Love and fear of water: Water dynamics around charged and apolar solutes
van der Post, S.T.

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A crucial parameter in any type of time-resolved vibrational spectroscopy is the excited state lifetime of the vibrational modes in the sample. In this thesis we almost exclusively make use of the OH- or OD-stretching vibration in pure or isotopically diluted water. The vibrational lifetime ($T_1$) thereby provides the limiting timescale over which observables like the reorientation dynamics or vibrational couplings can be measured. The $T_1$ of the OH-stretch vibration in pure liquid water has been measured to be very short ($200 \pm 50$ fs) in comparison to for example the $T_1$ of the OD-stretch vibration of HDO in H$_2$O ($1.8 \pm 0.1$ ps). This difference is probably due to the strong resonant coupling of the OH-stretch vibration to the overtone of the H$_2$O-bend. In this chapter we show that not for all OH-stretching modes in pure liquid water $T_1 = 200$ fs. Very weakly hydrogen-bonded OH-oscillators have a vibrational lifetime that is almost a factor of three slower compared to that of strongly hydrogen-bonded OH-oscillators. In addition, we demonstrate that weakly hydrogen-bonded oscillators dominate the overtone spectrum of the OH-stretch vibration. These results show that pure water is quite an inhomogeneous liquid.
5.1 INTRODUCTION

In previous work it was shown that in spite of the structure of the OH-stretch absorption band of water, spectral diffusion due to Förster transfer equilibrates any excited subset within hundred femtoseconds [40, 41, 42, 43]. It was also found that the vibrational lifetime of the OH-stretch is 200–240 fs, independent on the excitation frequency [44, 41].

The structure of the linear absorption spectrum of the OH-stretch vibration is still a topic of debate [45, 15, 46, 47]. Most interpretations involve contributions from the symmetric and asymmetric stretch, and the H$_2$O-bend overtone vibrations [48, 46, 40, 49]. It was also proposed that the H$_2$O-bend overtone leads to a Fermi-resonance with the symmetric OH-stretch vibration [46, 47, 50, 51]. Mixing of the wave functions of both modes forms a decreased cross section in the broad symmetric stretch band, known as an Evans window [47]. Surprisingly, the overtone spectrum of the OH-stretch vibration is extremely smooth [52, 53]. The underlying molecular origin of this smoothness is likely far from simple. The complexity becomes clear when considering the linear spectrum of a small percentage of HDO molecules in heavy water. In such a solution no H$_2$O-bend or (a)symmetric OH-stretch vibrations exist and the OH-stretch fundamental absorption spectrum is in this case almost a single gaussian. The OH-stretch overtone spectrum of HDO, however, shows a rich structure of several peaks [54]. The underlying structure of the smooth overtone spectrum in pure H$_2$O is thus expected to be rather complex [55].

Explanations of these phenomena have been sought in the structure of water [56, 55, 54, 45]. The OH-stretching vibration of the water molecule is a good probe of this structure. Its coupling to the hydrogen-bond causes the OH-stretch resonance frequency to be dependent on the hydrogen-bond strength: a stronger hydrogen bond lowers the resonance frequency. In this chapter we measure the vibrational lifetime and spectral response of OH oscillators in different spectral regions of the OH-stretch fundamental and overtone spectrum. We investigate whether the relaxation of the fundamental OH-stretch vibrational excitation is indeed as frequency independent as has been suggested previously. Subsequently we study the vibrational relaxation of the OH-stretch/H$_2$O-bend combination mode and of the OH-stretch overtone.

5.2 EXPERIMENT

5.2.1 EXCITATION OF THE FUNDAMENTAL TRANSITION

The experiments were performed with the two-color setup described in section 3.1.2. The absorption band of the OH-stretch fundamental vibrations of H$_2$O has a maximum at 3400 cm$^{-1}$ and a full width at half maximum (FWHM) of $\sim$300 cm$^{-1}$ (see linear spectrum in Fig. 5.1, band 1). We excited the band using an intense pump pulse (10 $\mu$J) with a center frequency tunable between 2900 cm$^{-1}$ and 3700 cm$^{-1}$. The spectral bandwidth of the pump pulses was 150 cm$^{-1}$ FWHM. The sample was probed at three different spectral positions:
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Figure 5.1. Logarithmic plot of the linear spectrum of the waterfilm (solid line) and that of pure water with 115 µm path length (dashed line, scaled from the spectrum of a 1 µm sample cell). In this chapter we focus on three bands: 1) the OH-stretch band centered at 3400 cm\(^{-1}\), 2) the OH-stretch/H\(_2\)O-bend combination band centered at 5150 cm\(^{-1}\) and 3) the OH-stretch overtone band centered at 6900 cm\(^{-1}\).

the \(\nu = 0 \rightarrow 1\) transition around 3400 cm\(^{-1}\), the \(\nu_{OH} = 1 \rightarrow 2\) transition around 3000 cm\(^{-1}\) and the \(\nu_{OH} = 1 \rightarrow 2\) transition of the H\(_2\)O-bend vibration at 1550 cm\(^{-1}\). The FWHM of the probe pulses was 300 cm\(^{-1}\), and the FWHM of the cross-correlate with the pump pulses (measured in a thin germanium window) was 150 fs. Most of the data was taken by probing the \(\nu_{OH} = 1 \rightarrow 2\) transition around 3000 cm\(^{-1}\), since a strong thermal difference spectrum obscures the response of the excited OH oscillators at the \(\nu_{OH} = 0 \rightarrow 1\) transition frequency.

For the measurements on the OH-stretch fundamental we used a sample cell consisting of two calcium fluoride windows of 0.5 mm thickness, pressed against each other with small drop of water in between. This procedure resulted in a water film of approximately a few micrometers thickness, at which path length the maximum absorbance of the OH-stretch vibration is \(\sim 2\) OD. Since water vapor in the air causes a strong absorption around 3600 cm\(^{-1}\) (rotation-vibrational lines of the free OH-stretch), the setup was purged with dry nitrogen to a humidity < 5%.

5.2.2 Excitation of Overtones

The OH-stretch/H\(_2\)O-bend combination band is centered at 5150 cm\(^{-1}\), and the OH-stretch overtone band is centered at 6900 cm\(^{-1}\) with a FWHM of \(\approx 600\) cm\(^{-1}\) (bands 2 and 3 in Fig. 5.1, respectively). Depending on the experiment either the signal (OH-stretch overtone) or the idler (OH-stretch/H\(_2\)O-bend combination) output of the TOPAS was used as a pump. The spectral bandwidth of the pump was 250 cm\(^{-1}\) FWHM. The pulse energy was typically 50 µJ for pumping
the combination band and 90 µJ for pumping the overtone.

The response of the system was probed at two different positions in the spectrum. First, we used the signal or idler output of the homebuilt OPA to directly probe the response of the overtone or combination band. Secondly, the OH-stretch vibration at the \( \nu_{OH} = 1 \rightarrow 2 \) transition at 3000 cm\(^{-1} \) was probed. In order to have sufficient absorption in the overtone region, the sample was made several tens to a hundred µm thick, resulting in an absorbance of > 30 OD at the OH-stretch fundamental vibration. For this reason the fundamental transition \( \nu_{OH} = 0 \rightarrow 1 \) could not be probed.

