Ultrafast vibrational dynamics of water

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1 Introduction
1.1 Water and hydrogen bonds

The ubiquitous presence of water on earth and in everyday life may suggest that the behavior of this liquid is fully understood. Whereas its macroscopic properties like the high specific heat and the high boiling temperature, are attributed to the ability of water to form hydrogen-bonds, its microscopic behavior, which underlies the macroscopic properties, still forms an intriguing puzzle. It is beyond doubt that water molecules play a crucial role in the stabilization of biomolecules, like proteins, and in (bio)chemical reactions, either as reactant themselves, as in the photosynthesis or the ATP/ADP cycle, or as solvent facilitating these reactions. In the latter case, it not only determines the solvation dynamics, but also acts as an acceptant of excess energy dissipated in the reaction. In this context, it is necessary to know the behavior of water molecules in the liquid phase. This is one of the central themes in this thesis.

Water (H\textsubscript{2}O) molecules can form up to 4 hydrogen bonds and because hydrogen bonds are cooperative in nature, they strongly affect the structure and dynamics of water. Hydrogen-bonding also plays a dominant role in the structure of macro- and biomolecules. The elementary building blocks for the secondary structure of proteins, the α-helices and β-sheets, owe their actual structure to hydrogen bonding. Hydrogen-bonding is much stronger than the intermolecular Van der Waals interactions, and is therefore expected to dominate the dynamic properties of hydrogen bonding liquids and solids. Breaking and making of hydrogen bonds on picosecond time scales, for example, are ubiquitous in liquid water. Chemical reactions, like acid-base reactions and excited state proton or hydrogen transfer, all involve the breaking of hydrogen bonds. Therefore, understanding water means understanding hydrogen-bonds.

Hydrogen bonding is an attractive interaction between proton donor (A-H) and proton acceptor (B) molecules. The atoms A and B are among the electro-negative atoms oxygen (O), fluorine (F) or nitrogen (N). Hydrogen bonds are directional and the energies associated with hydrogen bonding range from 4 to 40 kJ/mol [14]. In this thesis we will study the O–H····O system. In the case of liquid water, hydrogen bonds have an energy of 23.3 kJ/mol [93], while the covalent O–H bond is 492 kJ/mol [81]. Dynamical information on water, in particular on the reorientation time of water molecules in the liquid has been measured in NMR and dielectric relaxation experiments, and was shown to be 8 ps [3, 6, 42]. Infrared spectroscopy is one of the key tools to decipher the structure of gases, liquids and solids. The infrared absorption spectrum of a system is extremely sensitive for hydrogen bonding [28]. Position, width and the intensity of the O–H stretch absorption band changes dramatically, as will be shown in the next sections. This does not imply, however, that the ultrafast dynamics of water and other hydrogen bonded systems can be unraveled using the above mentioned methods, including linear absorption spectroscopy. As will be shown in the coming sections, short infrared pulses form a powerful means to get dynamical information on hydrogen bonding and the behavior of water molecules out of the absorption bands.
Molecular vibrations

Figure 1.1. Anharmonic (solid line) versus harmonic (dashed line) potential with the energies of their vibrational states. $r_0$ is the equilibrium distance, $D$ the dissociation energy.

1.2 Molecular vibrations

For the description of the A-H stretch vibration of the A-H···B system, we will first focus on a vibration in a di-atomic molecule. Given a harmonic potential $V = k(r - r_0)^2$, i.e. the potential energy depends on the displacement from the equilibrium position $(r - r_0)$ squared, it can be shown that the energies of the oscillator are given by [35]:

$$G_v = \hbar \omega_0 (v + 1/2)$$  \hspace{1cm} (1.1)

