

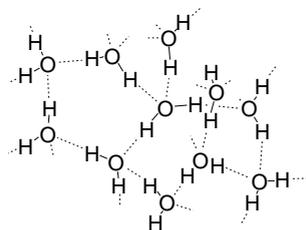
I INTRODUCTION

This thesis is about water and hydrogen bonding. That is: the properties of individual water molecules, whose collective behavior is responsible for how we experience water in everyday life. The first scientific knowledge of this kind was obtained by the end of the 18th century. At that time, chemists observed that ‘inflammable air’ (hydrogen), when burnt, would generate water vapor that fogged the glassware of their experiments. In 1781, Henry Cavendish was the first to synthesize water from correct proportions of hydrogen (which he assumed to be the element ‘phlogiston’ in pure form) and ‘dephlogisticated air’ (oxygen). Most likely, a considerable amount of shattered glass has been produced during the course of his experiments. Cavendish explained his observations in terms of the traditional alchemistic view that every material is composed of the elements earth, fire (phlogiston), water, and air. However, his discovery led Antoine Lavoisier, the founder of modern chemistry, to his demonstration in 1783 in front of a scientific audience that the summed weights of the oxygen and hydrogen gas in this synthesis were equal to the weight of the resulting water, that was ‘as pure as distilled water.’^{39,70} Though the concept of atoms and molecules was not very clear at the time, there was a notion that weights and chemical components are somehow conserved in chemical reactions. Therefore, we may regard these experiments as the first to prove that water is a compound consisting of hydrogen and oxygen in a fixed ratio. Nowadays, we learn at school that water has the chemical formula H_2O , but the simplicity of this formula is by no means reflected in the physical properties of this liquid. No other molecules with a comparable size and mass form a liquid at room temperature. The cause of water being liquid is the fact that every water molecule can form up to four hydrogen bonds with neighboring water molecules, which means that a three-dimensional network is formed, as shown in Fig. 1.1.

The hydrogen bonds in water are the attractive interactions between the H atom of a water molecule and the O atom of a neighboring water molecule. This attraction is 10 to 100 times weaker than the chemical bonds of the O–H groups. Due to this weakness, the network in liquid water is by no means static: hydrogen bonds are constantly formed and broken as the molecules change their position and orientation relative to one another.

Hydrogen bonds are not limited to attractions between water molecules. Generally, a

FIGURE 1.1. Hydrogen-bond network in liquid water. The dotted lines indicate hydrogen bonds, of which up to 4 can be formed per water molecule. On the average, a water molecule has 3.4 hydrogen bonds.¹¹⁶



hydrogen bond has the form



where the donating atom X is usually an N or O atom, and the accepting atom Y is usually either an N or O atom or a negative ion. For example, for the correct biological functioning of proteins and DNA molecules, two building blocks of life, the formation of $N-H \cdots O$ and $N-H \cdots N$ hydrogen bonds is essential.¹¹⁶ Further, the existence of hydrogen bonds between water molecules and the polarity of water molecules are responsible for water being an excellent solvent for polar molecules and salts, which is essential for many chemical reactions in both biochemistry and inorganic chemistry. Water is not only of chemical importance. As of today, a simple query on the scientific search engine INSPEC, which covers only the areas of physics and physical chemistry, generates 175,000 hits for articles with the word 'water' in the title or abstract, and 17,000 hits with 'hydrogen bond.'

The general importance of water is a constant motivation for seeking more knowledge about and understanding of the microscopic mechanisms that underly its properties. It has been suggested that the peculiar properties of liquid water, such as the temperature dependence of its density and viscosity,^{3,112} can be explained in terms of a two-state mixture model. In this view, molecules aggregate into clusters that come in two types of structure that have different properties.¹⁰² These aggregates would rapidly transform into one another. Whether water consists of two structures or not, the rapid breaking and forming of hydrogen bonds in liquid water does occur on an extremely rapid time scale, typically 10^{-12} seconds. Obtaining knowledge on processes requires experimental techniques that can resolve such processes. The next section concerns the effect of hydrogen bonds on the infrared spectrum of water, which is an ingredient for vibrational pump-probe spectroscopy, which satisfies this requirement and is used in this thesis.

