Ultrafast vibrational dynamics of water

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Hydrogen Bond Mediated Energy Transfer in Embedded Water Molecules

In this Chapter, we present results on embedded water molecules dissolved in a mixture of acetone and carbon tetrachloride. From both vibrational relaxation and anisotropy decay measurements, we conclude that two processes occur: the transfer of excitation energy from one OH-group to the other and the formation and breakage of hydrogen-bonds. It is shown that an intermediate state exists in which the water molecule has two hydrogen bonds, and in which the excitation energy is delocalized over the OH-groups.
8.1 Introduction

As stated in the Introduction, understanding water means understanding hydrogen-bonding in liquids. The study of the OH-stretch vibration of water is complicated due to the ultrafast energy equilibration with a time constant of 550 fs, as shown in Chapters 4 and 5, which stems from the large density of OH-oscillators and the strong inter- and intramolecular coupling present in liquid H$_2$O. Therefore, previous studies were mainly focused on dilute solutions of HDO in D$_2$O [20, 63, 64, 103, 104, 106, 108]. In this case, a single OH-oscillator is surrounded by OD-groups which makes it possible to study only the influence of the hydrogen bonding network on the OH-stretch oscillator, because there is no intra- and intermolecular OH–OH coupling. Recently, the rotational anisotropy decay was measured on pure water in a femtosecond mid-infrared pump-probe study [104]. The anisotropy is a measure for the degree of polarization induced by excitation of OH-stretch oscillators by the pump pulse. Because the transition dipole moments of the symmetric and antisymmetric OH-stretch vibration are orthogonal (see Figure 1.2), the anisotropy decay forms a measure for the population redistribution between these two modes. The anisotropy decay was observed to be instantaneous (<100 fs). This means that in pure water the vibrational energy is delocalized within the pulse duration. However, due to the large density of OH-groups and the ultrafast time scale, the intramolecular redistribution could not be distinguished from the intermolecular energy transfer.

In contrast to these measurements, the intramolecular coupling can still be studied in water monomers in apolar solutions [23, 26], because there is no influence of the hydrogen-bonding network on the OH-stretches. In a picosecond pump-probe study [26] it was shown that excitation of the antisymmetric stretch mode in a water monomer dissolved in an apolar solvent led to a fast (few ps) population redistribution with the symmetric stretch mode. It should be emphasized, that the pulse duration in this experiment was 14 ps.

Here we present a study on water-acetone complexes in apolar solution. This system enables us to study an isolated H$_2$O molecule with hydrogen bonds to acetone molecules. It allows for a study of both the intramolecular redistribution and the influence of hydrogen-bonding on the OH-stretch dynamics.

8.2 Experimental

The experimental setup used for the experiments described in this thesis has two major changes with respect to the setup described in Chapter 3.

First, the detection of the signal has been changed. The last mirror in the probe path (see Fig. 3.4) is replaced by a wedged CaF$_2$ window. The reflection from the back side forms the reference beam, which is now also focussed into the sample, but does not overlap with the pump beam. In order to measure the rotational anisotropy (see Section 3.2), the polarization of the probe beam was set at 45 degrees with
Respect to the pump beam. After the sample, an infrared beam splitter splits the probe beam into two parts. Due to polarizers in both pathways, two beams with polarization components perpendicular and parallel to the pump polarization are generated. These two beams, together with the reference beam, are focused by a 100 mm CaF$_2$ lens on the entrance split of an imaging spectograph. At the image plane three MCT detector arrays consisting of 32 pixels are placed above each other. In the experiments the arrays cover a spectral width of approximately 400 nm.

The measured intensities $I(\omega)$ are amplified and sent to a computer via an A/D-converter. In order to compensate for the pulse-to-pulse intensity fluctuations in the probe beam, the reference intensity $I_{\text{ref}}(\omega)$ is measured. Using a chopper, both the transmission of the probe beam in the presence of the pump beam ($T(\omega)$), and in the absence of the pump beam ($T_0(\omega)$) are measured. The transmission change $\ln(T/T_0)$ is calculated as a function of delay between pump and probe pulse, where $T(\omega)=I(\omega)/I_{\text{ref}}(\omega)$ and $T_0(\omega)=I_0(\omega)/I_{\text{ref}}(\omega)$.