Unfortunately, the high (photon) energy of the pump pulses used in this experiment creates a third order polarization in CaF\(_2\) windows resulting in white light generation. This broad-band light appears in our measurements as a very unstable background artefact, obscuring the signal of interest. To mitigate this problem, we used the wire flow cell described in section 3.4.1. Stable configurations of the waterfilm were obtained with film thicknesses of 25–125 µm. A linear spectrum taken from the film close to the nozzle using a fast flow rate resembled closely a linear spectrum from a water-filled conventional sample cell with a 115 µm spacer (Fig. 5.1). For this optical pathlength the absorbance of the sample is \( \sim 2 \) OD at the OH-stretch/H\(_2\)O-bend combination band and \( \sim 0.5 \) OD at the OH-stretch overtone band.

It should be noted that the pump energies used in this experiment are close to being able to excite electrons in the sample in a multi-photon absorption process. Such excited electrons would give rise to an induced absorption signal that is highly non-linear with the pump intensity. By comparing the amplitudes of the measured signals for different pump intensities, we found that such a contribution is not present in our data.

\[5.3\] OH-stretch: Results and Interpretation

Fig. 5.2 shows the transient response around 3000 cm\(^{-1} \) of a sample of pure water that was excited at the blue shoulder of the OH-stretch band (3600 cm\(^{-1} \)). The positive transient spectrum at early pump-probe delay times is due to the \( \nu_{OH} = 1 \rightarrow 2 \) absorption of OH oscillators that were excited by the pump. The negative transient response at longer delay times is the thermal difference spectrum: the excitation energy has been transferred from the OH stretch mode into low frequency modes, giving rise to an increased sample temperature.

As explained in section 4.2.2 it was found in previous work that the thermalization does not follow immediately the vibrational relaxation but is delayed [23]. To obtain an accurate estimation of the vibrational relaxation time \( T_1 \) we therefore globally fit a kinetic model to the data in which we take the delayed thermalization into account (for a detailed description of the model see section 4.2.2). The solid lines in Fig. 5.2A represent the results of this fit.

Delay traces recorded at 3050 cm\(^{-1} \) are shown in Fig. 5.3A for different central frequencies of the pump spectrum (thermalization subtracted data). There is a clear correlation between the pump frequency and the vibrational relaxation
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Figure 5.2. Transient spectra at different pump-probe delay times probed at the $\nu_{OH} = 1 \rightarrow 2$ transition. For this measurement the pump spectrum was centered at 3600 cm$^{-1}$.

dynamics. The maximum of the linear absorption spectrum of the OH-stretch band is at 3400 cm$^{-1}$. The dynamics become slower with an increasingly blue-shifted pump spectrum. Pumping the sample at frequencies red-shifted from this maximum, however, does not yield dynamics that are very different from when the sample is pumped at 3400 cm$^{-1}$.

The vibrational relaxation times obtained from the fits are summarized in Fig. 5.3B. For pump frequencies lower than 3400 cm$^{-1}$ $T_1 \approx 230$ fs. However, $T_1$ increases with frequency, and this increase becomes steeper. After excitation at 3700 cm$^{-1}$, we find that $T_1 = 540 \pm 70$ fs. From the fits we also obtain the transient spectra $\sigma(\nu)$ of the excited OH oscillators (shown for different pump frequencies in Fig. 5.4A). If the pump spectrum is tuned to higher frequencies the transient spectra also blue-shift. This observation indicates that on the timescale of the experiment no full spectral equilibration takes place. The vibrational relaxation in pure liquid water is thus frequency dependent.

So far we focussed on the transient response at the $\nu_{OH} = 1 \rightarrow 2$ transition, since this response is not so much obscured by the contribution of the thermal difference spectrum. To study the vibrational dynamics for different pump frequencies further, we measured the transient response at different probe frequencies. Firstly, the thermal difference spectrum of the OH-stretch has a zero crossing around 3500 cm$^{-1}$. At this frequency, the thermal contribution is therefore small compared to the excited state spectrum. Another mode of interest is the H$_2$O-bending mode at 1640 cm$^{-1}$. It has been shown that this mode gives an almost instantaneous response upon excitation of the OH-stretch vibration [46]. We probed the H$_2$O-bending mode at its $\nu_b = 1 \rightarrow 2$ transition at 1550 cm$^{-1}$. The raw transient delay plots for these probing frequencies are shown in Fig. 5.4B for a pump centered at 3400 cm$^{-1}$ and 3600 cm$^{-1}$. For all data the dynamics is significantly slower when the OH-stretch band is pumped at the blue shoulder.
Figure 5.3. (A) Delay traces taken at 3050 cm$^{-1}$ for measurements with the pump spectrum centered around various frequencies. The heat contribution is subtracted from this data according to the procedure described in the text. The vibrational relaxation is significantly slower when the OH-stretch band is pumped at its blue shoulder. (B) Relaxation time $T_1$ of the OH-stretch vibration obtained from the measured transient spectra as a function of the pump frequency. For low pump frequencies the relaxation time is similar to values that were found in other work. When the blue shoulder of the OH-stretch band is pumped, $T_1$ becomes up to a factor of 2.5 slower. The dotted line is the shape of the linear spectrum of the OH-stretch band. The solid line represents the result of a simulation, the details of which are elaborated on in the appendix, section 5.A.

By pumping the blue shoulder of the OH-stretch band we create an excited subset of OH oscillators that, at the time of excitation, are mainly in a weakly hydrogen-bonded state. This subset is clearly out of equilibrium. We can distinguish two processes that lead to relaxation to the equilibrium distribution. Firstly, the excitation energy may be transferred to another OH oscillator by Vibrational Resonant Energy Transfer (VRET), also called Förster transfer, a process that is caused mainly by dipole-dipole coupling [57, 58, 59]. This may be to a neighboring molecule or to an OH oscillator on the same molecule (intramolecular coupling). The donating and accepting oscillators should be in close vicinity of each other, since the rate of transfer is inversely proportional to the sixth power of their mutual distance. In addition, the rate of transfer is proportional to the overlap integral of the cross sections of both oscillators. A second contribution to the equilibration of the hydrogen-bond distribution is formed by translational motions of the water molecules that increase or decrease the oxygen-oxygen distance and thus the hydrogen-bond strength [60, 61, 62]. This last process is relatively slow ($\sim 1$ ps [63, 64, 65, 66, 60, 67, 68]).

VRET is known to cause extremely fast spectral diffusion in water [41]. It has even be claimed that within hundred femtoseconds all memory of the initial out-of-equilibrium excitation is lost and the excited subset smeared out over the full absorption band [69, 42]. Such a complete loss of memory is however
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Figure 5.4. (A) The excited state spectra obtained from fitting the kinetic model described in the text to the transient spectra. For increasingly blue-shifted pump spectra the excited state spectra blue-shift as well. This progression indicates that spectral diffusion is incomplete on the timescale of the measurements (~1 ps). The spectra are normalized to their maximum value. (B) Delay traces at the H$_2$O-bend $\nu_{\text{bend}} = 1 \rightarrow 2$ (dashed lines) and OH-stretch $\nu_{\text{OH}} = 1 \rightarrow 2$ (solid lines) response upon pumping the OH-stretch band at 3400 cm$^{-1}$ (red lines) and at 3600 cm$^{-1}$ (blue lines). For all measurements the dynamics are slower when the OH-stretch band is pumped in its blue shoulder compared to when it is pumped in the center of the band. No thermalization contribution was subtracted and the curves are normalized at 200 fs.

incompatible with our current findings. We find that the vibrational lifetime is dependent on the excitation frequency. The vibrational lifetime for a sample pumped at the peak position of the OH-stretch band is less than $T_1 = 300$ fs. If equilibration was to happen on a 100 fs timescale, any oscillator excited at much higher frequencies would have equilibrated fast enough to effectively decay with $T_1 < 300$ fs. Our results thus imply that at the blue side of the spectrum VRET must become less efficient.