with $\omega_0 = \sqrt{k/\mu}$, where $\mu$ is the reduced mass of the oscillator, $k$ the force constant and $v$ the quantum number. It follows from the above equation that all energy levels of the oscillator are equidistant. The selection rules for the harmonic oscillator are: $\Delta v = \pm 1$. The harmonic oscillator is, however, far from realistic. When the distance between the atoms gets too short, additional repulsive forces come into play, leading to a steeper slope for small internuclear distances. For distances larger than $r_0$ the slope becomes less steep than harmonic and decreases to zero for very large distances, i.e. the molecule is dissociated into two atoms. These effects can be taken into account using an anharmonic potential, i.e. a potential which contains a term $\propto (r - r_0)^3$ and higher order terms. An example of such a potential is the Morse potential: $V = D(1 - e^{-\beta(r-r_0)})^2$, which has a $(r - r_0)^3$ term in the expansion of the exponential. $D$ is the equilibrium dissociation energy and $\beta$ a constant. Figure 1.1 shows the Morse
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\[ G_v = \hbar \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 \]  

where \( \omega_e x_e \) is the anharmonicity constant. The anharmonicity between the 0→1 and 1→2 is given by \( \Delta = (G_1 - G_0) - (G_2 - G_1) = 2\omega_e x_e \). For an anharmonic oscillator the selection rules read: \( \Delta v = \pm 1, \pm 2, \ldots \). The levels are occupied following the Boltzmann distribution.

For polyatomic molecules, more vibrations come into play. These vibrations can be identified as normal mode vibrations, i.e. normal coordinates can be constructed along which the progress of a single vibration can be followed. If a vibration changes the dipole moment of the molecule, it is infrared active. If the polarizability changes, it is Raman active.

As a not completely arbitrarily chosen example, let’s inspect the normal modes of water. It belongs to the point-group \( C_{\infty v} \), and has three normal mode vibrations, shown in Figure 1.2. All these modes are infrared active. There are two stretching modes, the symmetric \( \nu_1 \), and the antisymmetric \( \nu_3 \), which absorb at 3657 and 3756 cm\(^{-1}\), respectively. The bending mode (\( \nu_2 \)) is the third normal mode, absorbing at 1595 cm\(^{-1}\). The dipole moments of the symmetric and antisymmetric stretch vibration, indicated by the dashed arrows in Figure 1.2, are orthogonal with respect to each other.

Strictly speaking, the normal mode analysis only holds for small amplitudes of the oscillations, i.e. only the quadratic terms in the potential are taken into account. As we have seen before, oscillations are anharmonic, and therefore, severe modifications are needed on the concept of normal modes. It is no longer possible to resolve the vibrational degrees of freedom in simple normal mode motions. In analogy with Eq. 1.2, the total vibrational energy for a tri-atomic molecule in cm\(^{-1}\) reads [35]:

\[ \text{Figure 1.2. Normal mode vibrations for gaseous water, the solid arrows indicate the displacement of each of the atoms, the dashed arrows give the direction of the dipole moment.} \]

potential together with the harmonic potential. The energy of vibrations in a Morse potential are given by [35]:
where $x_{ii}$ are the diagonal and $x_{ij}$ the cross anharmonicities. For gas phase water, the following anharmonicity constant were found [35]: $\omega_1=3825.25$ cm$^{-1}$, $\omega_2=1654.91$ cm$^{-1}$, $\omega_3=3935.59$ cm$^{-1}$, $x_{11}=-43.8$ cm$^{-1}$, $x_{22}=-19.5$ cm$^{-1}$, $x_{33}=-46.3$ cm$^{-1}$, $x_{12}=-20.0$ cm$^{-1}$, $x_{23}=-19.8$ cm$^{-1}$, $x_{13}=-155.0$ cm$^{-1}$. Using Eq. 1.3 the observed ir-frequencies can be calculated.

1.3 Vibrations in liquids

The validity of selection rules and the clear spectral positions of normal modes in the gas phase water, completely disappear in the liquid phase due to hydrogen bonding. Especially, the stretching vibrations in water, are extremely sensitive for hydrogen bonding. The A–H stretch frequency for a system A–H⋯B strongly depends on the distance between atoms A and B. For weak hydrogen bonds, i.e. long distances, the A–H stretch frequency resembles the gas phase frequency. For very strong hydrogen bonds, the A–H stretch frequency is shifted to the red. For water, the red shift is approximately 300 cm$^{-1}$. There is a strong correlation between the OH-stretch frequency and the O–O distance [58], as is generally the case for A–H⋯B systems. Recent calculations, however, have shown that for water not only the hydrogen bond length but also the hydrogen bond angle determines to a minor extent the stretch frequency [77]. The $\nu_2$ bending mode of water, undergoes a small blue shift upon hydrogen bonding.

