Love and fear of water: Water dynamics around charged and apolar solutes

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Citation for published version (APA):

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4.1 Transient Absorption Spectra

In our mid-infrared pump-probe experiment we use a probe pulse to measure the absorption change in a sample due to the excitation of a vibrational mode by an intense pump pulse. The difference between the transmission spectra with \( I(\nu, t) \) and without \( I_0(\nu) \) a preceding pump-excitation is called a transient spectrum \( \Delta \alpha(\nu, t) \) and can be written in terms of the measured intensities as,

\[
\Delta \alpha(\nu, t) = -\ln \left( \frac{I(\nu, t)}{I_0(\nu)} \right)
\]

where \( \nu \) denotes the frequency and \( t \) the delay time between the pump and the probe pulses. Typically the transmission spectra \( I \) are normalized to the spectrum of a reference pulse that is not overlapping with the pump pulse in order to divide out intensity fluctuations of the laser. Most pump-probe experiments in this thesis are performed on the OD stretch vibrational mode of the HDO molecule in isotopically diluted water (a few percent HDO in H\(_2\)O). The transient spectra measured on this and similar vibrational modes contain three main contributions. First, the pump excites the OD stretch mode of a small percentage of HDO molecules to their first excited state \( |\nu_s=1\rangle \). Due to the decreased population in the ground state, the excitation results in a reduced absorption at the \( \nu_s = 0 \rightarrow 1 \) transition frequency of this mode. The reduced absorption \( (\Delta \alpha(\nu, t) \) is negative) is called the ground state bleach. Second, stimulated emission out of the \( |\nu_s=1\rangle \) state occurs and contributes to the absorption decrease at the \( \nu_s = 0 \rightarrow 1 \) transition frequency. Finally, the absorption of the probe pulse due to the \( \nu_s = 1 \rightarrow 2 \) excitation of pump-excited modes leads to an induced absorption \( (\Delta \alpha(\nu, t) \) is positive). Since the OD stretch vibrational mode is anharmonic, the spectrum associated with the \( \nu_s = 1 \rightarrow 2 \) transition is red-shifted by \( \sim 180 \text{ cm}^{-1} \) from the \( \nu_s = 0 \rightarrow 1 \). With increasing pump-probe delay, an increasing number of excited HDO molecules have relaxed to their ground state, causing all three contributions to the transient spectra to decrease in amplitude. Time resolved transient spectra \( \Delta \alpha(\nu, t) \) thus contain information on the decay of the probed vibrational mode.
Figure 4.1. The transient absorption difference probed at 2500 cm\(^{-1}\) with a probe pulse with its polarization parallel (circles) and perpendicular (triangles) to the pump polarization. The parallel signal is initially larger due to the anisotropic excitation. After a couple of picoseconds both signals become identical due to molecular reorientation.

In case the excitation pulse was linearly polarized, the measured response depends on the polarization of the probe pulse. The reason is that the excitation probability scales with \(\cos^2(\alpha)\), where \(\alpha\) is the angle between the excitation polarization and the transition dipole moment of the vibrational mode. Immediately after excitation, the absorption changes probed parallel to the pump polarization will therefore be larger than those probed perpendicular to the pump polarization. After a certain delay time the OD stretch modes will be less ordered due to molecular reorientation. As a consequence, the absorption changes will depend increasingly less on the direction of the probe polarization, i.e. become more isotropic. An example of the parallel and perpendicular absorption changes probed in 8% HDO in H\(_2\)O at 2500 cm\(^{-1}\) for different delay times is shown in Fig. 4.1. The dynamical behavior of such a polarization resolved experiment thus not only depends on the vibrational decay of the excited mode, but on the reorientation dynamics as well. To obtain the transient spectra that are completely independent on molecular reorientation and thus reflect the vibrational decay only we have to take the weighted difference between the parallel and perpendicular signals according to,

\[
\Delta \alpha_{iso}(\nu, t) = \frac{\Delta \alpha_{||}(\nu, t) + 2 \Delta \alpha_{\perp}(\nu, t)}{3}
\]

(4.2)

where the perpendicular absorption changes appear twice to take into account the fact that we probe the three-dimensional sample in a two-dimensional plane orthogonal to the beam propagation. All probed dipoles are projected on this plane.

A parameter that exclusively depends on the reorientation of the excited
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transition dipole moments is the anisotropy $R(\nu, t)$ given by,

$$R(\nu, t) = \frac{\Delta \alpha_\parallel(\nu, t) - \Delta \alpha_\perp(\nu, t)}{\Delta \alpha_\parallel(\nu, t) + 2\Delta \alpha_\perp(\nu, t)}$$ (4.3)

Using Eq. (4.2) and Eq. (4.3), the parallel and perpendicular absorption changes can be written as a combination of the vibrational decay and reorientation dynamics according to,

$$\Delta \alpha_\parallel(\nu, t) = (1 + 2R(\nu, t))\Delta \alpha_{iso}(\nu, t)$$ (4.4)

$$\Delta \alpha_\perp(\nu, t) = (1 - R(\nu, t))\Delta \alpha_{iso}(\nu, t)$$ (4.5)

From the converging behavior of the parallel and perpendicular signals it is clear that the anisotropy of the OD stretch vibration in isotopically diluted water decays on a timescale of several picoseconds (Fig. 4.1). Both signals do not decay completely but rather reach an endlevel after $\sim 10$ ps. This response at long delay times is not due to excited OD oscillators, and needs to be subtracted from the data to obtain the anisotropy dynamics of the OD stretch transition dipole moment only. An important part of the data analysis of anisotropy measurements involves the subtraction of this endlevel and in the following sections we elaborate on a number of methods to achieve this.