1.1 THE INFRARED ABSORPTION OF WATER

Generally, molecules absorb light at infrared wavelengths with a spectrum that is characteristic for its structure.⁵² In water, the absorption by OH groups is especially interesting. Figure 1.2 shows two transmittance spectra. One is the spectrum of ambient air, which has a complicated structure of absorption lines around 3700 cm^{-1} due to the presence of water vapor. (see the Appendix on page 102 about spectroscopic units.) The source of the infrared absorption is formed by two types of so-called stretch vibrations in the H_2O molecule, one at 3652 and one at 3756 cm^{-1} .[↓] These vibrational frequencies are well-defined,¹¹⁰ but the overwhelming number of additional possible rotational excitations, each of them responsible for a separate narrow line, obscures this fact completely, at least at first sight. The other spectrum is of liquid water, which does not show any fine structure and which is broader and shifted towards lower frequencies. The widths of the liquid and vapor spectrum have different origins. In liquid water, rapid rotations such as those in the gas phase are not possible, mainly due to the ubiquitous presence of hydrogen bonds. In fact, both the lower average frequency of the liquid spectrum and its broadening can be explained from hydrogen bonds. It is a general property of hydrogen bonds that

[↓] These two vibrational modes are known as the symmetric and anti-symmetric stretch modes, respectively. There is a third mode, the bend mode, that has a frequency of 1595 cm^{-1} , but this mode is not part of the spectral region under consideration.

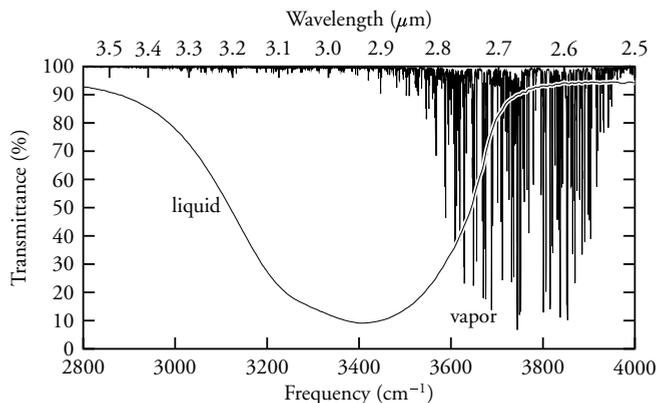


FIGURE 1.2. Transmittance spectrum of ordinary water (H_2O) vapor (~ 20 cm air of normal humidity at room-temperature) and transmittance spectrum of a water film with a thickness of $\sim 3 \mu\text{m}$.

they lower the vibrational frequency of the donating X–H group; this lowering effect is stronger for shorter XY-distances. References 77, 85, 92, 106 provide extensive data on the magnitude of this effect on O–H groups with various types of Y atoms; Ref. 114 provides a theoretical treatment. The presence of hydrogen bonds in liquid water and the variation in hydrogen-bond lengths, a consequence of the ever varying network structure in Fig. 1.1, cause the broad shape that ranges from 3200 to 3600 cm^{-1} .

The rapidly changing hydrogen bonds in liquid water cause the frequency of each participating OH group to fluctuate at a comparable rate. However, because an H_2O molecule has two separate independent vibrational frequencies that differ significantly, there is no single translation of vibrational frequency to hydrogen-bond length. However, if one H atom is replaced by a deuterium (D) atom, which combines chemical properties nearly identical to those of ordinary hydrogen with a mass that is twice as large, then the two vibrational modes will be clearly distinguishable. In such an HDO molecule, the OH stretch frequency is 3707 cm^{-1} in vapor¹¹⁰ and about 3400 cm^{-1} in the liquid phase, while the OD stretch frequency is 2727 cm^{-1} or 2500 cm^{-1} , respectively. Typically, we dissolve HDO molecules in D_2O , which has no significant infrared absorption in the range 3300–3700 cm^{-1} . Hence, in liquid HDO dissolved in D_2O , there is a reasonably well-defined relation between the OH stretch frequency and the hydrogen-bond length; Figure 1.3 shows the spectrum of liquid HDO and the corresponding hydrogen-bond lengths. However, this absorption spectrum only provides information on the variety of the hydrogen bonds and not on the time scale of the hydrogen-bond fluctuations.