In addition to the red shift, a broadening of the spectral bands occurs for the stretch frequencies. The broadening stems from the dephasing of an ensemble of excited oscillators. Different mechanisms are responsible for the broadening of absorption lines. In two limiting cases, they are either static or dynamic. Dynamic contributions to the line-broadening are responsible for the homogeneous broadening and described by the dephasing time $T_2$. This dephasing time reflects the loss of coherence of an ensemble of oscillators with the same center frequency. There are two causes for this loss: population relaxation to the ground state with time constant $T_1$ and pure dephasing with a time constant $T_2^*$. The latter time constant describes all very fast, small frequency jumps around the center frequency. A homogeneously broadened line shape is described by a Lorentzian with a width $\Gamma_{\text{hom}}$, which can be related to the time scales as follows:
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\[
\pi \Gamma_{\text{hom}} = \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^n} \quad (1.4)
\]

Static contributions to the line broadening are caused by static differences in the transition frequencies between different oscillators, i.e. different oscillators experience a different static environment. This leads to a Gaussian absorption line shape with a width that reflects the range of possible transition frequencies. The absorption band is inhomogeneously broadened.

A more general description of line broadening processes considers an oscillator with time-dependent transition frequency \( \omega(t) = \omega_0 + d\omega(t) \). If the Gauss-Markov assumption is applied for the second term, i.e. \( \langle d\omega(0)d\omega(t) \rangle = D^2 e^{-t/\tau_c} \), with \( D \) the width of the Gaussian distribution of the excursions \( d\omega(t) \) and \( \tau_c \) the typical frequency modulation time, the line shape can be calculated analytically \([61]\). The static and dynamic contributions to the line broadening are two limiting cases. The fast modulation limit \( (D\tau_c \ll 1) \) describes homogeneous broadening, whereas the slow modulation limit \( (D\tau_c \gg 1) \) describes inhomogeneous broadening.

For water, at least two line broadening mechanisms are present, a fast process leading to homogeneous broadening and a slow one leading to inhomogeneous broadening. In other words, the OH–stretch band consists of an inhomogeneous distribution of homogeneously broadened bands. If the changes in the transition frequency are neither very fast nor very slow, but change during the experiment, the process is called spectral diffusion. In this case, water molecules change orientations and positions, and continuously form and break hydrogen bonds towards neighboring water molecules on a picosecond time scale, which affects the OH–stretch frequency.

1.4 Non-linear spectroscopic techniques

All dynamical information, which can be extracted from the homogeneous line-width, is hidden under the inhomogeneous band. The band represents the average of an ensemble of oscillators. Therefore, other experimental techniques are necessary to reveal the broadening mechanism and the underlying dynamics.

These techniques can be grouped together as nonlinear spectroscopies, which means that the generated response scales with \( E^n \), with \( E \) the total E-field and \( n > 1 \). Among the techniques are two and three pulse photon echo spectroscopy \([75, 89, 91]\), coherent anti-Stokes Raman scattering (CARS) \([61]\) and various types of pump-probe spectroscopies, like hole-burning, saturation spectroscopy \([20, 25, 34, 37, 38, 46, 54, 64, 106, 107]\) and 2D-IR spectroscopy \([21, 31, 41, 111, 112]\), which all have been applied to vibrations in the condensed phase. The above mentioned techniques are all third-order nonlinear techniques, which means that the response from the sample is generated from three interactions with the total light field.

Photon echo spectroscopy is a fully time-domain technique and makes use of two coherence periods. A short pulse excites an inhomogeneous distribution of oscillators,
Non-linear spectroscopic techniques

Figure 1.3. Left: Inhomogeneous (top) and homogeneous (bottom) line broadening, right: the effect on the absorption spectrum after pumping an inhomogeneous (top) and a homogeneous band.

which will all dephase differently due to the different transition frequencies in the excited ensemble. The third interaction with the light field initiates a rephasing of the dephased oscillators, leading to the production of an echo, which is well defined in time. The temporal shape and the shift in time of the maximum of the echo, enables the experimentalist, for example, to determine the spectral diffusion time scale. Recently, this technique has been applied in the infrared for HDO dissolved in D$_2$O [91]. A $T_2^*$ was found of 90 fs.

