coupled with the ~220 cm^{-1} mode. The solvent dependence of the temporal frequency shift suggested that this structural change is closely related to the isomerization coordinate.

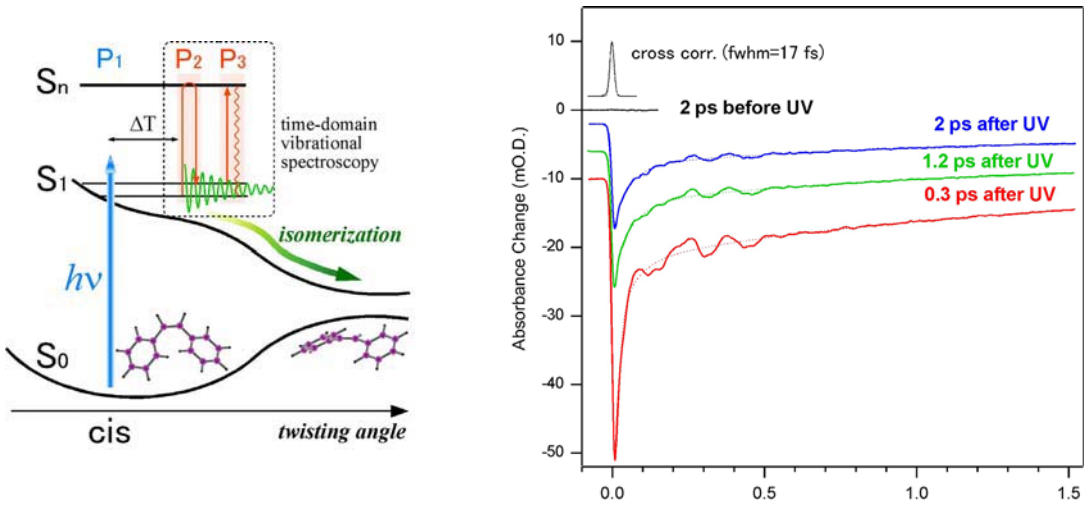

Fig.1 Scheme of TR-ISRS measurement (left) and the data of *cis*-stilbene in hexadecane (right).

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Base-Induced Solvent Switches in Acid-Base Reactions

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Modern discussions of acid-base reactions have evolved from the seminal studies of Eigen and Weller[1,2]. The general kinetic approach for acid-base reactions in aqueous solutions consists of three reaction branches[2]: (a) direct proton exchange between acid and base, (b) acid dissociation to solvent followed by proton scavenging by the base, and (c) water hydrolysis by the base followed by the neutralization reaction of the acid by the hydroxyl anion. Judging by the magnitude of the reaction radius in typical (diffusion-controlled) acid-base reactions it has been estimated that up to 2-3 water molecules separate when acid and base exchange a proton through pathway (a)[1]. In reality, however, this value is likely to be an averaged value of several encounter complexes (with n rearrangements steps) leading to proton transfer.

Proton transfer reactions have to be treated in the context of chemical equilibria, i.e. forward and backward reaction steps. Photoacids can be used as a means to follow proton transfer dynamics to a neutralising base in real time by photoinitiation. The outcome of the observed dynamics, i.e. the reaction rates and yields depend on the relative strengths and concentrations of acid and base. We have investigated the aqueous neutralization reaction of the photoacid pyranine and carboxylate bases ($^{-}OOCCH_{3-x}Cl_x$) (x = 0-3). Here we are able to dictate the outcome of the reaction dynamics by tuning the number of chlorine atoms x.

We have identified, using femtosecond infrared spectroscopy, two innermost types of encounter complexes (tight and loose), resulting in a sub-150 fs proton dissociation lifetime of the photoacid[3-5]. The proton transfer in both encounter complexes is found to be reversible. The step-wise, von-Grotthuss type[4-5], proton transfer in loose complexes involves a first step leading to a H_3O^+ like cation resembling the proton solvation core in the Eigen cation, $H_9O_4^+$, and a second and final transfer to the base on much slower picosecond time scales. The stability of the hydrated proton in the loose complex increases with decreasing reactivity (basicity) of the carboxylate base as measured in bulk water.

We have applied a unified reaction dynamics model in which we have approximated all possible configurations between acid and base by tight (n = 0), loose (n = 1) and solvent switch (n > 1) complexes, as well as acid and base fully separated by the solvent. Whereas the fully separated acid and base first have to diffuse, all other complexes are connected to each other through reversible proton transfer steps. Step-wise proton shuttling through water provides a route for proton transfer which circumvents further desolvating the acidic and basic groups necessary for direct transfer. We find that for HPTS and trichloroacetate (x = 3), the weakest of investigated carboxylate bases, the bulk of the proton transfer reaction occurs through n > 1 solvent switches[5], in contrast to the stronger bases where the observed kinetic data can be reproduced without the larger solvent switches, confirming our previous reports using less general kinetic models[3,4].

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Long-range proton transfer in aqueous acid-base reactions

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We studied the mechanism of proton transfer in aqueous environments between the photoacid 8-hydroxy-1,3,6-pyrenetrisulfonic acid (HPTS) and acetate with femtosecond visible-mid-infrared pump-probe spectroscopy. By directly probing the vibrational absorption of the proton, we were able to follow the trajectory of the proton from the HPTS donor to its eventual position on the acetate acceptor.

We observe a strong isotope effect of 1.5 in the rate at which the proton/deuteron is taken up by the acetate. This isotope effect is much larger than would be expected if the reaction rate would be controlled by mutual diffusion of HPTS and acetate. In that case the somewhat more viscous solution of acetate in D_2O would have slowed down the reaction by only 5%. The isotope effect of 1.5 is the same as the ratio of the proton/deuteron mobilities in pure H_2O/D_2O, for which proton/deuteron transfer has been found to occur via Grotthuss conduction. In addition, we observe that >50% of the proton transfer events occur on a time scale (< 10 ps) that is fast in comparison to the time scale required for HPTS and acetate to diffuse into contact. These observations indicate that the transfer of a proton between HPTS and acetate dissolved in water takes place via the same mechanism as proton transfer in pure liquid water: via Grotthuss conduction through a hydrogen-bonded water wire.

In a recent study, evidence was found that the reaction between HPTS and chloro-acetate involved an intermediate reaction complex in which the acid and the base are separated by one water molecule[1]. Here we find that there are, in fact, many different reaction complexes that differ in the number of water molecules separating the acid and the base. In the base concentration range of 1 to 4 M, ~90% of the proton/deuteron transfers takes place via water wires that vary in length from 1 to 4 water molecules.

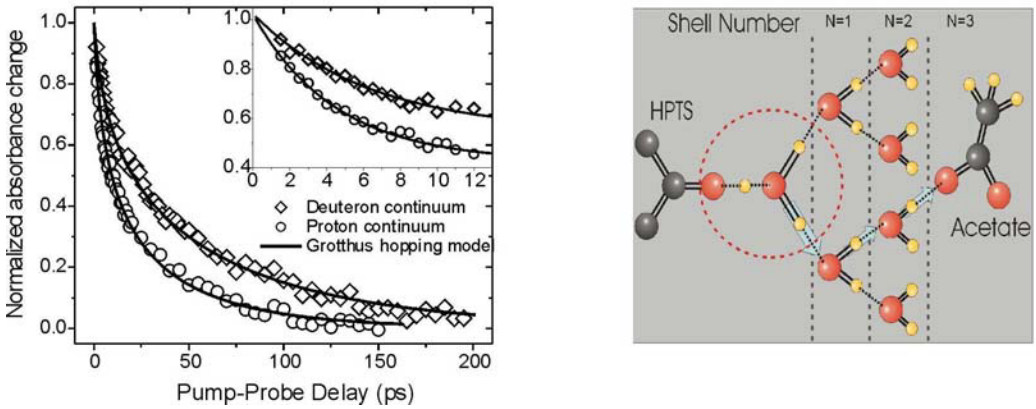

Figure 1 : Decay curves for the proton and deuteron continuum in 10 mM HPTS, 2 M acetate solutions in H_2O/D_2O. Early time dynamics (inset) are fit to single exponentials functions. The single exponential time constants are 4.5 ps (proton) and 6.3 ps (deuteron), showing an isotope effect of ~1.5. The solid curves are calculated using the Grotthuss hopping model illustrated in the right panel.

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Femtosecond IR Studies of Transients in Azides, Diazo Compounds, and MM Quadruply-Bonded Dinuclear Metal Complexes

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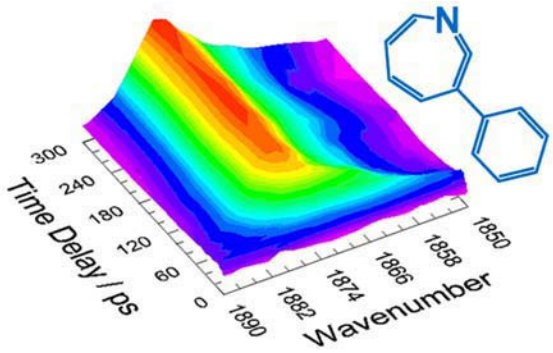
We are using fs UV/Vis and fs IR spectroscopy to probe the structure and dynamics of photogenerated intermediates in three important classes of molecules: azides[1-3], diazo compounds[4,5], and MM quadruply-bonded dinuclear metal complexes[6]. The combination of ultrafast electronic and vibrational spectroscopies provides a comprehensive picture of the important intermediates formed following photoexcitation. In this work we present our most recent investigations.

We have been investigating the intermediates formed following photoexcitation of aryl azides and diazo compounds[1-5]. The excited state of the parent molecules typically lives for ~300 to 700 fs before the extrusion of molecular nitrogen. The resultant singlet nitrene (from the azides) or singlet carbene (from the diazo compounds) can undergo a variety of processes, including intersystem crossing to the triplet, reaction with solvent, or other chemical transformations. Using fs transient IR we have observed the direct formation of ketenimine from hot phenylnitrene and *ortho*-biphenylylnitrene. (See figure.) The rise of the characteristic ketenimine vibration at ca. 1890 cm^{-1} is consistent with the decay time of the corresponding singlet nitrene, as observed using fs UV/Vis spectroscopy.



Femtosecond transient IR spectrum of the ketenimine formed following photoexcitation of *ortho*-biphenylyl azide in acetonitrile. (Pump: 270 nm)

We have observed the singlet metal-to-ligand charge transfer state (^{1}MLCT) in a series of MM quadruply-bonded dinuclear metal complexes (M = Mo, W) with aryl ligands bound to the metal center via carboxylate linkages[6]. The ^{1}MLCT state in these complexes lives for ca. 10-30 ps, owing to the coupling between the metal center and the ligand through the carboxylate group. The vibrational spectrum of the carboxylate linking group provides new insight into the coupling between the ligand and metal center in the ^{1}MLCT state.

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Photoinduced Bimolecular Electron Transfer Investigated by Femtosecond Time-Resolved Infrared Spectroscopy

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Since the pioneering work of Weller and coworkers[1,2], bimolecular photoinduced electron transfer (ET) reactions have been intensively investigated. These processes are the simplest bimolecular reactions and have thus been object of many theoretical treatments. Furthermore, they play an important role in many areas of chemistry and biology and are involved in several practical applications such as solar energy conversion, and photopolymerization. Despite the numerous studies carried out on bimolecular ET, important questions still remain unanswered[3], such as the nature of the primary ET quenching product and the various steps leading to the formation of free solvated ions in polar solvents.

A major experimental problem is that ion pairs and free ions cannot be easily differentiated from their electronic absorption spectra. Here, we report on an investigation of the bimolecular ET quenching reaction of the electron donor perylene (Pe) and the acceptors 1,4-dicyanobenzene (DCB), and tetracyanoethene (TCNE) in acetonitrile and dichloromethane using time-resolved IR spectroscopy. Following vibrational marker modes on both donor and acceptors sides in real time provides direct insight into the structural dynamics during the reaction. By recording transient IR absorption spectra of the radical ions generated upon photoinduced ET and analyzing height and width of the corresponding bands, we can directly follow the generation of both products under identical conditions, which is often difficult to impossible in all-visible experiments. With this approach we are able to distinguish strongly and weakly coupled ion pairs in the bimolecular electron transfer reaction.

With DCB as acceptor a band narrowing on a time scale of a few tens of picoseconds observed on the antisymmetric CN stretching vibration of the DCB radical anion indicates that a substantial part of the excess energy is dumped into vibrational modes of the product, despite the fact that the reaction is weakly exergonic. An additional narrowing of the same band on a time scale of several hundreds of picoseconds observed in acetonitrile only is interpreted as a signature of the dissociation of the geminate ion pairs into free ions[4].

Using TCNE as acceptor the obtained transient spectra clearly show two distinct components, permitting for the first time to clearly distinguish two independent sub-populations of the reaction product, strongly and weakly coupled ion pairs. The tightly coupled pairs originate from ultrafast “static” ET quenching and recombine to the neutral pair shortly after ET. The weakly coupled pairs are formed by diffusional quenching, undergo slower recombination and, thus, lead to free solvated ions. The relative yield of these sub-populations strongly depends on the TCNE concentration.

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Population and coherence dynamics of vibrationally excited states in perylene dyes in solution

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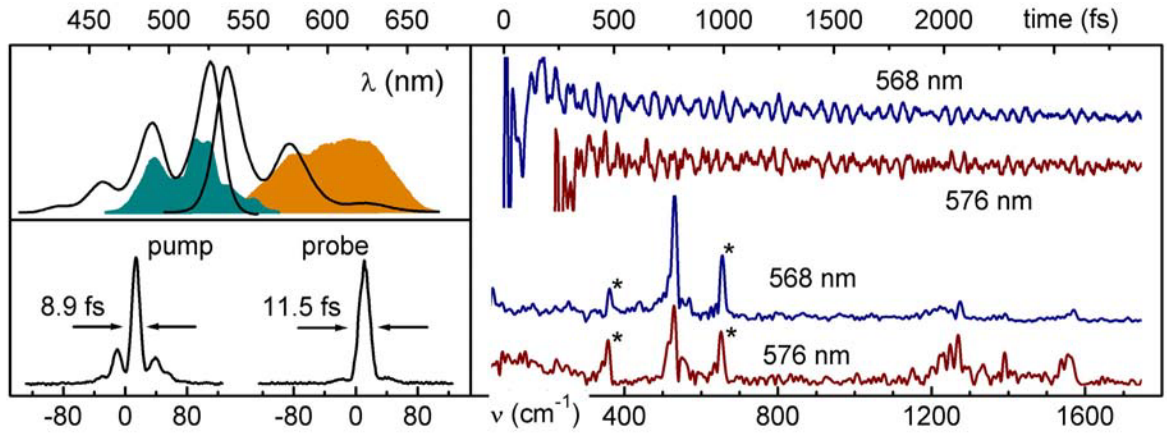
We investigate with femtosecond pump probe spectroscopy the interplay between the intramolecular redistribution of vibrational energy and the decoherence of coherently excited vibrations in perylene dyes in solution. In a first experiment selected vibronic transitions of the perylene bisimide dye S-19[1] are directly excited and sampled with two suitably tuned 45 fs pulses each matching a vibronic band of the absorption and emission spectrum. To reveal the population dynamics of the vibrational levels in the electronic S_1 state time traces of the stimulated emission are recorded from which a vibrational decay time of 1.3 ps is derived.

In a second set of experiments a wavepacket is prepared as a superposition of vibronic transitions using nearly Fourier limited ultra-broadband light pulses covering two vibronic bands in the absorption or emission spectrum (see left part of the figure). For the pulse compression custom designed chirped mirrors are used under Brewster's angle incidence[2] in combination with a fused silica prism pair.



Absorption and emission spectrum of S-19 and spectra of the pump and probe pulses (upper left panel). Autocorrelations of the pulses (lower left panel). Transient transmission changes detected at two different wavelengths selected with a fused silica prism (upper right panel). Fourier transforms of the time traces (lower right panel). The modes marked with an asterisk are attributed to chloroform vibrations.

With the reduced duration of 8.9 fs for the pump pulse centered at 510 nm and 11.5 fs for the probe pulse centered at 615 nm the time resolved stimulated emission contains oscillatory contributions up to 1600 cm^{-1} (see figure). They can be identified as vibrational modes of the dye[3] and the solvent molecules. From the damping of the oscillations a coherence lifetime for the different modes between 1.1 ps and 1.6 ps is derived. Since these numbers are very similar to the vibrational population lifetime we can conclude that pure dephasing and vibrational redistribution and/or relaxation contribute about equally to the dephasing of the vibronic wavepackets.

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Tuesday Afternoon Session

Biology III

Following photoinduced dynamics in bacteriorhodopsin with 7 fsec impulsive vibrational spectroscopy

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Sub ten fsec laser pulses are used to impulsively photoexcite bacteriorhodopsin suspensions, and probe the evolution of the resulting vibrational wave packets. Fourier analysis of the spectral modulations induced by transform limited as well as linearly chirped excitation pulses, allows the delineation of excited and ground state contributions to the data. On the basis of amplitude and phase variations of the modulations as a function of the dispersed probe wavelength, periodic modulations in absorption above 540 nm are assigned to ground state vibrational coherences induced by Resonance Impulsive Raman Spectral activity (RISRS). Probing at wavelengths below 540 nm - the red edge of the intense excited state absorption band - uncovers new vibrational features which are accordingly assigned to wave packet motions along bound coordinates on the short lived reactive electronic surface. They consist of high and low frequency shoulders adjacent to the strong C=C stretching and methyl rock modes respectively, which have ground state frequencies of 1008 and 1530 cm^{-1}. Brief activity centered at ~900 cm^{-1} which is characteristic of ground state HOOP modes and strong modulations in the torsional frequency range appear as well. Possible assignment of the bands, and their implication to photoinduced reaction dynamics in BR are discussed. Reasons for the absence of similar signatures in the pump-probe spectral modulations at longer probing wavelengths are considered as well.

Energy Transport in Peptide Helices

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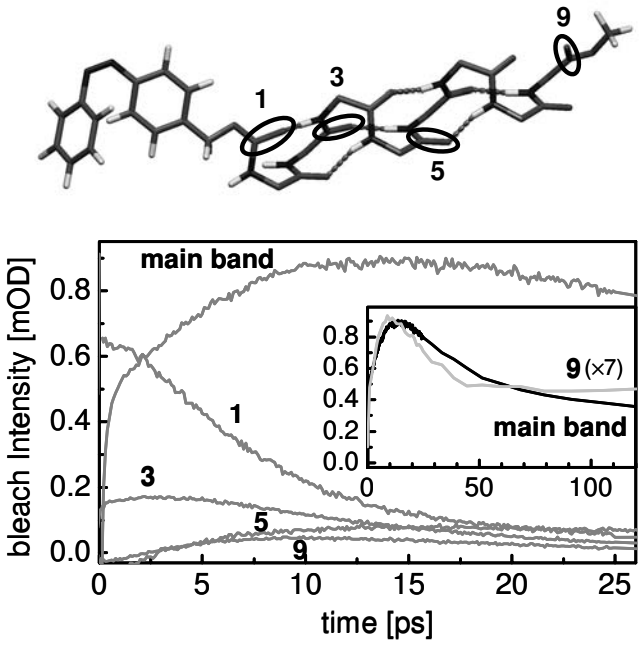
Proteins are the macromachines of life. They play a key role in the function of living organism. Protein action requires energy transport to and from proteins active site. It has been suggested that vibrational energy transport is possible through the helical part of a protein. In order to study this, we have constructed a stable 3_{10}-helix of 8 amino acids which a chromophore (azobenzene) attached at one side. Excitation of the azobenzene with a femtosecond laser pulse results in a large local temperature increase on short timescales (~200 fs) due to ultrafast isomerisation. The subsequent transport of energy through the helix is detected by molecular groups acting as local thermometers at specific locations with a second, non-perturbing laser pulse. The CO groups of the backbone of the peptide have been used for this, as the vibrational band shifts in frequency upon heating its surrounding.

Transport of energy along the helix is indeed observed (the maximum of the bleach intensity of group 3 comes later then the one of group 1, see figure), but has to compete with energy losses into the solvent on a ~7 ps timescale. The elevated temperature of the solvent also causes a bleach intensity which is reflected in the increase of band 5, 9 and the main band (all other CO groups) on the 7 ps timescale. From our data we can conclude that the diffusion constant of energy through the helix is ~2 $Å^2ps^{-1}$. The data are qualitatively in agreement with MD simulations.



Chemical structure of the backbone of the helix and the attached chromophore and time dependencies of the bleach intensities of bands 1 to 9 and the main band (all other CO groups). The inset shows the recovery of the main band and band 9 on a longer timescale. The tags **1** to **9** label the CO groups.

Understanding the Building Blocks of Life – Evidence of a High-Temperature Order-Disorder Transition in Peptide Model Compounds

N. T. Hunt,[1] N. Byrne,[2] C.A. Angell,[2] and K. Wynne[1]

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The ultrafast rotational-diffusive dynamics of the peptide linkage model compounds N-methylacetamide[1] (NMA), acetamide (A) and N,N-dimethylacetamide (DMA) have been studied as a function of temperature using optically heterodyne-detected optical Kerr-effect (OHD-OKE) spectroscopy.

The rotational diffusion times of NMA and A show a temperature dependence inconsistent with expectations for a normal Arrhenius-type fluid but can be fit to a combination of Arrhenius and Vogel-Fulcher-Tammann functions (see Fig. 1). The latter dynamics are more commonly observed in liquid-to-liquid phase transitions of super-cooled molecular liquids[2] but this represents the first observation of such phenomena at room temperature and in the normal liquid phase. In addition, differential scanning calorimetry measurements show that the change in rotational dynamics is accompanied by an increased heat flow as expected at a phase transition. No such effect is observed for the non-hydrogen bonding DMA, which exhibits perfect Arrhenius behaviour over a similar temperature range (see Fig. 1). These effects are assigned to an order-disorder transition between a low temperature hydrogen-bonded phase and a high temperature disordered phase.

The OHD-OKE responses of carboxylic acids, acetic acid (AcOH) and dichloroacetic acid (DCA) are also reported. These, along with the terahertz Raman and mid-infrared vibrational spectra, show no evidence of the effects observed in amide systems, but display trends consistent with the presence of an equilibrium between the linear and cyclic dimer structures at all temperatures and moderate-to-high mole fractions in aqueous solution. That these are not disrupted is attributed to stronger hydrogen bonding in these systems as compared to the amides.

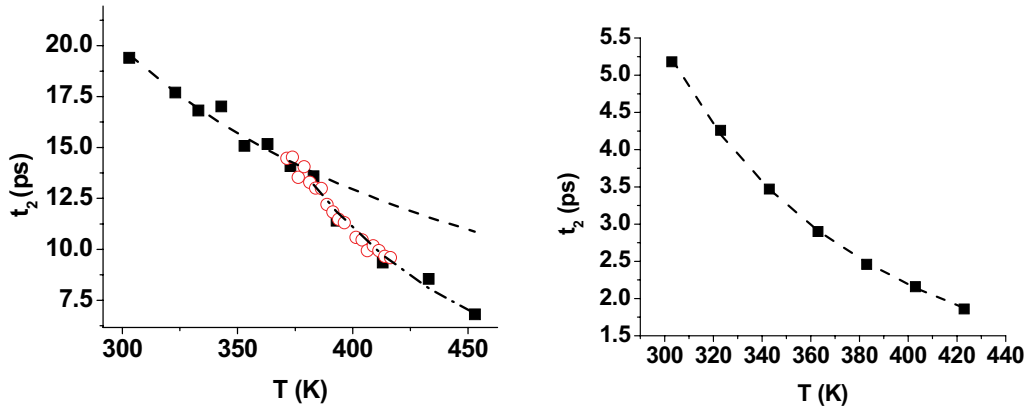

Figure 1 Rotational-diffusion times of liquid NMA (left) and DMA (right) as a function of temperature. Dashed curves beginning at low temperature show fits to Arrhenius functions while the high temperature portion of the NMA data is fitted to a Vogel-Fulcher-Tammann function consistent with a fragile-to-strong transition.

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Optical fingerprinting of peptides using two dimensional infrared spectroscopy: demonstration of principle.

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We demonstrate the viability of performing optical fingerprinting of peptides by using a particular form of picosecond two dimensional infrared (2D IR) vibrational spectroscopy[1]. The principle of this method is illustrated by measuring two dimensional spectra of a number of known peptides. Spectral features corresponding to vibrational ring modes of the aromatic group of tyrosine (Tyr) and phenylalanine (Phe) are identified as well as a methylene peak (figure a).

By measuring the integrated intensities of the Tyr and Phe peaks and using the methylene peak as an internal reference, we show that the ratio of the integrated intensities of Tyr and Phe peaks to the CH_2 integrated intensity is proportional to the known relative amount of Tyr and Phe in the sequence (figures b and c).

This demonstrates that this form of 2D IR spectroscopy has the potential to quantify the amount of a specific amino acid in peptides by measuring 2D vibrational features and that this can be done without any chemical or biological pretreatment.

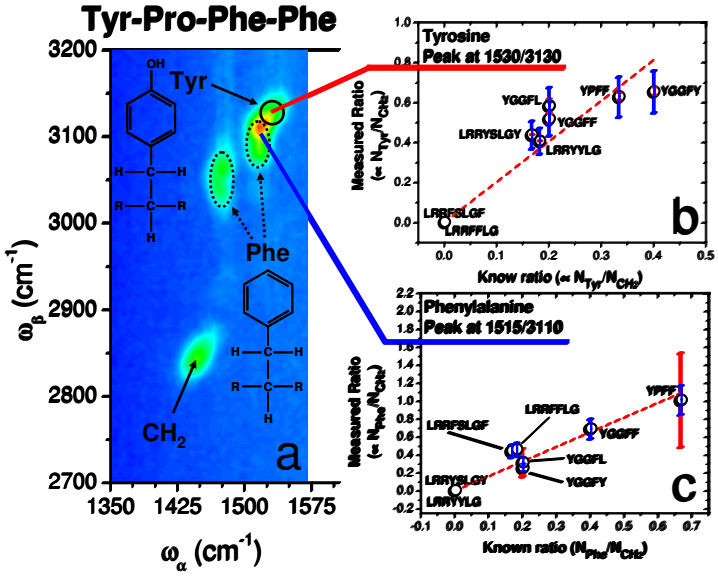

Figure a shows a 2D IR spectrum obtained for the YPFF peptide; the spectral features corresponding to CH_2, Tyr and Phe are indicated. By fitting the spectra it is possible to extract the parameters of each peak and to calculate the ratio of the integrated intensities of the features of interest to the reference peak (CH_2). Figures b and c show the measured ratio obtained for the eight samples studied (amino acid sequence indicated for each point), for one Tyr and one Phe peaks as a function of the known ratio: the data points show a linear correlation.

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Time-domain theoretical analysis of the IR, polarized Raman, and 2D-IR spectra of peptide chains in aqueous solution

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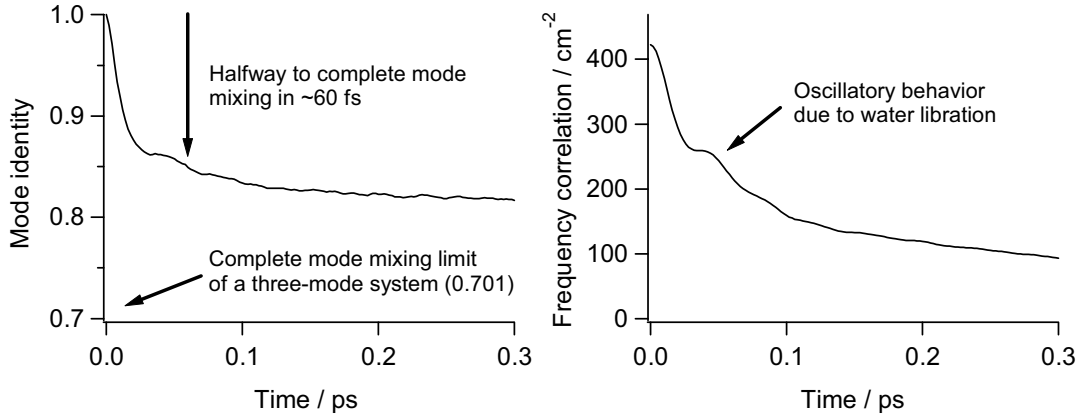
The profiles of the linear IR, polarized Raman, and 2D-IR spectra of the amide I mode of peptide chains in aqueous solution are analyzed theoretically by using a time-domain computational method. This method[1,2] includes both the frequency modulations induced by the interactions with solvent water molecules and the resonant vibrational couplings between peptide groups, so that the vibrational frequency crossings among peptide groups and the resultant non-adiabatic effects are taken into account in a natural way. It is shown that the negative noncoincidence effect (negative values of $\nu_{IR} - \nu_{iso}$ and $\nu_{aniso} - \nu_{iso}$) observed[3] for the amide I band of short alanine peptides is consistent with the structures dominated by the ppII and β-type conformations obtained from MD simulations. This negative noncoincidence effect arises from resonant vibrational coupling between the amide I vibrations of peptide groups and the resultant delocalization of vibrational modes. However, the effect of this delocalization cannot be clearly seen in the 2D-IR band profiles. In contrast, in the case of a longer peptide chain in the α-helical conformation, the effect of the delocalization of vibrational modes is easily recognized in the 2D-IR band profiles, although the magnitude of the noncoincidence is small.

To see the nature of the vibrational frequency modulations and the extent of the resultant changes in the characters of the normal modes, the time correlation functions of the frequency modulations $C_L(t)$ and the mode identity $M(t)$ are calculated. It is shown that the system proceeds halfway to complete mode mixing in ~60 fs. $C_L(t)$ also decays rapidly, giving rise to a motional narrowing effect on the band profiles. The oscillatory behavior of $C_L(t)$ in the first ~100 fs originates from the librational motions of solvent water molecules. The latter result is discussed by comparing it with the case of the OH stretching mode of liquid water.[4]



The time correlation functions of the frequency modulations $C_L(t)$ and the mode identity $M(t)$ calculated for the amide I mode of tetraalanine in aqueous solution at 298 K.