![Figure 8.1. Generation of the probe pulse. DM=dichroic mirror, RG1000=longwave pass 1000nm, L=lens, LWP=longwave pass 2500nm, AgGaS$_2$=nonlinear crystal, black bars represent gold mirrors.](image)

Secondly, the probe pulse is generated in a different way, as is depicted in Figure 8.1. An OPG/OPA-stage generates signal (1265 nm) and idler pulses (2180 nm). Difference frequency generation (DFG) in an AgGaS$_2$-crystal leads to pulses tunable up to 10 $\mu$m. A major advantage of using AgGaS$_2$ is that the generated pulses have a much larger bandwidth than pulses generated via parametric amplification in KTP. With these pulses, we can fully make use of the advantages of spectrally resolving the probe. The spectral width of the probe pulses used is approximately 300 cm$^{-1}$ (FWHM) and the duration is 100 fs.

The sample was prepared from a 4.0 mol/l solution of acetone (CH$_3$COCH$_3$, Biosolve, 99.8%) in carbon tetrachloride (CCl$_4$, Fluka, 99.5%). Water (Lichrosolv, Merck) was added to a concentration of 0.4 mol/l. For the HDO samples, liquid H$_2$O was mixed in a 1:10 ratio with D$_2$O. The measurements were performed on a 500 $\mu$m thick sample kept in between two CaF$_2$ windows. The transmission of the sample is
typically 10% at 3520 cm\(^{-1}\). In order to avoid the accumulation of heat produced by the pump pulses, the sample is rotated.

### 8.3 Linear absorption spectrum

The linear absorption spectra for the water-acetone complexes in carbon tetrachloride are depicted in Figure 8.2 for HDO and in Figure 8.3 for H\(_2\)O molecules. In case of HDO molecules, the OH-group is hydrogen-bonded to an acetone molecule, or it is not. In the latter case, the OH-stretch vibration is expected to behave similar as in the gas phase, i.e. it has a narrow absorption band at a high frequency. These free OH-groups are responsible for the peak at 3680 cm\(^{-1}\). We attribute the broad absorption band at 3530 cm\(^{-1}\) to hydrogen-bonded OH-groups. The absorption band for hydrogen-bonded molecules is expected to undergo a red-shift and a broadening, as is indeed observed.

For H\(_2\)O molecules, the absorption spectrum has a richer structure. We again observe peaks at about 3520 and 3690 cm\(^{-1}\). In analogy with the HDO molecule, we attribute these peaks to water molecules that only have one hydrogen-bond (see Fig 8.3, type A). If both OH-groups are hydrogen-bonded, the possible vibrations are the antisymmetric (\(\nu_{as}\)) and the symmetric stretch mode (\(\nu_s\)). We attribute the shoulder in the absorption spectrum at 3610 cm\(^{-1}\) to the antisymmetric stretch mode. The symmetric stretch mode is hidden underneath the broad band at 3520 cm\(^{-1}\), which is in close analogy with the gas phase, where the symmetric stretch mode is shifted 100 cm\(^{-1}\) to the red with respect to the antisymmetric band\[35\]. Furthermore, the symmetric stretch mode is expected to have a smaller cross-section than the antisymmetric stretch mode. Hence, both the symmetric stretch of the doubly hydrogen-bonded and the hydrogen-bonded OH-stretch of the singly hydrogen-bonded water molecule absorb at 3520 cm\(^{-1}\), but the major contribution at this frequency stems from the singly hydrogen-bonded OH-groups.

### 8.4 Vibrational and orientational relaxation

#### 8.4.1 Transient spectra

In order to gain insight in the vibrational relaxation behavior of the H\(_2\)O molecule, we first present the results for the HDO molecule. Figure 8.4a shows the transient spectra for HDO after pumping at 3530 cm\(^{-1}\), the frequency of the hydrogen-bonded OH-group. We observe a broad bleaching band around the pump-frequency and an asymmetrically shaped induced 1→2 absorption at 3350 cm\(^{-1}\). This implies that the anharmonicity for this system is 180 cm\(^{-1}\).