If it were possible to follow the frequency of an individual OH group in time, one would have enough information to calculate the hydrogen-bond length for this OH group at any moment. Time-resolved single-molecule spectroscopy, as this principle is called, is not (yet) possible for molecular vibrations, but it is possible to follow the behavior in time of a *subensemble* of the OH groups with the technique discussed in the next section.

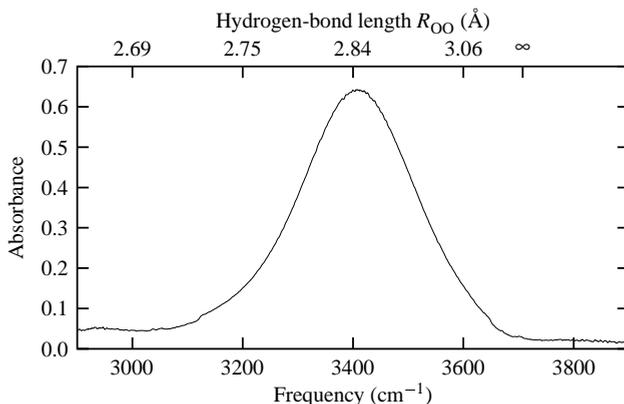


FIGURE I.3. Absorption spectrum of HDO in D₂O, corrected for the absorption of the solvent, D₂O, at an HDO concentration of $\sim 0.4\%$ and a sample thickness of $200\ \mu\text{m}$. In this thesis, the absorbance is defined as $A = -\ln(T)$, where T is the transmittance. (Other literature may also define $A = -\log_{10}(T)$.) On the top axis, approximate hydrogen-bond lengths corresponding to the OH frequencies are given (see also Fig. 8.2 on page 90).

I.2 VIBRATIONAL PUMP–PROBE SPECTROSCOPY

In a pump–probe experiment, a pulse of radiation creates an excitation in a sample, the effect of which is subsequently probed by a second pulse. A historical example of this technique applied on water consists of the nuclear magnetic resonance (NMR) experiments published by Bloembergen in 1948.⁴ He observed that, in a strong magnetic field, the hydrogen nuclei of water could be excited by a ‘pulse’ of 30 MHz radio waves that lasted half a minute. The effect of this excitation remained measurable for several seconds; by filming the screen of his oscilloscope using a movie camera, he was able to determine that the relaxation time of the proton excitation was 2.3 seconds. Over half a century later, we employ pulse durations of 2×10^{-13} seconds (200 fs) in vibrational pump–probe experiments to gain understanding of vibrational relaxation processes that occur on a timescale of 1 picosecond; the movie camera is now replaced by computer soft- and hardware. Vibrational pump–probe spectroscopy is now a technique widely employed, on the OH stretch,^{51,62,65,74,130} the OD stretch,⁷⁸ and the CO stretch.^{49,89,121} In a pump–probe experiment on the OH stretch vibration, a short laser pulse, or pump pulse, excites the OH stretch vibration of a significant fraction of the OH groups in the sample. The result of this excitation is a temporarily decreased absorbance, due to the fact that there are less OH groups left that are still capable of absorbing light.[†] This absorbance change is measured by means of a second, or probe, pulse that passes through the sample with a variable delay t after the pump pulse. Consider the simple case of a thin sample with a concentration ρ of OH groups per unit of surface, each capable of absorbing one photon at a particular

[†] More precisely: in thermal equilibrium, the OH stretch absorption results from the $0 \rightarrow 1$ transition. After excitation, there is still the possibility of absorption due to the $1 \rightarrow 2$ transition, which is generally at a lower frequency. Moreover, a population of the excited state leads to an additional decrease of the apparent $0 \rightarrow 1$ absorption due to stimulated emission caused by $1 \rightarrow 0$ transitions.