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Ultrafast dynamics in two-dimensional infrared spectroscopy: observing population transfer, spectral diffusion and rotational motion in peptides

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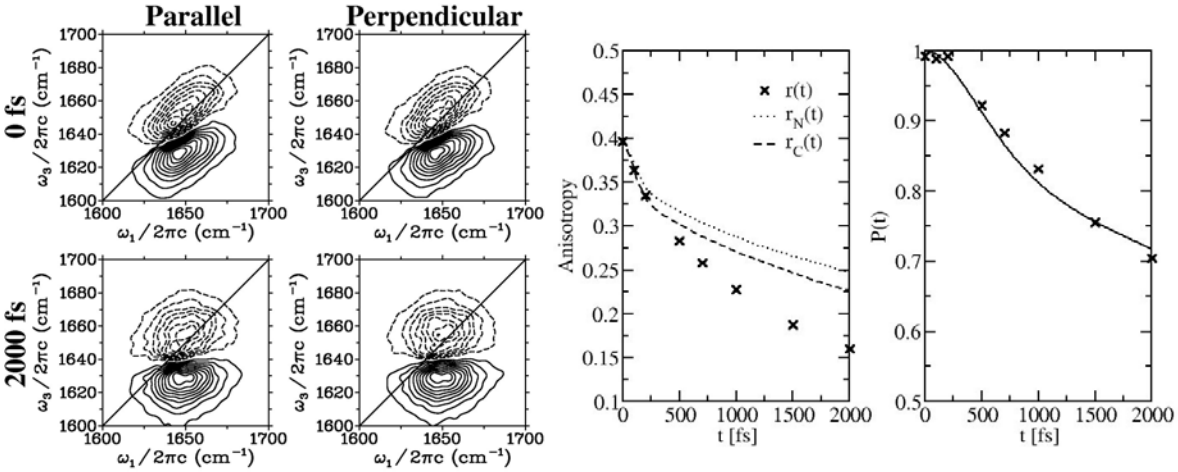
A method of simulating two-dimensional infrared (2DIR) spectra is presented that accounts for nonadiabatic effects and, thus, is able to describe the effect of population transfer, spectral diffusion and rotational motion simultaneously during the waiting time[1,2,3].

We demonstrate the new method on alanine dipeptide using the fluctuating vibrational Hamiltonian extracted from molecular dynamics simulations with high accuracy DFT models[4,5]. The calculated FTIR and 2DIR spectra are in very good agreement with experimental observations[6]. The polarization anisotropy, corresponding to that of a broad pump – narrow probe experiment, is calculated. It is shown that the rotational dynamics dominates the first few hundred femtoseconds. Thereafter, population transfer sets in and dominates the anisotropy decay. It is demonstrated that the population transfer can be extracted from the polarization anisotropy[1] using a procedure that should also be applicable to experimental spectra.



Left: The simulated 2DIR spectra of alanine dipeptide with different polarization configurations and waiting times. Middle: The anisotropy simulated for a broad pump-narrow probe experiment, r(t), together with the rotational correlation functions for the two sites, $r_N(t)$ and $r_C(t)$. Right: The directly calculated population transfer (solid) and the population transfer extracted from the anisotropy (crosses).

Furthermore, it will be demonstrated that the developed method can be applied to larger peptides. Here the population transfer that takes place during the waiting time is shown to strongly enhance the structural markers known for β-sheet structure[7].

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Wednesday Morning Session

Water II

Dynamics of Nanoconfined Water

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Liquid water displays a variety of unusual properties which originate from the fluctuating three-dimensional hydrogen bond network linking the highly polar water molecules. Recent spectrally resolved transient grating and two-dimensional (2D) correlation experiments on the OH stretching band have revealed very fast energy redistribution within the hydrogen-bond network of liquid water. It was therefore concluded that bulk liquid water essentially loses the memory of persistent correlations in its structure in about 100 fs[1].

In many biological systems water resides in nanometer-sized droplets, which properties are expected to differ considerably from those of bulk due to the truncation of the hydrogen bond network. To study such properties, reverse micelles have been proposed as a model system[2]. The reversed micelles are composed of nearly spherical water droplets, which are covered by a monolayer of the amphiphilic surfactant. Here we report on 2D femtosecond correlation experiments on H_2O confined in AOT (sodium di-2-ethylhexylsulfosuccinate) reverse micelles. The effect of nanoconfinement onto the ultrafast dynamics is investigated by varying the micelles diameter (d) between 1 and 10 nm.

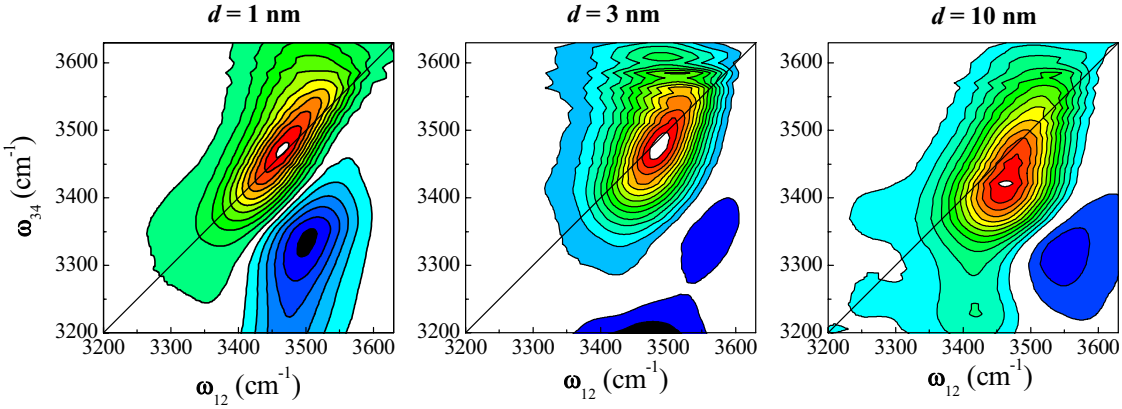

Fig.1. Two-dimensional correlation spectra obtained at 50 fs waiting time for micelles with diameters of 1, 3 and 10 nm. The maximum (red) and minimum (blue) of the signal are separated by sixteen equally spaced levels.

Figure 1 shows the experimental 2D spectra for the OH stretching band of H_2O in reverse micelles, measured for 50 fs waiting time. From the eccentricity of the ellipse[3] corresponding to the 0→1 transition (positive signal in Fig. 1) it can be deduced that the water dynamics considerably slow down upon nanoconfinement. For instance, the phase memory is considerably preserved for the 1-nm water core diameter while it is largely lost in the 10-nm case resembling the bulk water dynamics[1]. Our preliminary results also show signatures of slow dynamics in the high frequency region even in large micelles, most probably reflecting the properties of interfacial water.

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Anomalous Temperature Dependence of the 2D IR Spectrum of Liquid H_2O

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The dynamics and coupling within the fully resonant hydrogen bond network of liquid H_2O is directly linked to the special properties of water. The OH stretching vibration is a direct probe of these dynamics, and has been studied extensively with infrared pump-probe [1], and photon echo spectroscopy [2, 3]. Two-dimensional infrared spectroscopy has recently proven extremely useful in revealing the femtosecond timescales of the hydrogen bond network dynamics [4].

We have extended our previous studies of the 2D IR spectrum of liquid H_2O to include a temperature dependence. The experiments used the diffractive optic approach [5] with 70-fs pulses centered at 3,350 cm-1 in the OH stretching band. This work further advanced our recently developed nanofluidic cell technology to include active feedback, essential to maintaining uniform and stable 400 nm pathlengths with thermally isolated conditions.

The energy transfer dynamics are largely unaffected by temperature, however, the frequency correlations were found to be extremely sensitive to temperature, showing a marked increase in memory over ambient temperatures with as little as a 10 degree reduction in temperature. The coherence in the frequency correlations persist longer than the excitation hopping time suggesting a certain degree of delocalization of the vibrational excitation at even near ambient temperatures.

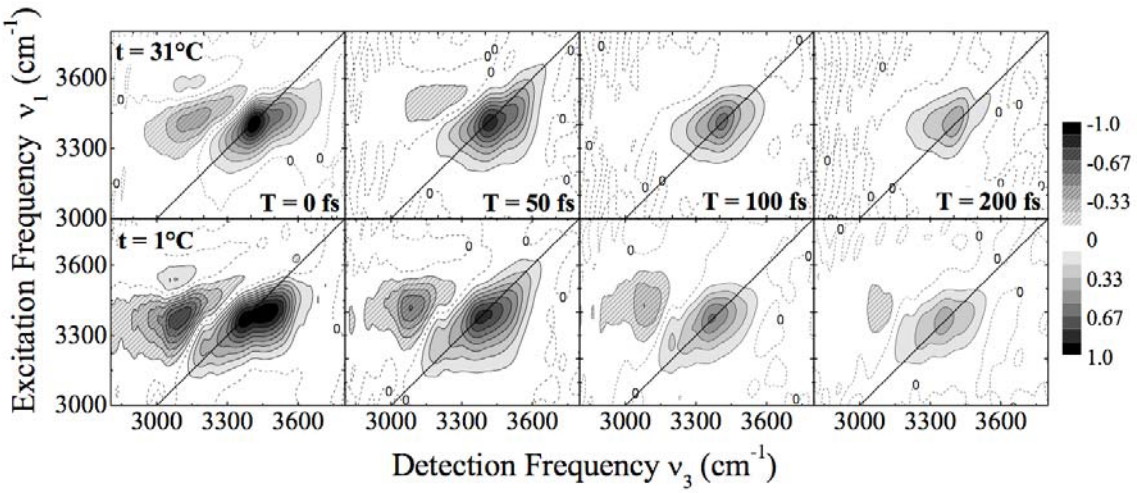

Figure: Representative data for the absorptive component of vibrational 2D spectra at population time T = 0, 50, 100, 200 fs (left to right). Structural correlations are lost within ~50 fs for ambient water temperature of 31°C (top), they persist significantly longer (~200 fs) for 1°C . Additional temperatures at 5, 10, 21 °C.

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Carbonyl stretch vibrational dynamics of acetic acid in water and alcohol studied by time-resolved IR spectroscopy

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Aqueous solution is an important field of chemical reactions in the natural world. The mechanism of the chemical reactions depends strongly on the intermolecular interaction between the solute and the solvent water molecules. Especially in aqueous solution, the intermolecular interaction should be mainly dominated by the solute-solvent intermolecular hydrogen bonding. To understand the chemical environment of the solute in aqueous solution, it is essential to elucidate the dynamics of the intermolecular hydrogen bonding.

In this study, we observed the vibrational dynamics of the carbonyl (C=O) stretch mode of acetic acid in D_2O by time-resolved IR spectroscopy. The C=O group forms hydrogen bond with the surrounding water molecules, resulting in the complex called "hydrated monomer"[1]. The vibrational dynamics of C=O stretching should, therefore, include important information on the dynamics of intermolecular hydrogen bonding.

We measured the IR absorption difference spectra of CH_3COOD in D_2O after the excitation of the C=O stretch vibration. In the result, the absorbance change and its decay were recorded at the wavenumbers in the range between 1610 to 1750 cm^{-1}. We observed negative absorbance change at 1710 cm^{-1}, corresponding to the bleaching of the ground state absorption band of the C=O stretch vibration, and positive one at 1660 cm^{-1}, corresponding to the transient absorption of the excited C=O stretch vibration (Fig. 1a). The delay time and wavenumber dependence of the absorbance change is well reconstructed by the following function,

$$A(\tilde{\nu},t) = a(\tilde{\nu})\exp\left(-\frac{t}{\tau_1}\right) + b(\tilde{\nu})\exp\left(-\frac{t}{\tau_2}\right),$$

where A is the observed absorbance change at wavenumber $\tilde{\nu}$ and delay time t, τ_1 and τ_2 are the decaying time constants common to all the wavenumbers, and a and b are the spectra of the τ_1 and τ_2 components. By global fitting, the time constants τ_1 and τ_2 are determined as 150 and 950 fs, respectively. The obtained spectra a and b are shown in Fig. 1b. There are two different species, 150-fs decaying component with a spectrum a and 950-fs decaying component with a spectrum b. The result probably indicates the presence of two or more different solvation species of CH_3COOD in D_2O.

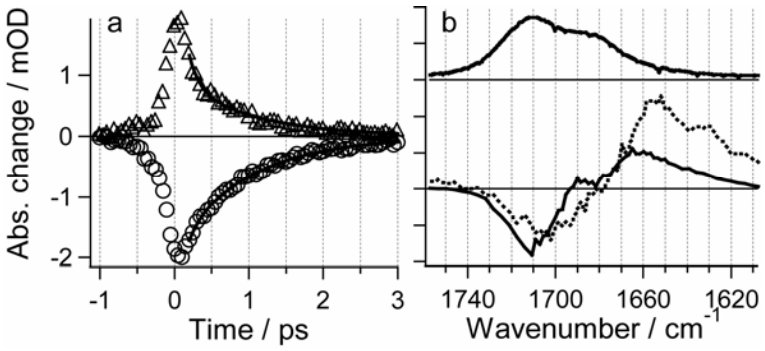

Figure 1.
(a) Delay time dependence of absorbance change at 1660 cm^{-1} (triangle) and 1710 cm^{-1} (circle). The solid lines are the best-fitted double-exponential functions.
(b) Ground-state absorption spectrum of CH_3COOD in D_2O (top), spectrum of 150-fs decaying component (*a*, dotted line) and 950-fs decaying component (*b*, solid line).

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Superheating of bulk ice. Transient temperature and pressure measurements.

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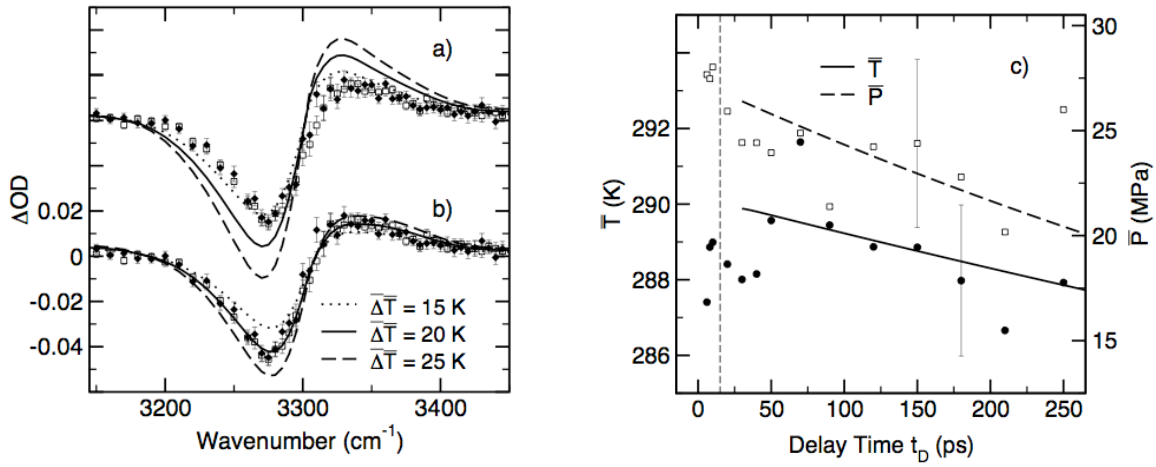
We have performed ultrafast temperature jump measurements in neat and isotopically mixed ice using IR double-resonance spectroscopy with one-picosecond time resolution. The hydroxilic stretching vibrations (OH or OD) possess sub-picosecond population lifetimes that allow a rapid energy redistribution and heating of the ice lattice. The same modes can be used as fast and sensitive probes of local temperature and structure.

The method is verified for an isotopic mixture of ice at 200 K and ambient pressure. It is also important to recall the isochoric character of the ultrafast temperature jump because of the slow volume expansion of the shock-heated sample (see Figs. 1a and b). In other words, a pressure increase is involved that is also measured with our technique. The temporal evolutions of temperature and pressure in the sample are determined by comparison of the measured time-resolved absorption changes to steady-state differential spectra[1,2].

The experiments close to the melting point show substantial superheating of the sample to more than 300 K that persists for more than 1.3 ns (see Fig. 1c)[2]. The thermal stability of the straight H-bonds in the crystal lattice near the melting point appears to be much higher as suggested by the common melting temperature. In this context the experimental determination of the maximum superheating temperature of neat and isotopically mixed ice will be presented for the first time[3].



(**a**) Transient differential spectra measured with tunable subpicosecond pulses 40 ps after OH- (hollow squares) or OD-pumping (filled diamonds) of the HDO:D_2O ice at 200 K. The curves represent steady-state differential spectra for ΔT = 15, 20 and 25 K and constant ambient pressure. (**b**) Same picosecond data (experimental points) as in (b) but compared to steady-state differential spectra for isochoric temperature jumps (calculated curves). (**c**) Average temperature and pressure of the probed sample volume after ultrafast heating of HDO:D_2O (15*M*) at 270 K. The initial temperature jump (filled circles, solid line, left ordinate scale) to a local quasi-equilibrium after ~ 15 ps (vertical line) is accompanied by an isochoric pressure increase (hollow squares, dashed line, right ordinate scale). Temperature and pressure develop differently later on.

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Vibrational energy dynamics in glycine/water solution studied with ultrafast IR–Raman spectroscopy

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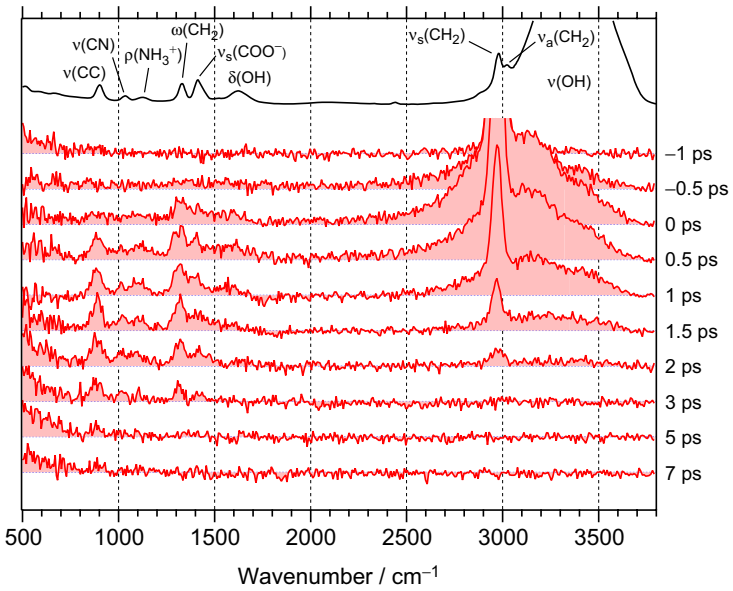
Elucidating vibrational energy dynamics of a solute and surrounding water molecules in an aqueous solution is one of the central subjects in the condensed-phase chemistry. It also provides insight into fundamental mechanisms underlying a variety of reactions that take place in biological systems. In order to trace how vibrational energy deposited on a solute flows within the solute and is transferred to surrounding water molecules, a vibrational spectroscopy with sufficient time resolution and spectral coverage is definitely necessary.

In this study, we use ultrafast IR–Raman spectroscopy with mid-IR pump and incoherent Stokes and/or anti-Stokes probe. Since the whole anti-Stokes and Stokes regions below 4000 cm^{-1} are covered in our experimental setup, we can study not only the energy flow from the parent vibration to daughter vibrations by looking at the anti-Stokes region, but the dissipation of the energy to surroundings by the Stokes part.[1] In the present paper, we study an aqueous solution of glycine, which is the simplest member of amino acids.

The figure shows transient anti-Stokes Raman spectra of a glycine/water solution (~1.8 M) with ~2970 cm^{-1} pumping. With this pumping, both the CH_2 symmetric stretch mode of glycine and the OH stretch mode of water are excited. Time evolution of the anti-Stokes transients of the solute glycine as well as the solvent water was successfully obtained. Transient anti-Stokes signals of glycine rise with a slight lag (<1 ps) from those of water, and decay away with time constants of 1–3 ps. Such a fast vibrational energy dynamics in the glycine/water solution can be attributed to hydrogen bonding between glycine and water molecules. Transient Stokes Raman spectra are analyzed using singular value decomposition and discussed in terms of a heat build-up of surrounding water.

This material is based upon work supported by the National Science Foundation under grant DMR-0504038.



Spontaneous Stokes Raman spectrum (top trace) and transient anti-Stokes Raman spectra of glycine/water solution measured with 2970 cm^{-1} pumping.

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Ultrafast vibrational energy transfer between surface and bulk water at the air-water interface

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We report a femtosecond time-resolved study of water at the neat water/air interface. The O-H stretch vibrational lifetime of hydrogen-bonded interfacial water is determined using a novel, surface-specific 4th-order non-linear optical spectroscopy with femtosecond infrared pulses. The O-H stretch vibration of interfacial water is resonantly excited with an intense, 100 fs IR pulse. The vibrational dynamics are investigated with femtosecond, time-resolved sum-frequency generation (SFG) spectroscopy, that allow for the specific detection of the ~1 monolayer of water molecules at the air-water interface.

Although the spectral response is strongly dependent on excitation and probe wavelength (see Figure), the vibrational dynamics in the frequency range of 3200 to 3500 cm^{-1} is found to closely resemble that of bulk water, indicating ultrafast exchange of vibrational energy between surface water molecules and those in the bulk. We find a vibrational lifetime of T_1=190 fs and an energy equilibration time τ_{eq}=400 fs (solid lines in Figure), with evidence for very fast spectral diffusion. The conclusion that energy exchange with the bulk occurs very rapidly is corroborated by polarization-resolved measurements that demonstrate ultrafast re-orientation of excited vibrational dipoles. [1]

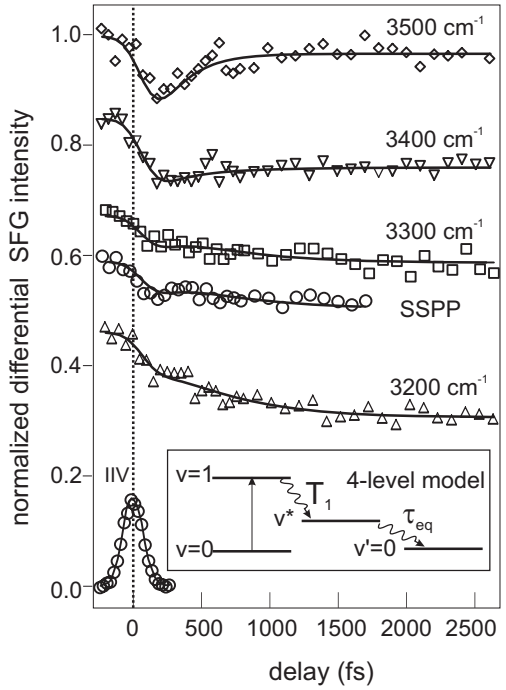

Figure : Time-resolved IR-pump, SFG-probe data for interfacial water for frequencies indicated in the graph (traces are offset for clarity). Polarizations of the SFG, VIS probe, IR probe and IR pump were S, S, P and S, except for the additional trace at ν_{pump}=3300 cm^{-1}, for which pump and probe polarization are parallel. The solid line is a calculation based on a four level system depicted in the inset. Relaxation from the vibrationally excited state (v=1) occurs to an intermediate state v*, from which further equilibration occurs to a situation with slightly elevated temperature (v'=0). The lower trace is an exemplary third-order IR+IR+VIS SFG signal, used to determine time zero and the time resolution in the experiment.

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Dynamical Properties of Water at Silica-Air Interface

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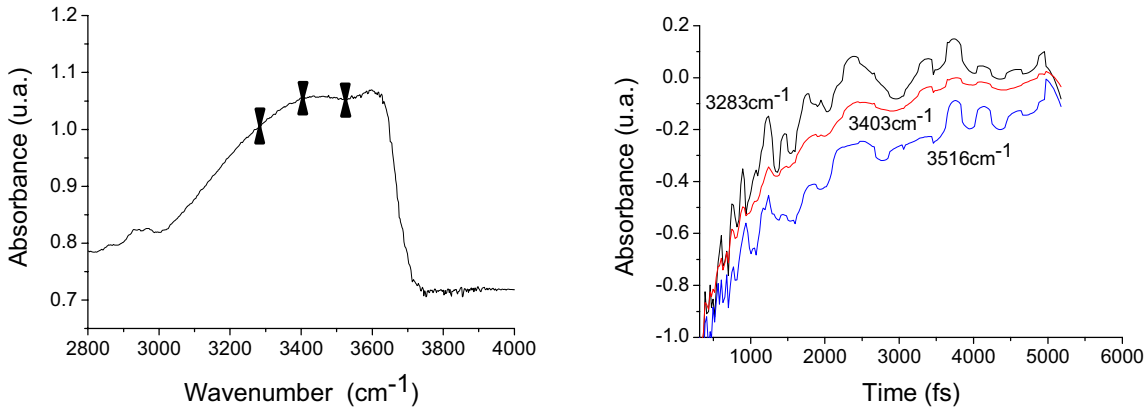
Water plays a major role in a multitude of physical and biological systems. The key feature of liquid water is the presence of a hydrogen bond network in a dynamical equilibrium that is responsible for water's unique properties[1]; hydrogen bond network dynamics in bulk water occurs over a range of time scales from tens of fs to ps[2]. In confined environments, the structure and dynamics of water are modified by the presence of surfaces, by a change of hydrogen bonding but also by the modification of the molecular motion that depends on the distance of water molecules from the surface[3,2].

IR pump IR probe experiments have been performed on a mixture of H_2O – D_2O i.e. HOD in D_2O confined in controlled pore glasses (CPG) sheets with different pore size (pore diameter = 1nm, 13nm, 50nm) in the OH stretch region (3420 cm^{-1}). Probing in the same region, at 3420 cm^{-1}, we have noticed, in the case of the dry samples, an important dependence of the OH vibrator lifetime upon the vibrator frequency, as can be clearly seen in figure 1. Thus, the lifetime is increased for larger frequencies (reaching a value of 2ps for 3516cm-1), and shorter for smaller frequencies (650fs at 3283cm-1). The lifetime of the OH vibrator depends on the structure and on the number of the H bond in the H bond network, which is deformed by the presence of the surface. At the same time, the relaxation of the OH vibrator in confined media is different from the bulk one (1.3ps). To the best of our knowledge it is the first time that such a dependence of the excited state lifetime upon the vibrator frequency has been highlighted.



(a) (b)

Figure1: (a) the IR spectrum of the dry 1nm CPG sheet; (b) the temporal evolution of OH absorption for three different probing frequencies: 3283 cm^{-1}, 3403cm^{-1}, 3516cm^{-1}. The pumping frequency is 3420 cm^{-1}.

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Wednesday Afternoon Session

FTIR

The Role of Protein Bound Water Monitored by trFTIR

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In the Postgenom era proteins are coming into the focus in the life sciences. Proteins are the nanomachines that perform the work in living organisms or are the receptors and mediators for external signals. By NMR and x-ray the three dimensional structural architecture of proteins are determined. In order to elucidate the function, time-resolved methods have to be applied.

FTIR difference spectroscopy can be used to monitor the reactions within proteins at the atomic level with ns time-resolution up to days [1]. In combination with site directed mutagenesis or isotopically labelling the IR bands can be clear cut assigned to specific amino acids or ligands. This provides in combination with structural models also spatial resolution.

Based on fast scan studies on bacteriorhodopsin the key catalytic residues, asp 85 and asp 96 and their protonation kinetics are identified and summarized in a first detailed proton pump model [2]. Their structural arrangement as resolved in succeeding X-ray experiments by several groups supports this proposal. The X-ray structural model at 1.55 Å resolves in addition the oxygens of internal water molecules. Based on succeeding step scan FTIR measurements the interplay between these water molecules, a strongly hydrogen bonded water, a dangling water and a protonated water complex is elucidated in detail. It results in a controlled Grothuis proton transfer from the central proton binding site to the protein surface. [3,4]. A similar mechanism might apply in the photosynthetic reaction center [5] and the cytochrome oxydase [6]. The step scan approach is also successfully applied to the photoactive yellow protein [7].

The difference technique requires fast triggering of the protein reaction, which is easy to accomplish for the chromoproteins as described before. Progress for the investigation of non chromophoric proteins is acquired by developing a micro mixing cell for FTIR studies, allowing mixing times in the sub ms time range. This cell is used to investigate protein folding reactions [8].

Alternatively, photolabile caged compounds can be applied. Using caged GTP the GTPase mechanism of the protooncogen Ras is investigated [9,10]. Also its protein-protein interaction with the GAP protein could be studied time-resolved [11,12]. This provides a detailed insight into the catalytic mechanism by which GAP activates the GTPase by five orders of magnitude. The activation by GAP proteins is a central process in the signal transduction. In oncogenic Ras this activation process is inhibited and involved in uncontrolled cell growth. The study proves that the approach can be extended to protein-protein interactions. Recently, beside rection within the active site of a protein, also the surface change of a protein leading to protein-protein interactions is monitored (13).

