Ultrafast vibrational dynamics of water

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Summary

The presence of hydrogen bonds in water strongly influences the macroscopic and microscopic properties of this liquid. The network of hydrogen bonds is by no means static: the formation and breakage of bonds occurs on an ultrafast time scale of a picosecond, which is on the same order as the relaxation time of vibrations in liquids. It is therefore expected that hydrogen bonding has a profound effect on vibrational relaxation in liquids like water and ethanol.

The absorption band of the OH-stretch vibration in liquid water is inhomogeneously broadened due to the different environment each water molecule experiences. In order to reveal the dynamics of water molecules, mid-infrared pump-probe spectroscopy is applied, in which a pump pulse excites a homogeneous sub-ensemble of oscillators with the same OH-stretch frequency. By tuning the frequency of the probe pulse, the response at the same or at other frequencies can be measured as a function of time, which enables us to deduce vibrational lifetimes.

The vibrational dynamics of the OH-stretch oscillator in liquid water, however, is not revealed in a straightforward way. In Chapter 4 we show that the measured pump-probe scans are governed by two time scales: the lifetime of the excited state of the OH-stretch oscillator and the so-called equilibration time. The latter time constant represents the redistribution time of the energy of the relaxed OH-stretch vibration over all degrees of freedom, i.e. over all low(er) frequency modes. This time scale is observed to be $550 \pm 50$ fs at all wavelengths and at all temperatures. The lifetime $T_1$ of the OH-stretch vibration at room temperature is found to be $260 \pm 18$ fs at all wavelengths. This means that spectral diffusion in pure water occurs on a time scale shorter than the pulse duration. The lifetime of the OH-stretch vibration is observed to increase with temperature to $320$ fs at $358$ K. The increase in lifetime can quantitatively be explained from the overlap integral between the OH-stretch mode and the first overtone of the H-O-H bending mode. These modes spectrally overlap which enables the transfer of energy from the stretch to the bend mode, but due to the change in hydrogen bond interactions at higher temperatures, the positions and shapes of these bands change, leading to a decrease in overlap, which leads to a longer lifetime of the OH-stretch mode.

In Chapter 5 we study the equilibration process. Here, we compare the equilibration time scales of water with other hydrogen-bonding solvents like the lower alcohols as methanol, ethanol and propanol. We observe that equilibration, or thermalization, leads to a shift of the position of the OH-stretch band and a decrease of its cross section. The equilibration times are observed to increase with the mass of the
Summary

molecule for the alcohols. This means that equilibration results from repositioning of the molecules in the liquid. The wavelength dependent equilibration behavior for alcohols indicates that at least two different processes are involved in the equilibration process. For water, the equilibration time is not observed to depend on frequency. This suggests that for water the equilibration rate is determined by the time scale at which energy can be transferred from a non-thermal intermediate state, likely the overtone of the bending mode, to the low frequency modes. Hence, water can adapt extremely fast to a deposition of energy.

The work presented in Chapters 6 and 7 was triggered by a time-resolved anti-Stokes Raman study by the group of Dlott. This group came up with a reinterpretation of the results presented in Chapter 4. In Chapter 6 we show that this reinterpretation is incorrect and is not able to explain our results. The long pulses used by the group of Dlott (1.4 ps) could not distinguish between the vibrational relaxation and equilibration time. It is shown in Chapter 7 that the subsequent action of these two processes leads to a deceleration of the vibrational relaxation rate of the still excited OH-groups. Because the pulse duration in our experiment was short compared with the lifetime of the OH-stretch vibration, this deceleration effect did not play an important role in our experiments. In the experiments by Dlott, however, long pulses are used. There still exist excited OH-groups, when the relaxation and equilibration of the OH-stretches excited by the front of the pulse have already changed the temperature of the sample. This leads to a deceleration of the vibrational relaxation of the still excited OH-groups. We present a numerical model describing this feedback effect on the lifetime for liquid water. The model accurately describes both the results presented in Chapter 4 and the results of Dlott and coworkers.

In Chapter 8, vibrational and reorientational measurements are presented for water monomers with one or two hydrogen bonds. In liquid water energy hopping to neighboring molecules and redistribution of energy among the antisymmetric and symmetric mode leads to a complete delocalization of vibrational energy over the molecule. For monomers, however, we can exclusively focus on the intramolecular energy redistribution. In all experiments two processes occur: the transfer of excitation energy and the change in excitation frequency due to the formation and breakage of hydrogen bonds. In all these processes an intermediate state occurs in which the energy is delocalized. From a comparison with HDO molecules, we have shown that the breakage and formation of hydrogen bonds occurs on a time scale of 1.3 ± 0.4 ps, the lifetime of the transient state is ~ 200 fs. From the rotational anisotropy we conclude that the molecular reorientation occurs on a 6.0 ± 1.0 ps time scale.

Chapter 9, finally, is devoted to the dynamics of two OH-groups that are coupled via an intramolecular hydrogen bond. The hydrogen-bond donating OH-stretch vibration has a slightly smaller OH-resonance frequency than the hydrogen bond accepting mode, 3570 and 3610 cm⁻¹, respectively. We show that the lifetimes of these vibrations are 3.5 ± 0.4 and 7.4 ± 0.5 ps, respectively. A 60 cm⁻¹ low-frequency mode is anharmonically coupled to the hydrogen-bond donating OH-groups, leading
to sidebands in the transient spectra. If we use broadband excitation of both OH-groups, oscillations with frequency components of 40 and 60 cm\(^{-1}\) are observed. We have modeled these oscillations using Feynman diagrams. The 60 cm\(^{-1}\) oscillation stems from the quantum interference of the hydrogen-bond donating group with its first sideband, the 40 cm\(^{-1}\) oscillation indicates the presence of a coupling between the hydrogen bond donating and accepting OH-stretch mode.