resonance frequency ω . The transmittance of such a sample is

$$T_o = e^{-\rho\xi_o\sigma}, \quad (I.1)$$

where σ is the absorption cross-section of an individual OH group (dimension m^2) and $\xi_o = 1/3$ is a geometrical factor to account for the fact that linearly polarized light preferentially excites OH groups that are approximately parallel to its polarization. If a pump pulse at a frequency ω , on resonance with the OH groups, excites N_x molecules per surface unit, then the partially excited sample has a temporarily changed transmittance that is different depending on the polarization ϵ with respect to the pump pulse. This transmittance is $T_\epsilon = \exp([2N_x\xi_\epsilon - \rho\xi_o]\sigma)$, where $\xi_{||} = 3/5$ and $\xi_\perp = 1/5$.[♯] The factor 2 results from the fact that both the ground-state depletion and the excited-state population affect the transmittance. A useful quantity is the absorbance change

$$\Delta\alpha_\epsilon \equiv -\ln(T_\epsilon/T_o). \quad (I.2)$$

Because excited molecules typically decay to the ground state with a time constant τ , the absorbance change at time t after the pump pulse becomes

$$\Delta\alpha_\epsilon(t) = -2N_x\xi_\epsilon\sigma e^{-t/\tau}. \quad (I.3)$$

In this simple case, we have assumed that all HDO molecules absorb at the same frequency, which is not very realistic in view of the dependence of the OH stretch frequency on its OH...O hydrogen-bond length. Therefore, we assume a distribution over frequencies that corresponds to a distribution over hydrogen-bond lengths. Let the normalized function $f_d(\omega)$ represent the distribution of HDO molecules over resonance frequencies. Further, $f_{pu}(\omega)$ is the normalized spectrum of the pump pulses, and $f_x(\omega, t)$ the distribution of excited molecules at time t after the pump pulse. Because of the fluctuations in hydrogen-bond lengths, this frequency distribution must be time-dependent in a way that mirrors the length fluctuations. Initially ($t = 0$), only OH groups within the small range of frequencies contained by the pump spectrum are excited, after which this distribution broadens, a process called spectral diffusion or spectral modulation. We assume that every HDO molecule absorbs within a narrow frequency band around a central frequency ω , such that we can describe the cross-section at frequency ω' by the ‘cross-section spectrum’

$$s(\omega' - \omega) = \delta(\omega' - \omega)\bar{\sigma}, \quad (I.4)$$

where δ is the Dirac- δ function and $\bar{\sigma} = \sigma / \max[f_d(\omega)]$. We can then write the equivalents of Eqs. (I.1) and (I.3):

$$\alpha_o(\omega) \equiv \ln(T_o(\omega)) = f_d(\omega)\rho\xi_o\bar{\sigma}, \quad (I.5)$$

$$\Delta\alpha_\epsilon(\omega, t) = -2N_x\xi_\epsilon\bar{\sigma}f_x(\omega, t). \quad (I.6)$$

[♯]The factors ξ_ϵ result from the fact that vibrational excitations are dipole transitions, whose excitation probability is proportional to $\cos^2(\theta)$, where θ is the angle between the OH bond vector and the polarization of the excitation light. We define σ as the cross-section of an OH group that is exactly parallel to the light polarization. Hence, for an isotropic population, $\xi_o = \int (1/4\pi) \cos^2(\theta) d\Omega = 1/3$, with $\int d\Omega \equiv \int d\phi \int \sin\theta d\theta$. If $g(\theta) = 3 \cos^2(\theta)/4\pi$ describes an anisotropic excited population, $\xi_{||} = \int g(\theta) \cos^2(\theta) d\Omega = 3/5$ and $\xi_\perp = \int g(\theta) \cos^2(\chi) d\Omega = 1/5$. Here, χ is the angle between a vector with polar coordinates (θ, ϕ) and the probe polarization vector $(\pi/2, \pi/2)$ and $\cos(\chi) = \sin(\theta) \sin(\phi)$.