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Frequency-comb FTIR spectrometer for snapshot (sub-µs), rapid spectra sequence (KHz), remote infrared probing

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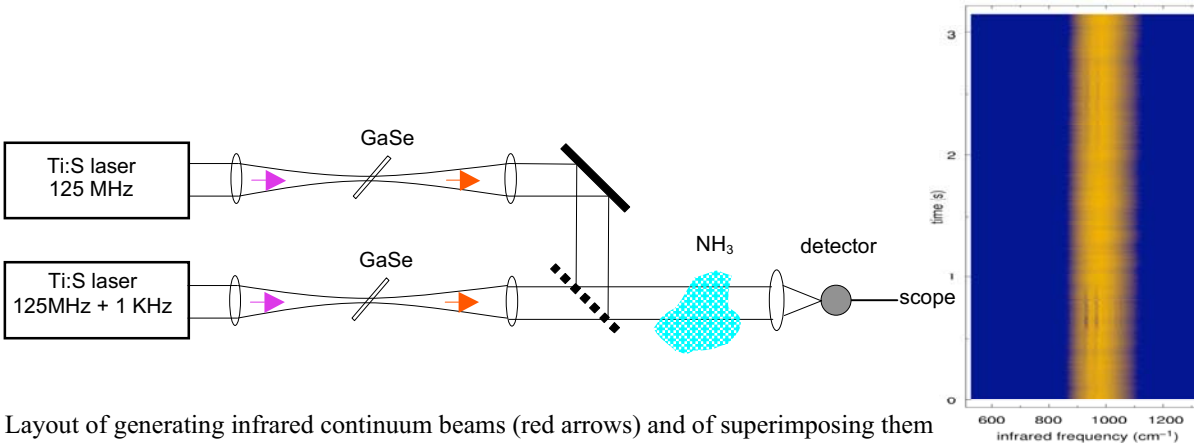
A novel Fourier-transform infrared spectrometer is reported that works without moving parts. It allows recording an interferogram in such short time (<1µs has been achieved) that it enables spectral snapshots of highly dynamic single events such as explosive combustion. The recording time and the time between snapshots can be varied over orders of magnitude by simple means. A continuous acquisition of 950 spectra/s has been demonstrated.[1]

Difference-frequency generation in GaSe is used to obtain, from the beam emitted by a 10 fs Ti:sapphire laser, a coherent mid-infrared beam that has a frequency-comb spectrum ranging from 9 to 12 µm. Its elements are exact harmonics of the laser's repetition rate $f_r \approx$ 125 MHz. The coherent frequency-comb spectrometer (c-FTIR) uses two such beams for its multi-heterodyne detection scheme.[2] This converts a beam's amplitude and phase spectrum into a radiowave replica that is easily measured. More precisely, the interference is self-scanned in the pure time domain, by interfering a sample beam with a reference beam that has slightly detuned repetition rate f_r + 1 KHz. Fig. 1 illustrates this setup and the achievement of continuous recording of spectra.



Layout of generating infrared continuum beams (red arrows) and of superimposing them to obtain self-scanned interferograms on an HgCdTe detector. Right panel: approx. 3000 spectra taken in 3s of continuous recording testify to a time-varying NH_3 mass in the beam path.

Recently we demonstrated asymmetric c-FTIR by placing a sample in one of the beams before the beam combiner. This measures the complex (i.e. amplitude and phase) transmission and allows operating a scattering-type infrared near-field microscope (s-SNOM).[3]

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Thursday Morning Session

Coherent Dynamics

Wavepacket motion of ultrafast proton transfer in the gas phase

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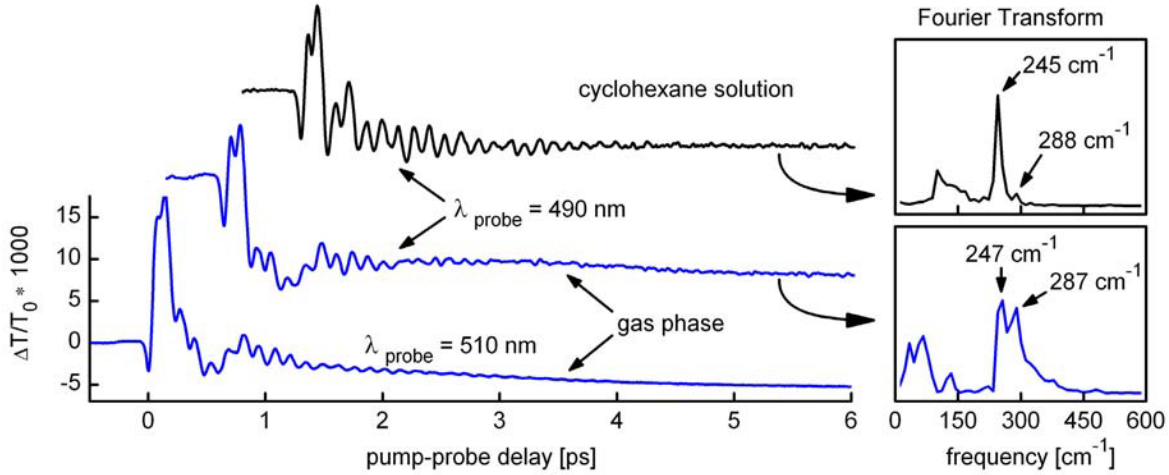
Ultrafast molecular processes are governed by intramolecular motions at the speed of skeletal vibrations as well as the interaction with the surrounding medium. To understand this interplay, we investigate the ultrafast intramolecular excited state proton transfer (ESIPT) of 2-(2'-hydroxyphenyl)benzothiazole (HBT) in the gas phase and compare the dynamics to the ones found in solution[1]. To measure the transient absorption of low vapour pressure molecules like HBT in the gas phase, a heatable gas cell was developed and a focusing geometry with an interaction length of 5 cm applied. A time resolution of 30 fs, achieved by using noncollinear optic parametric amplifiers as pulse sources, allows us for the first time to compare directly the coherent wavepacket motion of molecules in the gas phase and solution phase.

For various probe wavelengths, the dynamics are recorded both in the gas phase and in a 120 µm cyclohexane solution cell (see figure). In both environments similar behavior is found with respect to the initial delay time of the emission rise and the oscillatory components. A comparison with a precision of better than 5 fs shows that the intramolecular proton transfer itself is totally independent on the environment and proceeds in about 35 fs.



Transient absorption of the ESIPT in HBT in gas phase and in cyclohexane solution.

However, the wavepacket dynamics induced by the ESIPT and responsible for the signal oscillations differ between gas phase and solution. The gas phase traces exhibit an additional low frequency component which may reflect a torsional motion associated with a shallow excited state potential along the corresponding coordinate. In the condensed phase the friction induced by the interaction with the solvent molecules probably overdamps this motion. Surprisingly, the oscillatory signal contributions at higher frequencies are somewhat less pronounced and slightly faster damped in the gas phase than in solution. We presume that in solution part of the excess energy is already lost to the solvent within in the initial motion. In the gas phase this is not possible and the product molecules are formed with roughly 4.000 cm^{-1} of vibrational energy. Higher vibrational levels in the product potential are populated and if, due to anharmonicity, they are not equaly spaced in energy, they can lead to an efficient broadening of the wavepacket without the need of additional dephasing processes.

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Direct measurement of Fermi Resonance Coupling Energy in Benzene by 2D-Infrared Spectroscopy

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Fermi resonances of vibrational states are common features in the spectra of complex molecules. Being a mixture of two or more vibrational states and involving multiple anharmonic terms, the energies and intensities of Fermi resonance states are sensitive reporters on structure and environment.

We show that it is possible to both directly measure, and directly calculate from quantum mechanics the Fermi resonance couplings in Benzene. The measurement method used is a particular form of two dimensional infra-red spectroscopy known as Doubly Vibrationally Enhanced Four Wave Mixing (DOVE-FWM). By using different pulse orderings, vibrational cross peaks were measured either purely at the frequencies of the base vibrational states, or split by the coupling energy. This is demonstrated in Figure 1. Five cross peaks of the ring breathing mode ν_{13} with a range of combination bands were observed, spanning a region of 1500-4550 cm^{-1}. The coupling energy was measured for two states of the $\nu_{13}+\nu_{16}$ Fermi resonance tetrad and coherence dephasing rates measured in the time domain for ν_{13} and two $\nu_{13}+\nu_{16}$ Fermi resonance states. The electronic and mechanical vibrational anharmonicities were calculated to 2nd and 3rd order respectively, giving information on relative intensities of the cross peaks and enabling the Fermi resonance peaks of the combination band $\nu_{13}+\nu_{16}$ at 3050-3100 cm^{-1} to be treated, giving peak intensities that agreed well with the measured 2D-IR spectrum.

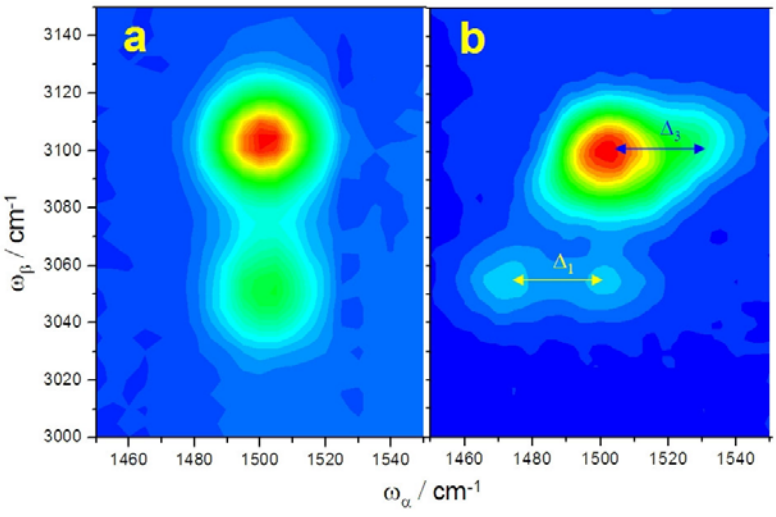

Figure 1. 2D-IR Fermi resonance cross peaks involving mode ν_{13} (~1500 cm^{-1}) and the $\nu_{13}+\nu_{16}$ Fermi resonance states, labelled as **1** (~3050 cm^{-1}) and **3** (~3100 cm^{-1}). Graph **(a)** shows a 2D-IR spectrum recorded using a pulse ordering that gives single cross peaks for each Fermi resonance state. Graph **(b)** uses a pulse ordering which gives the same cross peaks as in Graph **(a)** but with additional cross peaks shifted along the horizontal axis by the Fermi resonance coupling energies Δ_1 and Δ_3.

Coherent Control of Population Transfer and Vibronic Coherence

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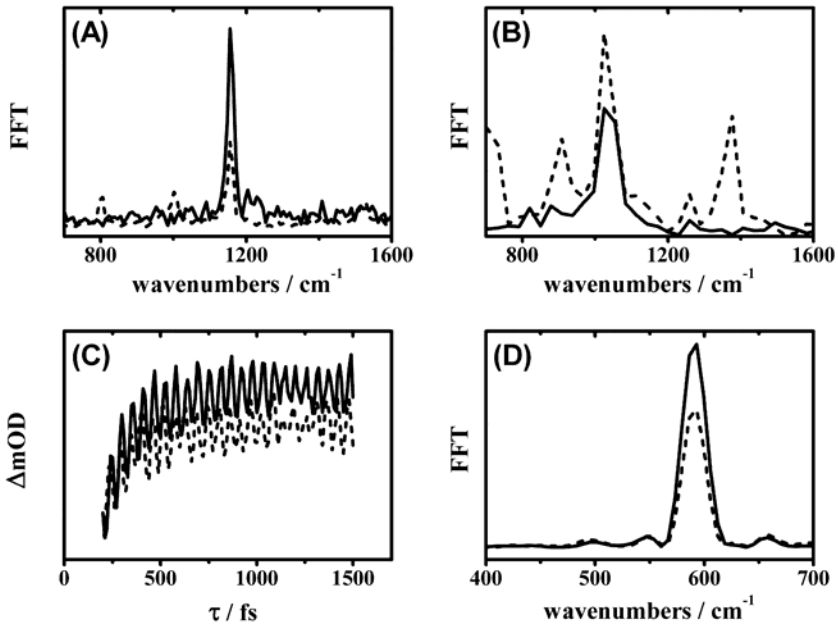
It has been a long term goal of coherent control to manipulate molecular oscillations, especially because they may represent motion along a reaction coordinate. Here we present two different control scenarios for vibrational motion and population transfer on two molecular systems using a spatial light modulator: Time-Resolved Degenerate Four Wave Mixing of all-trans-β-carotene[1] and Transient Absorption of Nile Blue (LD 6900)[2].

Vibrational modes were investigated under non-resonant, near-resonant and resonant excitation using tailored pulses. Pulse shapes to manipulate vibrations can be predicted to be trains of pulses with a temporal spacing between the sub-pulses equal to an integer multiple of the vibrational period. Excitation with purely resonant or only non-resonant excitation spectra show no enhancement, while by excitation slightly detuned from resonance (blue or red shifted) the vibrational modes can be strongly amplified. Showing a similar dependence on the excitation wavelength, the transferred population from the ground to the excited state is also subject to coherent control. A four-level (two pairs of vibrational levels separated by the electronic transition gap) density matrix simulation describes effectively the experimental findings, particularly the excitation wavelength dependence.



Shaped excitation (full line) is compared to unshaped excitation (dashed line) in DFWM (A and B) and in Transient Absorption (C and D). In (A), Raman modes of ß-carotene are shown after excitation with phase modulated pulses resonant (A) and non-resonant (B). The amplitude of the mode reached with a pulse train (shaped) exceeds the amplitude in the Fourier-limited case (unshaped) in the resonant case. In transient absorption, the transient and the respective Fourier-Spectra of Nile Blue are shown in C and D, respectively. Again, the excitation with a pulse train (full line in C) optimizes the vibration. Furthermore, a clear increase in population transfer (level of full line in C) is detected.

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Single-Shot Two Dimensional Time Resolved Four Wave Mixing

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We present a new experimental technique[1] of single-shot time resolved ultrafast Coherent Anti-Stokes Raman Spectroscopy (CARS), where we use the arrival time of different beams at the intersection of extended beams as controlled time delays. The three dimensional (BOXCARS) phase-matching configuration allows unique mapping of two independent time delays (pump-Stokes and pump-probe) onto the geometrical axes of the interaction region. Techniques based on delayed femtosecond beams have been used extensively for pulse diagnostics, and analyzed in detail (see e.g. Fourkas et al.[2]). The method paves the way to single-shot implementation of two dimensional time resolved experiments of the type reported earlier in experiments on Two-Dimensional Time-Delayed CARS[3].

Here we demonstrate time resolved measurement of field-free coherent vibrational evolution of bromoform ($CHBr_3$) on its ground electronic state. The entire measurement is completed within a **single laser pulse,** and the temporal resolution is determined by the pulse duration (~100fs). The image of the interaction region as taken by a simple CCD camera (left) depicts spatially resolved contributions from different interaction regions, which are mapped uniquely to a time resolved signal (right, inset) which in turn is Fourier transformed to a power spectrum (right). Within the bandwidth of the femtosecond pulse, two C-Br bending modes are clearly spectrally resolved (peaks at 152 and 224 cm^{-1} corresponding to asymmetric and symmetric modes), together with the homodyne beat at their difference frequency ($68cm^{-1}$).
The potential of this new methodology will be discussed.

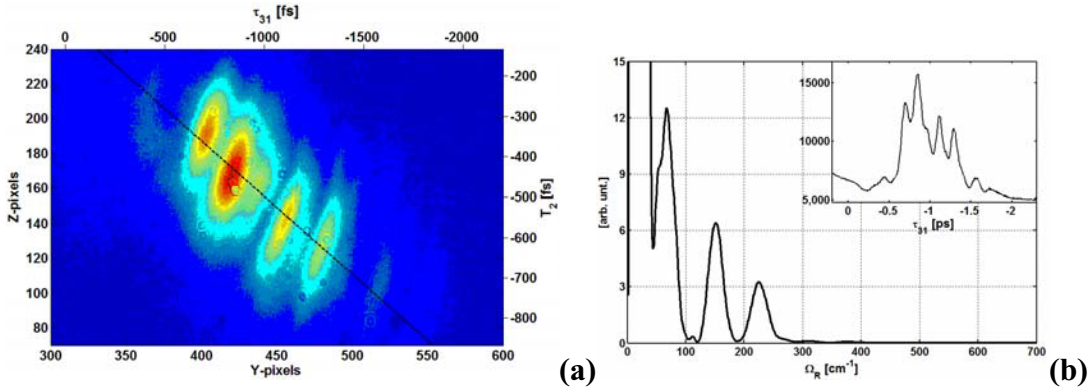

Figure 1 (a) Single-Pulse CARS image "as captured" of bromoform. The horizontal (upper) axis depicts the pump-probe delay. The vertical (right) axis depicts the arrival time of the Stokes pulse. (b) Power spectrum of the temporal signal (inset) of single-shot single pulse CARS of bromoform.

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Excited state vibrational dynamics near the S_2-S_1 conical intersection in all-*trans*-ß-carotene

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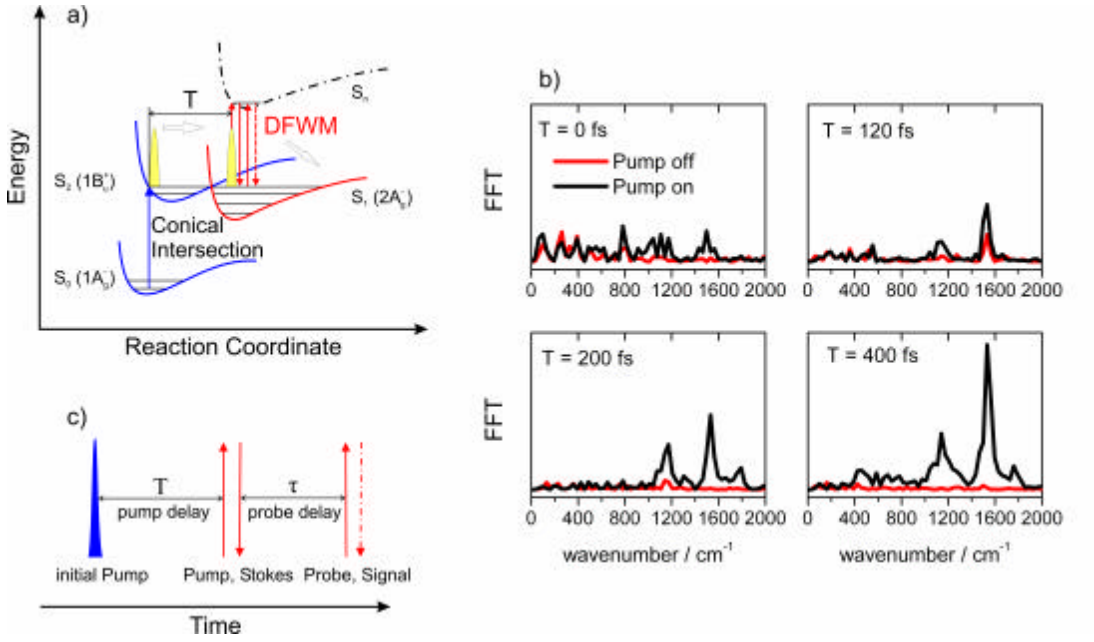
To determine the structural dynamics on short lived molecular excited states poses a challenging yet highly relevant field of ultrafast spectroscopy. We present a time domain technique which delivers highly resolved vibrational modes as well as information on the concerned electronic states. As a model system, we study the conical intersection between the lying excited states (S_2 and S_1) in ß-carotene.

The method of investigation is Pump-Degenerate Four Wave Mixing (Pump – DFWM)[1] with ultrashort pulses. Time resolved DFWM has already proven to be a versatile tool for studying and controlling vibrational dynamics on ß carotene's ground state.[2] Introducing an additional pump pulse preceding the DFWM – sequence opens the possibility to investigate excited state vibrations (see figure). The technique delivers a sub 20 fs time resolution and a spectral resolution better than 20 cm^{-1}.

In comparison to other transient Raman techniques, Pump - DFWM yields more than merely nuclear dynamics. Since the dephasing time of the DFWM – signal strongly depends on resonance conditions, changes in the electronic state can also be monitored. Hence, Pump DFWM offers a novel approach to study the important aspect of structural dynamics near conical intersections on an ultrafast time scale.



The employed excitation scheme is shown in a). When the initial Pump precedes the DFWM – sequence by time *T*, excited state dynamics become observable. When the probe delay time *t* (see c) between the probe and the other DFWM pulses is scanned for every pump delay *T*, Fourier spectra as seen in b) are obtained. The temporal evolution of the excited state vibrational modes can be investigated. In b) the development of the vibrational spectrum is depicted. Note the mode near 1800 cm^{-1}, which is characteristic to the S1 state.

[1] T.Hornung, H. Skenderovic, M. Motzkus, Chem. Phys. Lett., **2005**, 402, 283-288
[2] J. Hauer, H. Skenderovic, M. Motzkus, Chem Phys Lett., **2006**, 421, 523–528

Time-resolved polarization anisotropy study of doubly degenerate and nondegenerate vibrational states of $Mn(CO)_5Br$ in the condense phase

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The extension of vibrational spectroscopy into the time domain has driven further studies of structure and dynamics of complex systems[1], as well as prompted the application of coherent control methods to achieve various aims such as population transfer[2] and the possible implementation of molecular gates[3]. Here we use one color mid-infrared femtosecond pump-probe spectroscopy in order to investigate the ground state vibrational dynamics of a mono-substituted metal carbonyl complex[$Mn(CO)_5Br$] in solution, a recent canditate for molecular computation studies. In particular, we excite the two infrared active carbonyl stretches, namely the A and E normal modes which are separated by 50 cm^{-1}. Since both of these states lie within the bandwidth of our 130 fs pump and probe pulses, we can excite and monitor both states simultaneously. We present time dependent transient absorption spectra from which state lifetimes are measured and state anharmonicities are extracted.

Interestingly, we find varying relaxation state dynamics for these orthogonal vibrations. Specifically, at early times (< 8 ps) varying vibrational state relaxation rates are found. A time-resolved polarization anistotropy study reveals a doubly exponontential anisotropy decay for the doubly degenerate E state and a single exponetnial decay for the nondegenerate A state. We present the time dependent anisotropies for these states and the possible sources of these differences are explored.

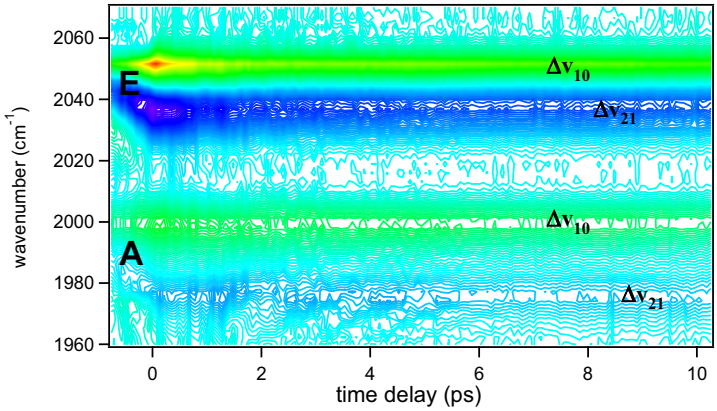

Figure 1. Time-dependent transient absorption spectra for both the A and E modes in Mn(CO)5Br .

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[3] F. Remacle and R.D. Levine, Appl. Phys. Sci., 101 (2004) 12091, B.M.R Korff, U. Troppmann, K.L. Kompa and R. De Vivie-Riedle, J. Chem. Phys., 123 (2005) 244509.

Ultrafast N-H vibrational dynamics in the DNA model base pair 7-azaindole dimer

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N-H hydrogen bonds are ubiquitous in nature and play a key role in genetic encoding through the complementarity of DNA base pairing. Infrared spectroscopic studies of N-H hydrogen bonds in native DNA are hampered by spectral overlap with the O-H stretching absorption of the aqueous solvent. To circumvent this problem we perform IR pump-probe measurements on the 7-azaindole dimer, a widely studied model nucleic acid base pair which is soluble in nonpolar solvents. This model system has the added advantage of being computationally tractable, thereby permitting theoretical investigations of experimentally measured vibrational dynamics. Recent efforts in ultrafast vibrational spectroscopy have revealed a large body of detailed information on the nature of the vibrational dynamics of hydrogen bonds[1], in particular for geometrically well-defined molecular systems with medium-strong hydrogen bonds, such as acetic acid dimers[2,3]. Following ultrafast vibrational dynamics in real-time allows for a separation of the different intra- and intermolecular couplings and the influence of the fluctuating solvent which is manifested in vibrational dephasing.

The IR-active N-H stretching band of 7-azaindole dimer exhibits a frequency downshift on the order of 400 cm^{-1} upon formation of the medium strong hydrogen bonded dimer with a pronounced substructure indicative of significant anharmonic couplings with fingerprint and low-frequency modes. We use two-colour femtosecond infrared pump-probe spectroscopy to investigate the role of these anharmonic couplings[4]. The N-H stretching vibration displays a 10 ps lifetime in the monomer. The lifetime is significantly shortened to ~100 fs upon dimer formation. The pronounced diagonal anharmonicity of the N-H stretching vibration in the dimers brought about by hydrogen bonding leads to a small energy mismatch between the $v = 1$ state and over-/combination tones, thereby facilitating an efficient relaxation pathway.

In addition to the ultrafast population dynamics, we observe coherent modulations of the spectrally integrated pump–probe signals of 7-azaindole dimer. These underdamped signals with a 110 cm^{-1} frequency are due to resonantly enhanced coherent Raman excitation by the pump pulse of the dimer in-plane hydrogen bond stretching mode strongly coupled to the N-H stretching vibration. Wavepacket motion in the $v = 1$ N-H stretching state is rapidly damped by the ultrafast population decay whereas the wavepacket in the $v = 0$ N-H stretching state oscillates for several picoseconds and modulates the N–H stretching absorption.

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Thursday Afternoon Session

Protein Dynamics

Transient 2D IR spectroscopy of ubiquitin unfolding dynamics

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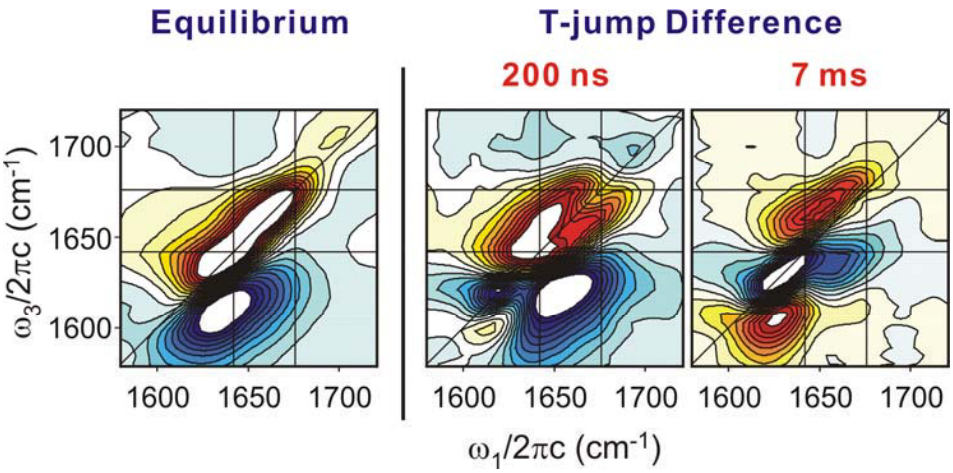
We have structurally resolved the unfolding of ubiquitin on nanosecond to millisecond time scales with transient amide I 2D IR spectroscopy following a temperature jump. The equilibrium 2D IR spectrum shows two spectral features that arise from delocalized vibrations of ubiquitin's β-sheet that differ by whether C=O oscillators vibrate in-phase along its strands ($\nu_{\parallel}$) or perpendicular to the strands ($\nu_{\perp}$). Spectral changes in the transient difference spectrum start with an abrupt blue shift of the $\nu_{\perp}$ diagonal region, which corresponds to the disruption of hydrogen bonds between water and solvent-exposed peptide groups. This change is followed by a blue shift of the $\nu_{\perp}$ region and disappearance of a cross peak between $\nu_{\perp}$ and $\nu_{\parallel}$ over μs to ms time scales. This change reflects the gradual unfolding of the β-sheet of the protein, beginning with the labile strands III-V. The antidiagonal linewidth, which characterizes the solvent-induced fluctuations, is observed to broaden as the sheet unfolds. The experiments are consistent with the observation of downhill unfolding by a sub-ensemble prepared at the unfolding transition state, followed by slower ms activated unfolding kinetics.

The free energy landscape for unfolding is evaluated with the help of modeling and simulation. Experiments are compared with 2D IR spectra calculated from molecular dynamics simulations of ubiquitin unfolding using a structure-based model for protein amide I spectroscopy. By calculating 2D IR spectra for transient structures, we evaluate the unfolding transition state. Proposed unfolding mechanisms are tested with a statistical mechanical model.



Equilibrium ZZZZ absorptive 2D IR spectrum of ubiquitin and two representative difference spectra following a 63ºC → 72ºC temperature jump.