Another technique to extract dynamical information from broadened absorption bands is CARS. In such an experiment, two incoming fields with frequencies $\omega_1$ and $\omega_2$ interact with the molecule. The frequency difference between the incoming fields is resonant with a transition to a state $v$ in the molecule: $\omega_1 - \omega_2 = \omega_v$. Field $\omega_1$ excites the molecules, whereas $\omega_2$ is the Stokes line back to the level $v$ in the molecule. The third interaction is again with light field $\omega_1$ and generates the anti-Stokes signal at $2\omega_1 - \omega_2$ [61, 84].

In a hole-burning experiment two pulses are used [99]. The first narrow-band pump selects a sub-ensemble of oscillators, with the same surroundings. Due to this excitation, a hole is created in the absorption profile, see Figure 1.3. A second, tunable laser, measures the transient absorption spectrum. From these measurements, the hole-width, which is related to the homogeneous line-width and lifetime of the excited
state [99] can be extracted. The broadening of the hole with time is a measure for the spectral diffusion.

The technique we used in this thesis is femtosecond mid-infrared saturation spectroscopy. This technique is similar to that of hole-burning, however, the emphasis lies more on time- than on frequency-resolution. It will be shown in Chapter 3, that ultrashort pulses can be generated with enough spectral selectivity. Saturation spectroscopy gives information on the lifetimes $T_1$, on anharmonicities and couplings of vibrations. Recent mid-infrared saturation spectroscopic studies of hydrogen-bonded systems were mainly focused on water monomers [23], dilute solutions of HDO in D$_2$O [20, 25, 64, 103, 104, 108] and alcohol clusters [27, 107, 48]. More recent work focuses on aqueous solutions of ions [43, 68], OD$^-$-ions dissolved in water [62] and proton transfer in photo-acids [78].

### 1.5 Outline of the thesis

The central theme of this thesis is the study of the vibrational relaxation of water and hydrogen-bonded systems. Before the presentation of pump-probe results, a formal description of the nonlinear polarization, with which wave mixing as well as pump-probe signals can be described, is given in Chapter 2. The third chapter deals with the generation of mid-infrared pulses and their usage in pump-probe spectroscopy.

The systems studied in Chapters 4-9 are depicted in Figure 1.4 together with the infrared absorption band of the OH-stretch region. As one can see from the large spread in positions, line shapes and band widths, the character of the hydrogen bond interaction is very different from sample to sample.

In Chapter 4, we study the temperature dependence of the lifetime of the OH-stretch vibration for pure liquid water and give an explanation for the observed behavior in terms of energy relaxation pathways. Chapter 5 focuses on the energy equilibration aspect in water. A comparison is made with the behavior measured in pure ethanol.

Dlott and coworkers [69] performed a coherent anti-Stokes Raman experiment with longer (picosecond) pulses on pure water. In their study, they present an alternative picture of the vibrational dynamics of liquid water. Chapter 6 forms the comment on this paper. In Chapter 7 an elaborate theoretical model is presented which both corroborates our findings and is able to explain their results.

The last two chapters are concerned with the study of OH-oscillators in dilute solutions. In contrast to earlier studies [23] where only water monomers without hydrogen bonds were studied, we investigate water monomers with one or two hydrogen bonds to acetone molecules. The results are presented in Chapter 8. The last Chapter is devoted to the study of an alcohol with two neighboring OH-groups that are hydrogen-bonded. Next to vibrational relaxation, we study the coupling between both groups.
Figure 1.4. Infrared absorption spectra of the molecules studied. From top to bottom: spectrum of pure water (H$_2$O), pure ethanol (C$_2$H$_5$OH), pinacol (2,3-dimethyl-2,3-butanediol) dissolved in CDCl$_3$ and water-acetone complexes dissolved in CCl$_4$. The OH–stretch bands can be found around 3400 cm$^{-1}$ and higher. The narrow bands around 3000 cm$^{-1}$ are the different CH-stretch modes.