Figure 8.4b shows the transient spectra after pumping of the free OH-stretch mode of the HDO sample. Immediately after excitation, bleaching is observed at the pumping frequency (3680 cm\(^{-1}\)), which decays as a function of time. At the
Figure 8.2. For HDO molecules, there is only one OH–stretch vibration that is either hydrogen-bonded ($\nu_b$) or free ($\nu_f$). Depicted is the absorption spectrum for the dilute solution of acetone-water complexes in CC\textsubscript{4}. The narrow peak at 3420 cm$^{-1}$ stems from the first overtone of the C=O stretch vibration of acetone.

The frequency of the hydrogen-bonded OH-groups (3530 cm$^{-1}$), however, an ingrowth of the bleaching is observed, which then decays for larger delay times. The induced absorption is found at 3350 cm$^{-1}$. Note that, for large delay times, the transient spectrum is similar to that of Fig 8.4a; the absolute signal, however, is much smaller.

The transient spectra for the H$_2$O molecules are displayed in Figure 8.5. The upper panel shows the results after pumping both the symmetric and hydrogen-bonded stretch mode at 3520 cm$^{-1}$. We observe a bleaching for frequencies higher than 3450 cm$^{-1}$ and induced absorption for frequencies lower than this value. The bleaching shows the fingerprints of the linear absorption spectrum (Fig. 8.3): bleaching features appear at 3520, 3610 and 3690 cm$^{-1}$. The induced absorption band is found at 3350 cm$^{-1}$, similar as in HDO. At the red side of this band at about 3180 cm$^{-1}$ a smaller induced absorption feature is visible.
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Figure 8.3. There exist two types of H$_2$O molecules in solution. Part of the H$_2$O molecules only has one hydrogen bond (type A), which gives rise to a hydrogen-bonded ($\nu_b$) and a free ($\nu_f$) OH-stretch mode. When both OH-groups are hydrogen bonded (type B), symmetric ($\nu_s$) and antisymmetric ($\nu_a$) OH-stretch modes exist. The latter absorb at 3520 and 3610 cm$^{-1}$, respectively. The peaks in the absorption spectrum are attributed to the four water vibrations, the narrow peak at 3420 cm$^{-1}$ belongs to acetone.

In Figure 8.5b the transient spectra are shown for pumping the antisymmetric stretch mode (3610 cm$^{-1}$). At a delay of 0.4 ps, a large bleaching signal is observed at the pumping frequency, while the bleaching at 3520 cm$^{-1}$ is negligible. For larger delay times, however, this band increases and then decays back to zero. The induced absorption is found to be centered around 3350 cm$^{-1}$. Furthermore, a small red-shifted induced absorption band is observed at the same frequency as in Fig. 8.5a.

Figure 8.5c displays the transient spectra after pumping the free OH-group at 3690 cm$^{-1}$. Here, instantaneous bleaching is observed at the pumping frequency. At 3520 cm$^{-1}$, bleaching is already present at short delay times. It shows an ingrowth and subsequently a decay. The response at 3610 cm$^{-1}$ is zero for short delay times.
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Figure 8.4. Transmission change for the HDO molecule as a function of probe frequency for different delay times after pumping at (a) 3530 cm\(^{-1}\) and (b) 3680 cm\(^{-1}\).

and grows in for longer delay times. The induced absorption peaks at 3350 cm\(^{-1}\) and also shows an ingrowth with time. The side band at 3180 cm\(^{-1}\) is again observed.