4.2 Modeling Heat Dynamics

As we have seen in the previous section, the transient pump-probe response in isotopically diluted water is virtually always superimposed on another response. This response is found to grow in on a similar timescale as the decay of the excitation and remains constant for longer delay times, at least on the timescale of the experiment (100 ps). The origin of this contribution is the rise in temperature of the sample due to dissipation of the vibrational energy into thermal bath modes. The typical pump energy used to excite OD-stretch oscillators in the experiment described in section 3.1.1 is 5 $\mu$J, focused in the sample on a spot with a radius of 100 $\mu$m. If we assume that about 90% of the energy is absorbed by the sample, the sample thickness is 25 $\mu$m and that energy diffusion in the direction orthogonal to the laser propagation direction is negligible on the timescale of the experiment, the probed volume of water experiences a temperature increase of about 10 Kelvin after vibrational relaxation is complete. As a response to the new energy content, the hydrogen-bonds in the solution will weaken. OD-oscillators with a weaker hydrogen-bond have a lower cross section and their resonance frequency is shifted towards blue frequencies. This explains the spectral shape of the thermal endlevel found in our experiments: a bleach at red frequencies and a much smaller induced absorption at blue frequencies. This spectral shape can be reproduced by subtracting the linear spectrum of the sample at room temperature from that at an elevated temperature: the thermal difference spectrum. The thermal endlevel thus forms an observable from our non-linear experiment that can be compared to an observable obtained with linear spectroscopy.
4.2.1 Simple Kinetic Model

In most of our work we are interested in retrieving the vibrational lifetimes and the reorientation dynamics of the excited OD oscillators. To isolate the OD-stretch response, we therefore need to subtract the contribution of the heat signal from the measured pump-probe data. Subtracting the thermal endlevel as a constant offset ignores the fact that in the first few picoseconds most energy is still present as localized vibrations rather than thermal modes. To account for this effect we use a kinetic model for vibrational decay in which the dynamics of the population in the thermalized ground state is related to the vibrational decay of the excitation through rate equations. In the simplest possible model the population in the excited state directly decays to the thermalized ground state. The population $N_1(t)$ in the excited state and the population $N_H(t)$ in the thermalized ground state are then obtained for all pump-probe delay-times $t$ by solving the differential equations,

$$\frac{d}{dt} N_1(t) = -k_1 N_1(t)$$

(4.6)

$$\frac{d}{dt} N_H(t) = +k_1 N_1(t)$$

(4.7)

where $k_1$ is the vibrational decay rate of the excited state. This can conveniently be written into a vector notation in which we introduce a rate matrix $M(k)$,

$$\frac{d}{dt} \mathbf{N}(t) = M(k) \cdot \mathbf{N}(t)$$

(4.8)

$$= \begin{pmatrix} -k_1 & 0 \\ +k_1 & 0 \end{pmatrix} \begin{pmatrix} N_1(t) \\ N_H(t) \end{pmatrix} .$$

(4.9)

where $k$ denotes the set of parameters of the model. The trivial solutions to these coupled equations are,

$$N_1(t) = N_1(0)e^{-k_1 t}$$

(4.10)

$$N_H(t) = N_1(0)(1 - e^{-k_1 t})$$

(4.11)

Typically the total population in the model is normalized and hence the initial condition is set to $N_1(0) = 1$. Both states thus have a time dependent contribution to the measured transient spectra $\Delta \alpha_{\text{iso}}(\nu, t)$ according to,

$$\Delta \alpha_{\text{iso}}(\nu, t) = \sum_{i=1}^{2} N_i(t)\sigma_i(\nu)$$

(4.12)

$$= N_1(t)\sigma_1(\nu) + N_H(t)\sigma_H(\nu)$$

(4.13)

where $\sigma_1(\nu)$ and $\sigma_H(\nu)$ represent the transient spectra associated with both states. The model is fit to the data by minimizing the following $\chi^2$ function by varying the rate of decay $k_1$,

$$\chi^2_{\text{iso}}(k) = \int \int dt \int d\nu \left( \frac{\Delta \alpha(\nu, t) - \sum_i N_i(t; k)\sigma_i(\nu)}{\epsilon_{\Delta \alpha}(\nu, t)} \right)^2$$

(4.14)
where $\epsilon_{\Delta\alpha}(\nu, t)$ represent the variances of the data points $\Delta\alpha(\nu, t)$ and $N_i(t; k)$ represent the population dynamics according to the model parameters $k$. The state spectra for a given set of population dynamics are obtained by calculating the minimum of $\chi^2_{iso}(k)$ with respect to the spectral amplitudes $\sigma_i(\nu_j)$ of every measured frequency $\nu_j$,

$$\frac{d}{d\sigma_i(\nu_j)} \int dt \left( \frac{\Delta\alpha(\nu_j, t) - \sum_i N_i(t; k)\sigma_i(\nu_j)}{\epsilon_{\Delta\alpha}(\nu_j, t)} \right)^2 = 0$$ (4.15)

The spectral contribution of heating the sample is isotropic and hence equal in both the parallel and perpendicular probed signal. To obtain the contribution to both signals that is solely from the OD-stretch excitation we subtract the contribution of the thermalization,

$$\Delta\alpha_{\parallel}(\nu, t) = \Delta\alpha_{\parallel}(\nu, t) - N_H(t)\sigma_H(\nu)$$ (4.16)

$$\Delta\alpha_{\perp}(\nu, t) = \Delta\alpha_{\perp}(\nu, t) - N_H(t)\sigma_H(\nu)$$ (4.17)

These pure signals can be used to calculate the anisotropy parameter $R(\nu, t)$ following Eq. (4.3),

$$R(\nu, t) = \frac{\Delta\alpha_{\parallel}(\nu, t) - \Delta\alpha_{\perp}(\nu, t)}{\Delta\alpha_{\parallel}(\nu, t) + 2\Delta\alpha_{\perp}(\nu, t)}$$ (4.18)

