Ultrafast vibrational dynamics of water

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Citation for published version (APA):
Strong Feedback Effect in the Vibrational Relaxation of Liquid Water

We show the presence of a strong negative feedback effect in the vibrational relaxation of the O-H stretch vibrations of liquid H₂O. The vibrational relaxation gets strongly decelerated as a result of the thermalization process that follows the relaxation. We present a model for the vibrational relaxation of water that includes this feedback effect. With this model we obtain a consistent interpretation of the experimental results of the femtosecond mid-infrared pump-probe experiments, presented in Chapter 4, and mid-infrared pump anti-Stokes Raman probe experiments.
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7.1 Introduction

Many of the anomalous properties of liquid water (H$_2$O) result from its extremely high density of O–H groups and strong directional hydrogen-bonds. These high densities lead for instance to exceptionally rapid energy transfer and relaxation dynamics. As a result of the rapid resonant intermolecular (Förster) energy transfer, an excitation of the O–H stretch vibration gets rapidly delocalized over many water molecules [104].

The energy relaxation of the O–H stretch vibrations of liquid water is also very fast, as has been shown with femtosecond mid-infrared pump-probe spectroscopy [51, 52] in Chapters 4 and 5 and with mid-infrared pump anti-Stokes Raman probe experiments in Refs. [12, 69, 101]. In Chapters 4 and 5, the relaxation was observed to take place in two subsequent processes. In a first process with a time constant of $\sim$300 femtoseconds, the O–H stretch vibration transfers its energy to a particular combination of accepting modes. This combination of accepting modes also relaxes, leading to an equilibration of the energy over all degrees of freedom. This equilibration takes place with a time constant of $\sim$550 fs, which is very fast in comparison to other hydrogen-bonded liquids. The same process takes about 3 picoseconds for methanol and 8 picoseconds for ethanol, see Chapter 5. In the mid-infrared pump anti-Stokes Raman probe studies by the group of Dlott [69, 101] a different relaxation behavior is reported. In these studies, the excitation of the O–H stretch mode is observed to lead to a blue shift of the anti-Stokes Raman spectrum with a time constant of $\sim$400 fs, and a vibrational relaxation with a time constant of $\sim$700 fs, that depends on frequency [69, 101]. The observations of the mid-infrared pump anti-Stokes Raman probe studies clearly differ from what is observed in the femtosecond mid-infrared pump-probe experiments. So far these differences are not understood.

An important consequence of the delocalized character of the O–H stretch vibrations in water is that the relaxation of an excited O–H stretch vibration will affect the relaxation of other still excited O–H stretch vibrations. For pure liquid bromoform (CHBr$_3$), a positive feedback effect was observed for the relaxation of the C–H stretch vibration, i.e. the relaxation was observed to get accelerated with an increasing occupation of the accepting modes [22]. For water a similar feedback effect is to be expected: the vibrational relaxation and thermalization processes will lead to the excitation of modes that affect the rates of these processes. This means that the relaxation dynamics of water will be essentially different from those of an electronically excited dye molecule in dilute solution, or even of the excited O–H stretch vibration of an HDO molecule in dilute solution in D$_2$O.

In this Chapter, we present a model that provides a complete picture of the vibrational dynamics of the O–H stretch modes of liquid water including the feedback effect on the vibrational relaxation. We will show that this model allows for a consistent description of all the experimental observations of recent femtosecond mid-infrared pump-probe studies and mid-infrared pump anti-Stokes Raman probe studies of the
vibrational dynamics of liquid water.

