

SUMMARY

This thesis describes experiments on liquid water that aimed at obtaining more information on and understanding of the microscopic properties of liquid water. The method is pump–probe spectroscopy on the *OH stretch vibration* in a diluted HDO in D_2O solution. The latter serves as a model system for normal water (H_2O), the macroscopic physical properties (melting point, boiling point, specific heat, etc.) of which are not very different from heavy water (D_2O). In pump–probe experiments on a sample consisting of liquid HDO/ D_2O , a short and very intense light pulse, or *pump pulse* vibrationally excites a fraction of the OH groups of the HDO molecules. These OH groups have a strong absorption around a frequency of 3400 cm^{-1} (i.e., a wavelength of $2.94\text{ }\mu\text{m}$). The effect of such an excitation is a temporary change in the absorption spectrum of the sample. This change can be observed by measuring the transmittance of a second pulse, or *probe pulse*. Since the normally low transmittance at 3400 cm^{-1} increases, this change is called *bleaching*. This bleaching is measurable during a few picoseconds. The transient spectrum of the bleaching (i.e., the bleaching as a function of the probe frequency) evolves in time and can be described as a spectral diffusion process with a *spectral correlation time* that is about 0.5 ps [Woutersen et al., Phys. Rev. Lett. 83, 2077 (1999)]. The spectral correlation time is directly related to the timescale of the length fluctuations of the hydrogen bonds in the liquid because in an $OH\cdots O$ hydrogen bond, the OH stretch frequency is related to the O–O distance.

The light pulses that have been employed in the pump–probe experiments were generated by a technique called optical parametric generation and amplification (OPG/OPA), but Chapter 3 discusses a new technique with promising features to generate tunable mid-IR pulses in the range $2.4\text{--}7.7\text{ }\mu\text{m}$ through a phase-matched four-wave mixing process in ordinary mid-IR window materials such as calcium fluoride and barium fluoride. In this process, the difference frequency $\nu_3 = 2\nu_2 - \nu_1$ is generated from pump fields ν_1 and ν_2 . The process can be phase-matched to different frequencies by adjustment of the angle between the pump fields.

The lifetime T_1 of an excited OH stretch vibration (in HDO: D_2O) is found to be 0.74 ps at room temperature. However, the lifetime of the bleaching is slightly longer with 0.85 ps and depends on the frequency at which is probed. The lifetime increases with temperature, a quite unusual fact compared to the typical behavior of molecular vibrations in other molecules. From these facts, we conclude that, upon relaxation of the OH stretch vibration, its energy flows into the hydrogen bond $OH\cdots O$ that is donated by the OH group. Moreover, we estimate that the resulting hydrogen-bond excitation decays with a time of $1.0 \pm 0.5\text{ ps}$.

We investigated to what extent the model system HDO: D_2O differs from pure H_2O by performing similar experiments on the OD stretch vibration of HDO dissolved in H_2O , in which the roles of all H and D atoms are exchanged. In the latter, the vibrational lifetime is $T_1 = 1.8\text{ ps}$, over 2 times longer than in the former. However, the spectral

correlation time is only slightly different with 0.40 ps instead of 0.5 ps, which justifies the use of HDO:D₂O as a model system to describe the hydrogen-bond dynamics in H₂O.

It is generally accepted from dielectric and NMR experiments that the random orientational motion of water molecules can be described with a time constant $\tau_2 \approx 2.5$ ps, which is the average value over all water molecules in the liquid. At any moment, water molecules in liquid water are oriented completely at random. However, by means of polarization-resolved pump-probe experiments, it is possible to use the excited OH stretch vibration to label those HDO molecules that happen to be oriented in a certain direction. This anisotropic orientation distribution can then be followed in time; it turns out that weakly hydrogen-bonded molecules have a much shorter orientation time, while strongly hydrogen-bonded molecules reorient very slowly. This differentiation is possible because pump and probe pulses at different frequencies are sensitive to different hydrogen-bond lengths. The average time constant of 2.5 ps is the result of the hydrogen-bond length fluctuations (that can be interpreted as the rapid making and breaking of hydrogen bonds). The temperature dependence of the frequency-dependent reorientation can be interpreted as an activated process, for which we estimate how the activation energy depends on the OH stretch frequency.

For most purposes, the potential in the OH stretch coordinate can be approximated as a harmonic potential with a small anharmonic perturbation. In this approximation, the OH stretch mode can be described as a harmonic oscillator, whose uniformly-spaced energy levels are slightly perturbed, which results in a $\nu = 1 \rightarrow 2$ transition energy that is lower than its $\nu = 0 \rightarrow 1$ transition. However, a more accurate model [Lippincot and Schröder, JCP 23, 1099 (1955)] of the potential $V(r, R)$ as a function of both the OH stretch coordinate r and the hydrogen-bond coordinate R shows that the approximation of a perturbed harmonic oscillator already breaks down for states $\nu \geq 2$, a fact that is reflected in the $\nu = 1 \rightarrow 2$ contribution in the transient spectrum of HDO:D₂O. The shape of this potential implies that the energetically most favorable path for the autodissociation reaction $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ is via the $\nu = 2$ state with a total activation energy of 79 kJ/mol. This value is comparable to the dissociation enthalpy that follows from the temperature dependence of the pH of water. With the potential $V(r, R)$ it is possible to describe the spectral relaxation more accurately than with the parabolic potentials of the Brownian Oscillator model; the correlation time is 950 ± 100 fs, larger than previously assumed values. A detailed analysis of data with a higher time resolution [Gale et al., Phys. Rev. Lett. 82, 1068 (1999)] show that, directly after excitation, excited molecules undergo a small and rapid inertial shift with a time constant of 170 ± 40 fs.

The hydrogen-bond network in water is completely disturbed if water is used as a solvent for sodium hydroxyde (NaOH). From pump-probe experiments on a 10 mol/l solution of NaOD in HDO:D₂O, we conclude that the broad absorption band of the OH stretch vibration consists of two separate classes of OH groups: (I) OH groups with DO-H...OD₂-like hydrogen bonds, suprisingly similar to those in HDO:D₂O. (II) OH groups with DO-H...OD⁻-like hydrogen bonds, which show a very rapid vibrational relaxation, possibly due to deuteron transfers. For component I, the lifetime of the OH stretch vibration is observed to increase with frequency, which can be explained from the accompanying decrease in the strength of the hydrogen-bond interaction. Spectral holes can be created in this component that change neither position nor width on a picosecond timescale. The spectral diffusion ($\tau \approx 0.5$ ps) in HDO:D₂O is completely absent, which indicates that, in this solution, the hydrogen-bond network is very static.