### 4.2.2 Delayed Heat

It has been demonstrated that the simple model of the previous section does not describe very well the isotropic transient spectra measured on the OD stretch in a few percent HDO in H$_2$O [22]. A much better description is obtained when the vibrationally excited state is allowed to decay to an intermediate state first [22]. The population in the intermediate state subsequently decays into the thermalized ground state. Effectively this leads to a delayed ingrowth of the heat. Such a delay is supported by measurements on the vibrational decay of the OH-stretch vibration and subsequent thermalization in pure liquid water [23]. While the vibrational lifetime of the OH-stretch in pure water is only $\sim 200$ fs, the thermal endlevel was found to grow in with a timeconstant of at least $\sim 600$ fs. In the formalism described in the previous section the rate equations for such a model look like,

$$\frac{d}{dt} N(t) = \begin{pmatrix} -k_1 & 0 & 0 \\ +k_1 & -k_{int} & 0 \\ 0 & +k_{int} & 0 \end{pmatrix} \begin{pmatrix} N_1(t) \\ N_{int}(t) \\ N_H(t) \end{pmatrix}$$ (4.19)

where $N_{int}(t)$ is the population dynamics and $k_{int}$ the decay rate of the intermediate state. This delayed thermal response can be due to the transient population of a particular non-thermal state in the vibrational relaxation of the OD stretch vibration. Such a non-thermal state may involve the HOD bending mode and/or the librational modes. However, the intermediate state was
observed to have no spectral signature [22], which means that its absorption spectrum is identical to that of the OD stretch vibration before the excitation by the pump. Therefore, the delayed rise of the thermal response is likely not due to the transient excitation of a specific mode like the HOD bending vibration, because such an excitation would lead to an anharmonic frequency shift of the absorption spectrum of the OD stretch vibration. Instead, the delayed rise is probably rather due to the relatively slow adaptation of the coordinates of low-energy degrees of freedom (hydrogen-bond bend and stretch) to the higher energy content that results from the relaxation of the OD stretch vibration. The relaxation of the OD stretch vibration leads to a rapid increase of the energy content of the lower-energy degrees of freedom, and these coordinates need some time to evolve to the new equilibrium positions corresponding to this higher energy content.

4.3 Direct Probe of Heat Dynamics

For increasingly complicated systems, as also described in this thesis, it may become more difficult to accurately describe the data with a kinetic model. Until now we considered systems that were homogeneous in the sense that the excited oscillators were evenly distributed over the absorption band at time-zero and could be treated as behaving identical. Although this is most of the time an approximation, it often provides a good description of the data. Some systems, however, are strongly inhomogeneous and the approximation breaks down. The vibrational lifetime may be strongly frequency dependent or the
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Figure 4.3. (A) Transient spectra for different delay times probed around 2900 cm\(^{-1}\) after exciting the OD stretch vibration in a sample of 8% HDO:H\(_2\)O with a pump centered around 2650 cm\(^{-1}\). The bleach that grows in with increasing delay time is the thermal difference spectrum of the red shoulder of the OH stretch vibration. (B) The dynamics that resulted from a decomposition of the spectra shown in panel A.

excitation is inhomogeneous. The latter case may happen by using a pump-pulse with a narrow spectral width. As described in section 2.2, this leads to spectral diffusion and as a result the transient state spectrum $\sigma_1(\nu)$ in Eq. (4.12) may not be constant in time anymore.

A kinetic model to describe the isotropic transient absorption data becomes in such a case quickly too complicated to obtain reliable values for the fit parameters. The main problem in obtaining the dynamics of the heat contribution from our data is that the contributions of both the thermalized ground state and the excitation are overlapping. A solution is to obtain the dynamics of the thermal difference spectrum by an independent method. Fig. 4.2 shows that upon heating a sample containing 8% HDO:H\(_2\)O by a few degrees, virtually all modes in the linear spectrum of water from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) either shift or change in amplitude. We are thus able to measure the dynamics of the thermal difference spectrum by probing an entirely different part of the spectrum.

An ideal window of probing has a strong thermal response, a not too strong linear absorption, and is free from any response due to the direct vibrational excitation. The spectral area around the H\(_2\)O bending mode at 1600 cm\(^{-1}\) is meeting these criteria very well. Probing in this region is experimentally relatively involved since the absorption of water vapor in the air requires the setup to be tightly flushed with dry air. A good alternative is the large thermal response at the red shoulder of the OH-stretch vibration around 3000 cm\(^{-1}\). The only potential complication is a possible contribution of OH-oscillators that are anharmonically coupled to excited OD-oscillators in HDO molecules. This is not a major problem, as will be shown later.
Fig. 4.3A shows the results of a measurement for which the OD stretch vibration is excited by using pump pulses of which the spectrum was centered around 2650 cm\(^{-1}\) and the probe around 2900 cm\(^{-1}\). For very short delay times there is an induced absorption at low frequencies. This feature quickly decays, after which a bleach at higher frequencies grows in at a much slower rate. We recognize the shape of the bleach as the thermal difference spectrum in this spectral region in Fig. 4.2. The spectral response at short delay times probably arises from the \(\nu = 1 \rightarrow 2\) transition of OH oscillators that are excited in the very far red wing of the OH stretch absorption band. As was shown in section 2.2, an excitation pulse of which the spectrum is very red-shifted from the center of the OH stretch band can still excite OH oscillators.

The OH stretch excited state spectrum \(\sigma_{OH}(\nu)\) and thermal difference spectrum \(\sigma_H(\nu)\) have quite a different shape. For this reason it is possible to disentangle the population dynamics of both states by doing a spectral decomposition of the transient spectra obtained at all delay times. To do this decomposition, we use for \(\sigma_H(\nu)\) the transient spectrum at long delay times (100 ps) and for \(\sigma_{OH}(\nu)\) the transient spectrum at 200 fs. At this delay time the pump and probe pulse are not overlapping anymore and the contribution of the coherent artefact becomes negligible. The results of such a spectral decomposition is shown in Fig. 4.3B. It should be noted that for the thermalization dynamics nearly identical results are obtained in case a delay trace of the raw data is taken at \(\nu \approx 3000\) cm\(^{-1}\) for which the OH stretch contribution is very small.

Fig. 4.4 shows the thermalization dynamics that were obtained for a solution of 8% HDO:D\(_2\)O. For the different curves the center frequency of the pump spectrum (FWHM of 60 cm\(^{-1}\)) was shifted from 2400 cm\(^{-1}\) to 2700 cm\(^{-1}\). The dynamics clearly depend on the excitation spectrum, with a faster initial rise in case the OD stretch band is not pumped in the center of its absorption
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A B

Figure 4.5. Temperature dependence of the thermalization dynamics after excitation at 2650 cm\(^{-1}\) in (A) neat 8\% HDO:H\(_2\)O and (B) a solution of 6 mol/kg TMU.