8.4.2 Delay time scans

Figure 8.6 shows delay time scans for pumping the HDO sample at the \(\nu_6\) frequency of 3530 cm\(^{-1}\) and probing in the center of the 0→1 and 1→2 band (upper two curves) and a delay time scan for pumping at 3680 and probing at 3530 cm\(^{-1}\) (lower curve).
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Figure 8.5. Transient spectra for H$_2$O at different delay times obtained after pumping (a) the symmetric and the hydrogen-bonded stretch mode at 3520 cm$^{-1}$, (b) the antisymmetric stretch band at 3610 cm$^{-1}$ and (c) the free OH–stretch band at 3690 cm$^{-1}$.
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The upper two scans show bi-exponential decay dynamics with time constants of 1.3 ± 0.4 and 6.3 ± 0.5 ps. In the lower curve, a slow rise with a time constant of 1.3 ps is first observed followed by a decay which is similar to the long time behavior found in the upper two scans.

**Figure 8.6.** Delay time scans for HDO. Upper curve: pumping and probing the 0→1 band of the hydrogen bonded OH-group at 3530 cm\(^{-1}\), middle curve idem now probing the 1→2 band (sign of curve inverted for clarity). The lower curve shows the response at 3530 cm\(^{-1}\) after excitation of the free OH-stretch mode at 3680 cm\(^{-1}\). The scans are vertically scaled for clarity.

In Figures 8.7-9 delay time scans are shown for the embedded H\(_2\)O molecule. In Figure 8.7, the pump frequency is resonant with the free OH-group (3690 cm\(^{-1}\)), the probe frequencies are 3520 (\(\nu_s\) and \(\nu_b\)), 3610 (\(\nu_{as}\)) and 3690 cm\(^{-1}\)(\(\nu_f\)), respectively. We observe for H\(_2\)O an ingrowth of the bleaching at 3520 and 3610 cm\(^{-1}\) with a time constant of 1.3 ps followed by a slower decay with a time constant of 6.3 ps. The same decay behavior is observed for probing at 3690 cm\(^{-1}\). Added to this slow relaxation behavior, is a fast decaying component for short delay times, which is similar to the rising time at the other two probe frequencies.

Figure 8.8 shows the delay times scans for pumping the antisymmetric stretch band at 3610 cm\(^{-1}\). The upper scan shows the relaxation behavior at 3610 cm\(^{-1}\), where a fast decay of \(\sim\) 200 fs is observed, followed by a slower decay of the bleaching with 6.3 ps. Tuning the probe to 3520 cm\(^{-1}\) leads to an ingrowth of the bleaching for short and a slow decay for long delay times. The ingrowth happens on the same \(\sim\) 200 fs observed at 3610 cm\(^{-1}\). The induced absorption signal is displayed in the

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third curve of Figure 8.8. Two time scales govern the dynamics: a fast relaxation together with the slow time scale, observed for all frequencies. Figure 8.9, finally, shows the delay time scans for pumping at 3520 cm\(^{-1}\). Probing at 3520 cm\(^{-1}\) gives a fast decay for short delay times (1.3 ± 0.4 ps) together with the slower relaxation time of 6.3 ± 0.5 ps. Probing at 3610 cm\(^{-1}\) shows a similar behavior, as does the 1→2 transition at 3350 cm\(^{-1}\). Probing at 3680 cm\(^{-1}\) shows a mono-exponential behavior with a time constant of 6.3 ps.

8.4.3 Orientational dynamics

As shown in Section 3.2, the rotational anisotropy can be calculated by measuring the signal with polarization parallel, \(\ln(T/T_0)_\parallel\), and perpendicular, \(\ln(T/T_0)_\perp\), to the pump pulse. The rotation free signal, i.e. the same signal as is observed in a magic angle measurement (see sections 8.4.1 and 8.4.2), is given by \(\ln(T/T_0)_\parallel+2\ln(T/T_0)_\perp\). Typical examples of \(\ln(T/T_0)_\parallel\) and \(\ln(T/T_0)_\perp\) are displayed in Figure 8.10.