At $t = 0$,

$$f_x(\omega, 0) = f_{\text{pu}}(\omega), \quad (1.7)$$

where we assume that all pump energy is absorbed by the sample [otherwise, multiply by $(1 - T_o(\omega))$].

Equation (1.6) describes the so-called transient spectrum at delay t . Its dependence on frequency and time is the essential ingredient of all pump–probe experiments described in this thesis, because it relates the dynamics of the hydrogen bonds to the time evolution of the absorbance change.

Up to now, we have assumed that the HDO molecules do not significantly change their orientations, which means that the orientation distribution $g(\theta)$ of excited molecules, that results from the polarization of the pump pulse, does not depend on time. With reorientation, $g(\theta)$ is time-dependent, e.g.

$$g(\theta, t) = \frac{1}{4\pi} \left(1 + [3 \cos^2(\theta) - 1] e^{-t/\tau_r} \right), \quad (1.8)$$

where τ_r is known as the rotational correlation time. If reorientation takes place, the geometrical coefficients ξ_{\parallel} and ξ_{\perp} will be time-dependent. An elegant way to circumvent the effect of reorientation is measuring the isotropic absorbance change

$$\Delta \alpha_{\text{iso}}(\omega, t) = (\Delta \alpha_{\parallel} + 2\Delta \alpha_{\perp})/3 = -2N_x \xi_o \bar{\sigma} f_x(\omega, t). \quad (1.9)$$

It can be shown that reorientational processes do not affect $\Delta \alpha_{\text{iso}}$. The isotropic absorbance change can be measured by means of polarizing optics or by simply choosing the polarization of the probe pulses such that the intensities of its parallel and perpendicular polarization components have a ratio 1:2. This ratio is obtained if the angle between pump and probe polarizations is $\arctan(\sqrt{2}) \approx 54.7$ deg, known as the magic angle. Most pump–probe studies in this thesis concern the behavior of the isotropic absorbance change, with the exception of Chapter 7, where we will use the difference between $\Delta \alpha_{\parallel}$ and $\Delta \alpha_{\perp}$ to obtain information on the reorientational dynamics in water. Equations (1.6) and (1.8) are a first approximation; I will discuss some refinements in §2.6.

All pump–probe experiments in this thesis, except for those in Chapter 5, were carried out on dilute HDO in D_2O , with or without dissolved substances. I already mentioned in §1.1 that HDO has a well-defined OH stretch vibration that is only weakly coupled to the OD stretch vibration in the same molecule. Further, the absorbed pump pulse energy is ultimately converted to heat; in a pure H_2O sample, this effect overwhelms any other signal contributions almost completely.⁷⁴ In a dilute HDO in D_2O solution, however, the thermal effects are rather small (§2.8). Finally, the short average distance between OH groups in pure H_2O or in concentrated HDO: D_2O (which contains H_2O as well) enables resonant energy transfer from one OH group to another.¹³⁰ This energy transfer (Förster transfer²⁹ in the limit for long-range interactions) would complicate the analysis.

Finally some remarks on notational conventions. The OH stretch vibration can be treated as quantum-mechanical (hence the distinction between ground-state and excited-state OH groups) with the quantum number ν (vee), that can take the values $0, 1, 2, \dots$, with $\nu = 0$ corresponding to the ground state. In this thesis, I will use the symbol ν exclusively for OH or OD stretch vibrations. Similarly, the symbol R will be used exclusively for the O–O distance of a hydrogen bond. Error margins in experimental values will be denoted in parentheses, e.g. 1.32(2) means 1.32 ± 0.02 .