Figure 4.5B shows the thermalization dynamics in 8\% HDO:D\(_2\)O for several sample temperatures. The OD stretch band is in this case excited homogeneously by a spectrally broad pump (FWHM of 150 cm\(^{-1}\)). For increasing temperatures the dynamics become faster, which is a result of the faster decay time \(T_1\) of the OD stretch vibration. It should be noted here that the rate of thermalization is not exactly proportional \(T_1\), due to the delay in thermalization that was discussed in section 4.2.2 of this chapter.

Finally, by the use of kinetic models it has been shown that the thermalization dynamics in water becomes slower upon the addition of the small amphiphilic molecule tetramethylurea TMU [24]. We therefore compare the thermalization dynamics of a concentrated solution of TMU in water (6 mol/kg) for different temperatures in Fig. 4.5B. It is evident that the dynamics is slower compared to neat 8\% HDO:H\(_2\)O. However, the dynamics at short delay times does not seem to show the characteristics of a long delay of the thermalization after vibrational decay. Fig. 4.6 shows a comparison of the thermalization dynamics for both neat isotopically diluted water and a solution of 6 mol/kg TMU obtained by the two methods described in this chapter: Direct measurement by probing the red shoulder of the OH stretch band and by fitting a kinetic model to the data that includes an intermediate state accounting for the delayed thermalization. Both methods yield thermalization dynamics that are similar at longer delay times, but have a quite different character at short delays. The kinetic model thus seems to underestimate the contribution of the thermal difference.
Figure 4.6. Comparison of the thermalization dynamics in neat 8% HDO:H₂O and 6 mol/kg TMU as obtained from a fit of a kinetic model to the isotropic transient spectra (lines) and from a spectral decomposition as described in this section (symbols). For short delay times there is a considerable deviation.

spectrum in the first few picoseconds. How much influence the underestimation of the thermal contribution has on the calculation of the anisotropy parameter depends on the relative size of the excited state with respect to the thermal difference spectrum. At short delay times, the excited state contribution is still relatively large and an incorrect subtraction of the thermal contribution does not affect the anisotropy as calculated by Eq. (4.18) much.

The thermalization dynamics obtained by the methods described above can be used to subtract the heat component from a measurement on the excitation (eg. the OD stretch vibration) for which an identical pump is used. To this end, a multi-exponential function is fitted to the thermalization curve to capture the dynamics $N_H(t)$. No assumptions are made on the fit based on physical interpretation, since it merely serves the purpose of describing the measured dynamics. Typically, a function of three exponentials were found to accurately describe the curves. For the thermal difference spectrum $\sigma_H(\nu)$, the transient spectrum at long delay time is used of the dataset of which the thermal contributions is to be subtracted. For improved signal-to-noise, typically the average transient spectrum of at least three delay times between 70 and 100 ps were used. Having obtained a description of $N_H(t)$ and $\sigma_H(\nu)$, finally Eq. (4.16) is used to obtain the heat subtracted transient spectra.

4.3.1 Multiple Species

In section 4.2.1 we implicitly assumed in the kinetic model that all OD-oscillators decay with equal decay rate $k_1$. For neat isotopically diluted water this is shown to provide an accurate description of the data [22], as long
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the spectrum of the pump pulse is broad enough to overlap with the whole OD-stretch absorption band. This condition is required since spectral diffusion (see section 2.2) is for most systems studied happening at a similar timescales as the vibrational relaxation. In some more complicated solutions there may be different species of oscillators $i$ that have different excited state transient spectra $\sigma_i(\nu)$, population dynamics $N_i(t)$ and reorientation dynamics $R_i(\nu, t)$. Information on $N_i(t)$ and $\sigma_i(\nu)$ can be obtained from a fit of a kinetic model to the isotropic transient spectra, which are free from any contribution of the reorientation dynamics. In order to do so, we need to extend the model described in Eq. (4.19) with an additional excited state to incorporate the excited state response of the second species. The rate equations that follow are written as,

$$ \frac{d}{dt} \mathbf{N}(t) = \begin{pmatrix} -k_1 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 \\ +k_1 & +k_2 & -k_{int} & 0 \\ 0 & 0 & +k_{int} & 0 \end{pmatrix} \begin{pmatrix} N_1(t) \\ N_2(t) \\ N_{int}(t) \\ N_H(t) \end{pmatrix}. \quad (4.20) $$

where $k_1$ and $k_2$ are the vibrational decay rates of species 1 and 2, respectively. The initial conditions are $(N_1(0), N_2(0), N_{int}(0), N_H(0)) = (1-p, p, 0, 0)$, where $p$ is a free fit parameter and denotes the relative initial population in the second state. $p$ must assume values between 0 and 1 to assure the total population in the model is normalized to one. In this model it is assumed that both excited states decay to the same intermediate state, which subsequently decays to the thermalized ground state.

The parallel and perpendicular signals can then in analogy to Eq. (4.4) and Eq. (4.12) be written as the sum of both contributions,

$$ \Delta \alpha_{\parallel}(\nu, t) = [1 + 2R_1(t)]N_1(t)\sigma_1(\nu) + [1 + 2R_2(t)]N_2(t)\sigma_2(\nu) + N_H(t)\sigma_H(\nu) \quad (4.21) $$

$$ \Delta \alpha_{\perp}(\nu, t) = [1 - R_1(t)]N_1(t)\sigma_1(\nu) + [1 - R_2(t)]N_2(t)\sigma_2(\nu) + N_H(t)\sigma_H(\nu) \quad (4.22) $$

Assuming that we have subtracted the heat contribution, the anisotropy that would be obtained using Eq. (4.3) yields,

$$ R(\nu, t) = \frac{2}{\sum_{i=1}^{2} R_i(t)N_i(t)\sigma_i(\nu)} \sum_{i=1}^{2} N_i(t)\sigma_i(\nu) \quad (4.23) $$