The qualitative molecular picture of the reduced rate of VRET is probably as follows. The concentration of oscillators that absorb on the blue extreme of the spectrum is low. Therefore the probability of finding other oscillators that are spectrally overlapping is also low. All adjacent oscillators likely have a considerably lower resonance frequency, and energy transfer to those oscillators is unfavorable. The transfer of vibrational energy from weakly bound oscillators to more strongly bound oscillators by VRET is thus suppressed. A quantitative description of this suppression is found in the appendix (section 5.A), in which we set up a model to simulate this effect. The solid line in Fig. 5.3 are the values of $T_1$ that result from this simulation and reproduce our experimental data very accurately.

The above arguments are based on the assumption that initially weak hydrogen-bonds remain weakly bound at least on the timescale of the vibrational relaxation (~500 fs). This is perfectly consistent with the timescale
Figure 5.5. Transient spectra obtained for a measurement in which the OH-stretch overtone was pumped at 7000 cm$^{-1}$ and the $\nu_{OH} = 1 \rightarrow 2$ transition was probed. The transient spectra show an induced absorption. This can be explained by an extremely fast relaxation of the overtone from the $\nu_{OH} = 2$ state to the $\nu_{OH} = 1$ state. The $\nu_{OH} = 1$ state decays significantly slower.

of translational motions. The translation of water molecules to increase or decrease the oxygen-oxygen distance occurs with a time constant of $\sim$1 ps [66, 63, 65, 68, 67, 64, 60]. The suppression of the rate of spectral diffusion due to VRET is further evidenced by the shifted transient state spectra presented in Fig. 5.4A. For a pump spectrum that is tuned to 3600 cm$^{-1}$, the transient response is blue-shifted by more than 100 cm$^{-1}$ compared to the transient response of a sample pumped at the maximum of the OH-stretch spectrum. An OH oscillator initially excited at the blue side of the spectrum thus remains blue on timescales on the order of 0.5 ps.

5.4 OVERTONES: RESULTS AND INTERPRETATION

5.4.1 OH-STRETCH OVERTONE

The most straightforward way to investigate the relaxation of the OH-stretch overtone vibration is to pump and probe the overtone band directly. The cross section of the overtone, however, is a factor $\sim$500 times smaller than that of the OH-stretch fundamental (see Fig. 5.1). In a one-color experiment, the pump=probe signal is proportional to the square of the absorption cross section, and the signals would be too small to measure with our signal-to-noise ratio. We therefore pump the overtone and probe the $\nu_{OH} = 1 \rightarrow 2$ transition. The results from a measurement in which the pump was tuned to the maximum of the overtone band at 7000 cm$^{-1}$ are shown in Fig. 5.5. The transient spectra have a strong resemblance to those obtained with the pump spectrum tuned to
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Figure 5.6. The vibrational relaxation times $T_1$ of $\nu_{OH} = 1 \rightarrow 0$ after excitation of the OH-stretch overtone at different frequencies (horizontal axis). Excitation of the blue shoulder of the overtone leads to a longer $T_1$ compared to an excitation at the red shoulder. The dotted line is the shape of the linear spectrum of the overtone band.

the blue side of the OH-stretch fundamental, shown in Fig. 5.2A. For early delay times we observe an induced absorption, which decays to a bleaching signal caused by the thermalized ground state. We use the same approach as before and globally fit a kinetic model for vibrational decay to the data to obtain the time constants $T_1$. The results are summarized for various center frequencies of the pump spectrum in Fig. 5.6. The first thing to notice is that the $T_1$ values are again much larger than 200 fs. Secondly, there exist a dependence on the pump frequency: in case the overtone band is pumped at higher frequencies, the relaxation of the induced absorption measured at 2850 cm$^{-1}$ decays slower.

When populating the $|\nu_{OH} = 2\rangle$ state, one naively may expect a bleach at the $\nu_{OH} = 1 \rightarrow 2$ transition (due to stimulated emission) and an induced absorption at the $\nu_{OH} = 2 \rightarrow 3$ transition. It may therefore seem somewhat surprising that the excitation of the OH-stretch overtone gives rise to an induced absorption at the frequencies of the $\nu_{OH} = 1 \rightarrow 2$ transition. The spectra of Fig. 5.5 thus imply that the overtone excitation is nearly instantaneously transferred to the $|\nu_{OH} = 1\rangle$ excitation, either by vibrational relaxation or by splitting of the overtone excitation into two $|\nu_{OH} = 1\rangle$ excitations.

The subsequent $\nu_{OH} = 1 \rightarrow 0$ relaxation occurs significantly slower than 200 fs. In addition, the transient state spectrum (transient spectrum at early delays in Fig. 5.5) is shifted to higher frequencies compared to the transient state spectrum after excitation of the OH stretch fundamental at 3300 cm$^{-1}$ (Fig. 5.4A). There is thus a strong resemblance with the results obtained when the OH-stretch fundamental is pumped at 3600 cm$^{-1}$. Additionally, the vibrational lifetime $T_1$ increases when tuning the pump spectrum from 6600 cm$^{-1}$ to 7100 cm$^{-1}$, similar to the increase in $T_1$ when tuning the pump spectrum...
over the fundamental transition from 3400 cm$^{-1}$ to 3600 cm$^{-1}$. Our interpretation of these results is that the OH-stretch overtone spectrum is dominated by weakly hydrogen-bonded OH oscillators. By pumping the maximum of the overtone band at 6900 cm$^{-1}$ we apparently excite mainly those OH oscillators that have a weak hydrogen-bond, for which Förster transfer and vibrational decay is slower as was pointed out in section 5.3. This interpretation is supported by the spectral position of the OH stretch overtone spectrum. The OH oscillator is anharmonic and the $\nu_{OH} = 0 \rightarrow 2$ transition maximum is expected to be at a frequency of $\sim 6500$ cm$^{-1}$ (3400+3100), considerably lower than twice the fundamental transition energy (6800 cm$^{-1}$). From Fig. 5.1 it is clear that the maximum of the $\nu_{OH} = 0 \rightarrow 2$ band is actually higher than 6800 cm$^{-1}$. This maximum shift indicates that the $\nu_{OH} = 0 \rightarrow 2$ transition is much stronger for weakly hydrogen-bonded OH oscillators than for strongly hydrogen-bonded OH oscillators.