Figure 8.11 shows the anisotropy decay curves. The probe frequencies lie for all decays in the 1→2 band at 3314 cm\(^{-1}\), i.e. the singly hydrogen-bonded OH-group is mainly probed. In Figure 8.11a, the anisotropy decay for HDO is displayed. A mono-exponential decay is observed starting from 0.4. Figure 8.11b,c show the decay for H\(_2\)O, pumped at 3520 and 3610 cm\(^{-1}\), respectively. In Figure 8.11b, the anisotropy
Figure 8.8. Delay time scans for H$_2$O: pumping the antisymmetric stretch mode at 3610 cm$^{-1}$, probe frequencies are from top to bottom: 3610, 3520, 3350 and 3690 cm$^{-1}$, respectively. Again, the scans are scaled vertically for clarity.

decays from 0.4 to 0 in a bi-exponential manner. The observed decay for pumping the antisymmetric stretch mode (Fig. 8.11c), shows an instantaneous decay from 0.4 to 0.1 followed by a slower mono-exponential decay.

8.5 Hydrogen bond mediated energy transfer

8.5.1 The HDO molecule

The interpretation of the transient spectra of the water-acetone complex would not be possible without by the HDO-spectra. It is for this molecule that only two kinds of OH-groups are present: hydrogen-bonded and non-hydrogen-bonded. Let’s therefore first have a look at the results obtained for HDO.

We attribute the fast component observed for short delay times in Figure 8.6 to the breaking and formation of a hydrogen-bond. Therefore, a fast decay is observed when pumping and probing the hydrogen-bonded OH-groups: bond breaking forms an extra relaxation channel. Pumping the free groups and probing the hydrogen-bonded groups leads to an increase of the bleaching, i.e. the amount of excited hydrogen-bonded OH-groups increases (see Figures 8.4b and 8.6). A bi-exponential fit of these data leads to a lifetime of the OH-stretch vibration $T_1$ of 6.3 ±0.5 ps for both the free as the hydrogen-bonded OH-groups, the hydrogen bond breaking and making time,
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Figure 8.9. Delay time scans for H$_2$O: pumping the symmetric and hydrogen bond stretch mode at 3520 cm$^{-1}$, probe frequencies are from top to bottom: 3520, 3610, 3690 and 3350 cm$^{-1}$, respectively. The scans are vertically scaled for clarity.

$\tau_{hb}$ is found to be 1.3 ± 0.4 ps, as shown in the previous section.

The anisotropy decay for the HDO molecule (Figure 8.11a) can be well fitted with a single exponential. This gives a reorientation time of 6.0 ± 1.0 ps. The excitation of the hydrogen-bonded OH–stretch oscillators gives rise to an anisotropy in the sample. We attribute this time to the reorientation of the molecule in the liquid. It should be noted that hydrogen-bond breaking dynamics, as observed in the vibrational relaxation experiments, lead to a shift of the absorption frequency from $\nu_h$ to $\nu_f$. Hence, it will not lead to a decay of the induced anisotropy, because the breakage of the bond does not induce a change in the polarization in the probe window.

The orientational relaxation time of water monomers was found [26] to range from 1.7 ps in solvents like carbon tetrachloride up to 6 ps in solvents with a large dipole moment, like acetonitrile. In view of this, it is not surprising that we find a reorientation time of 6 ps, as the dipole moments of acetonitrile and acetone are comparable.

### 8.5.2 H$_2$O: the intermediate state

The results for H$_2$O can be explained using the model depicted in Figure 8.12. In this model two processes are described: the formation and breakage of hydrogen bonds and the transfer of excitation energy between the two OH-groups in water. This gives
four different initial states in which an excited OH-group can be. These states are denoted with Roman numbers I, II, III and IV.

The direct transfer of excitation between the OH-stretches is very unfavorable due to the almost perpendicular dipole moments of both vibrations. Therefore, an intermediate or transient state is needed in which the energy is delocalized. Secondly, most water molecules prefer to have one hydrogen-bond. Breakage of this bond is very unfavorable unless the molecule gets in an (intermediate) state with two hydrogen-bonds. In this case, it would be preferable to break one hydrogen bond. Both conditions are fulfilled in the situation where the water molecule has two hydrogen-bonds. Therefore, we identify the situation in which a symmetric and antisymmetric mode exist as an intermediate state, which is necessary for the hydrogen-bond dynamics. This state is denoted by $T$ in Figure 8.12.