Protein ligand migration mapped by nonequilibrium 2D-IR exchange spectroscopy

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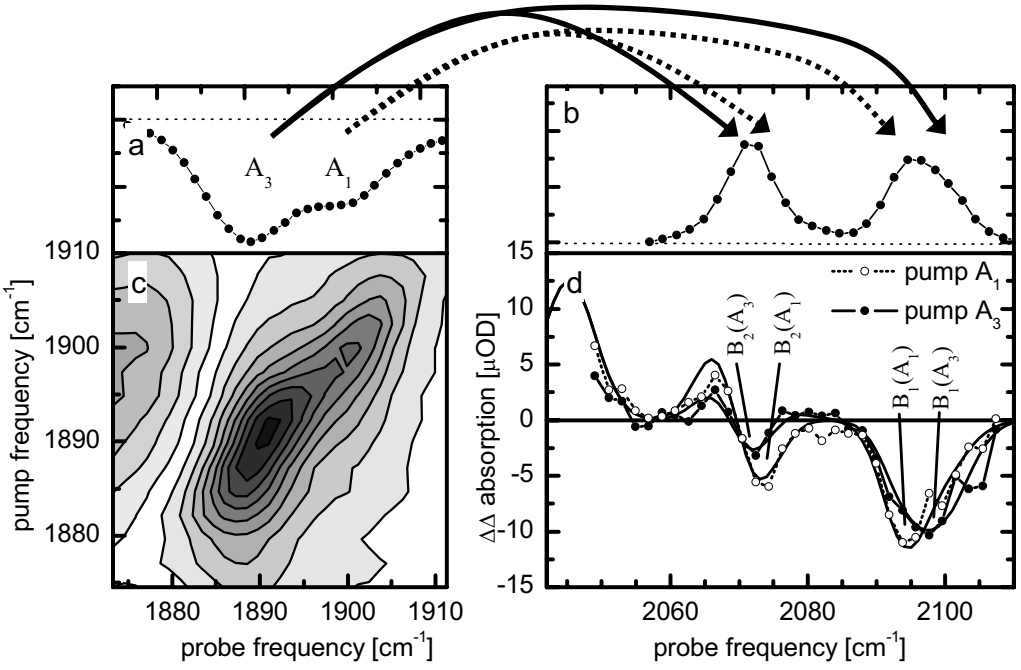
Two-dimensional exchange spectroscopy (2D-EXSY) has been introduced in the field of nuclear magnetic resonance (NMR) already three decades ago[1]. Since then, 2D-NMR-EXSY has grown into a powerful tool for mapping networks of interconverting chemical species in dynamic equilibrium. Only recently, the concept of 2D-EXSY has been transferred to IR spectroscopy[2], opening up the sub-picosecond range of exchange phenomena for real-time studies. In a regular 2D-IR-EXSY experiment, exchange between species occurs spontaneously during the waiting time between IR pulses. Here we demonstrate an extension of 2D-IR-EXSY, where a UV/Vis pulse during the waiting time triggers the exchange process (T2D-IR-EXSY). In this fashion the connectivity between transient species can be mapped in a nonequilibrium situation. We demonstrate the application of this technique to map the migration of a ligand (carbonmonoxide) between different sites in a protein (myoglobin) upon its release by a visible laser pulse[3].



(a) TRIR spectrum of the CO ligand, 5 ps after photodissociation from the binding site (A states) in myoglobin. Depletion of the A_3 and A_1 conformation can be seen. (b) The ligand populates different docking states (B states) within 5 ps. (c) 2D-IR spectrum of the ligand at the binding site showing the bands of the A_3 and A_1 conformation. (d) Cuts through the EXSY cross peaks between the A and B states at the frequency of the A_1 and A_3 conformation. Each conformation is connected to a separate set of B states: $A_1 \longrightarrow B_2(A_1)$, $B_1(A_1)$, $A_3 \longrightarrow B_2(A_3)$, $B_1(A_3)$, according to the arrows in the upper part of the figure.

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[3] J. Bredenbeck, J. Helbing, K. Nienhaus, G. U. Nienhaus, P. Hamm, Proc. Natl. Acad. Sci., **2007**, in press

Observation of Primary Structural Changes of Photoreactive Proteins by Picosecond Time-Resolved Ultraviolet Resonance Raman Spectroscopy

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Photoreactive proteins utilize the photoenergy to promote signal transduction and to produce the physiological function. In the primary steps of the photocycle, the chromophore responds to the light and changes its structure due to the electronic relaxation, isomerization, and etc. The local structural change around the chromophore transforms into large structural changes in the entire protein. To understand the mechanism of the protein function, it is essential to clarify how the changes of the chromophore enhance the structural change of each specific site in the protein. Picosecond time-resolved ultraviolet resonance Raman (UVRR) spectroscopy can probe the primary changes in the protein structure through the selective enhancement of vibrational bands from aromatic amino acid residues as well as the polypeptide skeletal structure. In such timescales, we can characterize the structural change of the protein backbone in early intermediates, which is one of the key steps in the photocycle. However, a few investigations on the picosecond protein dynamics have been reported by using this useful technique[1,2]. In this presentation, we discuss the ultrafast structural dynamics of the aromatic amino acid residues in photoactive yellow protein (PYP). This protein serves as a good model for understanding the signal transduction of photoreactive proteins because of the well defined tertiary structure and photostability.

PYP is a blue-light sensor involved in bacteria. The primary photochemistry of PYP relies on the trans-cis photoisomerization of its chromophore, an anionic form of *p*-coumaric acid. PYP involves a single tryptophan residue and five tyrosine residues. Picosecond spectral changes of the both tyrosine and tryptophan UVRR bands were selectively observed. The spectrum in the figure is the transient UVRR difference spectrum between the intermediate at 0 ps and dark-state PYP. Especially for tyrosine, the intensity loss was observed at the Y8a, Y7a, and Y9a bands. Time-resolved measurements revealed that the Y8a band intensity decreased within the instrumental response, partially recovered with a time constant of ~8 ps, and maintained a constant negative value up to 1 ns. Because one tyrosine residue (Y42) is directly hydrogen-bonded to the chromophore, it is reasonable that the ultrafast structural change of Y42 induces the observed spectral change.

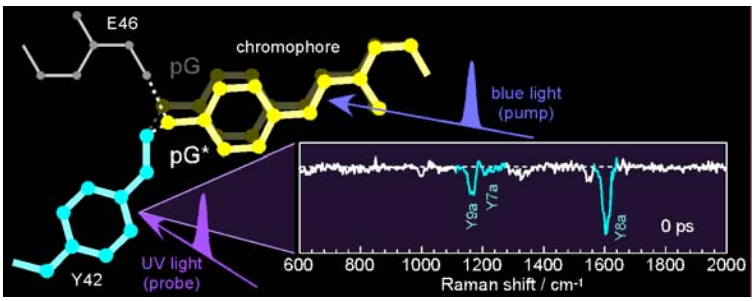

Fig. Ultrafast structural change around the PYP chromophore

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Primary Protein Response Following Ligand Photodissociation in Carbonmonoxy Myoglobin

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Proteins are endowed with both stiff and flexible properties; hence their dynamics are closely associated with structure and function. Because allosteric proteins in general propagate conformational changes over considerable distances, how these conformational changes are generated and transmitted is of major interest for understanding the regulatory, kinetic, and recognition properties of proteins. A variety of experimental evidences suggests that rapid and long-range propagation of conformational changes through the core of protein plays a vital role in allosteric communication. For example, the cooperative oxygen binding properties of hemoglobin (Hb) result from a change in quaternary structure, which is initiated by ligand binding/release at the heme (ligand binding site). Therefore, if the pathway by which one quaternary structure is converted to the other quaternary structure is structurally characterized, our understanding how a protein performs its function will be greatly advanced. The ligand-induced dynamics of myoglobin (Mb) are a basic subject for studying such features in proteins. Although Mb is a monomeric protein, the three-dimensional structure of Mb is closely similar to that of a subunit of Hb. Thus, the structural changes of Mb can be regarded as a model for the tertiary structural events that cause the quaternary structural change of Hb. Previously, we report preliminary work on primary protein response of Mb following ligand dissociation[1]. Here, we present our most recent work on Mb dynamics.

Time-resolved ultraviolet resonance Raman (UVRR) spectroscopic studies of wild-type and mutant Mb were performed to reveal the dynamics of protein motion following ligand dissociation. After dissociation of carbon monoxide (CO) from the heme, Raman bands of Tyr showed a decrease in intensity with a time constant of 2 ps. The intensity decrease was followed by intensity recovery with a time constant of 8 ps. On the other hand, Raman bands of Trp residues located in the A helix showed an intensity decrease that was completed within the instrument response time (~3 ps). The intensity decrease was followed by an intensity recovery with a time constant of about 50 ps and lasted up to 1 ns. The time-resolved UVRR study of the Mb mutants demonstrated that the hydrophobicity of environments around Trp14 decreased while that around Trp7 barely changed in the primary protein response. The present data indicate that displacement of the E helix toward the heme occurs within the instrument response time and that movement of the F helix away from the heme and that of the FG corner take place with a time constant of 2 ps. The finding that the E helix motion precedes the F helix motion strongly suggests a mechanism in which protein structural changes are propagated from the heme to the A helix through the E helix motion. In this pathway, a change of interaction between CO and the side chain of Val68 would mediate transmission of the structural events to the A helix.

[1] A. Sato and Y. Mizutani, *Biochemistry* **44**, 14709-14714 (2005).

Amide I-II Two-Dimensional Infrared Spectroscopy: Characterizing vibrational couplings and solvation of protein secondary structure

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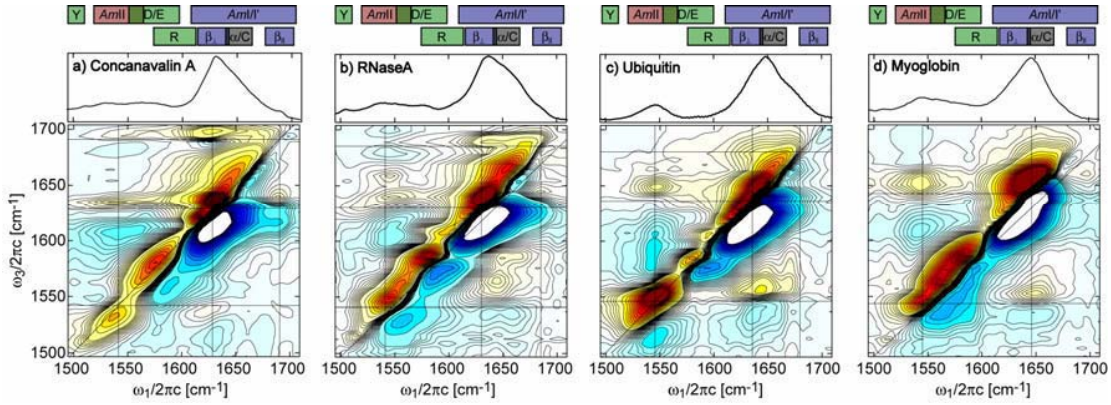
The amide vibrations are widely used for investigating conformation and dynamics of peptides and proteins due to their unique sensitivity to the local environment. A significant effort has been made to develop the structural sensitivity of amide I 2D IR spectroscopy of peptides and proteins.[1] We will report on two studies of amide I-II vibrational couplings, and how these can be used to probe solvent exposure of protein secondary structures.

N-methylacetamide, a model amide group, is investigated to characterize the anharmonic vibrational potential, coupling, and vibrational relaxation of the amide I and II modes.[2,3] Analysis of these eigenstates under isotopic substitution shows distinct changes in local mode character of the vibrations, and indicates that the modes experience relatively strong anharmonic couplings and rapid vibrational relaxation.

NMA provides the basic framework for understanding amide vibrational shifts and dynamics in proteins. In particular, the sensitivity of amide II to deuteration state of the amide proton provides a mechanism for isolating regions of larger systems based on solvent accessibility. By correlating the solvent-exposure sensitivity of amide II with secondary-structure sensitivity of the amide I vibration in proteins, a direct probe of solvent-inaccessible residues embedded in the hydrophobic core or those involved in strong hydrogen bonds in secondary structures is obtained.[4] Information on solvent penetration is obtained from amide I-II 2D IR spectra in conjunction with hydrogen-deuterium exchange (HX) experiments. Distinct spectral signatures of the cross-peak region arising from the coupling of the amide I and II modes imply significant stability of hydrogen-bonded contacts in α-helices and β-sheets (Figure). In the specific case of ubiquitin, the loss of the β-sheet signature in the cross peaks region indicates a thermally labile structure, while the α-helix remains unchanged.



FTIR and absorptive amide I/I'-II HX 2D IR spectra of series of proteins with decreasing β-sheet content including (a) Concanavalin A, (b) RNaseA, (c) Ubiquitin, and (d) Myoglobin. Spectral regions corresponding to the amide vibrations and side chains absorptions are labeled above the spectra.

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Ultrafast infrared spectroscopy of a versatile nanomachinery: Photoinduced processes in retinal proteins

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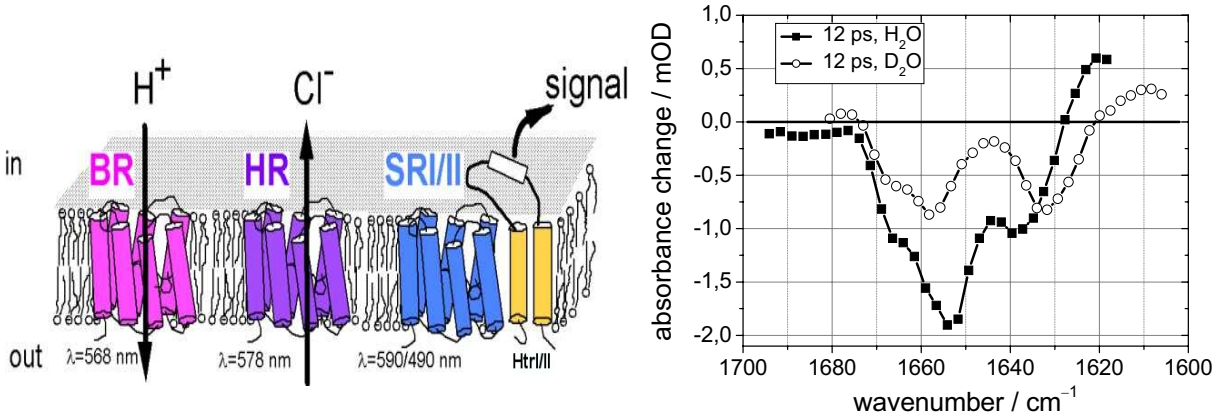
Protein function is often mediated by protein conformational changes. Systems incorporating an intrinsic chromophore which excerts a perturbation on the protein upon photoexcitation offer the opportunity to study ultrafast protein dynamics. Important prototypes in this regard are proteins exhibiting cis-trans photoisomerization of a bound cofactor, as e.g. bilin binding phytochromes and retinal binding proteins. Here, the steric part of the perturbation is realized by the torsional movement of the isomerizing chromophore moiety. We have studied the primary photoreactions of the bacterial phytochrome Agp1-BV from *Agrobacterium tumefaciens* and of the three retinal proteins bacteriorhodopsin (BR), halorhodopsin (HR) and sensory rhodopsin (SR) by means of ultrafast transient absorption spectroscopy in the IR. Whereas the chromophore vibrational dynamics along the retinal isomerization reaction in the various systems have been well characterized already[1,2,3], the corresponding protein contributions can now be revealed. As an example, in the figure IR difference spectra of SRII in H_2O- and D_2O-buffer in the amideI region are shown. The bleach bands at 1658 and 1665 cm^{-1} (D_2O spectrum) are assigned to protein vibrations that respond within less than 12 ps to the retinal photoisomerization. Similar observations were made in BR and HR. Analogies and differences are discussed.



Left: Sketch of the three most prominent bacterial retinal proteins bacteriorhodopsin (BR), halorhodopsin (HR) and sensory rhodopsin (SR), including their function. Right: Example for ultrafast protein response to isomerization in a retinal protein. Shown are IR difference spectra of SRII in H_2O- and D_2O-buffer in the amideI region, 12 ps after photoexcitation at 500 nm.

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Sunday Evening

Postersession I

Trans-cis reaction dynamics in retinal proteins by sub-ps time-resolved IR spectroscopy: protein and chromophore dynamics

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Transient vibrational spectroscopy, which provides insights into processes associated with protein-based photoreactions such as structural changes of the chromophore, its vibrational relaxation and the associated dynamics of the protein environment has been performed on sensory rhodopsin II from *Natronomonas pharaonis* at sub-picosecond time resolution.

We present new data on the dynamics of the chromophore and the surrounding protein due to the primary all-trans to 13-cis retinal photoisomerization. Three time constants (0.5 ps, 4 ps ans 11 ps) were obtained[11]. It was found that the isomerization takes place within 0.5 ps, followed by an electronic ground state relaxation (4 ps) which corresponds to experiments in the visible spectral region[22].

For the 11 ps time constant two possible processes are discussed: a vibrational cooling process of the chromophore and a relaxation of protein modes which are sterically or electrostatically disturbed due to the ultrafast chromophore isomerization. Including the results taken from BR and HR the first process would indicate a mode specifity of the time constant for vibrational cooling. The second process would demonstrate for the first time protein dynamics in retinal proteins on that timescale.

A comparison of the three systems SRII, BR and HR should give important conclusions about fast reaction dynamics in protein environment.

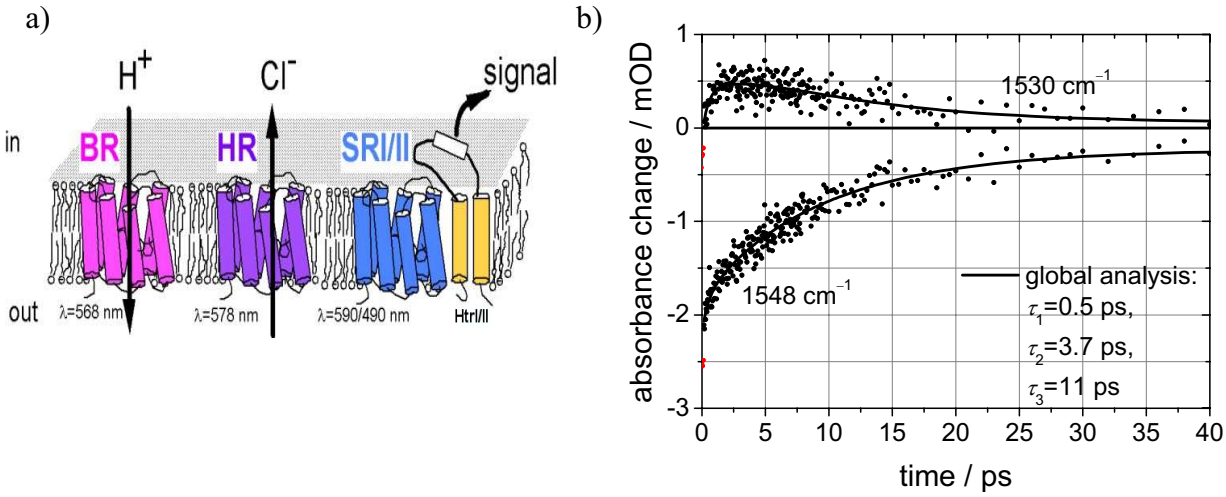

Fig.1: a) Function of the retinal proteins BR, HR and SRII, b) kinetics at 1548 and 1530 cm^{-1} and corresponding global analysis.

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Hydrogen Bond and Proton Transfer Dynamics in Complexes of Formic Acid with Amines

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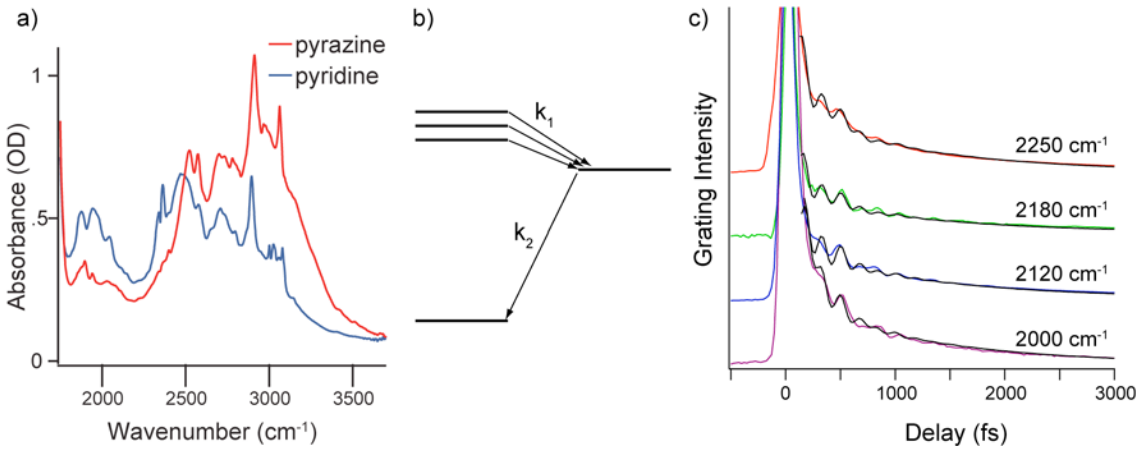
Strongly hydrogen bonded complexes like those of formic acid with amines such as pyridine and pyrazine exhibit dramatically broad, structured O-H stretching bands. The origins of this broadening and structure are the subject of ongoing study and debate, and several possible contributions have been suggested by previous theoretical and experimental studies. We have measured excitation wavelength dependent transient grating decays in the O-H stretching band of complexes of formic acid with pyridine and pyrazine. The grating transients decay on two timescales and show coherent oscillations whose intensity varies with the excitation wavelength. We have developed a model that extends the usual nonlinear response-function formalism to include a sequential kinetic scheme to describe the population relaxation. Using this model for a set of three coupled oscillators, we are able to accurately reproduce the essential features of our grating measurements. These results suggest that the broadening and structure of the O-H stretching band in these complexes arise from strong anharmonic coupling of the O-H stretch to overtones and combination bands that lie in the region between 2000 and 3000 cm^{-1}. We use electronic structure calculations on the complexes to suggest likely candidates for the states probed in our measurements.



a) The infrared absorption spectra of formic acid complexes with pyrazine and pyridine. b) The kinetic model used to describe our results. c) Typical excitation wavelength dependent transient grating decays and fits to the nonlinear response calculated using the kinetic model for hydrogen-bonded complexes of formic acid with pyridine.

Ultrafast Infrared-Spectroscopy on Flavin Systems

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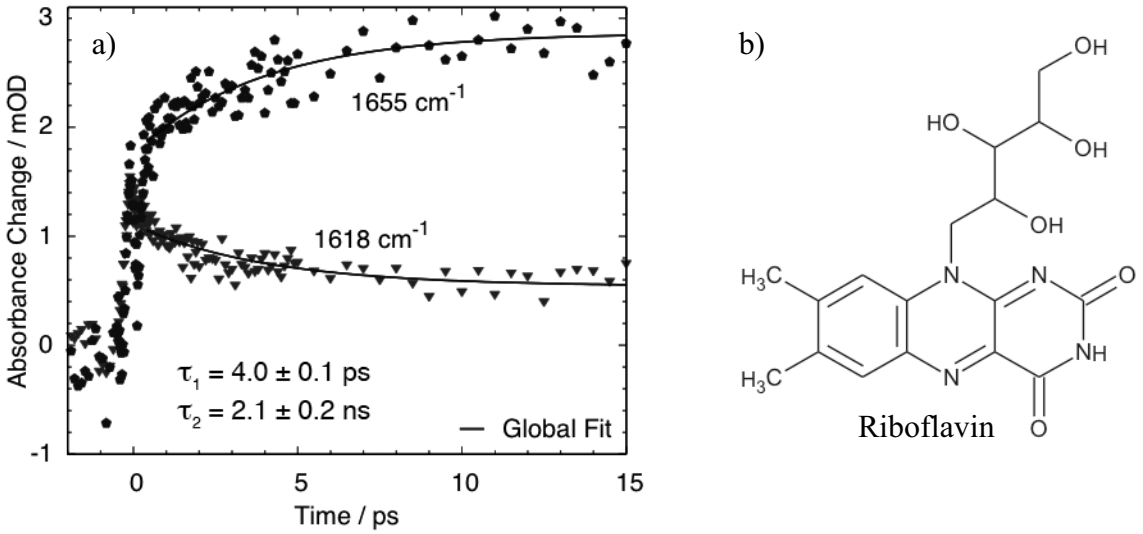
Flavin chromophores are well known for their absorption of blue light and their strong yellow color. In nature they are found as chromophores bound to proteins that act as blue light receptors, like the protein class of Phototropins which is commonly found in plants. We investigated the vibrational dynamics of two different Flavin chromophores in solution after photoexcitation on a ps-timescale.

We present sub-picosecond time resolved infrared spectroscopy of Riboflavin and Flavin-Adenine-Dinucleotide (FAD) in DMSO solution in a spectral region from 1100 cm^{-1} to 1750 cm^{-1}. Both Flavins show fast dynamics with time constants of 4 and 6.6 ps, respectively. A characteristic blue shift of all product bands within this time constant identifies the fast kinetic component as vibrational cooling of the excited electronic state.

This spectral and kinetic feature, characteristic for vibrational cooling, enables us to identify a set of excited state vibrations and to determine their spectral position, even if they are superimposed by strong bleaching bands of the electronic ground state.

Additionally both Flavins show slow kinetic component on a ns-timescale, which is due to the excited electronic state decay, as indicated by fluorescence experiments[1].

In addition we present first measurements of the Flavin-Mononucleotide binding protein domain LOV1 of the Phototropin 1 of the green algae *Chlamydomonas Reinhardtii*.



All product bands of the investigated Riboflavin (**b**) in DMSO solution show a blue shift on a time scale of a few picoseconds after photo excitation at 387.5 nm (**a**), which is is characteristic for vibrational cooling.

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Self-trapped vibrational excitations in synthetic ß-helical polymers

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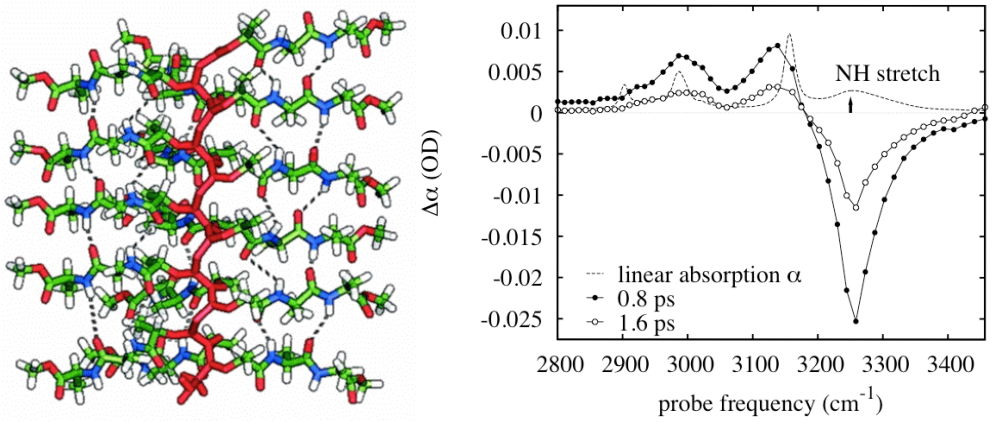
Polymerization of isocyanopeptides results in polymers that fold in a proteinlike fashion to give helical strands in which the peptide chains are arranged in β-sheets.[1] The peptide conformation in these polymers is different from the β-helices found in proteins: they have a central helical core acting as a director for the β-sheet-like arrangement of the peptide side arms (see figure). The structure of isocyanopeptide polymers can be controlled by tailoring of the side branches forming the β-sheets.[1] We present evidence for self-trapped NH-stretch vibrational excitations in these β-helical polymers. Such self-trapped states, in which distortion of the hydrogen-bond network localizes vibrational excitations, have recently been demonstrated in an α-helix,[2] and are believed to play a role in energy transport in proteins.[3]

We use femtosecond vibrational pump-probe spectroscopy to measure the nonlinear response of the NH-stretch mode of alanine-based β-helical polymers. In polymers containing dialanine side chains (having one amide group), the transient absorption change upon exciting the NH-stretch mode exhibits a negative Δα at the fundamental frequency (due ground-state bleaching and stimulated emission), and *two* positive Δα bands at lower frequencies (see figure; in the monomer only one positive Δα band is observed). These two bands, which are similar to the ones observed in an α-helix,[2] can be assigned to states in which the vibrational excitation is trapped at the same, or at two neighboring peptide units in the hydrogen-bonded ⊣[NH···OC]⊢ chain.[3] In trialanine-based polymers, each side chain contains two amide groups, and hence participates in two different hydrogen-bonded ⊣[NH···OC]⊢ chains. Interestingly, only the ⊣[NH···OC]⊢ chain closest to the polymer core exhibits NH-stretch self-trapping, whereas the chain farthest from the core does not, probably as a consequence of differences in hydrogen-bond strength and/or molecular geometry.



Left: Structure of a trialanine-based β-helical polymer, containing two amide groups per side chain. Right: Conventional absorption spectrum (dotted curve) of a dialanine-based polymer, and the absorption change upon excitation of the NH-stretch mode. The two positive Δα bands indicate NH-stretch self-trapping.[3]

References:

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Sub-picosecond infrared spectroscopy of green-absorbing proteorhodopsin chromophore isomerization

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Proteorhodopsin (PR), found in marine γ-proteobacteria, is a light-driven proton pump similar to bacteriorhodopsin (BR). Widespread distribution of γ-proteobacteria in worldwide oceanic waters indicates this retinal containing protein may contribute significantly to global solar energy input into the biosphere[1]. Different variants of proteorhodopsin are spectrally tuned to absorb different wavelengths of light. A previous study using low-temperature FTIR examined the structural changes during the primary photoreaction (PR→K) of wild-type green-absorbing proteorhodopsin (GPR)[2] and showed that the primary photoreaction involved an all-*trans* to 13-*cis* isomerization of the retinal chromophore. In this study we employ sub-picosecond visible-pump infrared-probe spectroscopy to investigate the all-*trans* to 13-*cis* chromophore isomerization in GPR by characterizing the C=C ethylenic stretching vibration (1500 – 1570 cm^{-1}). Global analysis of the data set yields two time constants of 700 fs and 3.2 ps corresponding to the formation of the 13-*cis* photoproduct at 1519 cm^{-1} and the partial recovery of the ground state at 1539 cm^{-1}, respectively. In addition, comparison of the time-resolved difference spectra with that obtained at low-temperature shows that there are differences between the PR chromophore structure trapped in the K-intermediate at low-temperature and several ps after photon absorption at room temperature. This work was supported by NIH grant GM069969-01 to KJR and NIH grant R37GM27750 and the Robert A. Welch foundation to JLS.