5.4.2 Bend-Stretch Combination Tone

Since the H$_2$O-bend/OH-stretch combination tone is stronger than the OH-stretch overtone, a direct pump-probe measurement (in which we probe the excited mode) could be performed. The transient spectra for different delay times obtained with both the pump and probe spectra centered at 5100 cm$^{-1}$ are shown in Fig. 5.7. At short delay times an induced absorption is present at 5200 cm$^{-1}$. This signal is small, however, and rapidly decays into the much larger thermal difference spectrum. Close examination of the delay dependence at the frequencies for which the thermal difference spectrum is negligible ($\sim 5190$ cm$^{-1}$), reveals that the induced absorption decays on a $\sim 0.5$ ps timescale. A detailed analysis is unfortunately challenging due to the overwhelming heat contribution.

For this reason we again probe the response of the $\nu_{OH} = 1 \rightarrow 2$ transition of the fundamental OH stretch vibration. The results of such a measurement for which the pump spectrum was centered at 5000 cm$^{-1}$ are shown in Fig. 5.8A. The transient spectra show an induced absorption that is very similar to that observed when exciting the overtone (see Fig. 5.5). Since we excite the H$_2$O-bend/OH-stretch combination tone, this response can be naturally identified as the excited state absorption of the OH stretch vibration. The decay of the induced absorption is considerably slower than 200 fs. We analyzed the spectra in a similar fashion as was done in the previous sections. For three pump spectra, overlapping with different regions of the H$_2$O-bend/OH-stretch combination band, the normalized decay traces of the excited state are shown in Fig. 5.8B. We find that an excitation of the band at 5170 cm$^{-1}$ results in a slightly slower relaxation time ($590 \pm 70$ fs) than an excitation at the red shoulder of the band ($500 \pm 70$ fs).
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Figure 5.7. Transient spectra obtained for a measurement in which the OH-stretch/H$_2$O-bend combination tone is pumped and probed around at 5100 cm$^{-1}$. Already at quite short delay times the thermal difference spectrum is the dominant contribution. Around 5150 cm$^{-1}$ the transient spectra are positive for short delay times, decay through zero at about 550 fs and eventually equilibrate at negative values. This behavior is indicative for an induced excited state absorption at early delays.

Figure 5.8. (A) Transient spectra obtained with the pump spectrum centered at 5000 cm$^{-1}$ and the probe at the $v_{OH} = 1 \rightarrow 2$ transition of the OH-stretch. (B) Delay trace of the measurement in panel A compared to a measurement in which the OH-stretch was pumped directly at 3400 cm$^{-1}$. The dynamics of the combination mode is considerably slower.

5.4.3 Calculation of the Overtone Spectrum of Hydrogen-bonded OH Groups

In this section we will demonstrate that for strongly hydrogen-bonded oscillators, a cancelation occurs in the transition dipole moment to the overtone. This
Figure 5.9. (A) The Lippincott-Schroeder potential as a function of the OH bond length $r$ for an hydrogen-bonded OH-group of a water molecules. For the potential shown we used a hydrogen-bond length (oxygen-oxygen distance) of $R_{OO} = 3.1\,\text{Å}$, corresponding to an oscillator donating a weak hydrogen-bond. The energy levels were calculated using a Numerov integration scheme. (B) The transition frequencies of $\nu_{OH} = 0 \rightarrow 1$ (dashed), $\nu_{OH} = 1 \rightarrow 2$ (dashed-dotted) and $\nu_{OH} = 0 \rightarrow 2$ (solid line, right axis) calculated for different hydrogen-bond lengths $R_{OO}$. Only weakly hydrogen-bonded OH groups have a $\nu_{OH} = 0 \rightarrow 2$ transition frequency higher than 6600 cm$^{-1}$.

cancellation explains why the OH-stretch overtone spectrum is dominated by weakly hydrogen-bonded OH oscillators. We analyze the linear overtone spectrum in the context of the Lippincott-Schroeder (LS) model, which has been shown to provide a good description of the coupling between the OH stretch vibration and the hydrogen-bond (see also section 2.1.3).

We calculate the wave functions of the LS-potential using a Numerov integration scheme for different hydrogen-bond lengths $R_{OO}$. Fig. 5.9A shows the LS-potential for an oxygen-oxygen distance of $R_{OO} = 3.1\,\text{Å}$, with the calculated wave functions of the first four energy levels. The transition energies that correspond to the $\nu_{OH} = 0 \rightarrow 1$, $\nu_{OH} = 1 \rightarrow 2$, $\nu_{OH} = 2 \rightarrow 3$ and $\nu_{OH} = 0 \rightarrow 2$ transitions are shown as a function of hydrogen-bond length in Fig. 5.9B.

The transition probability of an excitation from the $|\nu_{OH}\rangle$ state to the $|\nu'_{OH}\rangle$ state is proportional to transition dipole moment $\mu_{\nu_{OH}\nu'_{OH}}$, which is the matrix element of the dipole moment operator $\hat{\mu}$ given by

$$\mu_{\nu_{OH}\nu'_{OH}} = \langle \nu'_{OH} | \hat{\mu} | \nu_{OH} \rangle,$$  \hspace{1cm} (5.1)

where $\hat{\mu}$ is the dipole moment operator, defined in section 2.1.3. As discussed there, the transition dipole moment can be expanded for small displacements
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![Graph A](A) The matrix elements of the linear, quadratic and cubic displacements of the \( \nu_{OH} = 0 \rightarrow 2 \) transition (the vertical axis is in units of Å, Å² or Å³, respectively). The matrix elements were calculated for different hydrogen-bond lengths, which were mapped to the \( \nu_{OH} = 0 \rightarrow 2 \) transition frequency according to the relation in Fig. 5.9B. 

![Graph B](B) The second derivative of the transition dipole moment as a function of the \( \nu_{OH} = 0 \rightarrow 2 \) transition frequency.

**Figure 5.10.** (A) The matrix elements of the linear, quadratic and cubic displacements of the \( \nu_{OH} = 0 \rightarrow 2 \) transition (the vertical axis is in units of Å, Å² or Å³, respectively). The matrix elements were calculated for different hydrogen-bond lengths, which were mapped to the \( \nu_{OH} = 0 \rightarrow 2 \) transition frequency according to the relation in Fig. 5.9B. (B) The second derivative of the transition dipole moment as a function of the \( \nu_{OH} = 0 \rightarrow 2 \) transition frequency.