This expression poses a problem. If one of the species has slower population dynamics, $R(\nu, t)$ will represent a weighted sum of the reorientation dynamics of both species with weighting factors $N_i(t)$ that differ for every pump-probe delay time. It is much more instructive if both $R_1(t)$ and $R_2(t)$ could be resolved separately, which is in fact possible in case also the spectral response of both
species (ie. $\sigma_1(\nu)$ and $\sigma_2(\nu)$) is different. In such a case it is more convenient to consider the not-normalized difference between the parallel and perpendicular signals $D(\nu, t)$ given by,

$$D(\nu, t) = \frac{\Delta \alpha_\| (\nu, t) - \Delta \alpha_\perp (\nu, t)}{3} = \sum_{i=1}^{n} R_i(t) N_i(t) \sigma_i(\nu)$$

With the knowledge of the population dynamics and spectral responses of both species from the isotropic fit, we can resolve the reorientation dynamics by performing a spectral decomposition analogous to Eq. (4.15),

$$\frac{d}{dR_i(t_j)} \int d\nu \left( \frac{D(\nu, t_j) - \sum_i R_i(t_j) N_i(t) \sigma_i(\nu)}{\epsilon_{D}(\nu, t_j)} \right)^2 = 0$$

Alternatively, the heat subtracted parallel and perpendicular transient spectra can be decomposed directly to obtain the dynamical components from both species,

$$\frac{d}{dA_i(t_j)} \int d\nu \left( \frac{\Delta \alpha_\| (\nu, t_j) - \sum_i A_i(t_j) \sigma_i(\nu)}{\epsilon_{\Delta \alpha_\|}(\nu, t_j)} \right)^2 = 0$$

and similar for the perpendicular transient spectra. $A_{i,\|}(t)$ and $A_{i,\perp}(t)$ contain all the dynamical behavior of species $i$,

$$A_{i,\|}(t) = [1 + 2R_i(t)]N_i(t)$$

$$A_{i,\perp}(t) = [1 - R_i(t)]N_i(t)$$

The anisotropy of both species is thus evaluated by,

$$R_i(t) = \frac{A_{i,\|}(t) - A_{i,\perp}(t)}{A_{i,\|}(t) + 2A_{i,\perp}(t)}$$

The multiple-species model can in principle be extended to incorporate any number of species. Whether such an extension does not lead to an over-determination of the data depends on how well separated the species are spectrally, how different the vibrational lifetimes are and the quality of the data.

### 4.4 Anisotropy

#### 4.4.1 Modeling of Anisotropy Dynamics

In the previous section we described how we obtain the anisotropy dynamics $R(\nu, t)$ from a polarization resolved measurement. In the following discussion we assume that $R(\nu, t)$ is the anisotropy of the transition dipole moment of the OD or OH stretch vibration of water, since this is most relevant for this thesis. It can be shown that the anisotropy is proportional to the second order orientational correlation function of the transition dipole of vibration $\mu_s$ [25],

$$R(t) = \frac{2}{5} \langle P_2(\mu_s(0) \cdot \mu_s(t)) \rangle$$
where $P_2$ is the second order Legendre polynome. Immediately after excitation, the anisotropy thus has a maximum value of 0.4. Its subsequent decay depends on the chemical environment and is primarily governed by four different processes. First, librational motions make the transition dipole wobble over a cone. The librational decay process takes place on a very fast timescale ($\sim 100 \text{ fs}$). Since the angle of the cone is often limited by the chemical environment (e.g., the hydrogen-bond of the OD/OH oscillator), this reorientation process does not lead to a complete decay of the anisotropy. Secondly, an OD/OH oscillator may jump to a new hydrogen-bonding partner. Although the actual jump takes only a few hundred femtoseconds, the rate of jumps is on the order of $\sim 0.5 \text{ ps}^{-1}$. Such a jump is found to involve a rotation of the transition dipole moment over a large angle ($\sim 60^\circ$) [2], and thus results in a complete loss of orientation. The third process of anisotropy decay is frame rotation. A transition dipole moment that remains hydrogen-bonded to the same partner will on average point along the oxygen-oxygen coordinate. As a result of the dynamic hydrogen-bond network surrounding it, this coordinate also experiences a slow reorientation. Finally, $R(\nu, t)$ can decay due to the resonant transfer of the vibrational excitation from the initially excited mode to a neighboring oscillator. This is not a reorientation process, but the transition dipole moment of the accepting mode can be different from that of the donating mode. As a result, the orientational correlation decreases. The rate of transfer strongly depends on the distance between the donating and accepting modes and is extremely fast in pure liquid water ($< 100 \text{ fs}$), but can be neglected in solutions of sufficient isotopic dilution [26].

After a short equilibration time, all OD oscillators in a solution of 8% HDO in H$_2$O can be approximated as belonging to a single species due to fast spectral diffusion (see section 2.2). The anisotropy in such a solution therefore decays mono-exponentially after a few hundred picoseconds. In previous sections we also considered systems in which two different species can be identified. In particular, it was assumed that the species have different population dynamics, spectral response and reorientation dynamics. In a solution containing multiple species, there are in fact a number of relevant situations that may occur, for some of which a spectral decomposition as described above is not possible. First, it can happen that although the population dynamics are different for both species, their spectral response may overlap. If the species with slower vibrational relaxation also has slower reorientation dynamics, the total anisotropy can show a recurrence behavior. This was observed for water in reverse micelles, for which the anisotropy was found to increase again after an initial decay [27]. Secondly, both the spectral response and the population dynamics can be very similar for both species. The bimodal behavior will then only become apparent in the anisotropy dynamics and $R(t)$ will in such case not be a mono-exponential function anymore. This has been observed for solutions of amphiphiles in water [28] (see also chapter 7 and chapter 10). It was typically found that the anisotropy could be modeled with a separate exponent for both species, yielding separate reorientation times and amplitudes. Finally, the spectral responses
of the species can be different, but their vibrational lifetimes are the same. In this case a spectral decomposition is still possible if the excited state spectra are known, but it is not possible to obtain those spectra from the isotropic data using a kinetic model as described in section 4.3.1. An indication of this situation is when the anisotropy has a frequency dependence even if the isotropic relaxation has not.