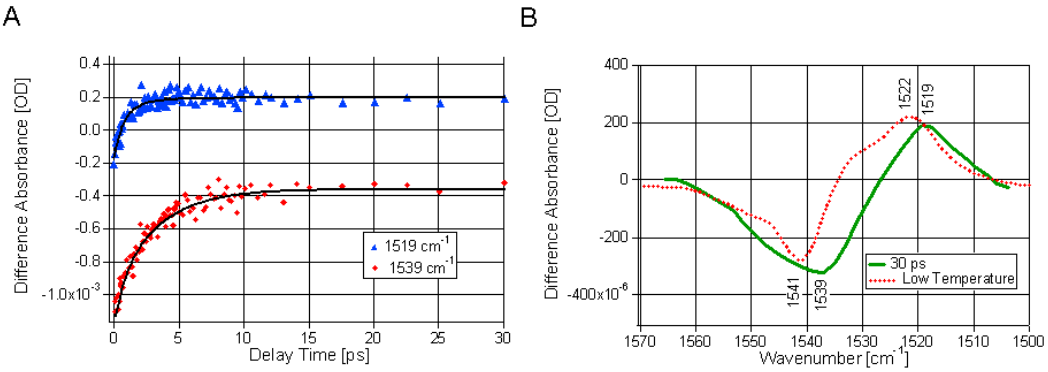

Figure: A. Results of global fit displayed for 1519 cm^{-1} and 1539 cm^{-1} bands. B. Comparison of 30 ps time-resolved spectrum recorded at 25ºC and low-temperature (80K) spectrum.

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Solvent Effects on Vibrational Cooling: Differences Between Cytidine and para-Nitroaniline

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Rapid (< 1 ps) internal conversion after excitation with a UV pump pulse leads to "hot" molecules in the electronic ground state, which exhibit a non-thermal distribution of vibrational excitation in various modes. The excess energy in these modes is redistributed between the normal modes and eventually transferred to the solvent. These processes can be experimentally observed by a delayed mid-infrared probe pulse[1].

In this study we investigate the influence of the solvent on these processes for the nucleoside cytidine (cyd) and para-nitroaniline (pNA) where fast ground state recovery is found. In both cases we chose protic and aprotic solvents. For the reference molecule pNA, the bleach recovery time constant of the NO_2 stretch mode of pNA at 1315 cm^{-1}, which is a measure for the vibrational cooling, depends strongly on the solvent, ranging from 0.7 ps in water to 4.4 ps in methanol and 7.5 ps in deuterated dimethylsulfoxide (DMSO-d6).

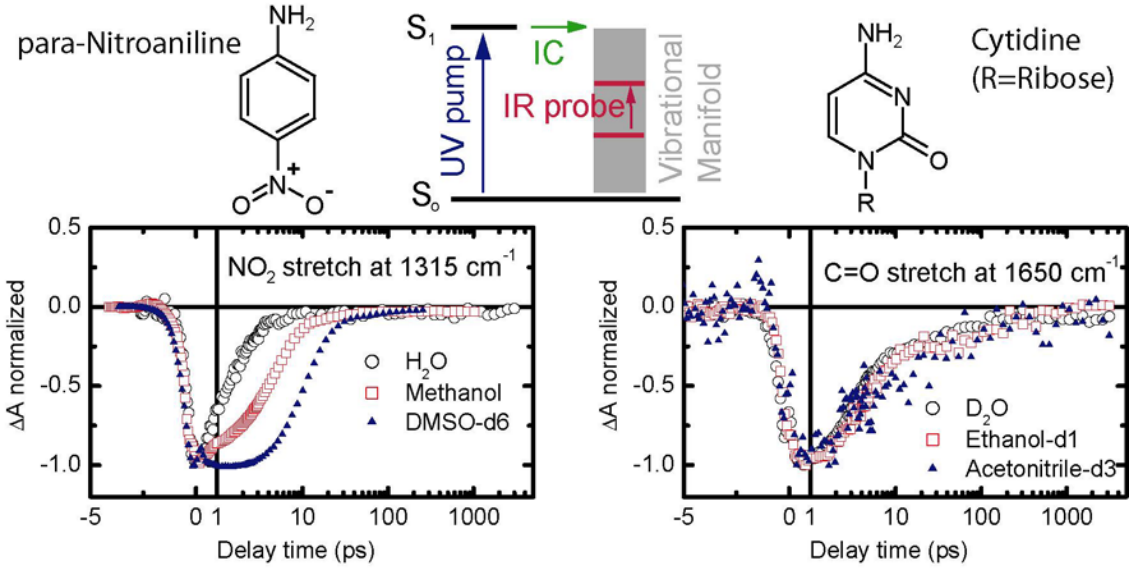

Figure 1: (top) Schematic overview of the experimental approach followed in this study. (left) Molecular structure of pNA and observed bleach recovery of its NO_2 stretch mode at 1315 cm^{-1}. (right) A similar data set for cytidine and its C=O stretch vibration.

On the other hand for cytidine, a time constant of 3 ps is observed for cooling, as inferred from the bleach recovery at 1650 cm^{-1}. Contrary to pNA this early phase of the recovery does not depend on the solvent. This vastly different energy redistribution behavior is discussed in the context of molecular structure and normal mode frequencies.

[1] T. Schrader, A. Sieg, F. Koller, W. Schreier, Q. An, W. Zinth, P. Gilch, Chem. Phys. Lett., **2004**, 392, 358-364

Water as a molecular hinge in amide-like structures

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Water plays an important role in a wide variety of chemical interactions. In protein folding, single embedded water molecules can form connections between oxygen atoms of different amide groups through double hydrogen bond formation[1]. In this way water holds together bio-molecular chains and assists in the formation of tertiary structures. Here we study the molecular motions and energy dynamics that single water molecules exhibit in interaction with such amide groups.

As a model system, we used a dilute solution of water dissolved in N,N-Dimethylacetamide (DMA). DMA possesses the same characteristic O=C−N group that is also present in amides while the N−H groups are substituted by amino-methyl groups ($N-CH_3$) to avoid spectral interference with the O−H groups of water in our measurements. From the linear spectra, we derived that each water molecule was embedded between DMA molecules through double hydrogen bond formation. Using polarization-resolved pump-probe spectroscopy, we examined the depolarization of three different directions of transition dipole moments of the OH stretch vibration of the water molecules (OH-stretching mode in HDO and symmetric and asymmetric stretching modes in H_2O). By combining these measurements we extract detailed information about the specific reorientation of this water around different axes.

We found that the system exhibits bimodal rotational dynamics with two distinct timescales: a slow (7±1 ps) reorientation of the entire DMA-water-DMA complex and a fast (0.5±0.2 ps) 'hinging' motion of the water molecule around the axis parallel to the connecting hydrogen bonds (i.e. parallel to the asymmetric mode of H_2O). We found that this hinging motion is not cylindrically symmetric but instead limited to a range of about a quarter circle (52 ± 8^o) around the equilibrium position. Additionally, we observed an exchange of energy between the two normal modes of H_2O at a timescale of 0.8±0.1 ps and found that the vibrational excitation decays almost exclusively through the symmetric stretch normal mode with a time constant of 0.8±0.2 ps.

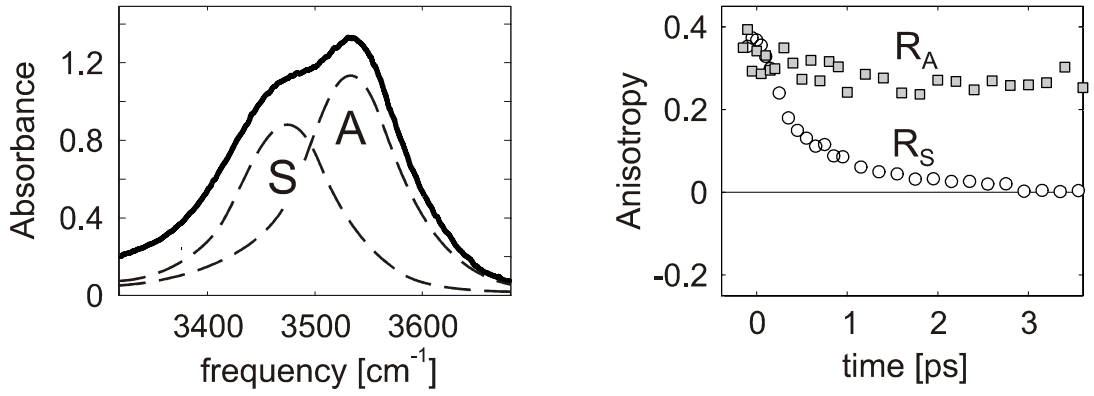

Figure 1: Left: linear absorption spectrum of H_2O in DMA showing the symmetric (S) and asymmetric (A) normal modes. Right: Anisotropy of water pumped and probed in the symmetric normal mode (R_S) shows a faster initial decay than water pumped and probed in the asymmetric normal mode (R_A)

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STRUCTURAL DYNAMICS OF HEMOGLOBIN ENCAPSULATED IN SILICA GELS

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Encapsulating hemoglobin (Hb) in silica gels[1] can slow quaternary structural changes extremely and is very useful for investigation of allosteric mechanisms because only tertiary structural changes on R and T quaternary structure can be observed. We applied this technique to investigate structural dynamics of Hb fixed in R and T quaternary structures following CO dissociation by time-resolved resonance Raman (TR^3) spectroscopy.

Three kinds of CO-bound Hb (HbCO) samples were prepared: Hb associated with CO before the encapsulation (denoted by *R* gel), Hb associated with CO after the encapsulation of deoxyHb (*T* gel) and HbCO in solution. There was a small difference in steady state resonance Raman spectra of HbCO between R and T quaternary structures. It is suggested that the frequency of ν_4 band observed in 1350-1380 cm^{-1} is proportional to that of Fe-histidine stretching [ν(Fe-His)] band[2], which is known to be sensitive to structure of proximal side of the heme pocket and is not observed for CO-bound form[3]. On the other hand, the frequencies of Fe-CO stretching [ν(Fe-CO)] band observed around 500 cm^{-1} and C-O stretching band [ν(C-O)] observed around 1950 cm^{-1} are known to be sensitive to structure of distal side of the heme pocket[4]. These results show that the structure of the heme pocket on both proximal and distal side of CO-bound heme is independent from quaternary structure.

Nanosecond TR^3 spectra upon CO photolysis were measured for the three samples. The temporal changes of the ν(Fe-His) frequency (Fig. 1), the γ_7 frequency and the ν_8 band intensity were different among the three kinds of samples. In delay time later than 100 ns, the ν(Fe-His) frequencies of *R* gel exhibited a deviation from these of HbCO in solution, while the frequencies were similar to each other in 10-100 ns. This suggests that quaternary structure of *R* gel is fixed in R structure. In the case of *T* gel, the ν(Fe-His) frequency at 10 ns was different from those of *R* gel and HbCO in solution. This is in contrast to that there was the small frequency difference for the ν_4, ν(Fe-CO) and ν(C-O) bands for the CO-bound forms among the three samples.

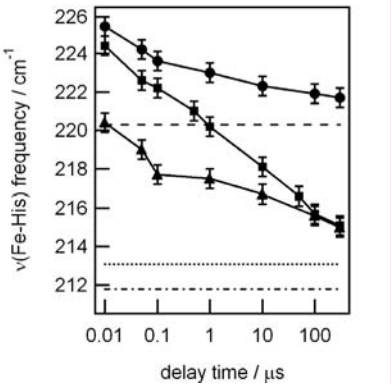

Fig. 1 Temporal changes of the ν(Fe-His) frequency upon CO photolysis for *R* gel (circles), *T* gel (triangles) and HbCO in solution (squares). The ν(Fe-His) frequencies of the deoxy forms are also shown : *R* gel (dashed line), *T* gel, dotted line and HbCO in solution (dash-dotted line).

Picosecond TR^3 spectra upon CO photolysis were also measured for the three samples. A 7-cm^{-1} frequency difference between *R* gel and *T* gel was observed in the time-resolved spectrum at 10 ps. This suggests that the structural difference in the heme pocket between *R* gel and *T* gel has appeared within 10 ps after CO dissociation.

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Real time investigation of turn opening and hydrogen bond breaking upon thiopeptide isomerization

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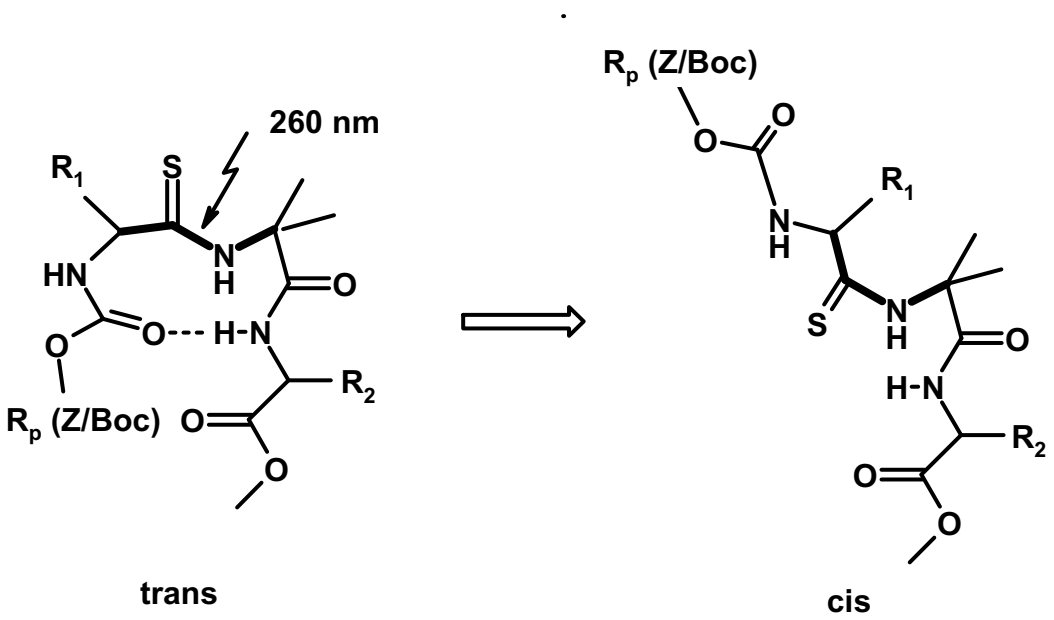
To investigate peptide dynamics on ultrafast time scale molecular photo switches can be incorporated to trigger conformational change. We use the substitution of the oxygen in one peptide bond with a sulphur atom. The resulting thionated peptide bond can now be excited and isomerized selectively from trans to cis because its electronic absorption is red-shifted compared to the one of a normal peptide bond[1]. It has been shown that this minimal modification does not perturb the structure of a peptide significantly[2,3].

Aib-containing peptides are known to stabilize β-turns and 3_{10}-helices. A number of different Aib-containing thiopeptides (Z/Boc-AA_1(thio)-Aib-AA_2-OMe, AA = Amino Acid) have been investigated[4,5]. X-ray crystallography has shown that some of the Aib-containing thiopeptides exhibit an intramolecular hydrogen bond[5]. In solution, the IR spectra of the molecules indicate the presence of two different conformations, one of them involving an intramolecular hydrogen bond. The equilibrium between the different conformations depends strongly on the amino acid sequence. 2D-IR-spectroscopy and conventional methods have been used to characterize the different thiopeptides. We show by transient infrared spectroscopy that it is possible to break the hydrogen bond upon UV excitation. The dynamics and quantum efficiencies of different thiopeptides have been compared.



Schematic representation of the ring opening upon thiopeptide isomerization.

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Noninvasive Tissue Oxygenation Monitoring by Resonance Raman Spectroscopy

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Readings of oxygen saturation percentages of venous blood being returned to the lungs from major organ systems provide important indications of the adequacy of the supply and utilization of oxygen. These levels can be lowered from normal values by the presence of hemorrhage, or raised by sepsis. Both of those conditions are life threatening and can be difficult to detect via the traditional vital signs.

Methods currently used for the measurement of acute oxygen levels in tissue and venous blood include gastric tonometry (Figure 1) and pulmonary artery catheterization. Gastric tonometry has some inherent problems. Pulmonary artery catheterization involves threading a catheter through the chambers of the heart, and is risky to the patient. A long sought goal has been to replace such procedures with non-invasive methods that are as easy to implement as pulsed oximetry, a method which is now universally employed for the measurement of oxygen saturation levels in arterial blood.

Spectroscopic methods based on the absorption of tissue penetrating near-infrared light by hemoglobin in blood are complicated by the competition of signals from myoglobin in deep tissue. We have utilized low powered deep violet excitation at externally accessible oral mucosal surfaces which are metabolically active. Such excitation does not significantly penetrate tissue, and provides strong resonance Raman signals from hemoglobin in the surface vasculature.[1-3]

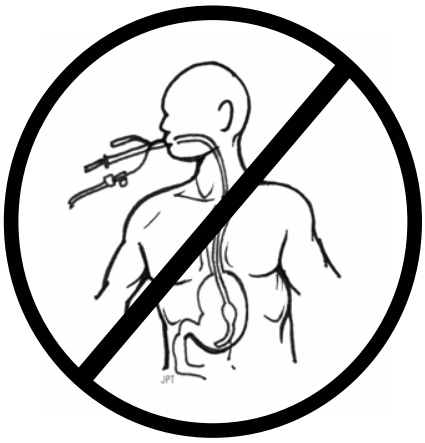

Figure 1. It would be beneficial to be able to replace methods such as gastric tonometry diagramed here, used for the measurement of oxygenation of tissue and venous blood, with non-invasive alternatives.

Financial support is acknowledged from NIH grant GM-57042.

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Site-selective information on α-helix formation on a photoswitchable peptide gathered by means of time-resolved IR spectroscopy

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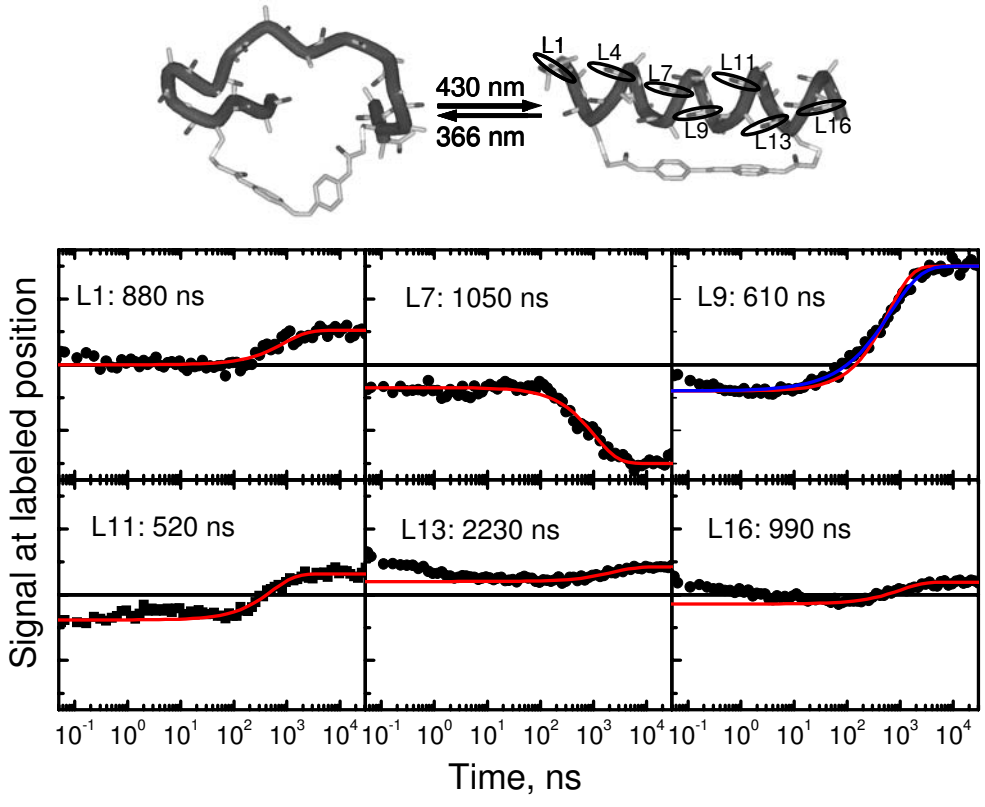
Position dependent α-helix formation kinetics is studied by utilizing single $^{13}C=^{18}O$ isotope labeling and time-resolved IR spectroscopy on a photoswitchable peptide. The folding time-scales between different sites spread with a factor of two among each other and in the middle of the peptide a non-exponential kinetics is observed. Moreover, the lifetimes from each site show strong temperature dependence, as does the averaged signal reported earlier. Surprisingly, one of the studied site (site 7) shows a decrease of hydrogen bonding upon folding of the peptide, instead of "normally detected" increase of the hydrogen bonding. This implies that considerably conformational changes take place during α-helix folding, but more importantly, the unfolded state is not as unstructured as thought before.

In order to detect a direct lifetime of a single specific H-bond formation during α-helix formation transient-2D-IR experiments on a site-selectively isotope labeled peptide are on progress.



Time-dependent amplitudes of the amide I' difference signal between the non-labeled and labeled (assigned as circles in the sketch of the molecule, upper panel) signals during the folding process. The solid red lines are exponential fits of the curves and in the case of L9 (isotope label position 9) also stretched exponential fit is shown.

Nonadiabatic Coupling Mechanism for Ultrafast Electron Transfer in Reaction Centers of Bacterial Photosynthesis

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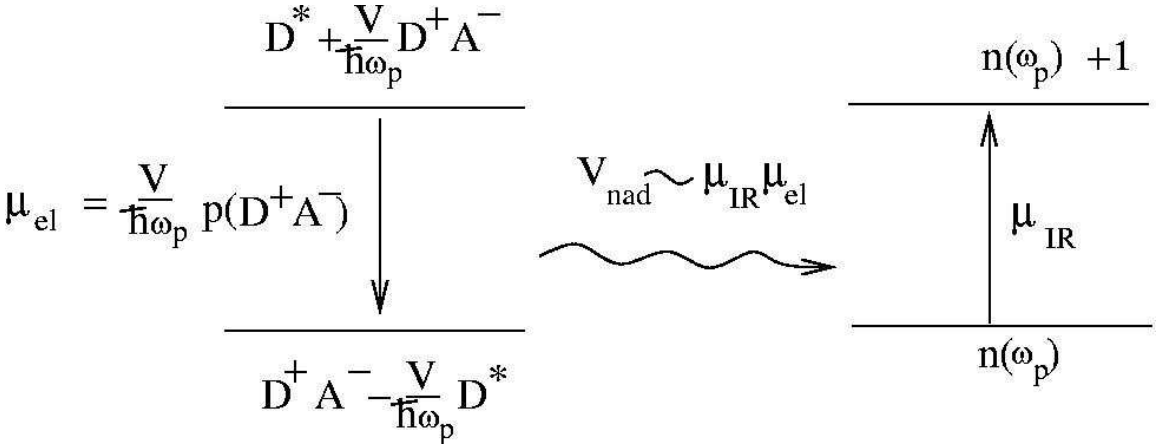
Electron transfer from the special pair dimer to the BChl monomer and further to the Pheophytine is analyzed as a nonadiabatic transition between delocalized Born-Oppenheimer states. Initial and final states are considered as adiabatic states which already incorporate the resonance coupling between molecular orbitals at different sites. Nonadiabatic coupling matrix elements and partial reorganization energies are evaluated for the normal modes of a model system which is representative for the reaction center. We find a rather broad distribution of weakly coupled accepting modes from the low frequency region $\hbar\omega << kT$ up to the region of stretching modes with $\hbar\omega >> kT$. The nonadiabatic coupling is interpreted as a transition dipole type coupling involving the optical transition dipole between the adiabatic states and the infrared dipole of the promoting mode. Such a mechanism is highly efficient for the reaction center where the optical transition dipole is borrowed from the large permanent dipole of the charge separated state and the infrared dipole of the promoting mode can be enhanced by coupling to the low lying IR transition of the special pair cation



Nonadiabatic coupling via a transition dipole coupling mechanism: The localized optical excitation D* and the pure charge transfer state D^+A^- are mixed by the resonance interaction V to form the adiabatic initial and final states. The nonadiabatic coupling V_{nad} can be visualized as an electronically allowed transition occurring simultaneously with creation of one quantum of the promoting mode ω_p .

Ultrafast β-Turn Opening Observed by Transient 2D–IR Spectroscopy

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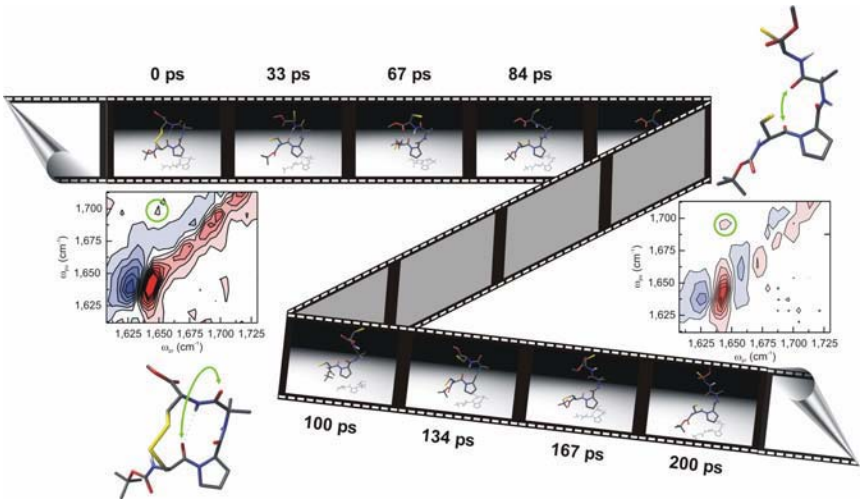
2D-IR spectroscopy offers means to resolve distributions and dynamics of fast interconverting structures in *equilibrium*. Transient 2D-IR[1] (T2D-IR) can be understood as an extension of the 2D-IR experiment to the *non-equilibrium* regime, which allows to take full advantage of the high time resolution.

We used T2D-IR to investigate the opening of a β-turn in a small cyclic peptide.[2,3] The β-turn is stabilized by an intramolecular hydrogen bond and clasped by a disulfide bridge, providing a predetermined "breaking point", which can be cleaved by UV light generating *non-equilibrium* conditions.[4] In the 2D-IR spectra we observed a set of crosspeaks that arises from coupling of neighbouring C=O vibrators and a crosspeak due to through space coupling between the two hydrogen-bonded peptide units. Upon cleavage of the disulfide bridge the latter coupling is most strongly affected as the β-turn opens and starts to adopt a more floppy and random structure. This leads to a *transient* crosspeak in the T2D-IR spectra. Its intensity changes in good agreement with the times scales extracted from pump-probe experiments and MD-simulations.

We believe that the combined use of MD simulations and direct structural information from T2D-IR will provide new insights into fast biomolecular processes.



MD snapshot structures (film reel), closed and open structures and corresponding T2D-IR spectra of the β-turn peptide.

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Sub-Picosecond Time-Resolved Infrared Spectroscopy of Phytochrome

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Phytochromes are photoreceptor proteins in plants and bacteria incorporating a bilin chromophore. Their photocycle contains two interconvertible metastable states Pr and Pfr linked by several thermally driven relaxation steps. The primary process of the Pr to Pfr reaction is a light-induced Z to E isomerization of the C_{15}=C_{16} methine bridge of the bilin chromophore connecting the pyrrole rings C and D.

Here we present the first sub-picosecond time-resolved vibrational spectroscopy data on the Pr photoreaction of the biliverdin-binding phytochrome Agp1-BV from *Agrobacterium tumefaciens*. Three kinetic components with time constants of τ_1=0.7 ps, τ_2=3.3 ps and τ_3=33.3 ps could be extracted from the transient IR absorption data of bond-specific marker bands. On the grounds of the corresponding decay associated spectra and accompanying sub-picosecond VIS-VIS experiments, a first reaction scheme for the Pr photoreaction of Agp1-BV is proposed. It involves several steps on the S_1 surface and a vibrationally excited electronic ground state O_r. The obtained results are discussed in the context of the literature on the primary reaction of bacterial and plant phytochromes.

Further, the isomerization quantum yield ϕ_{Pr} of the primary process could be determined to 0.094. Comparison with ϕ_{Pr} obtained by biochemical methods clearly shows that the quantum yield of the Pfr formation is fully determined by the Pr photoreaction.

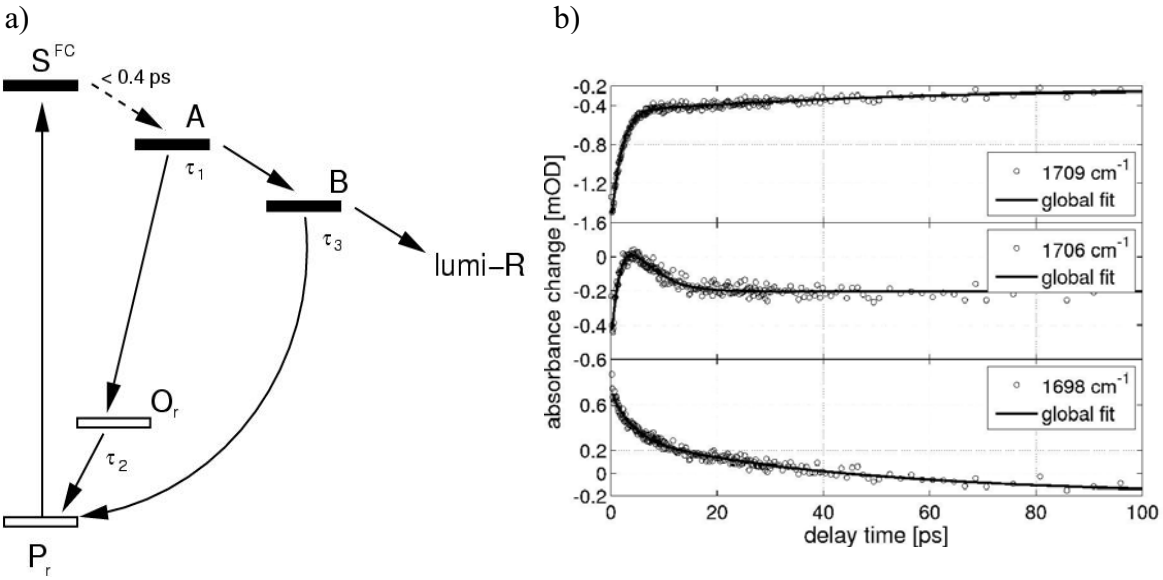

Fig. 1 a) Proposed reaction scheme for the primary process of the Agp1-BV Pr reaction. b) Infrared absorbance transients from the ring D carbonyl stretch region of the bilin chromophore together with the triexponential global fit.