Using the wave equations of the LS-potentials, we calculate the matrix elements for the \( \nu_{OH} = 0 \rightarrow 2 \) transition of the linear, quadratic and cubic displacements,

\[
\mu_{\nu_{OH}'\nu_{OH}} = \left( \frac{d\hat{\mu}}{dQ_{OH}} \right)_0 \langle \nu_{OH}' | Q_{OH} | \nu_{OH} \rangle + \quad (5.2)
\]

\[
\frac{1}{2} \left( \frac{d^2\hat{\mu}}{dQ_{OH}^2} \right)_0 \langle \nu_{OH}' | Q_{OH}^2 | \nu_{OH} \rangle + \cdots
\]

for various hydrogen-bond lengths. The results are shown in Fig. 5.10A. The linear and quadratic displacements are of leading order, while the cubic (and higher, not shown) order contributions are much smaller. Note that the vertical axis shows the values in units of Å, Å² or Å³, depending on the order of the displacement. Due to the opposite signs of the linear and quadratic displacements, a cancelation between the first and second term in Eq. (5.2) can occur. The first derivative of the dipole moment \( \hat{\mu} \) increases with increasing hydrogen-bond strength (i.e. decreasing \( R_{OO} \)) and was empirically found to depend on
the fundamental transition frequency according to [54],

\[
\frac{d\hat{\mu}}{dQ_{OH}}(\omega) \approx \left( 1.21 + \sqrt{3.34 - \frac{2.15\omega}{\omega_f}} \right) \cdot 10^{-18} C; \tag{5.6}
\]

where \( \omega_f = 3719.65 \text{ cm}^{-1} \) is the absorption frequency of the free OH-stretch mode in the gas phase. The overtone absorption cross section \( \sigma_{0,2}(\omega) \) is written as a function of the transition dipole moment as,

\[
\sigma_{0,2}(\omega) = \frac{\pi\omega}{3\hbar \varepsilon_0} |\mu_{0,2}(\omega)|^2 \tag{5.7}
\]

The transition dipole moment \( \mu_{0,2}(\omega) \) is given by Eq. (5.2). We used the calculated linear and quadratic displacements (Fig. 5.10A) and \( d\hat{\mu}/dQ_{OH} \) from Eq. (5.6) to directly obtain \( d^2\hat{\mu}/dQ_{OH}^2 \) from Eq. (5.2) by ignoring the terms of higher order than \( Q_{OH}^2 \). The overtone spectrum was described by the values of \( d^2\hat{\mu}/dQ_{OH}^2 \) shown in Fig. 5.10B. Fig. 5.11 demonstrates that for the values of the second derivative shown indeed a cancelation occurs between the first and second order terms in Eq. (5.2) for strongly hydrogen-bonded OH oscillators. The value of \( d^2\hat{\mu}/dQ_{OH}^2 \) increases for increasing hydrogen-bond strength (lower transition frequencies). This dependence has an intuitive rationalization: the stronger coulomb interaction of the OH group with the lone pair of the hydrogen-bond acceptor makes the transition dipole more non-linear in the \( Q_{sOH} \) displacement. However, due to the opposite signs of the \( \langle 2|Q_{OH}|0 \rangle \) and \( \langle 2|Q_{OH}^2|0 \rangle \) matrix elements, this leads to a cancelation of the first two terms in the transition probability (Eq. (5.2)) for strongly hydrogen-bonded OH oscillators and a domination of weakly hydrogen-bonded OH oscillators in the OH-stretch overtone band.

## 5.5 Discussion

### 5.5.1 Frequency Dependence of the OH-Stretch Vibrational Lifetime

Relaxation of the OH-stretch vibration leads to a very strong thermal response that almost completely obscures the transient response at the \( \nu_{OH} = 0 \rightarrow 1 \) transition frequencies [23]. This effect is similar in nature and even stronger than for example the thermalization response shown for the \( \text{H}_2\text{O-bend/OH-stretch} \) combination band in Fig. 5.7. To improve the determination of the vibrational lifetime of the OH-stretch vibration we therefore probed the induced absorption at the \( \nu_{OH} = 1 \rightarrow 2 \) transition in most experiments presented in this chapter. In pure liquid water this induced absorption is believed to arise from a combination of six transitions between the symmetric and asymmetric stretching vibrations [40], causing it to be significantly broader than the fundamental transition. Due to the anharmonicity of the OH-stretch mode the \( \nu_{OH} = 1 \rightarrow 2 \) band is red-shifted from the fundamental transition. It seems natural to assume
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Figure 5.11. Calculated OH stretch overtone spectrum for the first-order contribution to the transition dipole moment $\mu_{02}$ (dashed line), the second order contribution to $\mu_{02}$ (dashed-dotted line) and both contributions (solid line). When both contributions are taken into account, an interference occurs for strongly hydrogen-bonded OH oscillators. The linear absorption spectrum of the overtone is with both terms well described.

that the lifetime of the $\nu_{OH} = 1 \rightarrow 2$ transition is identical to that of the $\nu_{OH} = 0 \rightarrow 1$ transition. However, in ice it was found that the $\nu_{OH} = 1 \rightarrow 2$ decay is about 10% faster than the $\nu_{OH} = 0 \rightarrow 1$ decay due to an intermediate state that is present in the decay channel [70, 71, 72]. The time constant of the $\nu_{OH} = 1 \rightarrow 0$ decay may therefore be 10% slower than the vibrational lifetime that we obtained from probing the $\nu_{OH} = 1 \rightarrow 2$ transition.

Various studies found a value of the OH-stretch vibrational lifetime $T_1 = 200$ fs [23, 73, 46, 44]. Ample evidence exists that the main pathway of vibrational decay is the H$_2$O-bend overtone centered at 3250 cm$^{-1}$ [48, 74, 67, 46, 44, 75]. At elevated temperatures, the average hydrogen-bond strength decreases, leading to a blue-shift of the OH-stretch band and a red-shift of the H$_2$O-bend overtone. As a result the spectral overlap decreases, leading to an increase of $T_1$ [74, 67]. Even though the H$_2$O-bend overtone band overlaps with the red shoulder of the OH-stretch band, $T_1$ was always considered to be independent of frequency [46, 44]. This was explained by the paradigm that any inhomogeneity in the OH-stretch band is averaged out within 50 fs by spectral diffusion. The underlying mechanism of this rapid spectral diffusion is the ultrafast hopping of vibrational energy quanta between oscillators (Förster transfer) [57, 58, 59]. Blue-excited oscillators thus spectrally migrate within 50 fs to the red side of the spectrum by Förster transfer, where the overlap with the H$_2$O-bend overtone band acts as a sink for vibration decay.

In this chapter we have shown clear evidence that the vibrational lifetime in fact does depend on the excitation frequency. Such a dependence requires the excitation to keep its frequency for at least as long as the vibrational lifetime, in apparent contradiction to the presence of rapid Förster transfer within 50 fs.
However, we also observe a blue-shift of the transient spectrum with increasing excitation frequency (Fig. 5.4A), which implies that for high excitation frequencies (> 3600 cm\(^{-1}\)), the excited oscillators do not spectrally equilibrate within 0.5 ps.

In the appendix we show that this observation is in fact consistent with the presence of Förster transfer. An oscillator that is excited in the very blue shoulder of the OH-stretch band, first needs to spectrally diffuse to overlap with the H\(_2\)O-bend overtone band in order to decay. However, the spectral overlap with this spectral region required for Förster hopping is very small. In addition, the probability of finding an oscillator with a more favorable spectral overlap nearby is small since the number density of such oscillators in the blue wing is small. As a result, the rate of Förster transfer from a donating OH oscillator resonant at 3700 cm\(^{-1}\) to an accepting OH oscillator overlapping with the H\(_2\)O-bend overtone band is about 20 times smaller than the rate from a donating oscillator at 3250 cm\(^{-1}\) to the same acceptor (Fig. 5.13). This result is in line with previous work that suggested that weakly hydrogen-bonded OH oscillators undergo slower spectral diffusion than strongly hydrogen-bonded OH oscillators [41]. Förster transfer thus strongly decelerates with increasing OH frequency. However, a significant deviation from the 200 fs decay time constant occurs only in the very blue shoulder of the absorption band, and this may explain why the frequency dependence was not noticed before [46, 44].