4.4.2 Self-Consistent Fit

It may happen that in a system with two species the spectral separation between the associated transient state spectra \( \sigma_i(\nu) \) is small. A decomposition of the anisotropy according to the procedure described in the section 4.3.1 may in such a case be prone to cross-talk (assignment of spectral amplitude to the incorrect state). One solution to this problem is found in fitting simultaneously a kinetic model for vibrational decay to the isotropic data and functional forms of the reorientation dynamics to the heat corrected anisotropy data. Instead of minimizing only Eq. (4.14) for a two-species model, we thus need to minimize at the same time an error function that incorporates a model for the reorientation dynamics. To that end we consider again the difference \( D(\nu, t) \) between the measured parallel and perpendicular transient spectra, which is expressed in terms of our state model as,

\[
D(\nu, t) = \sum_{i=1}^{2} R_i(t; p) N_i(t; k) \sigma_i(\nu) \tag{4.31}
\]

where both the third and fourth term from the original equation (Eq. (4.24)) vanish as a result of the assumptions that \( \sigma_{int}(\nu) = 0 \) and that the thermal ground state is isotropic. \( R_1(t; p) \) and \( R_2(t; p) \) are the functional forms of the reorientation dynamics of OD-oscillators of the first or second species, respectively, for a set of free fit parameters \( p \). The population dynamics \( N_i(t) \) and state spectra \( \sigma_i(\nu) \) are obtained from the results of Eq. (4.14) and Eq. (4.15).

We can thus extend the \( \chi^2 \) function of Eq. (4.14) by,

\[
\chi_{ani}^2(p) = \int \int dtd\nu \left( \frac{D(\nu, t) - \sum_i R_i(t; p) N_i(t; k) \sigma_i(\nu)}{\epsilon_D(\nu, t)} \right)^2 \tag{4.32}
\]

where \( \epsilon_D(\nu, t) \) are the variances of \( D(\nu, t) \). The additional restriction on the fit by Eq. (4.32) comes from the choice of the functional forms of the anisotropy functions \( R_i(t; p) \). Datapoints obtained by the conventional calculation of the anisotropy dynamics, as described earlier in this chapter, are frequently fitted with exponential functions [22, 28, 29, 30]. A logical choice is thus to have \( R_i(t; p) \) decay exponentially. Depending on the system studied and previous observations, more than one exponential component can be included. A self-consistent fit with such a choice of \( R_i(t; p) \) gives a large penalty to \( \chi^2 \) for parameters \( p \) that lead to anisotropy dynamics that increase with time or that do not decay to zero. The advantage over a
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conventional fit after which a similar functional form is fitted to \( R_i(t) \) is thus that unphysical description are excluded from the solutions.

This approach does not resolve the data points of the anisotropy of both species. To obtain the data points \( R^D_i(t) \) of the anisotropy decay of a single species \( i \), the fitted contribution of the other species is subtracted from the raw data according to,

\[
R^D_i(t) = \frac{D(\nu, t) - [R(t)N(t)\sigma(\nu)]_{i=2}}{[N(t)\sigma(\nu)]_{i=1}}
\]  

(4.33)

This method strictly yields an overestimation of systematic errors in the data, since the same error ends up in both collection of anisotropy points \( R^D_1(t) \) and \( R^D_2(t) \).

4.4.3 Anisotropy and Exchange

In section 4.3.1 we considered the possibility of having multiple species of OD oscillators with different spectral response and dynamics. An example of such systems are aqueous salt solutions, in which OD oscillators hydrogen-bonded to anions and those hydrogen-bonded to other water molecules can be treated as two different species. However, the two species are both OD stretch modes and are thus intrinsically not different. They reflect different chemical environments and it is expected that the two species exchange population as a result of dynamics in the liquid. This chemical exchange occurs by a large rotational motion in or out the anion hydration shell and is accompanied with a large loss in orientation. This mechanism is discussed in chapter 8 and in this section we elaborate on the effects of such jumps on the observed anisotropy decay of both species.

The kinetic model from Eq. (4.20) is extended to incorporate this exchange. The exchange model is described by the rate equations,

\[
\frac{d}{dt} \begin{pmatrix} N_1(t) \\ N_2(t) \\ N_{int}(t) \\ N_H(t) \end{pmatrix} = \begin{pmatrix} -k_1 - k_{1\to 2} & +k_{2\to 1} & 0 & 0 \\ +k_{1\to 2} & -k_2 - k_{2\to 1} & 0 & 0 \\ +k_1 & +k_2 & -k_{int} & 0 \\ 0 & 0 & +k_{int} & 0 \end{pmatrix} \begin{pmatrix} N_1(t) \\ N_2(t) \\ N_{int}(t) \\ N_H(t) \end{pmatrix}.
\]  

(4.34)

where \( k_1 \) and \( k_2 \) are again the vibrational decay rates of species 1 and 2, respectively, and \( k_{1\to 2} \) and \( k_{2\to 1} \) are the rates of exchange between the species. The initial conditions are defined identically to the model described in Eq. (4.20). A graphical representation of this model is shown in Fig. 4.7.

In the coming discussion we denote an OD oscillator that at the time of excitation resides in chemical environment 1 or 2 as \( 1 \) and \( 2 \), respectively. At any given time after excitation the OD oscillator may either still be in the same chemical environment, denoted by \( \to 1 \) and \( \to 2 \), or may have exchanged to the other chemical environment, denoted by \( 1\to 1 \) and \( 2\to 1 \). We can of course consider even higher order processes, like \( 1\to 2 \) and \( 2\to 1 \), but we will not do this for a number of reasons. First, in case the vibrational lifetime is shorter than the exchange
time, the probability of higher order exchange processes decreases quickly. In the studied system this is indeed the case. Secondly, a quick back-exchange is likely accompanied with a recovery of the orientation of the OD oscillator. Further decay of the orientation will in such a case thus be independent on the temporary excursion. For simplicity we assume that an OD oscillator that exchanges from one chemical environment to the other loses its orientation completely. It can be shown that this is the case for a jump over an angle of 54.7°, which is in fact very close to the physical situation when considering exchange in and out of the anion hydration shell (see chapter 8).