Ultrafast Structural dynamics in BLUF Domains: Transient infrared Spectroscopy of AppA and its Mutants

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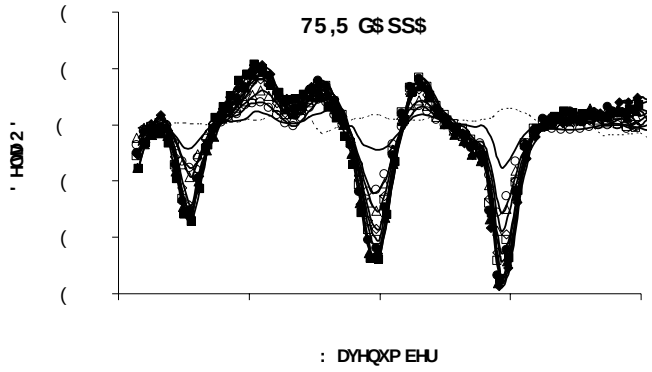
In this paper we will describe ultrafast vibrational studies of the dynamics underlying the operation of blue light sensing using FAD (flavin adenine dinucleotide) (BLUF) proteins. The BLUF domain of AppA, a transcriptional antirepressor from the photosynthetic bacterium *Rhodobacter sphaeroides* will be studied as an example. Under low light conditions, the dark state of AppA binds to PpsR forming an AppA-$PpsR_2$ complex that is unable to bind DNA. Upon blue light photoexcitation, AppA dissociates from PpsR, allowing formation of the repression-competent PpsR tetramer which binds to DNA and inhibits gene transcription.

AppA is an unusual photoactive protein. In PYP and the rhodopsin family electronic excitation is followed by a fast structural change in the excited state which acts as the trigger for formation of the signaling state of the protein. In contrast for FAD in AppA there is no apparent excited state structure change. All that is seen is a 10 nm red shift in the absorption spectrum between dark (dAppA) and light (lAppA) adapted states. Structural studies point to changes in the interaction between FAD and the protein, probably through modified H-bonding interactions.[1] Recently we have shown that time resolved IR spectroscopy is a powerful tool in investigating ultrafast structural changes in proteins.[2] Here we apply this method to dAppA, lAppA and two mutants. Some typical transient IR data are shown in the figure. All transients appear on a sub-picosecond timescale. Many can be assigned to FAD, though modified compared to the spectrum in solution.[3] Through mutagenesis we identify one transient which is uniquely a marker for the capability to form the signaling state. The assignment will be discussed.



TRIR spectra of dark adapted AppA recorded *1 (filled squares) 5 (filled diamonds) 10 (filled triangles) 20 (filled circle), 50 (open square) 100 (open diamond) 300 (open triangle) 500 (open circle) and 2000 ps (line) after excitation. Note that data for 1,5,10 ps are overlapped*

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An experimental setup for FTIR step scan spectroscopy of membrane proteins with a non-cyclic photo reaction

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The method of Step Scan FTIR spectroscopy has been developed over 15 years ago [1]. It combines the excellent signal to noise ratio of FTIR measurements with a time resolution of nano seconds. For this, the movable mirror of the spectrometers Michelson interferometer is not moving continuously back and forth, but at each sampling position of the interferogram the mirror is kept fixed while a transient recorder card measures the reaction-induced changes of the interferogram with a sampling rate of up to 200MHz. After this, the mirror is moved to the next sampling position where another transient data set is taken and so on. 540 mirror positions are needed to represent the IR interferogram for the spectral range up to 1975cm^{-1} with a spectral resolution of 8cm^{-1}. Finally, Fourier transformation renders difference absorbance spectra for each time slice the transient recorder has measured after triggering the reaction.

Step scan spectroscopy has been successfully applied to a variety of photoactive systems in the last 15 years. All these samples had one property in common: the photoreaction is reversible, i.e. the system undergoes a photocycle. In addition to the excitations at each mirror position, also signal averaging has to be performed. The same sample has to be triggered at least 5000 times for one step scan measurement to be complete. One possibility to overcome the limitation of reversible systems is the replacement of the sample after each excitation, and a set-up with a micro-illuminator and an x-y translation stage has been described, although no real measurements on irreversible photoreactions of proteins have been reported [2]. It is clear that larger amounts of protein are required.

In order to reduce the protein quantity, one has to balance the number of triggering events which are possible with a given protein quantity and a given focus diameter against the reduction of IR intensity caused by the micro-illuminator. We realized that the use of IR microscope objectives as micro-illuminators with a 100 µm focus caused a dramatic reduction of IR intensity, counterbalancing the larger number of possible excitations. A satisfactory compromise is a micro-illuminator with a focus of 1 mm, and a sample area of 7 cm^2 which is scanned via an x-y translation table. With this arrangement, the number of possible sample excitations is somewhat larger than the number of sampling positions of the interferogram.

We will demonstrate the feasibility of the method for the case of the visual pigment rhodopsin which bleaches irreversibly after excitation. Approx. 20 nMol of rhodopsin are required to cover the 7 cm^2 sample area. In order to improve the quality of the spectra, we had to correct the laser flash-induced signals for variations in flash energy and in protein concentration at each sample position. The noise in the spectra is further reduced by averaging several measurements. The spectra represent the first time-resolved measurements of rhodopsin in the infrared covering the µs and ms time regime. Difficulties and possible improvements of the method will be discussed.

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A novel imaging system:

Femtosecond Stimulated Raman Microscopy (FSRM)

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Raman microscopy allows to trace the distribution of molecules, for instance in cells, in space and time. Microscopy techniques relying on linear Raman spectroscopy suffer from low Raman cross sections which result in long acquisition times. This can hamper "real time" monitoring of such distributions. By applying non-linear Raman techniques these acquisition times can be drastically reduced. Presently the common approach relies on coherent anti-Stokes Raman scattering (CARS)[1]. CARS microscopy is highly sensitive but often yields strongly distorted Raman spectra due to a non-resonant background. Further it features a quadratic concentration scaling which hampers a quantitative analysis of CARS micrographs.

We have recently presented femtosecond stimulated Raman microscopy (FSRM)[2] as a possible alternative delivering undistorted Raman spectra which scale linearly with the sample concentration. A femtosecond white light pulse (Raman probe) and an intense picosecond pulse (Raman pump) both derived from the output of a 1 kHz CPA system are coupled into a scanning microscope (Fig. 1). At the focus, stimulated Raman interaction modulates the white light spectrum. This spectrum is read-out in multi-channel fashion. By raster-scanning the sample, complete Raman spectra of each point of the sample are recorded and converted into chemical maps. To demonstrate the feasibility of the approach "chemical" pictures of polystyrene beads suspended in water have been recorded (see Fig. 1).

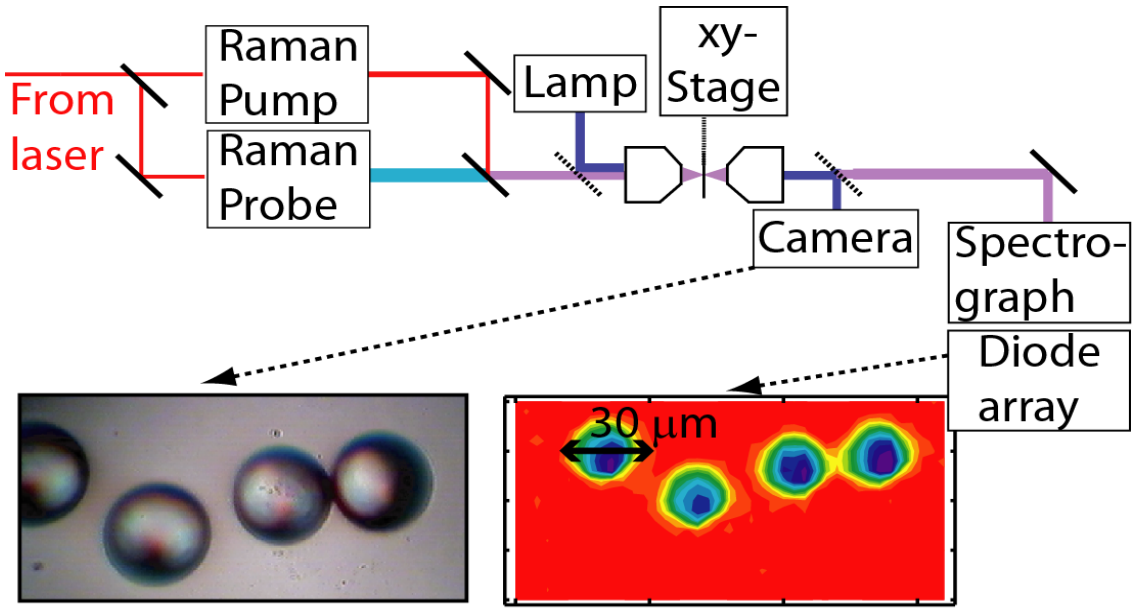

Fig. 1: Schematic of the FSRM set-up. The picture on the left shows a conventional micrograph of polystyrene beads dispersed in water. The false color image on the right is based on a two-dimensional array of Raman spectra. Spectral integrals covering the C-H stretch region are indicative for the polystyrene concentration and are contour-plotted here.

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Femtosecond Photo-initiation of Protein Folding.

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UV visible pump-probe spectroscopy is used to investigate and validate the use of *bis* (maleimide) derivatives of aryl diaryl disulfides as 'triggers' with which to quickly and easily intimate folding in proteins. Structurally, these triggers are product mutations of *(p)*-aminophenyldisulfide (PAPDS) in which optically induced homolytic photolysis of the disulfide bond coupled with monitoring of the temporal evolution of thiyl radical absorption in the visible region allows direct confirmation of the triggering method.

The thiyl concentration history upon photocleavage of (*p*)-aminophenyldisulfide is recorded as a function of optical density change in a series of solvents of increasing viscosity. This data is subsequently compared to a model obtained from a diffusional and kinetic treatment of molecular translational motion to investigate the effects of thiyl geminate recombination and solvation on thiyl pair survival probability. *Bis*-maleimide derivatives, 4-maleimide phenyldisulfide, cysteine maleimide disulfide along with an *ortho* class 2-maleimide phenyldisulfide are also examined in an identical fashion to PAPDS to determine their suitability for use as cross-linking reagents. Of these, the cysteine maleimide ligand is considered the most promising bridging moiety.

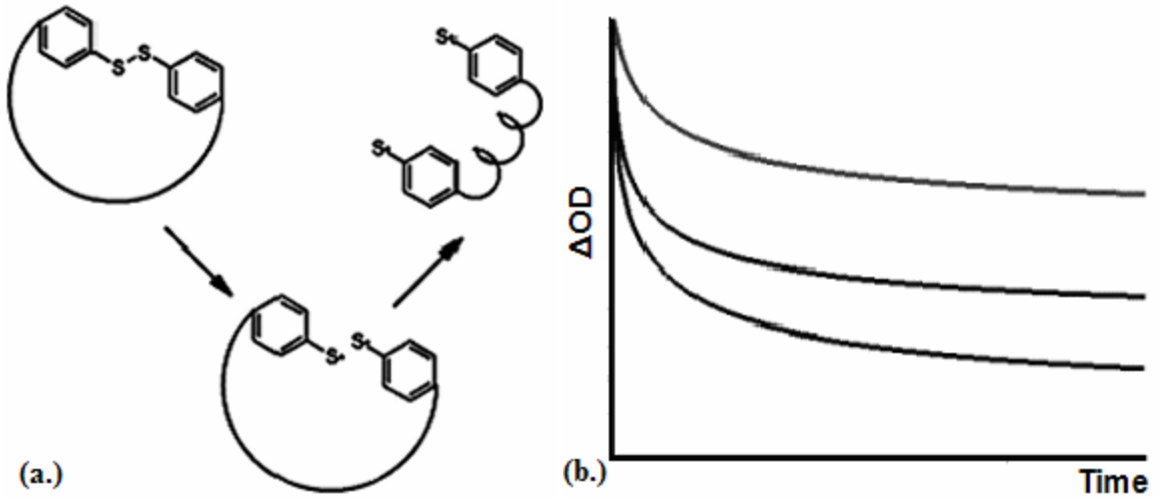

Figure (a.) Aryl disulfide cross-linking groups were incorporated to link the protein ends constraining the protein in a cyclic, less helical conformation. Photocleavage of the disulfide bond on the sub-picosecond timescale removes this constraint and the peptide begins to fold into its native more helical structure. This approach allows the earliest events of helical formation to be observed. **Figure (b.)** Evolution of the radical absorption signal after photolysis of PAPDS in solvents of increasing viscosity. The vertical axis is the change in absorption relative to the starting disulfide (ΔOD) in arbitrary units.

The initial folding kinetics of the proteins are finally monitored using femtosecond mid-infrared (MWIR) pump probe experiments. The folding of each protein is monitored by preliminary examination of the cysteine maleimide carbonyl response upon photo cleavage of the crosslink thus giving an insight into the environment change local to the photolysed region. Secondary experiments probing carbonyl absorption changes in the amide I region are also conducted with the ultimate objective to obtain information about the folding pathway via monitoring of secondary structural change.

Monday Evening

Postersession II

Water and proton transfer at the alumina-air interface

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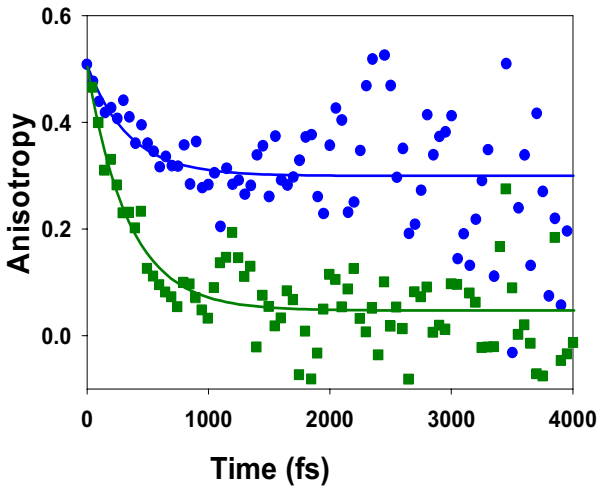
The present study aims at understanding the dynamical properties of water and OH groups layered on a γ-alumina surface mainly by means of femtosecond IR-pump IR-probe transient absorption spectroscopy.



Evolution of the anisotropy as a function of the pump frequency: blue circles: pump and probe at 3460 cm^{-1}; green squares: pump and probe at 3200 cm^{-1}. The decays have been fitted with a single exponential decay (lines corresponding to a*exp(-t/τ)+b). The fitted values are: τ = 400 ± 100 fs, a = 0.2 and b = 0.3 for a pump at 3460 cm^{-1} and τ = 400 ± 100 fs, a = 0.45 and b = 0.05 for a pump at 3200 cm^{-1}.

The experimental results obtained demonstrate the existence of several kinds of O-H vibrators on the surface of alumina membranes, distinguishing them by their behavior on the femtosecond time scale and by their anisotropy. In the high frequency region (> 3400 cm^{-1}) the absorption is due to well-packed aluminol groups and to physisorbed water patches on the surface. When pumping at 3200 cm^{-1} physisorbed water hydrogen-bonded to $AlOH_2^+$ groups is observed. The anisotropy measurements demonstrate the existence of an efficient energy transfer mechanism among the water molecules characterized by a time constant of 400 ± 100 fs (Figure). The persisting anisotropy at long times especially in the case of AlOH groups and of the structured physisorbed water layer on top of them proves the anisotropic structuring induced by the surface (Figure, blue circles). The ratio of the time constants associated to the anisotropy in the case of neat water (τ_{3D} = 75 fs)[1] and in the case of surface water (τ_{2D} = 400 fs) is τ_{2D}/τ_{3D} ~ 5. This ratio reflects the change of dimensionality in the energy transfer and the specificity of surface chemistry.

The excitation at 3000 cm^{-1} enables the detection of a photon induced proton transfer reaction. The proton back-transfer reaction time constant is 350 ± 50 fs. From anisotropy measurements, we estimate the proton hopping time to be 900 ± 100 fs in a locally extended water network lying on the surface. This time is consistent with recent studies on proton transfer in water[2] which support the idea of a proton jump within the picosecond time range. Moreover our value is consistent with ~ 1 ps time calculated using molecular dynamics[3].

Laserlab Europe is gratefully acknowledged for financial support under contract RII3-CT-2003-506350.

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Simple Analysis of 2D IR Correlation Spectra

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Optical 2D spectroscopy has matured to become a powerful tool for probing system dynamics because of its ability to resolve individual transitions hidden under featureless inhomogeneously broadened lines[1,2]. Recently, a simple way of data analysis was proposed[3] that allows for a quick but accurate estimate of the correlation function (i.e., the amount of the transition frequency memory loss) from the eccentricity of the 2D correlation spectra.

In this Contribution we extend the proposed model to a three-level system that is the most adequate model in the IR domain. The method yields both intuitive clues and a quantitative measure of the system dynamics. The developed approach is applied to 2D experiments to reveal dynamics of HDO molecule embedded in the acetonitrile matrix (Fig.1). The elliptical peak shape is indicative of substantial inhomogeneity at short waiting times. Nevertheless, about 50% of the phase memory is lost within the first 500 fs. As the waiting time increases, both peaks become more symmetric. However, even at the waiting times of 2.5 ps there still is some residual inhomogeneity. This is totally different from the case of the HDO molecule in D_2O where the phase memory totally disappears by 2 ps.

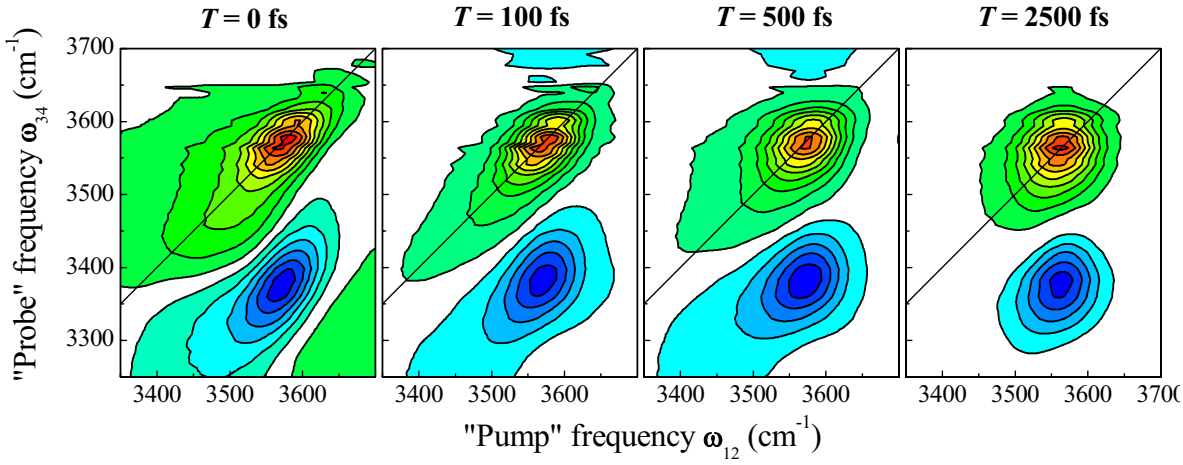

Fig.1. Two-dimensional correlation spectra obtained at different waiting times *T* for an HDO molecule dissolved in acetonitrile. The maximum (red) and minimum (blue) of the signal are separated by sixteen equally spaced levels.

The value of the *cross*correlation function of the lower and upper transitions can be derived directly from the 2D spectra. This paves the way to the direct experimental verification of the validity of the linear response approximation that is implicitly used throughout nonlinear spectroscopy. Furthermore, such cross correlations can be particularly useful for studying the through-bond correlations such as the symmetric/asymmetric stretching modes in water and through-space correlations of the process of energy transfer in light-harvesting proteins and molecular wires. The applicability of the simple analytical relation for realistic experimental situations is further verified through numerical calculations.

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Time-domain analysis of the rotational relaxation of water and aqueous salt solutions within the context of glass-forming behaviour

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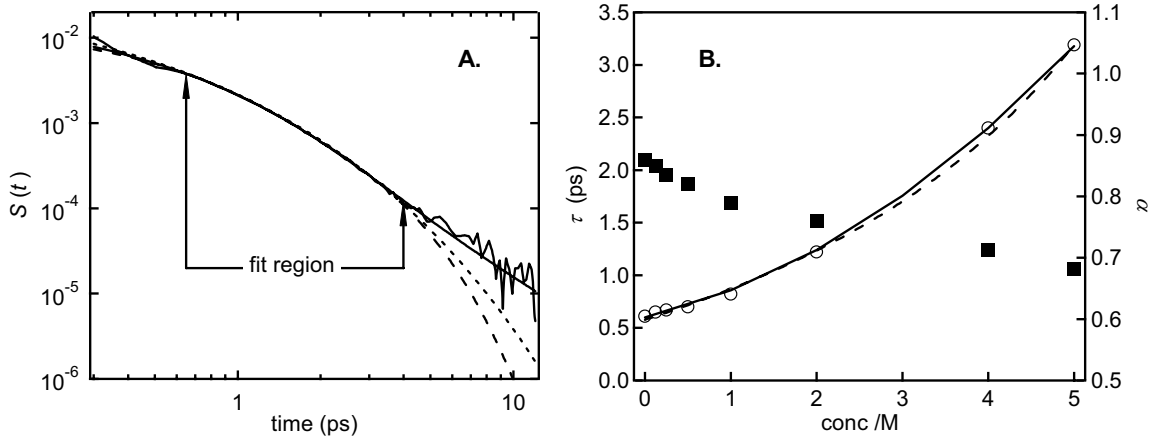
The rotational relaxation decay provides insight into the degree of structuring in a liquid and has been used in both temperature- and concentration-dependence studies of water and aqueous salt solutions. Conventionally, rotational relaxation in the time domain has been analysed as a double exponential or "stretched exponential" decay[1]. The origin of the double exponential decay is not clear and, furthermore, the measured parameters show poor consistency from study to study. In the frequency domain, the corresponding band has been fit successfully by the Cole-Cole function, $\chi(\omega) = 1\Big/\left(1+(i\omega\tau)^{\alpha}\right)$. Related to the Debye function, the Cole-Cole function has the additional parameter α ($0<\alpha<1$) which allows for a distribution of relaxation lifetimes, of average τ, consistent with a distribution of hydrogen-bonding environments. The lack of an analytical time-domain expression for the Cole-Cole function means it has not been applied in the time domain.

Ultrafast optical heterodyne-detected optical Kerr-effect (OHD-OKE) spectroscopy[2] is superior to depolarised Raman scattering for measuring slow rotational decays, and we show that fitting in the time domain by the Fourier transform of the Cole-Cole function gives greater accuracy—for high quality data—than given by the alternatives and apply this approach to the study of the concentration dependence of the relaxation lifetime for aqueous salt solutions.



A. Rotational relaxation in water measured by OHD-OKE. The fit by the Cole-Cole function (solid curve) is more accurate, over a longer timescale, than a double exponential (dashed) or stretched exponential (dotted).

B. Concentration dependence for aqueous $MgCl_2$ of the fitted parameters, τ (○) and α (■). The solid curve is a function consistent with glass forming behaviour.

In our presentation, we will discuss the slowing down of relaxation rates on increasing concentration and the broadening of the distribution as measured through α. We will discuss the results in the context of glass formation and supercooled water.

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Ultrafast dynamics of water in ionic micelles

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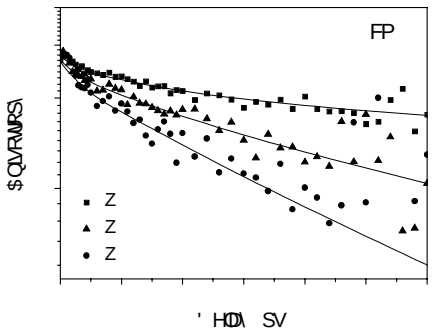
We study the properties of small water droplets by probing the vibrational dynamics of the OH-stretch vibration using nonlinear femtosecond mid-infrared spectroscopy. Droplets with a diameter ranging from ~1-10 nanometre are prepared using reverse micelles, which form spontaneously in a mixture of water (HDO dissolved in D_2O), an apolar solvent, and a surfactant. We study the dynamics of confined water both in anionic micelles and in cationic micelles, using the surfactant salts AOT and CTAB, respectively. By differences in the vibrational relaxation rate and the absorption frequency, we can distinguish water molecules in the core and in the outer shell of the micelles (e.g. for AOT micelles, T_1=0.7 and 2.6 ps, respectively). We find that the mobility of water in the outer shell of the micelle is strongly decreased (τ_{or}>15ps), while water in the core of the micelle behaves much like bulk water (τ_{or}~2.5-4ps)[1].

For cationic micelles, we observe a lowering of the orientational mobility when the water content of the micelles is decreased, as illustrated in Fig. 1. We also find that for these micelles the OH-stretch relaxation rate can be used to determine the distribution of counterions (anions) inside the micelles. We find that the counterions predominantly reside at the interfacial (Stern) layer.

The orientational mobility of interfacial water is found to be different for anionic and cationic micelles. For cationic micelles, the interfacial water molecules show an additional fast component in their orientational mobility (in addition to the dominant slow component). This component is not observed for the anionic micelles. This difference can be explained from the hydrogen bonds formed by the interfacial water molecules in the two types of micelles, as illustrated in Fig. 2. For the anionic micelles, the interfacial water forms highly directional hydrogen bonds to the negative head-groups of the AOT surfactant molecules. For the cationic micelles, the interfacial water molecules form hydrogen bonds to large bromide anions, allowing fast reorientation over a relatively large angle θ.



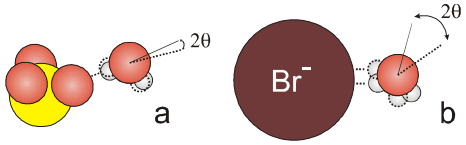


Fig. 1 (Left): Anisotropy decay of the OH-stretch vibration of water in three sizes of cationic CTAB reverse micelles. w_0 equals the molar ratio [water]/[surfactant], being proportional to the size of the micelles.

Fig. 2 (Right): water near the AOT headgroup (a) experiences a more directional hydrogen-bond than water near an interfacial Bromide ion in cationic CTAB micelles (b), leading to different orientational mobilities.

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Vibrational Dynamics of the CO Stretching of Fluorenone in Various Alcohols

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[3] CREST/JST, 1-1, Rokkoutyo, Nada-ku, Kobe 657-8501, Japan

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Hydrogen bond plays an important role in determining three-dimensional chemical structures and reactivity of many chemical and biological systems. Especially, reactivity of the hydrogen-bonded complexes is considered to be influenced by strength of the hydrogen bond and fluctuation of structures formed by hydrogen-bond. Fluorenone is an interesting molecule because the excited state dynamics is strongly affected by hydrogen-bonding interaction. Fluorenone has a carbonyl group, which forms an intermolecular hydrogen-bonded complex in alcoholic solvents.[1] In this study we have studied IR spectra of the CO stretching of fluorenone in various alcohols and measured vibrational dynamics of this mode by IR pump-probe spectroscopy.

The CO stretching of fluorenone shows a sharp band in non-hydrogen bonding solvents. For example, in cyclohexane the peak is located at 1720 cm^{-1}. In alcohols the spectrum shows a broad and asymmetric band in the region of 1690-1740 cm^{-1} as shown in Figure 1(a). There are two peaks at around 1713 cm^{-1} and 1721 cm^{-1}, and sometimes the third peak is observed in the lower frequency region. The relative intensities of the two bands at 1713 cm^{-1} and 1721 cm^{-1} depend on the solvent and temperature. We are performing molecular orbital calculations at DFT/B3LYP 6-31G(d) level of theory to study a frequency change of the CO stretching of fluorenone by modeling complexes with alcohols. Preliminary results show that the peak shifts to the lower frequency side by forming complexes. Therefore, we assign the observed bands in the IR spectrum to different complexes of fluorenone and solvent molecules.

We have performed pump-probe experiments on these bands in 1-octanol using a ~160 fs IR pulse. The ground state recovery at 1724 cm^{-1} is shown in Figure 1(b). The signal shows a bi-exponential feature with time constants of 405 fs and 4.46 ps. On the other hand, the dynamics at 1713cm^{-1} is much faster than this band. This suggests that difference of the hydrogen bond strength in the complex leads to the different vibrational relaxation processes.

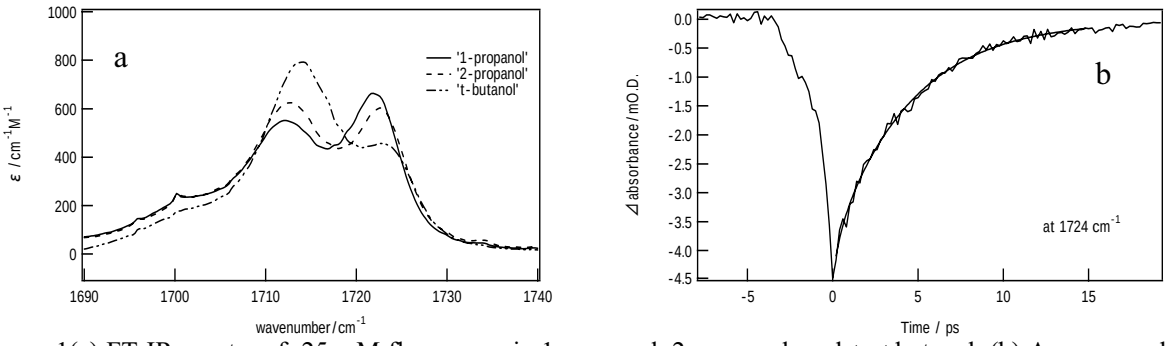

Figure 1(a) FT-IR spectra of 25 mM fluorenone in 1-propanol, 2-propanol, and *tert*-butanol. (b) A pump-probe signal of fluorenone in 1-octanol at 1724 cm^{-1}.