The lower Förster rate also has consequences for the reorientation dynamics probed by polarization resolved fs-IR pump-probe spectroscopy. This technique measures the reorientation dynamics of water by probing the decay of an anisotropically excited subset of OH-stretch oscillators [22]. In pure liquid water the anisotropy was found to decay nearly instantaneously [69, 40, 42]. This fast decay is not due to the reorientation of independent OH groups, but to the ultrafast hopping of the vibrational excitation to accepting OH modes with different orientation than the donating modes. Due to the slower Förster rates for OH oscillators with high OH-stretch frequencies, the anisotropy is expected to decay much slower upon excitation of the high-frequency wing of the absorption band. This is indeed what we observe (Fig. 5.12).

### 5.5.2 The Stretch Overtone and Stretch-bend Combination Spectra

It is surprising that excitation of the OH-stretch overtone (\(\nu_{OH} = 0 \rightarrow 2\)) leads to an induced absorption at \(\nu_{OH} = 1 \rightarrow 2\) frequencies, where a bleach due to \(\nu_{OH} = 2 \rightarrow 1\) stimulated emission would be expected. There are two possible explanations for this observation. First, the induced absorption may arise from a \(\nu_{OH} = 2 \rightarrow 3\) or even \(\nu_{OH} = 2 \rightarrow 4\) transition. We performed an analysis in the framework of the Lippincott-Schroeder model and find that especially the \(\nu_{OH} = 2 \rightarrow 4\) transition can have a considerable cross section in the probed spectral region. Both cross section and transition frequency however strongly depend on the hydrogen-bond strength (defined by the oxygen-oxygen distance). Since we do not see such a strong difference of the transient response
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Figure 5.12. The anisotropy dynamics of the OH stretch vibration in pure water after excitation at 3650 cm\(^{-1}\) (circles) or 3400 cm\(^{-1}\) (triangles). The probed frequency is 3500 cm\(^{-1}\), at which the thermal response is zero. Excitation at 3400 cm\(^{-1}\) is followed by an instantaneous drop of the anisotropy to zero. Consistent with the lower rate of Förster transfer, the reorientation dynamics after excitation at 3650 cm\(^{-1}\) have a component that is much slower than those after excitation at 3400 cm\(^{-1}\).

For different pump frequencies, this explanation can be ruled out. The induced absorption can more likely be identified as the \(\nu_{OH} = 1 \rightarrow 2\) transition. The presence of this feature in the transient spectrum for pump-probe delay times of 200 fs therefore implies an ultrafast relaxation of \(\nu_{OH} = 2 \rightarrow 1\). Possibly, a single OH oscillator excited in the \(|\nu_{OH} = 2\rangle\) state rapidly transfers one quantum of vibrational energy to a neighboring oscillator, resulting in two \(|\nu_{OH} = 1\rangle\) excitations.

The subsequent \(\nu_{OH} = 1 \rightarrow 0\) decay is \(T_1 = 450\pm 50\) fs, much slower than the main relaxation time after excitation of \(\nu_{OH} = 0 \rightarrow 1\) fundamental transition directly (\(T_1 \approx 200\) fs). In addition, we observe that the \(\nu_{OH} = 1 \rightarrow 2\) induced absorption spectrum is more blue-shifted after excitation of the overtone compared to the induced absorption after excitation of the fundamental transition at 3400 cm\(^{-1}\) (Fig. 5.4A). It rather resembles the \(\nu_{OH} = 1 \rightarrow 2\) spectrum after excitation of the very blue wing of the fundamental transition. It may be argued that these effects are due to a temperature increase of the environment in close vicinity of the excited oscillator due to the thermalization of one of the two OH stretch quanta. The thermalization of the vibrational energy was however found to be on a picosecond timescale, much slower than the vibrational lifetime of the OH stretch [23, 46, 75]. In addition, the temperature dependence of \(T_1\) that has been reported is too small to account for the large effect that we observe [74, 67]. Instead, we assign the blue-shifted induced absorption and slower \(T_1\) to the predominant excitation of weakly hydrogen-bonded OH groups. This is because that the OH stretch overtone spectrum is dominated by such species. This interpretation is in line with previous work that suggested that
the overtone spectrum of the OH stretch vibration of HDO molecules in D$_2$O can be explained by a strong dependence of the transition dipole moment on the hydrogen-bond strength [54], see also section 5.4.3.

The rich structure of bands in the OH-stretch overtone band of HDO has in several studies been interpreted as arising from different hydrogen-bonding species in water [76, 56, 45]. Similar suggestions have been made for pure liquid water: By dissolving a small amount of pure water in acetone, the otherwise smooth overtone spectrum breaks up in several peaks of which the relative amplitudes change with temperature [55]. These studies made a very discrete separation of 1, 2 or 3 hydrogen-bonded species [76, 56, 55, 45], a picture that is not supported by modern molecular dynamics simulations [77, 78]. Based on a theoretical interpretation of the linear absorption spectrum of HDO:D$_2$O, the overtone spectrum could be well explained from a destructive interference effect in the cross section of the overtone transition of strongly hydrogen-bonded water molecules [54]. Hence, instead of a discrete division in species, the calculations show that the electrical and mechanical anharmonicities have different dependencies on the hydrogen-bond strength. Their contributions to the transition dipole moment destructively interfere for some hydrogen-bond strengths and yield a net transition dipole moment for others.

We find strong evidence that in pure liquid H$_2$O a similar cancelations occurs. The absorption spectrum of the OH stretch overtone in pure H$_2$O has its maximum at 6900 cm$^{-1}$, more than twice the average frequency of the fundamental transition. The strongly anharmonic potential of the OH stretch vibration rather predicts a frequency maximum around 6500 cm$^{-1}$ (Fig. 5.9B). This would indeed be the case if non-Condon effects could be neglected. Non-Condon effects, the dependence of the transition dipole moment on the low-frequency (hydrogen-bond) coordinates, are however strong in water [15]. The transition dipole moment of the fundamental OH stretch transition $\mu_{01}$ strongly depends on the hydrogen-bond strength of the oscillator. In fact, the number density of weakly hydrogen-bonding OH groups that have their resonance frequency at 3600 cm$^{-1}$ has been found to be quite large. However, since their $\mu_{01}$ is much smaller than that of strongly hydrogen-bonded OH groups, their contribution to the linear spectrum of the fundamental transition is small [15, 68, 79, 7]. For the overtone transition dipole moment $\mu_{02}$, the dependence on the hydrogen-bond strength is reversed due to the interference of the electrical and mechanical anharmonicities (section 5.4.3). We found that $\mu_{02}$ strongly depends on the hydrogen-bond strength and almost completely disappears for strongly hydrogen-bonded OH oscillators. The overtone spectrum is thus dominated by weakly hydrogen-bonded OH oscillators.