The effect of exchange events on the reorientation dynamics as obtained from the analysis elaborated on in section 4.3.1 can now be described as follows. Immediately after excitation, the transient state spectrum \( \sigma_1(\nu) \) of OD oscillators in chemical environment 1 represents the response of the collection of all 1. Therefore, the resolved anisotropy \( R_1(\nu, 0) \) reflects the orientation of all 1. As time evolves, an increasing number of oscillators become \( \gamma_2 \). Since those oscillators now contribute to the spectral response of \( \sigma_2(\nu) \) (they increase \( N_2(t) \)), their orientation is not contributing to \( R_1(\nu, t) \) anymore. However, at the time of excitation there will be 2 that at later times become \( \gamma_1 \). Since those oscillators now have their spectral response at \( \sigma_1(\nu) \) (increase of \( N_1(t) \)), they will contribute to \( R_1(\nu, t) \). In the process of exchange they lost all their orientation and therefore they effectively lower \( R_1(\nu, t) \). This process can be formalized by treating the \( \gamma_1, \gamma_2, \gamma_2 \) and \( \gamma_1 \) as four separate species. Let us assume that the thermal contribution is already subtracted from the data obtained for such a system. The rate equations describing the population dynamics of the species of Eq. (4.20) can then be rewritten as,

\[
\begin{pmatrix}
-k_1 & \quad 0 & \quad 0 & \quad 0 \\
+k_1 & -k_1 & \quad 0 & \quad 0 \\
0 & \quad 0 & -k_2 & -k_2 \\
0 & \quad 0 & +k_2 & +k_2 \\
\end{pmatrix}
\begin{pmatrix}
N_{1\gamma_1}(t) \\
N_{1\gamma_2}(t) \\
N_{2\gamma_1}(t) \\
N_{2\gamma_2}(t) \\
\end{pmatrix}.
\]

(4.35)

where the dynamics of \( N_{int}(t) \) and \( N_H(t) \) are omitted. The total isotropic
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Transient spectra are then written as,

\[ \Delta \alpha(\nu, t) = \sum_{i,j=1}^{2} N_{i\gamma j}(t)\sigma_j(\nu) \] (4.36)

and in a similar fashion the difference signal \( D(\nu, t) \) as,

\[ D(\nu, t) = \sum_{i,j=1}^{2} R_{i\gamma j}(t)N_{i\gamma j}(t)\sigma_j(\nu) \] (4.37)

We assumed that orientation is completely lost in a jump and using the previous two expressions and the definition of the anisotropy we can write,

\[ R_{1\gamma 1}(t) = \sum_{i=1}^{2} \frac{N_{i\gamma 1}(t)R_1(t)}{N_{i\gamma 1}(t)} \] (4.38)

where \( R_1(t) \) is the anisotropy that resulted from the spectral decomposition. All the rates needed to calculate the dynamics from Eq. (4.35) were already determined from the isotropic fit, and the intrinsic anisotropy dynamics \( R_{1\gamma 1}(t) \) and \( R_{2\gamma 2}(t) \) can thus readily be evaluated.

In case the state spectra \( \sigma_1(\nu) \) en \( \sigma_2(\nu) \) are of very similar shape and strongly overlapping, the exchange rates \( k_{12} \) and \( k_{21} \) are hard to obtain from a free fit of the kinetic model to the isotropic data. However, the anisotropy data provides additional information that can aid in determining these rates. To this end, we use the fact that in case the pump spectrum is tuned over the absorption spectrum, different ratio’s of the initial \( N_{1\gamma 1}(0) \) and \( N_{2\gamma 2}(0) \) populations are excited. In case the pump has a stronger overlap with \( \sigma_1(\nu) \) than with \( \sigma_2(\nu) \), the response measured for the second species will represent more \( 1\gamma 2 \) relative to \( 2\gamma 2 \) and vice versa. As a result, the anisotropy dynamics as obtained from a spectral decomposition \( R_{1i}(t) \) are different for various spectral positions of the pump. The intrinsic anisotropy dynamics \( R_{1\gamma 1}(t) \) and \( R_{2\gamma 2}(t) \) are by definition invariant under the change of the pump spectrum and the relation between them was given in Eq. (4.38). The exchange parameters \( k_{12} \) and \( k_{21} \) can therefore be constraint in a fit that includes data obtained with different pump frequencies. The additional weight \( \chi_{ex}^2 \) to the \( \chi^2 \) function of the isotropic fit is provided by the requirement of the invariance of the intrinsic anisotropy dynamics. For \( n \) datasets with different center frequencies of the pump spectrum \( \chi_{ex}^2 \) can be written as,

\[ \chi_{ex}^2 = \frac{1}{2} \int dt \sum_{i \neq j}^{n} \frac{(R_{i\gamma 1}(t; k) - R_{j\gamma 1}(t; k))}{\epsilon_{Ri}(t) + \epsilon_{Rj}(t)} \] (4.39)

and similar for the intrinsic \( R_{2\gamma 2}(t) \) anisotropy. Here is \( \epsilon_{Ri}(t) \) the variance of the intrinsic anisotropy of dataset \( i \) and \( k \) the parameters of the kinetic model including the exchange parameters.
4.5 Dielectric Relaxation

In this section we describe how the complex permittivity spectra obtained by either THz or GHz dielectric relaxation spectroscopy (DRS) are analyzed. To this end, we first elaborate a bit on the molecular origin of the permittivity spectrum of pure liquid water.

DRS measures the correlation function of the macroscopic polarization of the sample as a response to an externally applied electric field. Generally, an applied electric field partially aligns the permanent dipoles of the water molecules against the thermal fluctuations. The resulting induced macroscopic polarization is proportional to the applied field,

\[ P = \varepsilon_0 (\varepsilon(\nu) - 1)E \]  

(4.40)

where \( \varepsilon_0 \) is the permittivity in vacuum and \( \varepsilon(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) \) is the frequency-dependent complex permittivity. At frequencies lower than the characteristic timescale at which reorientation processes of water molecules take place, the dipoles can follow the electric field oscillations and the built-up polarization is only limited by the thermal fluctuations of the dipole orientations. At high frequencies, the dipoles fail to follow the oscillations of the applied electric field. The transition from the low-frequency to the high-frequency domain is marked by a strong response in the imaginary dielectric function due to a phase lag in the reorienting dipoles relative to the externally applied oscillating electric field (the out-of-phase response).