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Coherent Optical Phonons in Diamond and Graphite

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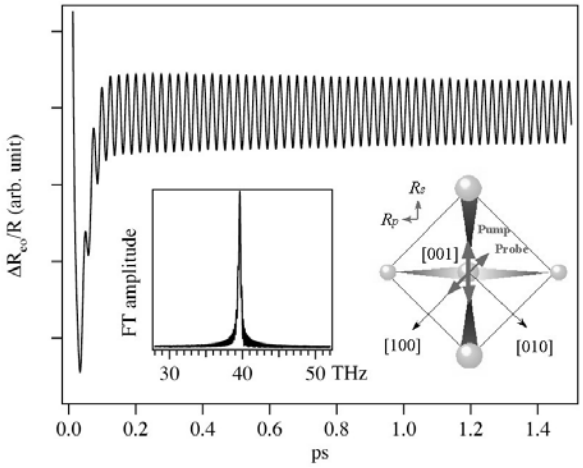
Recent development of materials science and nanotechnology cast a new light on carbon materials such as carbon nanotubes and superconducting diamonds. Electronic and phononic properties in these novel carbon materials, especially their ultrafast dynamics, will dominate their functionality in future electrical and electro-optical devices. In the present study, we present transient reflectivity measurements on synthetic single-crystal diamond[1] and highly oriented pyrolytic graphite (HOPG) excited with sub-10 fs laser pulses with center wavelength of 400 nm.

Anisotropic reflectivity of diamond features an oscillation with a period of 25 fs. The frequency of 40 THz, or 1330 cm^{-1}, agrees well with the Raman active optical phonon of diamond. The oscillations persist for more than 300 cycles before dephasing on 8 ps time scale. The coherent phonon signal essentially vanishes after rotating the sample by 45° within the surface plane, being consistent with the off-diagonal $\Gamma_{25'}$ symmetry Raman tensor. With increasing pump power, the amplitude of the coherent phonon increases linearly. Since our excitation photon energy of 3.14 eV is too low for the one-photon indirect (5.48 eV) or direct (7.3 eV) band gap excitation, the linear power-dependence indicates the off-resonant Raman nature of the coherent phonon generation.



Transient anisotropic reflectivity $\Delta R_{eo}/R=(\Delta R_p - \Delta R_s)/R$ of the (001) surface of type IIa single crystal diamond. Pump and probe polarizations are illustrated with respect to the crystal in the inset. Fourier transform of the reflectivity signal after t=0 is shown in the left inset.

Graphite exhibits a coherent oscillation with a period of 21 fs in the anisotropic reflectivity, which is assigned to the E_{2g2} phonon (in-plane C-C stretching). Contrary to other materials under intense excitation, the phonon frequency upshifts with increasing pump power. Time-windowed analysis shows that the frequency is highest at t=0 and relaxes to a lower frequency within 0.5 ps. We attribute the observation to transient stiffening of the C-C bonds in the presence of non-thermal occupations of photo-excited electrons, followed by electron thermalization on the electron-phonon scattering time scale.

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Structural Dynamics of the Organic Pigment Yellow 101

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The bisazomethine colorant Pigment Yellow 101 (P.Y. 101) exhibits unusual photochemical and photophysical properties, since it does not obey empirical rules for solid state fluorescence. Calculations of P.Y. 101 and three derivatives employing density functional theory (DFT) and time-dependent DFT (TDDFT) methods[1,2] reveal their energy relaxation pathways. It was shown, that the OH-groups are essential for the fluorescence of the pigments. Recent experiments with visible transient absorption spectroscopy[3] propose an excited state intramolecular proton transfer (ESIPT) and a biexponential decay of the excited state of P.Y. 101, which is assigned to the relaxation of two different configurations of the S_1 state, namely an enol and a keto tautomer. In addition, a long-lived photoproduct is identified.

We present studies of the structural dynamics of a P.Y. 101 dispersion in CCl_4 by vis-pump/IR-probe spectroscopy in the range of 1530 cm^{-1} to 2535 cm^{-1}. The data are analyzed by a global fit analysis. The revealed time constants of 15 ps and 350 ps are in perfect agreement with those found in the visible experiment of pigment crystals dispersed in a film, corresponding to the decay of the two S_1 populations. The positive absorbance change in the range of 1640 cm^{-1} to 2535 cm^{-1} and a red shift of all bands immediately after excitation are explained by altered resonance frequencies of the excited state. The observed photoproduct is stable on the timescale of our measurement and its characteristic features appear within our experimental time resolution.

Investigations of pigments lacking the essential OH-groups will allow to address molecular mechanisms of the deexcitation pathway and the possible role of an ultrafast enol-keto tautomerism found in related molecules[4,5,6].

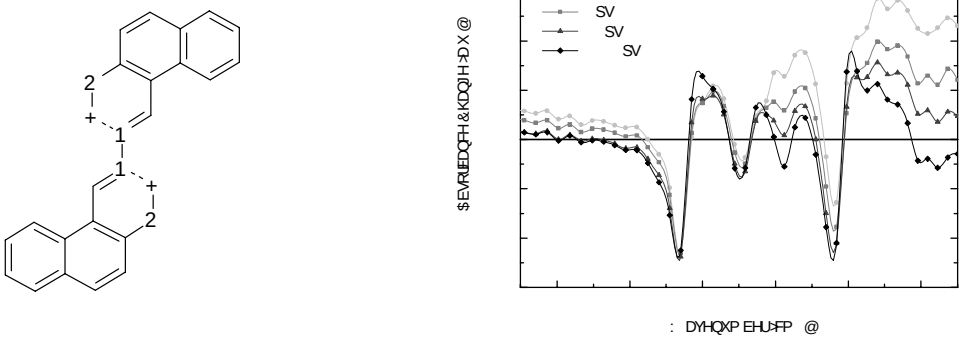

Fig 1: Structure of P.Y. 101 (left), Transient spectra at selected delay times after electronic excitation (right)

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Vibrational Population Relaxation of Hydrogen-Bonded Phenol in Solution Studied by Ultrafast Infrared Pump-Probe Spectroscopy

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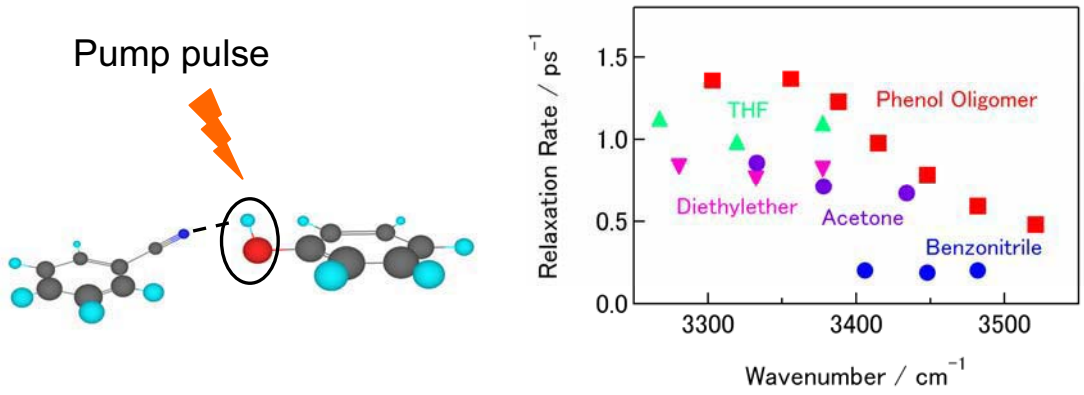
[2] Molecular Photoscience Research Center, Kobe University, CREST/JST, Nada-ku, Kobe 657-8501, JAPAN
E-mail address kohta@kobe-u.ac.jp

Understanding the structural and dynamical properties of hydrogen-bonded complexes has attracted great attention from many researchers because the hydrogen bonds play an important role in many chemical and biological systems. Ultrafast infrared (IR) spectroscopy has been shown to be powerful technique to obtain information on the vibrational dynamics for hydrogen bonded systems. In this contribution, we will present the results of the vibrational dynamics of hydrogen-bonded complexes using ultrafast IR pump-probe spectroscopy. Here we focus on the vibrational population relaxation of the OH stretching modes of hydrogen-bonded complexes of phenol with various bases (benzonitrile, acetone, diethylether, and tetrahydrofuran) and hydrogen-bonded phenol oligomers in carbon tetrachloride (CCl_4). By using different bases which act as a hydrogen-bond acceptor, we can change the strength of the hydrogen bond in the complex and thus investigate the influence on the vibrational dynamics in detail.

From the decay of the IR pump-probe signals of phenol-benzonitrile complex, it is found that the vibrational population relaxation takes place on 5 ps time scale. The time scale of the decay of the IR pump-probe signals does not depend on the probe frequency. We also measured the IR pump-probe signals for the other hydrogen-bonded complexes. The time constants of the decay of the IR pump-probe signals for phenol-diethylether, phenol-acetone and phenol-tetrahydrofuran complexes are about 1.4 ps, 1.3 ps and 1.0 ps, respectively. We found that the time scales of the vibrational population relaxation for these complexes are correlated with the strength of the hydrogen bond, i.e., a stronger hydrogen bond leads to a faster vibrational population relaxation. On the other hand, we observed that the decay time constants of the IR pump-probe signals for hydrogen-bonded phenol oligomers in CCl_4 depend strongly on the probe frequency (0.7 ps~2.1 ps). We will discuss the origin of this dependence.



We investigated the vibrational population relaxation of the OH stretching mode of hydrogen-bonded phenol in solution by ultrafast infrared spectroscopy. We focus on the probe frequency dependence of the decay of the pump-probe signals for hydogen-bonded phenol with various bases and phenol oligomers in carbon tetrachloride.

Vibrational relaxation of OH and OD stretching of methanol in isotopically diluted solutions

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The interactions and dynamics of hydrogen bonding liquids such as water and alcohol play an important role in many chemical and biological processes. A network structure formed by hydrogen bond dynamically fluctuates by making and breaking the bond. Methanol is the simplest alcohol, and the OH and OD stretching vibrations are sensitive to enviroment around the hydogen bond. The vibrational relaxations of the OH and OD stretching also depend on the strength of the hydrogen bond. In CCl_4 methanol forms clusters, and time-resolved measurements of OH[1] and OD[2,3] streching have been perfomed. Furthermore vibrational energy relaxation in pure methanol (CH_3OH) has been extensively studied by Dlott and coworkers by the IR pump-Raman probe technique.[4,5] In this work we have measured vibrational relaxation times (T_1) of the OH and OD stretching in isotopically diluted methanols and compared with the vibrational dynamics of these modes in CCl_4. In addition, we have also studied an isotope effect of the methyl group on the vibrational relaxations of the OH and OD stretching.

We studied the following solutions; CH_3OH/CH_3OD, CD_3OH/CD_3OD, CH_3OD/CH_3OH, and CD_3OD/CD_3OH. The ground state recovery was measured by IR pump-probe technique with about 160 fs-pulse. In the experiment the wavenumbers of the pump and probe pulses were set to the absorption peaks of the OH or OD stretching spectra.

Figure 1 shows the pump-probe signals of the four systems. The results were fitted well by a single exponential function ($A_1\exp(-t/T_1)+A_0$). This is a sharp contrast to the results in CCl_4 which shows a complicated dynamics in the excited vibrational states.[2,3] We also observed an isotope effect of the methyl group on the vibrational relaxation, indicating importance of the intermolecular process on the vibrational relaxation.

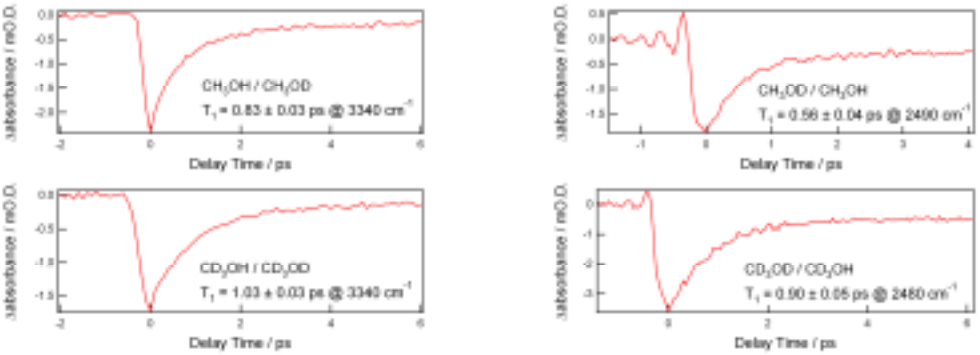

Figure 1. Pump-probe signals of the OH and OD streching of methanols.

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[3] J. B. Asbury, T. Steinel, C. Stromberg, K. J. Gaffney, I. R. Piletic, and M. D. Fayer, *J. Chem. Phys.*, **2003**, 119, 12981-12997.

[4] Lawrence K. Iwaki, Dana D. Dlott, *Chem. Phys. Lett.*, **2000**, 321, 419-425.

[5] Lawrence K. Iwaki, Dana D. Dlott, *J. Phys. Chem. A*, **2000**, 104, 9101-9112.

Vibrational dynamics of benzoic acid in solutions studied by sub-picosecond time-resolved infrared spectroscopy

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Biological macromolecules such as nucleic acid and proteins often express and control their functions by rearranging hydrogen bonds (HB). Hydrogen bonded complexes of carboxylic acids (CA) in solutions are important model systems for studying HB. Benzoic acid (BA) is one of the CA and forms cyclic dimer or complex with other molecules in various solutions.[1] Intermolecular HB of these complexes have much effect on dynamics of the vibrational modes associated with HB. In this work we have studied vibrational energy relaxation of the OH stretching of the BA complexes in various solvents by IR pump-probe spectroscopy.

The solvents we used are; CCl_4, $CDCl_3$, benzene-d_6, THF-d_8, acetone-d_6, and acetonitrile-d_3. We obtained IR short pulses by difference frequency mixing with signal and idler pulses in the near-infrared region generated by a home-made optical parametric amplifier. We splitted the pulse into pump and probe pulses with frequencies at a peak of the OH stretching band in the solutions.

Figure 1 (a) shows solvent dependence of IR spectra of the OH stretch of BA. In the solvents which do not form strong HB with the hydroxyl group (CCl_4, $CDCl_3$, and benzene-d_6), the peak wavenumber is located at around 3000 cm^{-1}, and the spectra show complicated structures. The spectra of the three solutions are identical to each other. From the dependence of the IR spectrum on the concentration of BA, the broad band at 3000 cm^{-1} is assigned to the dimer of BA. On the other hand, for the other solvents forming strong HB (THF-d_8, acetone-d_6, and acetonitrile-d_3) the peak is shifted to the higher frequency side depending on the solvents, indicating that the strength of HB of these complexes is weaker than that of dimer in the former solvents. In addition, the spectra are structure-less compared to those in the former solvents. In these solvents, BA may exist as dimer or BA-solvent complex. This is under investigation by measuring concentration dependence of IR spectra in detail.

In all the solutions, transient absorption signals showed a double exponential decay (730 fs, 8 ps in CCl_4, Figure 1 (b)). We assigned the fast and slow components to the population relaxation of the excited vibrational state and the cooling process in the local environment heated by the vibrational excitation. Furthermore, in the solvents which do not form strong HB, we observed a quantum beat in the signal. A spectrum obtained by Fourier transforming the beat shows a band at 100 cm^{-1}, and the same band was observed in all these solutions (Figure 1 (c)). The quantum beat is due to coupling of the OH stretching mode and intermolecular vibrations of BA dimer similarly to the case of acetic acid dimer.[2, 3]

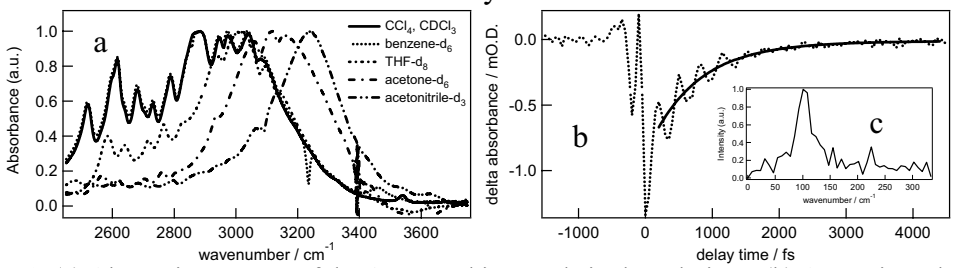

Figure 1. (a) Absorption spectra of the OH stretching mode in the solutions. (b) A transient absorption signal of 120 mM BA-d_5 in CCl_4 at 3000 cm^{-1}. (c) A spectrum of the beat in CCl_4.

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[3] K. Heyne et al., *Chem. Phys. Lett.*, **2003**, 369, 591.

Vibrational Dynamics in Hydronge-Bonding and Non-Hydrogen Bonding Liquids and Complexes

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Interactions between solute and solvent play an important role in chemical reaction dynamics and in many relaxation processes in condensed phases. Recently third-order nonlinear infrared spectroscopy has shown to be useful to investigate solute-solvent interaction and dynamics of the vibrational transition.[1,2] These studies provide detailed information on the energy relaxation of the vibrationally excited state, and the time scale and the magnitude of the time correlation functions of the vibrational frequency fluctuations.

We have studied vibrational energy relaxation (VER) of solutions and molecular complexes by nonlinear spectroscopy, especially pump-probe method, to understand the microscopic interactions in liquids. So far VER in liquids has been often discussed in terms of short-range interactions between solute and solvent molecules. Recently, importance of dielectric interaction, which is intrinsically long-range, in the VER has been pointed out theoretically and experimentally, and studies on the detailed mechanism of the relaxation are necessary to understand nature of VER in liquids. In order to further investigate how the vibrational dynamics is affected by the nature of the solute-solvent interaction, it is important to know the dynamical properties of the vibrational transitions in various types of solvents. In this work we have extended our studies to investigate the vibrational relaxation of the anti-symmetric stretching mode of SCN^- in polar solvents by IR pump-probe method. It is found that the VER times in hydrogen bonding solvents are longer than twice of those in non-hydrogen bonding solvents. Among the hydrogen bonding solvents the VER in formamide and *N,N*-dimethylformamide are slower than those in methanol and water. We have also found correlation between the band width of the absorption spectrum and the VER time. This indicates that the hydrogen bond plays an important role in the VER. We will also discuss the resutls of the hydrogen bonding liquids and complexes and frequecny fluctuations of these systems.

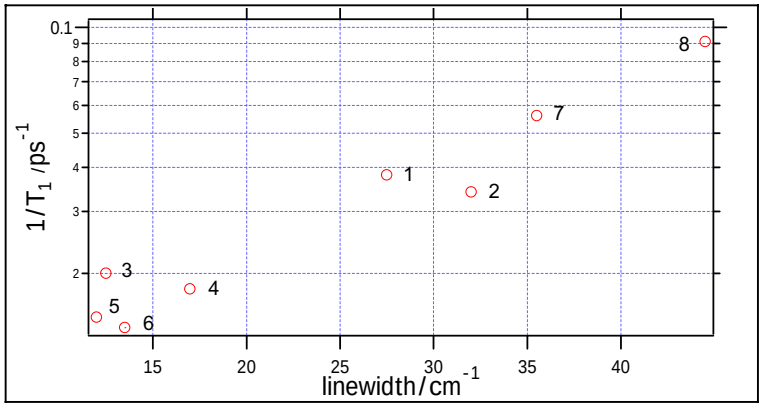

Figure 1. Plot of vibrational relaxation rates vs. linewidth of the absorption spectra. The relaxation rates are inverses of the relaxation times for the v = 0-1 transition. 1: formamide, 2: *N*-methylformamide, 3: DMF, 4: methyl acetate, 5: acetonitrile, 6: DMSO, 7: methanol, 8: D_2O

[1]K. Ohta and K. Tominaga, *Bull. Chem. Soc. Jpn.* **78**, 1581 (2005).
[2]K. Ohta and K. Tominaga, *Chem. Phys. Lett.* **429**, 136 (2006).

Ultrafast Chelation Dynamics of Model Photoswitches: Arene Chromium Tricarbonyl Derivative with Pendant Sulfide

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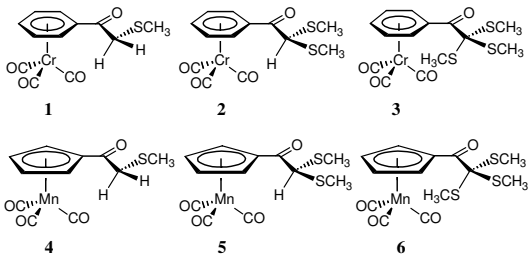
The chelation dynamics of three new $[Cr\{\eta^6\text{-}C_6H_5C(O)R\}(CO)_3]$ complexes **1** (R = $CH_2(SCH_3)$), **2** (R = $CH(SCH_3)_2$), and **3** (R = $C(SCH_3)_3$) have been investigated on the picosecond to millisecond time scale by UV-pump IR-probe transient absorption spectroscopy following photodissociation of CO in room temperature *n*-heptane, tetrahydrofuran (THF), and acetonitrile. In *n*-heptane, UV irradiation of **1**, **2**, or **3** dissociates CO to initially yield a Cr-S chelate and a transient Cr-heptane solvate in approximately 1:2, 1:2, and 2:1 ratios, respectively. The Cr-heptane solvate is unstable and converts to the Cr-S chelate within 30 ns in each case. Irradiation of **2** or **3** in THF yields both the Cr-S chelate and Cr-THF solvate in approximately 1:3 and 1:1 ratios, respectively. The Cr-THF solvate converts to the Cr-S chelate on the second or longer time scale. All three complexes appear to yield the Cr-$NCCH_3$ solvate exclusively within 50 ps following irradiation in acetonitrile. The solvent effect on chelation is in striking contrast to that previously reported for the analogous $(C_5H_4R)Mn(CO)_3$ derivatives, **4**-**6**. While irradiation for both the Cr and Mn series in heptane or THF results in picosecond chelation and solvent coordination, only chelation is observe for the Mn series while only solvate is observed for the Cr series in acetonitrile. The study highlights how subtle structural changes may be used to tailor picosecond processes for the design of ultrafast switches.



Femtosecond (Stimulated Raman) Spectroscopy of the Photo-Tautomerisation of Nitrotoluene

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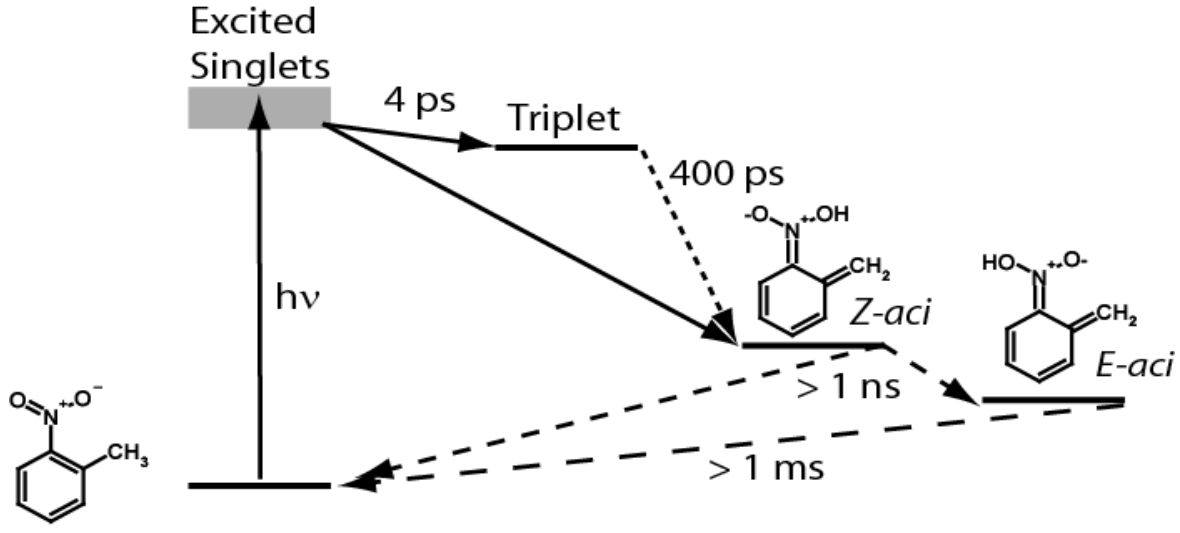
Nitroarene moieties are the central building blocks for many photolabile protecting groups[1]. Such groups are widely applied in biotechnology, e.g. in caged compound experiments and in the in-situ synthesis of DNA chips. Photo-active nitroarenes usually carry a substituent ortho to the nitro group from which the group can accept a hydrogen atom. We have recently given evidence for the ultrafast (~ 400 fs) nature of this hydrogen transfer in one nitroarene, *ortho*-nitrobenzaldehyde.[2] *Ortho*-nitrotoluene also undergoes such a photo-induced transfer yielding the *aci*-nitrotautomer[3]. It is structurally very closely related to "real" protecting groups and can serve as a model of the processes occuring there.

Here, we will present a combined femtosecond transient absorption and stimulated Raman (FSRS) study on the mechanism of this transfer. The FSRS experiments rely on a novel set-up[4] particularly suited for chromophores absorbing in the UV. In the transient absorption experiment three characteristic times of 0.2 ps, 4 ps, and 400 ps are discernible. The shortest time constant is tentatively associated with the transition between two excited singlet states. The other two mark the formation of a species absorbing at 400 nm commonly assigned to the *aci*-nitrotautomer[4]. The 400 ps time constant also characterizes the decay of an absorption band peaking at 650 nm believed to be designative of the triplet state of nitroarenes[5]. Further the 400 nm species spectrally evolves on timescales much longer than one nanosecond. These results suggest that singlet and triplet excited states are involved in the hydrogen transfer and at least two isomers of the *aci*-nitrotautomer are intermediately formed. These assigments will be compared with findings from FSRS measurements and DFT calculations.



Kinetic model of the photo-tautomerisation of *ortho*-nitrotoluene.

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[5] R.W. Yip et al. J. Phys. Chem. **1984**, 88, 5772-5574

Ion-Molecule reactions in XB-NH_3 clusters: Determining the structure of the reactants' arrangement through Franck-Condon simulations

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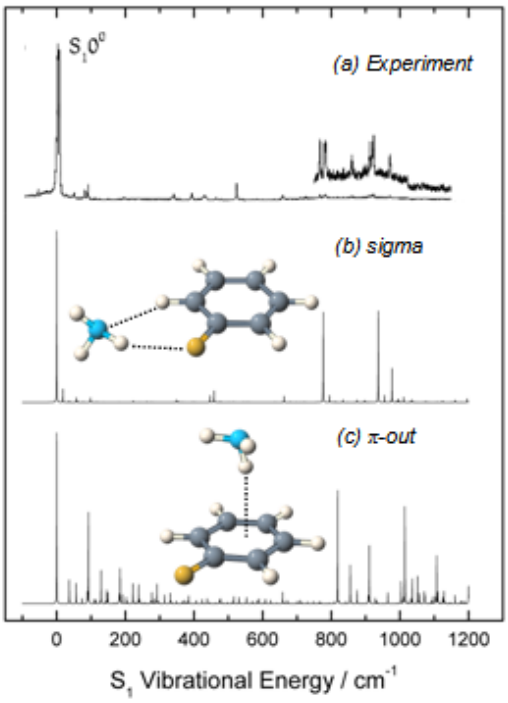

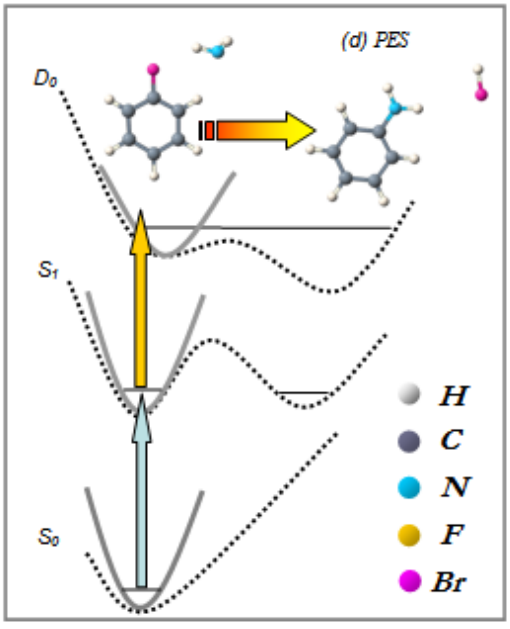

Figure: REMPI spectrum (a) and Franck-Condon simulations (b) and (c) of FB-NH_3. PES for the BrB-NH_3 to aniline ion-molecule reaction.

Clusters between aromatic systems and key reagents such as ammonia are ideal systems to study ion-molecule reactions as the cold conditions of a molecular beam provide a noise and solvent free environment and allow for state selective preparation of the reagents though interaction with laser radiation. Crucial in this endeavour is the determination of the possible equilibrium structures of the cluster as this corresponds to the arrangement of the reagents prior to reaction.

For the case of Fluorobenzene-NH_3 presented here, an extensive ab initio study with the RI-CC2 method reveals the existence of two stable structures (see figure (b) and (d)). While FB-NH_3 does not react upon ionisation, its heavier relative BrB-NH_3 displaying a REMPI spectrum analogous to that of FB-NH_3 (figure (a)) forms aniline upon ionisation. Due to the possible different arrangements of the reagents in the different cluster structures, different reaction mechanisms would be responsible for the conversion to aniline. However, only the Franck-Condon simulations of the sigma complex match the experimental REMPI spectrum indicating that the components of the cluster prior to reaction are in a sigma arrangement. This and the fact that the Franck-Condon factors are preserved during the ion-molecule reaction and a spectrum analogous to (a) is obtained in the aniline mass channel (while in FB-$(NH_3)_2$ which also undergoes an ion-molecule reaction to aniline, a broad REMPI spectrum is observed) strongly suggests that the reaction only occurs after ionisation, on a possibly barrierless D_0 PES as shown in figure (d) with the relevant bonds being broken and made in a concerted fashion.