Starting from situation I in Figure 8.12, a hydrogen-bond is present between the excited OH-stretch oscillator and the acetone molecule. We can end up in four different situations. In situation I and II, the excitation stays on the OH-group which was initially excited, whereas in situation III and IV the excitation is transferred to the other OH-group. Furthermore, in situation I and III the hydrogen bond is not broken, whereas in situation II and IV the hydrogen-bond is broken and formed at the other OH-group. Transitions between these states all involve the intermediate state $T$. Both the vibrational and the orientational dynamics measurements for $H_2O$ can

Figure 8.10. Pump-probe scans for HDO sample. The signal measured with polarizations parallel and perpendicular to the pump polarization are indicated by closed and open circles, respectively. From these two contributions, the anisotropy is calculated.
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Figure 8.11. The measured anisotropy $R$ as a function of delay for (a) HDO pumped at 3530 cm$^{-1}$, (b) H$_2$O pumped at 3610 cm$^{-1}$ and (c) H$_2$O pumped at 3520 cm$^{-1}$. The probe frequency lies in the 1$\rightarrow$2 band.
be explained by the model presented in Figure 8.12. In the process I—I, for example, the excitation stays on the initially excited OH-groups, but a hydrogen bond is broken and formed at the other group. This process contributes to the rotation free signal, but not to the anisotropy decay.

8.5.3 \( \text{H}_2\text{O}: \) interpretation of the measurements

In analogy with HDO, we attribute the ingrowth observed for \( \text{H}_2\text{O} \) when pumping at 3690 cm\(^{-1} \) and probing at 3520 and 3610 cm\(^{-1} \) to the formation of a hydrogen-
bond, as shown in Figure 8.7 (process II/III→T→I/IV. When the pump and probe frequencies are equal, hydrogen-bond breaking and making forms an extra and faster relaxation channel and will therefore appear as a peak on the bleaching signal (see Fig 8.7 upper curve and 8.9 second curve). The observed signals for pump and probe frequencies at 3610 cm\(^{-1}\) need special attention. It should be noted that the antisymmetric stretch forms the transient T state. Therefore, the ingrowth observed at 3520 cm\(^{-1}\) (middle curve of Fig. 8.8) is the result of breaking of one hydrogen bond and strengthening of the other. As stated before, the fast time scales observed for Figure 8.8 upper two curves, are similar; they are, however, much faster than the hydrogen bond breaking and making time which is in the order of 1 ps. This fast decay and fast ingrowth occurs on a \(\sim\)200 fs time scale. This fast time scale can be well understood using the model from Figure 8.12. The transition state is an energetically unfavorable state, therefore breakage of one of the hydrogen bonds out of this state occurs faster than in case the initial state was one of the four stable states.

The small absorption band at 3180 cm\(^{-1}\) observed for H\(_2\)O is due to a combination band from the transition \(\nu_b=0, \nu_f=1 \rightarrow \nu_b=2, \nu_f=0\). The calculated energy for this transition is \((3520 + 3350) - 3690 = 3180\) cm\(^{-1}\), which matches with the observed absorption feature. The dynamics of the band is similar to that of the 1→2 transition, which corroborates our assignment. Because we observe this band at all three pump frequencies, this implies that at all three pump frequencies excited free OH-stretches are present, either due to energy transfer (Figure 8.5a) or due to direct excitation with (the wings of) the pump pulse (Figure 8.5b,c).

For the H\(_2\)O molecule, the observed anisotropy decay is more complicated. By pumping at 3520 cm\(^{-1}\) in the H\(_2\)O sample, mainly singly hydrogen-bonded OH-stretches are excited. In contrast to the HDO molecule, breakage of a hydrogen-bond now affects the anisotropy. Passing the transient state \(T\), the excitation can end up in four different states. Because there is no preferred state, the excitation energy will be equally distributed over both OH-groups. Therefore, breakage of the hydrogen-bond leads to a decay of the anisotropy with \(\tau_{hb}\). The data can be fitted with a bi-exponential function with time scales of 1.0 ±0.4 ps and 6.0 ± 1.0 ps. We attribute the faster component to hydrogen-bond breaking dynamics, the slower decay component is the reorientation time of the molecule as observed for HDO.