These considerations based on the linear spectra and the Lippincott-Schroeder model are perfectly in line with our experimental results. OH oscillators with a $\nu_{OH} = 0 \rightarrow 2$ transition frequency at the overtone maximum of 6900 cm$^{-1}$, have a fundamental transition of $\sim$3600 cm$^{-1}$. The relatively large number density that was found for oscillators resonant at 3600 cm$^{-1}$ therefore also contributes to the large overtone cross section at 6900 cm$^{-1}$. The vibrational lifetimes that we find after an excitation at 3600 cm$^{-1}$ or 6900 cm$^{-1}$ match perfectly.
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The results on the H$_2$O-bend/OH-stretch combination band suggest a similar frequency dependence of the transition dipole moment. After excitation of this band, we find an induced absorption at the $\nu_{OH} = 1 \rightarrow 2$ frequencies with similar characteristics as we found after excitation of the OH stretch overtone band: a blue-shifted excited state response and a relatively long vibrational lifetime ($T_1 = 500 \pm 70$ fs). In analogy to the overtone band, the combination band shows a very asymmetric tail towards lower frequencies and has a maximum at a higher frequency (5150 cm$^{-1}$) than the sum of the H$_2$O-bend and OH-stretch band maxima ($\omega_{01,bend} + \omega_{01,OH} = (1640 + 3400)$ cm$^{-1}$). The anharmonic coupling between the two vibrations [80], would rather suggest a lower transition frequency for the combination band.

For the transition dipole moment $\mu_{(0,0),(1,1)}$ of an excitation of the H$_2$O-bend/OH-stretch combination tone $\nu_{bend,OH} = (0,0) \rightarrow (1,1)$ a similar analysis as for the overtone (Eq. (5.2)) can be made. The first and second-order contributions to $\mu_{(0,0),(1,1)}$ can be written as,

$$
\mu_{(0,0),(1,1)} = \left( \frac{d\hat{\mu}}{dQ_{OH}} \right)_0 \langle \nu_{bend,OH} = 1 | Q_{OH} | (0,0) \rangle + 
\frac{1}{2} \left( \frac{d^2\hat{\mu}}{dQ_{OH}^2} \right)_0 \langle \nu_{bend,OH} = 1 | Q_{OH}^2 | (0,0) \rangle + 
\frac{1}{2} \left( \frac{d^2\hat{\mu}}{dQ_{OH} dQ_{bend}} \right)_0 \langle \nu_{bend,OH} = 1 | Q_{OH} Q_{bend} | (0,0) \rangle
$$

(5.8)

where the bend/stretch combination wave function can be written as a mixed state,

$$
| \nu_{bend,OH} = 1 \rangle = \alpha | (1,1) \rangle + \beta | (0,2) \rangle + \gamma | (0,1) \rangle, \quad (\alpha^2 + \beta^2 + \gamma^2 = 1)
$$

(5.9)

in which the wave function of the H$_2$O-bend/OH-stretch combination tone is a superposition of the product wave function $| (1,1) \rangle$ of the $\nu = 1$ states of the uncoupled stretch and bend vibrations, the wave function of the OH stretch first excited state $| (0,1) \rangle$ and that of the OH stretch overtone state $| (0,2) \rangle$. The amplitude of $\mu_{(0,0),(1,1)}$ does not only depend on the amplitudes of the dipole moment derivatives, but also on the anharmonic coupling between the H$_2$O-bend and OH-stretch modes. Evidence exists that the wave functions of the vibrational modes in water all show a very mixed behavior [9]. The $| (0,1) \rangle$ term will add a large contribution to the transition dipole moment, which could explain the surprisingly large cross section of the combination band. These latter wave functions are admixed by anharmonic couplings like $Q_{OH}^2 Q_{bend}$ or even by a linear coupling $Q_{OH} Q_{bend}$. The shape and position of the combination band suggest that for this band a similar destructive interference effect in the cross section occurs as for the overtone band. The mixing of the overtone wave function for example yields a similar interference behavior as was described above in the first and second term in Eq. (5.8) in case the $| (1,1) \rangle$ state is replaced by the superposition state Eq. (5.9).
5.6 CONCLUSIONS

We studied the inhomogeneity of some of the most important vibrational absorption bands of pure water: the OH stretch fundamental band, the OH stretch overtone band and the H$_2$O-bend/OH-stretch combination band. We measured the vibrational relaxation of the $|\nu_{OH} = 1\rangle$ state by probing the induced absorption at the $\nu_{OH} = 1 \rightarrow 2$ transition after excitation of these bands at different frequencies. We find that the spectral position of the induced absorption blueshifts for excitation frequencies that are higher than the average OH stretch absorption frequency ($>3400$ cm$^{-1}$). The excited vibrations thus keep the same resonant frequencies on the timescale of the experiment ($\sim 0.5$ ps). Normally, ultrafast spectral diffusion by vibrational resonant excitation (Förster) transfer would equilibrate any inhomogeneity within a few hundred femtoseconds. However, the number density of oscillators in the high frequency wing of the absorption band is relatively small and have an unfavorable spectral overlap with nearby chromophores. The Förster transfer rates are therefore low for these oscillators and spectral diffusion is mostly determined by structural diffusion (1 ps). Excitation of the OH stretch fundamental band at frequencies $\geq 3600$ cm$^{-1}$ yields a much longer $T_1$ than excitation at the center or on the low frequency wing of the band. The longer $T_1$ for high excitation frequencies follows from an unfavorable overlap of the resonance frequency of high-frequency OH oscillators with the H$_2$O-bend overtone band at 3250 cm$^{-1}$, which is the main decay channel of the OH stretch vibration.

After excitation of the OH-stretch overtone at 6900 cm$^{-1}$, the oscillators decay within $<100$ fs to the $|\nu_{OH} = 1\rangle$ state. For this reason we observe an induced absorption at the $\nu_{OH} = 1 \rightarrow 2$ transition that is very similar to the response after excitation of the OH stretch fundamental. The induced absorption after excitation of the OH-stretch overtone is equally blue-shifted and its vibrational decay is equally slow as after direct excitation of the OH stretch fundamental at 3600 cm$^{-1}$. This shows that the overtone band is dominated by weakly hydrogen-bonded OH oscillators. An analysis in the context of the Lippincott-Schroeder model of the OH stretch vibration reveals that a cancellation occurs in the transition dipole moment of strongly hydrogen-bonded OH oscillators. The OH oscillators that are probed after excitation of the OH stretch overtone band at 6900 cm$^{-1}$ have the same hydrogen-bond strength as the oscillators excited in the OH stretch fundamental band at 3600 cm$^{-1}$. This explains why their spectral response and vibrational lifetime are identical. For the stretch-bend combination tone we observe similar results, i.e. a blue-shifted spectrum and a relatively slow vibrational relaxation. This result indicates that for the stretch-bend transition a similar destructive interference effect occurs as for the overtone.
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Figure 5.13. Relative Förster rates (solid line) from donating oscillators (horizontal axis) to a distribution of oscillators overlapping with the H$_2$O-bend overtone (dashed-dotted line). At 3600 cm$^{-1}$ the rate of transfer is more than 10 times lower than for oscillators resonant around 3250 cm$^{-1}$.