Time-Resolved UV/Vis-Pump IR-Probe Spectroscopy on Photochromic Indolylfulgides

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Photochromic organic molecules have the potential for important applications in the wide field of optical data handling. The high flexibility of organic chemistry allows the synthesis of special compounds optimized for very different purposes. In this context fulgides play an important role for storage application since they exist as thermally stable conformers (Fig. 1a) and can be switched selectively by laser pulses at different wavelengths (Fig. 1b). In order to characterize the switching dynamics and to understand the reaction principles we performed intensive femtosecond experiments on different fulgides.

In this study we present UV/Vis pump mid-IR probe investigations on a fluorinated indolylfulgide in order to obtain information on the ring opening (C→Z) and ring-closure (Z→C). The combination of visible and IR spectroscopy allows to determine the life time of the excited electronic state, which limits the switching speed of the molecules. In addition we are able to record the vibrational spectra of the excited electronic states and to correlate the observed absorption dynamics with distinct molecular reaction steps.

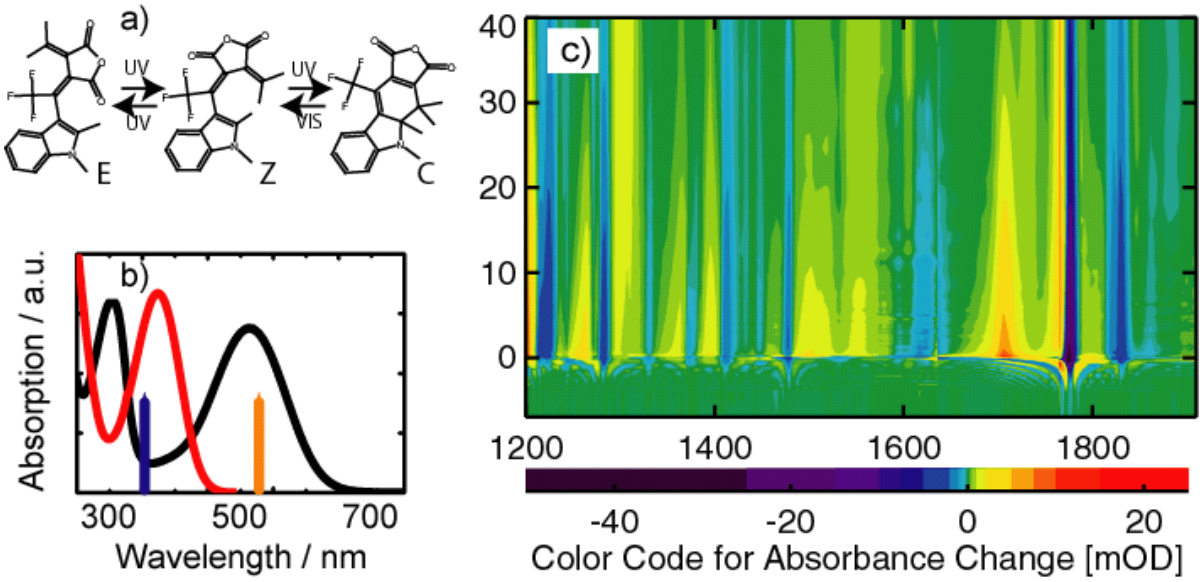

Figure 1: (a) Schematic structures of the conformers of the investigated indolylfulgide. (b) Vis absorption spectra of the closed C-form (black) and the open E-form (red); the arrows indicate the excitation wavelengths. (c) 2D-representation of the time-resolved date for the ring-closure reaction in deuterated acetonitrile.

Both C→Z and Z→C reactions show similar cooling behavior with time-constants of about 15 to 20 ps; the life-times of the excited state (ES) lie in the range of ~3 to ~18 ps, whereas in a polar solvent the ES life-time is slightly increased. After about 50 ps no more spectral changes can be observed. Comparing ring-closure and opening, the spectral signatures of the ES differ from each other.

Vibration of metal nanoparticles induced by laser excitation

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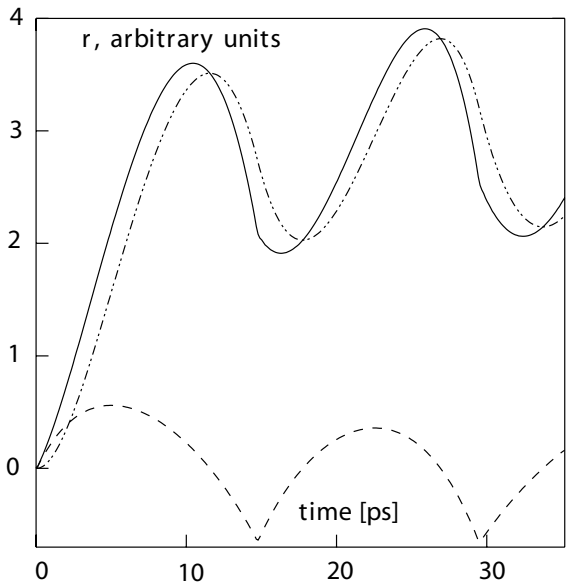
We consider the vibrational dynamics of metal nanoparticles following excitation with fs-laser-pulses[1]. The induced electronic and lattice pressure contributions cause excitation of breathing modes in spherical particles. We pay special attention to the role of the excitation of overtones, which affect the short-time dynamics substantially. For instance, the expansion of clusters increases linearly with time and the slope becomes discontinuous at certain time points. The overtones also lead to shifts of the position of the minima and maxima of the cluster radius as compared to those of the fundamental vibration mode. They are of comparable size as the shift due to inclusion of electron pressure effects in addition to the lattice pressure. The theoretical treatment we propose is well suited to describe the control of excitation of acoustic vibrations of nanoparticles



Electronic (dashed curve) and lattice (dash-dotted curve) contribution to the vibration (full curve) of a model gold cluster of radius r=24.2 nm. The electronic contribution is extremely anharmonic and determines the slope at t=0. The total vibration, and especially that part of it that is due to electronic pressure change, can be seen to have a discontinuous slope due to the sudden change of pressure.

[1] F. Dufey and S. F. Fischer, *Short time vibrational dynamics of excited metal nanoparticles*, J. Phys. Chem. C, accepted for publication.

A Time-Resolved Transient Infrared Study of a Bistable Photochromic Organometallic Compound Based on Linkage Isomerization

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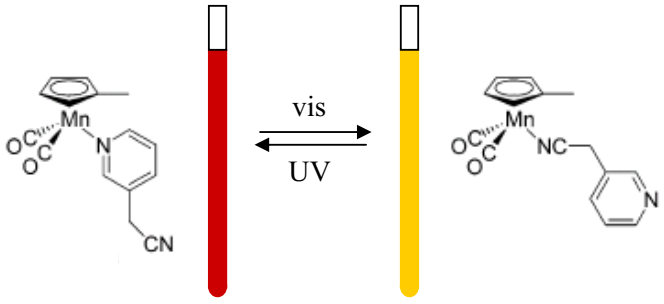
Previous work has shown that the cyclopentadienylmanganese complex (η^5-$C_3H_4CH_3$)$Mn(CO)_2$(3-cyanomethylpyridine) can act as a bistable photochromic organometallic complex via linkage isomerization.[1] Steady-state room temperature experiments in solution show that the red-orange pyridine nitrogen bound complex, Mn-Py, isomerizes to the yellow cyano bound isomer, Mn-NC, upon visible irradiation. Further irradiation with UV light reverses ligand coordination back to the pyridine ring, restoring the red-orange solution color.

A time-resolved transient infrared study was performed to investigate the mechanism and time-scale of this linkage isomerization. To date, only the visible pathway has been studied in isooctane. Strong bleach features are observed at 1932 and 1868 cm^{-1}, corresponding to loss of the pyridine-coordinated complex. An absorption feature at 1985 cm^{-1} appears immediately and decays completely within 400 ps, while absorption features at 1952 and 1888 cm^{-1} grow in at a similar rate to the loss of the 1985 cm^{-1} peak. Previous FTIR experiments have shown that absorbances corresponding to the final cyano-coordinated complex appear at 2025, 1943, and 1885 cm^{-1}.[1]

Based on these results we propose the following mechanism. Following absorption of a 400 nm photon, the cyanomethylpyridine ligand dissociates from the Mn center. The peak at 1985 cm^{-1} corresponds to a "bare radical", triplet state, or some other form of ring-slipped intermediate that relaxes to form an isooctane-solvated complex. The unstable alkane solvate then converts to the chelate product on the >nanosecond timescale. Additional confirmation of this mechanism was obtained by comparing to transient infrared studies of methylcyclopentadienyl manganese tricarbonyl (MMT) in isooctane where both MMT and (η^5-$C_3H_4CH_3$)$Mn(CO)_2$(3-cyanomethylpyridine) form an identical transient Mn-alkane solvate (and CO-stretch absorption features) upon UV and visible irradiation, respectively.

In summary, our results indicate that the linkage isomerization pathway for (η^5-$C_3H_4CH_3$)$Mn(CO)_2$(3-cyanomentylpyridine) from the pyridine-coordinated to the nitrile-coordinated isomer proceeds through a solvated intermediate. Future work will include studying the reverse isomerization, and exploring the photochemistry of tethered bifunctional ligands to potentially eliminate the solvated intermediate.



Scematic depiction of color change that occurs with (η^5-$C_3H_4CH_3$)$Mn(CO)_2$(3-cyanomethylpyridine) linkage isomerization.

[1]T.T. To, C.E. Barnes, T.J. Burkey, Organometallics, **2004**, 23, 2708-2714.

Picosecond Stokes- and anti-Stokes Raman spectroscopy of excited state intramolecular proton transfer

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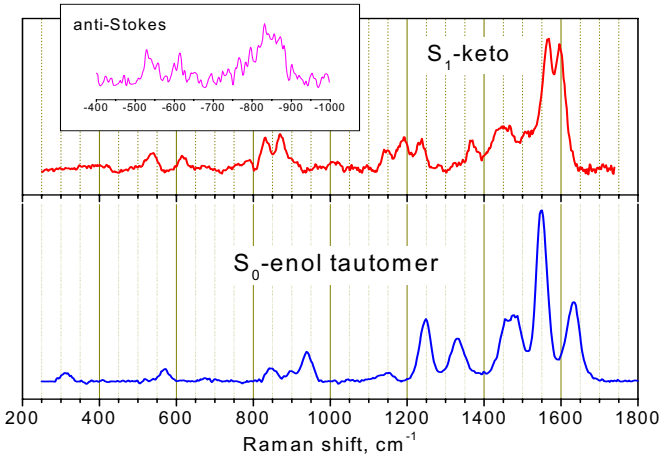
Vibrational populations after excited state intramolecular proton transfer (ESIPT) in 2-(2'-hydroxyphenyl)benzoxazole (HBO) were investigated using transient Raman spectroscopy. After electronic photoexcitation of the enol tautomer of HBO with a C–O-H↑N hydrogen bond, the keto tautomer with a C=O↑H-N hydrogen bond is formed in the first excited singlet state S_1.

Using resonance probe within the S_1-S_N absorption band, we measured time-resolved Stokes and anti-Stokes Raman spectra of this species for the first time. The Figure shows the resonance Raman spectrum of the transient (upper panel) which was recorded by probing at 395 nm, 5 ps after excitation of a solution of HBO (5×10^{-3} mol/l in cyclohexane) with a pulse centered at 336 nm. The ultrashort rise time of the transient Stokes Raman line-intensities and a decay time of about 200 ps confirm their assignment to the S_1-keto tautomer. In the insert, an anti-Stokes spectrum of the transient recorded 2 ps after UV-excitation with a 402 nm probe pulse is shown. The lower panel displays a stationary Stokes Raman spectrum of the stable enol tautomer of HBO. The observed vibrational modes were assigned with the help of normal mode calculations both for the S_0-enol and S_1-keto tautomers. Based on CIS/6-31 G(d,p) calculations the two most intense high-frequency Raman lines of the S_1-keto tautomer are assigned to delocalized vibrations with substantial CO-stretching or NH-bending components.



The study of time-resolved anti-Stokes resonance Raman spectra reveals excess populations of the modes at 535 cm^{-1}, 610 cm^{-1} and 832/871 cm^{-1} at early times after excitation. In contrast, modes of higher frequencies do not show excess population at any delay time. The measured excess populations have fast rise times close to our time-resolution and decay times of about 8 ps for the 535 cm^{-1} and 610 cm^{-1} vibrations and 5 ps for the 832/871 cm^{-1} doublet.

A comparison of the estimated maximum possible vibrational temperature of 425 K, which can be reached after distribution of the excess energy between all vibrational modes with the measured anti-Stokes to Stokes Raman intensity ratios shows that the S_1-keto tautomer is close to thermal equilibrium 2 ps after proton transfer. Afterwards it cools down to ambient temperature with a $(\approx 8\ ps)^{-1}$ rate.

In conclusion, the study revealed that the high-frequency modes of the S_1-keto tautomer of HBO are not vibrationally excited by the ESIPT reaction. Instead, modes below 1000 cm^{-1} display substantial excess population.

Surface Specific 2D-IR Spectroscopy of a Molecular Monolayer

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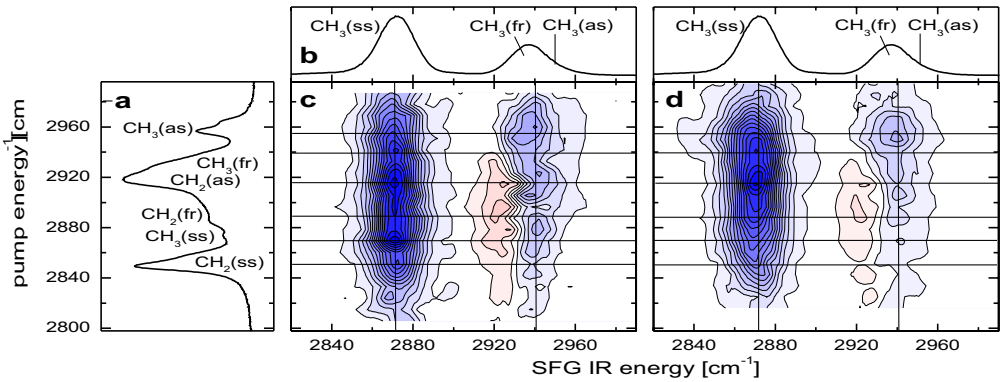
We present a novel 2-dimensional vibrational spectroscopy, which provides information on coupling between vibrational modes of surface molecules. As a 4th order non-linear vibrational technique, it is bulk-forbidden in centrosymmetric materials and hence surface specific. Analogous to bulk 2D-IR spectroscopy, a 3rd order vibrational coherence is created by an infrared pulse sequence. In our surface specific 2D-IR experiment, however, the 3rd order coherence is upconverted to a 4th order coherence by an additional (nonresonant) narrow-band 800 nm pulse in the process of sum-frequency generation (SFG). The 4th order coherence radiates the 2D-IR signal at the sum frequency of the 3rd order coherence and the 800 nm pulse. Here we report the first 2D-IR-SFG spectrum of a self-assembled monolayer of dodecanol on water (fig. **a**, **b**). The spectra are characterized by intense cross peaks at pump frequencies where no SFG intensity was observed. This can be traced back to the fact that the pump and probe processes are governed by different selection rules, namely IR activity and IR *and* Raman activity, respectively. Along the probe axis (x-axis) only SFG active modes appear (static SFG spectrum in fig. **c**), while the pump process on the y-axis follows the infrared selection rules (static IR spectrum of solid dodecanol in fig. **d**). The appearance of intense cross-peaks between SFG active and SFG inactive modes reflect the large degree of coupling between the various C—H modes in this system.



a, **b**—2D SFG spectra of a self-assembled monolayer of dodecanol on water in the C—H stretch region of the alkyl chain for p and s polarization of the pump pulse. **c**—1D SFG spectrum as measured during the 2D experiment. **d**— linear IR absorption spectrum of solid dodecanol as an approximation of the IR spectrum of the monolayer (surface freezing temperature 39°C).

In summary, we have demonstrated the successful implementation of surface 2D-IR spectroscopy. This novel surface vibrational spectroscopy allows for detailed information on the coupling of vibrational modes at surfaces, which is of importance for a variety of fields including electrochemistry, catalysis and membrane physics.

Methyl groups and vibrational energy relaxation of *para* - nitroaniline

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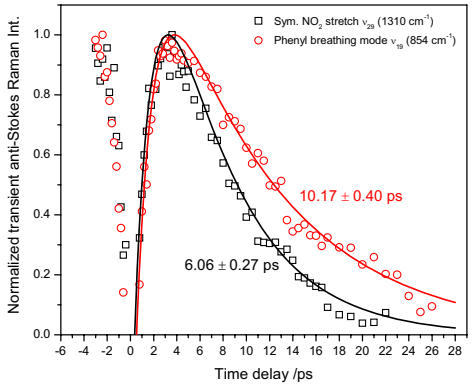
Para-nitroaniline (pNA) belongs to the important push-pull class of molecules, characterized by an electron donating group connected via a conjugated linker to an electron withdrawing group. The large dipolar change that accompanies charge-transfer (CT) electronic excitation makes these promising nonlinear optical materials. The electronic and vibrational dynamics of pNA have been studied by several groups, most recently using UV–visible transient absorption[1-4], fs transient grating[5], and time-resolved anti-Stokes Raman[6-10] and IR[10]. In our group, single color, sub-ps anti-Stokes resonance Raman studies at several pump wavelengths previously indicated that pNA S_1 dynamics are very fast relative to the intersystem crossing rate and found no evidence for inhomogeneous broadening of the CT absorption band[9]. In the current study, the impact of structural factors on vibrational dynamics has been explored by incorporating methyl groups at various positions on the pNA template. The vibrational excitation patterns and lifetimes of pNA, 2-methyl pNA, 2, 6–dimethyl pNA and N, N – dimethyl pNA have been compared. Findings are interpreted in terms of access of the excited pNA system to dissipative pathways, in which consideration is given to the effectiveness of an individual substitutent, the number of substituents, and the pattern of substitution.



Analysis of anti-Stokes resonance Raman intensities of N, N – dimethyl pNA dissolved in DMSO, obtained using narrow band, 403.5 nm pump-probe spectroscopy. The experimental intensities are normalized to unity at their maximum. The solid lines represent bi - exponential fits to the experimental data.

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Nonlinear Vibrational Response of Coupled Anharmonic Systems — Towards the 2D IR Spectrum of H_2O

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The recent experimental observation of extremely fast memory loss in pure water[1] is still pending a full understanding of the underlying mechanisms and theoretical description, mainly due to difficulties in treating the resonant energy transfer in the pure liquid. We present a new method of numerical propagation of the vibrational dipole moments that allows for nonlinear signal calculations, fully treating the coupled fluctuating Hamiltonian and Non-Condon effects. This approach will, for the first time, allow us to calculate two-dimensional (2D) spectra of the OH-stretching vibration in pure water.

We use molecular dynamics simulations in combination with an ab initio electrostatic map[2] to gain the fully anharmonic, fluctuating vibrational Hamiltonian and transition dipole moments. We then numerically propagate initially excited dipole moments in the molecular basis according to the different Liouville pathways necessary to calculate the 3rd order signal. In this model, all nonlinear signals arise from anharmonicities in the two-particle excitations. We thus fully treat the coupled fluctuating Hamiltonian, as well as non-Condon effects.

As a first application, we studied the effect of intermolecular couplings on nonlinear vibrational response using the OH stretching mode in pure HOD as a model system. Resonant dipole-dipole coupling is used as intermolecular coupling term. In Figure 1, we compare the nonlinear response of the coupled and the uncoupled OH-stretching system. Fig. 1(a) shows the polarization anisotropy decay calculated from impulsive pump-probe signal. This allows quantification of the effect of the intermolecular coupling on the resonant energy transfer times. Figure 1(b) shows impulsive 2D spectra at populations times t_2 = 0, 200, 500 fs, exhibiting a faster loss of frequency correlations in the coupled system.

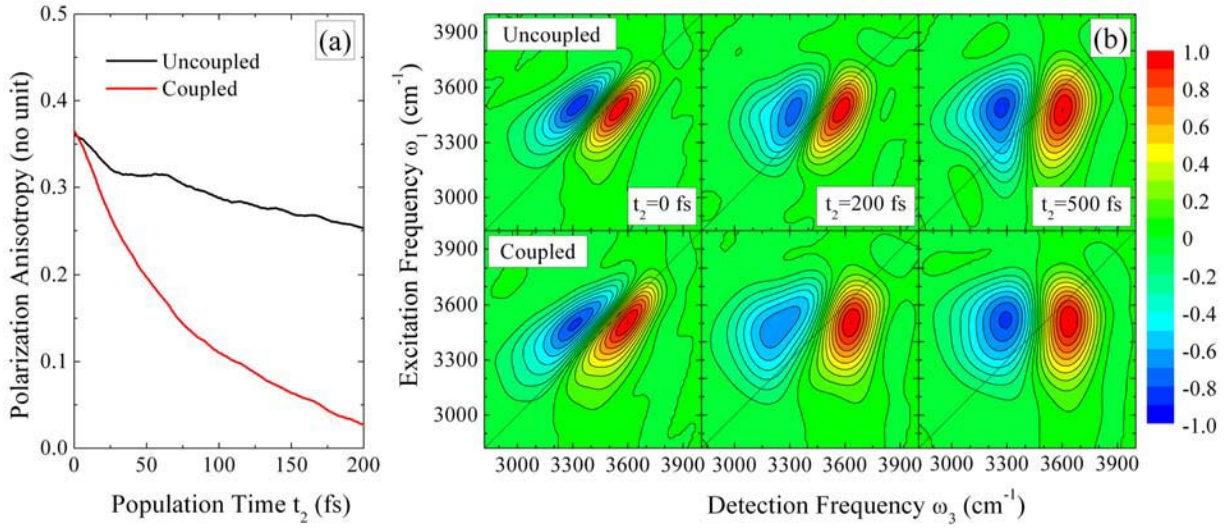

Figure 1. (a) Transient polarization anisotropy of the OH-stretching vibration, calculated from spectrally integrated, impulsive pump-probe signal. Upon coupling, resonant energy transfer accelerates the signal decay. (b) 2D spectra at population times t_2 = 0, 200, 500 fs. The coupled system shows faster decay of frequency correlations.

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The photo-induced decomposition of aryl peroxycarbonates studied by time-resolved infrared spectroscopy

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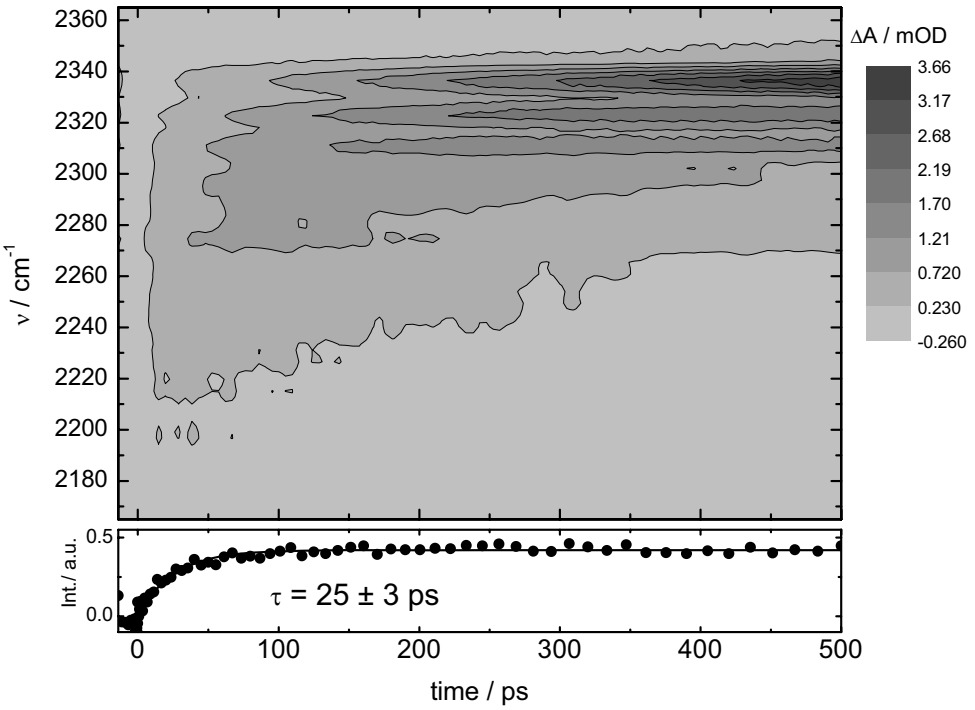
The ultrafast photo-fragmentation of organic peroxides of the type Ar-O–C(O)O–O-t-Bu (Ar = naphthyl, phenyl) is studied using UV excitation at 266 nm and mid-infrared laser pulses to elucidate the dissociation mechanism. Two modes of bond scission are discussed in the literature[1], namely a sequential process where the peroxide bond O–O breaks almost instantaneously (<100 fs) followed by decarboxylation of the carbonyloxy intermediate to yield CO_2 plus radicals Ar-O and O-t-Bu, and simultaneous breakage of O–O and O–C bonds.

Our experiments show that the rate of fragmentation is limited by the S_1-lifetime of the peroxide, i.e. the time constants of S_1 decay and of CO_2 and Ar-O formation are identical. The fragmentation times are solvent dependent and for the naphthyl peroxycarbonate vary between 24 ps (in CH_2Cl_2) and 52 ps (in n-heptane). In the case of the phenyl peroxycarbonate the decomposition takes 5.5 ps in CD_3CN and 12 ps in n-heptane. The CO_2 fragment is formed vibrationally hot with an excess energy of about 5000 cm^{-1}. The cooling times are 200 ps in CCl_4 and 50 ps in n-heptane, respectively.



Spectral evolution of the asymmetric stretch absorption band of CO_2 produced in the photo dissociation of tert-butyl 2-naphthyl peroxycarbonate in CCl_4. The 12 cm^{-1} progression results from anharmonic coupling to the bend vibration initially populated in the vibrationally hot CO_2 molecule. The lower panel shows the integrated band intensity.

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Femtosecond Infrared Spectroscopy of the Photo-Rearrangement of a Heterocyclic-N-Oxide

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The photo-rearrangement of organic N-oxides is a useful synthetic tool in organic chemistry. It allows to synthesize chemicals difficult to access by other methods. A large variety of N-oxides have been shown to be photo-reactive[1]. In contrast to this wealth of empirical data information on the kinetics and mechanism of this reaction is scarce. In particular, no spectroscopic experiments with a suitable time resolution have yet been published. We here report on a combined femtosecond UV/VIS and IR study on the rearrangement of a heterocyclic N-oxide (2-benzoyl-3-phenylquinoxaline-1,4-dioxide, structure see figure). Photoexcitation of this N-oxide results in drastic structural changes finally yielding the depicted imidazolone.

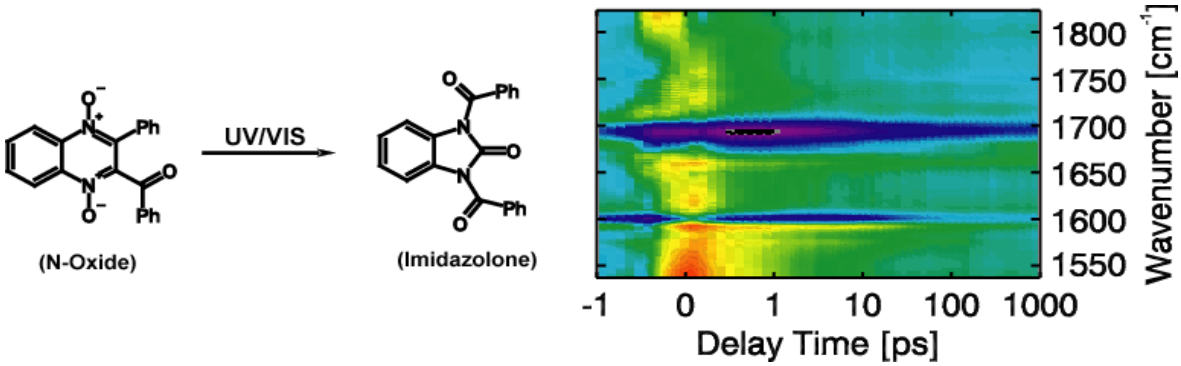

Photo-reaction of the N-oxide under study (left). IR difference spectra recorded after femtosecond excitation of the N-oxide at 400 nm. Blue coloring stands for absorption bleaches, green and red coloring for positive absorption changes. The reduction of the bleach contributions with time marks the partial ground state recovery. Note the absence of a positive signal at 1770 cm^{-1}.

Steady state experiments[2] afforded an overall yield of 0.1 for that reaction. The same study excluded the involvement of triplet states. Transient absorption (VIS) experiments on that reaction reveal multi-exponential kinetics with time constants of 1 ps, 10 ps, and 200 ps. The 1 ps component is assigned to the S_1 decay and does not go along with the repopulation of the starting material. The two subsequent processes result in total in a ~ 70% ground state recovery. Matching observations are made in the IR. As inferred from a cw illumination experiment the final photo-product can be identified via the characteristic C=O stretch vibration of the imidazolone ring at ~ 1770 cm^{1}. In the time window covered (≤ 3 ns) in our fs-IR-experiment this resonance does not show up. The final product formation takes longer than some nanoseconds.

So the photo-rearrangement of the N-oxide involves at least four intermediates (in addition to the primarily excited state) with widely spanned lifetimes. Based on the transient IR spectra and with the help of DFT calculations molecular structures for the intermediates will be suggested. This approach should allow to verify the involvement of three-membered rings often postulated in the literature[2].

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