1.2.1 ABSOLUTE MAGNITUDE OF THE PUMP-PROBE SIGNALS

We can use Eqs. (1.3) and (1.6) to estimate how large the absorbance changes $\Delta\alpha$ will be for given experimental parameters. A pump pulse containing N photons per unit area will excite $N_x = N(1 - T_o)$ molecules, where we assume that $N_x \ll \rho$. If an appropriate HDO concentration and sample thickness are chosen, then $1 - T_o \approx 1$, which is optimal for the sensitivity of the experiment. If the pump pulse has an energy E_{pu} per unit surface, the absorbance change in Eq. (1.3) is

$$\Delta\alpha_\epsilon = \frac{-2E_{pu}\xi_\epsilon\sigma}{\hbar\omega} \quad (1.10)$$

The OH stretch of HDO in D₂O has a cross-section $\sigma \approx 8.0 \times 10^{-23}$ m² (Ref. 135), which can also be estimated from the linear spectrum in Fig. 1.3. For a pump pulse at 3400 cm⁻¹ with $E_{pu} = 1$ μJ in a focus of 100 × 100 μm², we can expect an isotropic absorbance change $\Delta\alpha_{iso} \approx -0.1$. Of course, the pump energy must be contained within a pulse that is shorter than the vibrational lifetime, because most of the excited population would otherwise relax to the ground state before the pump pulse is finished.

If the spectral distribution f_x is to be incorporated, the expression in Eq. (1.10) should be multiplied roughly by the ratio Δ_d/Δ_{pu} , where Δ_d is the width of the linear absorbance spectrum and Δ_{pu} is the width of the pump pulse spectrum. This correction factor holds in the case of spectral modulation that is slow compared to the pulse duration. Otherwise, Eq. (1.10) applies.

In our experience, the observed pump-probe signals are smaller (typically a factor 3) than the estimated signal amplitude, possibly due to geometrical effects in the overlap region of pump and probe pulses. However, it is worth to note that the fraction of excited molecules can be written as

$$\frac{N_x}{\rho} = \frac{-\xi_o\Delta\alpha_\epsilon}{2\xi_\epsilon\alpha_o} \quad (1.11)$$

Thus, a typical sample transmittance $T_o = 0.05$ and an absorbance change $\Delta\alpha_{iso} = -0.1$ imply that only 1.7% of the HDO molecules is excited, which justifies the assumption at the beginning of this section.

1.3 OUTLINE OF THIS THESIS

Pump-probe experiments on water and the resulting information on the dynamics of hydrogen bonds constitute the central theme of this thesis. In Chapter 2, I will discuss the various experimental setups that have been used in the rest of the thesis, along with a practical considerations and additional contributions to the pump-probe signal that have to be taken into account. All experiments were carried out with pulses at wavelengths in the range 2.8–4.2 μm that were generated by means of optical parametric generation and amplification (OPG/OPA), that has become standard practice in time-resolved spectroscopy. However, Chapter 3 discusses a novel way to generate infrared pulses with wavelengths up to 7.2 μm by means of a 4-photon mixing process, which has the potential of being extended to even longer wavelengths.

The following chapters describe experimental pump–probe studies on water. First, Chapter 4 describes the vibrational relaxation of the OH stretch vibration of HDO dissolved in D_2O . Here, the donated $OH \cdots O$ hydrogen bond shows its influence by acting as an acceptor for the vibrational energy. Next, Chapter 5 is concerned with the difference between the OH stretch vibration of HDO in D_2O and the OD stretch vibration of HDO in H_2O . It turns out that the OD stretch vibration is affected by hydrogen-bond dynamics at a timescale somewhat faster than those affecting the OH stretch, but that the lifetime of the OD stretch is significantly longer. In Chapter 6, dissolving sodium deuterioxide ($NaOD$) in $HDO:D_2O$ turns out to have a strong impact on the fluctuations in the hydrogen-bond network. The OD^- ions that are embedded in this network strongly distort its structure, with the result that the fluctuations in the hydrogen-bond lengths become slower by at least an order of magnitude. Returning to $HDO:D_2O$, we will find in Chapter 7 how the orientational motions of water molecules are related to the making and breaking of hydrogen bonds. Finally, in Chapter 8, we use the transient spectrum of excited $HDO:D_2O$ to obtain information on the shape of the potential surface in terms of the OH stretch coordinate and the hydrogen-bond coordinate, which has interesting implications on the mechanism of the autodissociation reaction that is responsible for the fact that pure water has a pH of 7.