Direct excitation of the transient state leads to an instantaneous decay of the anisotropy from 0.4 to approximately 0.1. This means that the energy redistribution among both OH-groups, and thus the delocalization of the excitation, occurs on an ultrafast time scale. It can be shown that the rotational anisotropy decays from \(\frac{2}{5}\) to \(\frac{2}{5} \* P_2(\cos\delta)\), with \(P_2\) the second-order Legendre polynomial, if the total excitation polarization is transferred from a donor molecule to an acceptor molecule that has its transition dipole under an angle \(\delta\) with respect to the donor dipole [26, 94]. Because the angle between both OH-groups is 104 degrees, delocalization of the excitation leads to a decrease of the anisotropy to \(\frac{1}{2}*(\frac{2}{5} + \frac{2}{5} * P_2(\cos(104\text{°})))\approx 0.12\), as is indeed observed for short time scales. It should be noted that also in Figure 8.11b a first
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decay of the anisotropy to the value of 0.12 is observed. Because here, the initial situation was state I or IV instead of the intermediate $T$, the time scale at which this level is reached is different.

Transfer mechanisms between two resonances influence the observed population dynamics. When the transfer time is slow compared to the lifetime, the individual lifetimes of the separate states are not affected. In this case, we would have different lifetimes for the hydrogen-bonded, the free, the symmetric and the antisymmetric OH-stretch. We observe, however, similar dynamics at all probe frequencies. This means that the transfer times between two resonances are faster than the lifetime, and that the lifetime decays with an average value. In fact, all observed transfer times, either the hydrogen-bond dynamics (1.3 ps) or the bond breakage time out of the transient state (200 fs), are faster than the lifetime. All measured delay time scans for $\text{H}_2\text{O}$ can be well fitted with a bi-exponential decay. The longer time component, the lifetime of the OH-stretch vibration is observed to be $6.3 \pm 0.4$ ps, the slower time depends on the initial state. When starting from situation I-IV the hydrogen-bond dynamics time is $1.3 \pm 0.5$ ps.

8.6 Conclusions

We have studied both vibrational and rotational relaxation of a single water molecule with hydrogen bonds. Using a solution of water, acetone and carbon tetrachloride, we have shown that for HDO two different OH-stretch vibrations are present: those of free OH-groups ($\nu_f$, 3680 cm$^{-1}$) and those of hydrogen-bonded OH-groups ($\nu_b$, 3530 cm$^{-1}$). For $\text{H}_2\text{O}$ instead of HDO, two OH-stretch vibrations come into play. A water molecule which donates two hydrogen bonds, has two OH-stretch vibrations: the symmetric ($\nu_s$) and the antisymmetric ($\nu_a$) mode, which absorb at 3520 and 3610 cm$^{-1}$, respectively. We have shown that the state in which the $\text{H}_2\text{O}$ molecule has two hydrogen bonds acts as an intermediate state for excitation transfer and hydrogen-bond dynamics. From the vibrational relaxation experiments we observe that in $\text{H}_2\text{O}$ three time scales are present. Next to the life time of the OH-stretch vibration, which is found to be $6.3 \pm 0.5$ ps for all types, two other time scales are found. Hydrogen bond breaking and making is observed to occur on a $1.3 \pm 0.4$ ps ps time scale starting from one of the states I-IV. Starting from the intermediate state a characteristic time of 0.2 ps is found for ending up in one of the four states I-IV. From the rotational anisotropy measurements we conclude that molecular reorientation has a characteristic time scale of $6.0 \pm 1.0$ ps. Pumping the intermediate state gives an instantaneous decrease of the anisotropy from 0.4 to 0.12, the signature of a state in which the energy is delocalized, followed by the molecular reorientation with 6 ps.