5.A Appendix: Förster Transfer

The rate for Förster transfer $k_{DA}$ from a donating oscillator $D$ to an accepting oscillator $A$ is proportional to the overlap integral of their spectra $\sigma_D(\nu)$ and $\sigma_A(\nu)$, respectively, and inversely proportional to their distance $\vec{R}$ to the sixth power according to [58],

$$
k_{DA} \propto \frac{C}{|\vec{R}|^6} \int d\nu \sigma_D(\nu)\sigma_A(\nu) \quad (5.10)$$

where $C$ is a prefactor containing the transition dipole moments of both oscillators and a geometrical factor that accounts for the relative orientations of the oscillators. Here, we will consider relative values of $k_{DA}$ and assume an isotropic distribution of oscillators such that $C$ can be treated as a constant. All oscillators are assumed to have a Lorentzian line profile at a certain center frequency $\nu_c$,

$$
\sigma(\nu) = L(\nu - \nu_c) = L\nu_c(\nu), \quad (5.11)
$$

with the homogeneous linewidth gradually increasing from 40 cm$^{-1}$ at the low frequency wing of the spectrum to 80 cm$^{-1}$ at the high frequency wing of the spectrum.

We calculate $k_{DA}(\nu_{c,D},\nu_{c,A})$ for a single donating oscillator with center frequency $\nu_{c,D}$ and an accepting oscillator with center frequency $\nu_{c,D}$. The density of oscillators in the bath as a function of their center frequencies is assumed to follow a distribution function $G(\nu)$ that is normalized such that,

$$
\int d\nu G(\nu) = 1 \quad (5.12)
$$
Eventually, we will take the normalized linear spectrum of the OH-stretch band as the distribution function. This is an approximation, as the cross section of blue OH oscillators is in fact smaller than that of red oscillators. If \( \rho \) is the density of oscillators, then \( R_0 = (3/4\pi \rho)^{1/3} \) denotes the radius around an oscillator that contains one other oscillator. With the distribution function \( G(\nu) \) the number of oscillators \( \eta(r, \nu_{c,A}) \) that have their center frequency at \( \nu_{c,A} \) in a sphere of radius \( r \) is then given by,

\[
\eta(r, \nu_{c,A}) = \left( \frac{r}{R_0} \right)^3 G(\nu_{c,A}) \quad (5.13)
\]

The exact value of \( R_0 \) will be divided out when normalizing the rates and is thus of no importance. The number density \( N(R, \nu_{c,A}) \) of accepting oscillators at \( \nu_{c,A} \) at a spherical shell of radius \( R \) and thickness \( dR \) around the donating oscillator is thus given by,

\[
N(R, \nu_{c,A}) = \frac{3R^2}{R_0^3} G(\nu_{c,A}) dR \quad (5.14)
\]

The rate \( k_{DA} \) for Förster transfer from an excited oscillator with center frequency \( \nu_{c,D} \) to an accepting oscillator with center frequency \( \nu_{c,A} \) is thus,

\[
k_{DA}(\nu_{c,D}, \nu_{c,A}) = \int_{R_0}^{\infty} dR \int d\nu \frac{C}{|R|^6} N(R, \nu_{c,A}) L_{\nu_{c,D}}(\nu) L_{\nu_{c,A}}(\nu) \quad (5.15)
\]

where the integration over \( R \) has a lower boundary cut-off at the radius \( R_0 \).

As a first comparison we assume a distribution of accepting modes \( B(\nu)G(\nu) \), where \( B(\nu) \) is the lineshape of the overtone of the bending vibration. The exact shape of this band is not known for pure liquid water, but for our purpose we assume a linewidth which is 1.5 times that of the fundamental bend (88 cm\(^{-1}\)) and a center frequency of 3250 cm\(^{-1}\). The total rate \( K(\nu_{c,D}) \) for transfer from a subset of donating oscillators \( L_{\nu_{c,D}}(\nu) \) to the distribution overlapping with the bend overtone is found when we integrate over the accepting modes distribution,

\[
K(\nu_{c,D}) = \int d\nu_{c,A} k_{DA}(\nu_{c,D}, \nu_{c,A}) B(\nu_{c,A}) G(\nu_{c,A}) \quad (5.16)
\]

This integral is evaluated for different center frequencies \( \nu_{c,D} \) of the donating oscillator. The results are normalized to the maximum rate and shown in Fig. 5.13. There is a strong frequency dependence of \( K \). At 3600 cm\(^{-1}\) the transfer rate is more than a factor of 11 slower compared to 3250 cm\(^{-1}\).

To get a description of the population dynamics, we performed a simulation that also includes dynamics effects other than Förster transfer. To this end, we divide the OH stretch linear absorption spectrum between 3000 cm\(^{-1}\) and 3800 cm\(^{-1}\) in bins with a lorentzian absorption profile with central frequencies \( \nu_i \), 2 cm\(^{-1}\) apart. Förster transfer from bin \( i \) to bin \( j \) is calculated according to
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Figure 5.14. Population dynamics simulated for an initial population in frequency bins between 3000 cm$^{-1}$ and 3700 cm$^{-1}$, with steps of 100 cm$^{-1}$ (red to blue curves) according to the model described in the text. The population dynamics becomes much slower at blue excitation frequencies in spite of ultrafast Förster transfer. The time constants of exponential fits to the curves between 0.2 and 1 ps are shown in Fig. 5.3B.

The rates are normalized such that the rate from an oscillator in the center of the band to any other oscillator is,

$$\int d\nu k_{DA}(3400, \nu) = 20 \text{ps}^{-1}. \quad (5.17)$$

In addition to Förster transfer, reorientational jumps and structural diffusion also lead to spectral diffusion. The jump rate is assumed to be $k_j = 0.5 \text{ps}^{-1}$ for bins higher than 3500 cm$^{-1}$ and zero for others. Oscillators that undergo a reorientational jump are distributed over all other bins according to the distribution function $G(\nu)$. Structural diffusion is described by letting bins exchange population with their neighbors with rate constants that depend on the slope of $G(\nu)$,

$$k_{s,i\rightarrow i+1} = k_g G(\nu_{i+1})/G(\nu_i) \quad (5.18)$$

where $k_g$ is related to the time constant of the frequency correlation function $\tau_c = 700 \text{fs}$ according to $k_g^{-1} = \tau_c(1-\sqrt{1-4/w^2})$ [81]. Here is $w$ the half width at 1/e of the maximum of the equilibrium distribution. For our simulation and bin size, this yields $k_g^{-1} = 1.0 \text{fs}$.

The decay rate of the OH stretch vibration is assumed to be proportional to the spectral overlap of the lorentzian lineshape of a certain bin and the H$_2$O-bend overtone,

$$k_b(\nu_i) \propto \int d\nu L_{\nu_i}(\nu)B(\nu) \quad (5.19)$$

The rates are normalized such that the rate for oscillators with the maximum spectral overlap $k_b(\nu = 3250) = 1/170 \text{fs}^{-1}$. Bins at lower frequencies that 3250 cm$^{-1}$ are all assumed to have a decay rate of 1/170 fs$^{-1}$ (due to strong
coupling). As initial condition, one bin at a particular frequency contains a population (is assumed to be excited). The subsequent population dynamics are obtained by iteration over time with a step size of 0.2 fs. For a number of excitation frequencies (bins), the results are shown in Fig. 5.14. Exponential fits to the dynamics between 0.2 and 1 ps yield the vibrational relaxation times that are shown as a solid line in Fig. 5.3B. The experimental results are very well reproduced.