Fig. 4.8 shows the real and imaginary part of the complex permittivity for pure water. For single-component molecular liquids, for which the polarization decays with a single-exponential functional shape, the measured permittivity
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can often be described by a Debye relaxation model,
\[ \varepsilon(\nu) - \varepsilon_\infty = \frac{S}{1 + 2\pi \nu \tau}, \]  

where \( \varepsilon_\infty \) is the permittivity at infinite frequency, \( \tau \) is the characteristic relaxation time and \( S \) the amplitude of the Debye mode. The maximum of the out-of-phase response in pure water is found at 20 GHz, corresponding to a timescale \( \tau_{\text{bulk}} \) of \( \approx 8.4 \) ps [31]. This time constant is often referred to as the Debye relaxation time and has been assigned to the timescale of the spontaneous restructuring of the hydrogen-bond network. At higher frequencies (\( \sim 0.9 \) THz, \( \tau_{\text{fast}} \approx 350 \) fs), a contribution with a much lower amplitude has been found. This additional mode has been assigned either to quick jumps of undercoordinated water [2, 32], interaction-induced components in the water relaxation mechanism [33, 34] or a small angular rotation preceding a large angle jump [8].

The dielectric function \( \varepsilon(\nu) \) of water is thus modeled as a sum of two Debye modes with time constants \( \tau_{\text{bulk}} \) and \( \tau_{\text{fast}} \),
\[ \varepsilon_{H_2O}(\nu) = \frac{S_{\text{bulk}}}{1 + 2\pi \nu \tau_{\text{bulk}}} + \frac{S_{\text{fast}}}{1 + 2\pi \nu \tau_{\text{fast}}} + \varepsilon_\infty, \]  

The fraction of water molecules that reorient with time constant \( \tau_n \) is proportional to the amplitude \( S_n \). For pure water \( S_{\text{bulk}} \approx 70 \) and \( S_{\text{fast}} \approx 2 \).

To compare the reorientation time obtained with dielectric relaxation spectroscopy with the reorientation time obtained with fs-IR pump-probe spectroscopy, it should be realized that they differ by a linear conversion factor. The reason for this difference is that both experiments measure a different observable. GHz-DRS measures the first order correlation function \( C_1(t) \). The decay time \( \tau_{\text{bulk}} \) of \( C_1(t) \) thus represents the collective reorientation of all water molecules. The fs-IR experiment measures the second order correlation function \( C_2(t) \) of the transition dipole moments of the OD stretch vibration. The decay time \( t_{\text{bulk}} \) of \( C_2(t) \) is a measure of the reorientation of single water molecules. Assuming a jump-reorientation model or diffusive reorientation model (small amplitude angular reorientations) yields an ratio \( \tau_{\text{bulk}}/t_{\text{bulk}} \) of the two time constants of 2.5 and 3, respectively. Dipole-dipole coupling between water molecules however leads to a further increase of \( \tau_{\text{bulk}} \). The ratio between the rotational correlation times of the two different experiments including dipole-dipole coupling was found to be 3.4, independent on the temperature [35].

For a mixture of different dipolar species that show distinct time constants, it can be assumed that each species is described with a separate Debye mode. The amplitude \( S \) of each relaxation mode is proportional to the corresponding concentration \( c \) of dipoles and their effective dipole strength \( \mu_{\text{eff}} \) through the Cavell equation [36],
\[ S = \frac{\varepsilon_s}{3(\varepsilon_s + 1) \left( \varepsilon_s + \frac{1}{3} \left( 1 - \varepsilon_s \right) \right)} \frac{N_A}{k_B T \varepsilon_0} \mu_{\text{eff}}^2 c, \]  

where \( \varepsilon_s \) is the static permittivity.
For electrolyte solutions the translation of the ions, as determined by the macroscopic conductivity $\sigma_c$, gives rise to an additional contribution $\kappa(\nu)$ to the imaginary part $\varepsilon''$ of the permittivity, given by,

$$
\kappa(\nu) = \frac{-i\sigma_c}{2\pi\nu\varepsilon_0}
$$

(4.44)

Due to its $\nu^{-1}$ dependence, this conductivity term becomes dominating for low frequencies. Typically, this contribution is subtracted from the data by assuming $\varepsilon'' = \kappa(\nu)$ for the low frequency domain [37, 19].

The addition of a solute often leads to a (concentration dependent) decrease of $\dot{\varepsilon}(\nu)$ (depolarization), as a result of three contributions. First, in a constant volume there is a decreased number of water molecules that contribute to the signal because of dilution when a solute is added. This effect is corrected for by calculating the water density in the solution from the solution density and water concentration. Secondly, the water molecules in the hydration shell of the solute molecules may have different reorientation dynamics. As a result they no longer contribute to the bulk water Debye mode but to a separate mode at different frequencies. In case of strongly hydrating cations, water molecules are bound so strongly that their contribution to $\dot{\varepsilon}(\nu)$ is shifted out of the measurement window [38]. Finally there is the effect of kinetic depolarization that results from the movement of charges in an electric field. This depolarization component $\Delta S_{kd}(c)$ is proportional to the macroscopic conductivity and given by [39, 38, 37],

$$
\Delta S_{kd}(c) = -\frac{2}{3}\tau_D\sigma_c(c) \cdot \frac{\varepsilon_s(0) - \varepsilon_\infty(c)}{\varepsilon_s(0)\varepsilon_0}
$$

(4.45)

where $\varepsilon_s(0)$ is the static permittivity of pure water and $\varepsilon_\infty(c)$ the permittivity at infinite frequency for a solution of solute concentration $c$.

It should finally be noted that the THz-DRS experiment described in chapter 3 probes at frequencies between 0.4 and 1.2 THz and is not very sensitive to the frequency dependence of the dielectric relaxation modes that peak at much lower frequencies. The frequency window of the generated THz pulses does not reach down to the maximum of the main Debye response of water at 20 GHz, but the high frequency wing of this response extends to THz frequencies. The depolarization of the main Debye mode of water can therefore be measured by THz-DR. Conversely, the GHz-DRS experiment measures in the range of 10 MHz to 70 GHz. The low amplitude high frequency mode at 0.9 THz in pure water can therefore be neglected in the analysis of the permittivity spectra measured in this range.