7.2 Model for the vibrational relaxation of liquid H$_2$O

Following the results of Chapters 4 and 5, the vibrational relaxation of pure liquid H$_2$O occurs in two subsequent relaxation processes. In the first process the population $n_1$ of the excited $v = 1$ state of the O-H stretch vibration is transferred with time constant $T_1$ to an intermediate state. In the second process, the population $n_0^*$ of this state relaxes with time constant $\tau_{eq}$, leading to an increase in temperature that can change the vibrational lifetime $T_1$ of the first process. In view of the above, the vibrational excitation and relaxation of water can be described with the following four coupled equations:

$$\frac{dn_0}{dt} = -I_p(t)\sigma_{0\rightarrow1}(\omega, T)n_0 + \frac{n_0^*}{\tau_{eq}}, \quad (7.1)$$

$$\frac{dn_1}{dt} = I_p(t)\sigma_{0\rightarrow1}(\omega, T)n_0 - \frac{n_1}{T_1(T)}, \quad (7.2)$$

$$\frac{dn_0^*}{dt} = \frac{n_1}{T_1(T)} - \frac{n_0^*}{\tau_{eq}}, \quad (7.3)$$

$$\frac{dT}{dt} = \frac{bn_0^*}{\tau_{eq}}, \quad (7.4)$$

with $n_0$ the population of the $v = 0$ (ground) state, $I_p(t)$ the intensity profile of the pump pulse, $T$ the temperature, $\sigma_{0\rightarrow1}(\omega, T)$ the infrared cross-section depending on frequency $\omega$ and temperature $T$, and $b$ a parameter relating the relaxed population $n_0^*$ to a temperature increase. The cross-section $\sigma_{0\rightarrow1}(\omega, T)$ is obtained from an interpolation of the infrared absorption spectra at 25°C and 85°C that are shown in Fig. 7.1a.

The O–H stretch vibrations of liquid H$_2$O show an extremely rapid spectral diffusion. This diffusion is even faster than that of a dilute solution of HDO in D$_2$O, because for H$_2$O the spectral diffusion results from both the hydrogen-bond dynamics and the rapid intermolecular (Förster) energy transfer. This latter transfer takes place with a time constant <100 fs [104]. As a result of the rapid spectral diffusion, excitation of the O–H stretch absorption band with a narrow-band pump pulse does not lead to the formation of a spectral hole [101]. In fact, already at short delays after the excitation, the observed spectral response is very similar to the linear spectrum, and shows very little dependence on the pump frequency [12, 69, 101]. The vibrational dynamics also shows little dependence on the pump frequency: very similar time constants for $T_1$ and $\tau_{eq}$ are observed when the O–H stretch vibration is excited at 3250 cm$^{-1}$ (Chapter 4) and when it is excited at 3550 cm$^{-1}$ (Chapter 6).
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Figure 7.1. Infrared absorption spectra of liquid water at 25 and 85 °C (a), and Raman (Stokes) spectra of liquid water at 30 and 90 °C (b).
Model for the vibrational relaxation of liquid $\text{H}_2\text{O}$

Because of the rapid spectral equilibration of liquid $\text{H}_2\text{O}$, the experimentally observed $T_1$ represents an average over the spectral distribution of O–H oscillators. The experimentally observed relaxation rate $T_1^{-1}(T)$ can thus be approximated by integrating over the spectral distribution $S(\omega, T)$ of O–H oscillators multiplied by the frequency-dependent relaxation rate $T_1^{-1}(\omega)$ that would be observed if there were no spectral diffusion:

$$\frac{1}{T_1(T)} = \int d\omega S(\omega, T)T_1^{-1}(\omega)/\int d\omega S(\omega, T), \quad (7.5)$$

The experimentally observed value of $T_1$ will depend on temperature $T$ because the spectral distribution $S(\omega, T)$ depends on temperature. In the calculations we approximate the temperature-dependent spectral distribution with the cw Raman spectrum $R(\omega, T)$. A similar temperature dependence of $T_1$ is obtained when the calculations are performed when the temperature-dependent infrared absorption spectrum $\sigma(\omega, T)$ is used to describe the spectral distribution.

The use of Equation 7.5 to approximate the experimentally observed $T_1$ does not critically depend on the spectral diffusion time constant. The equation can be used provided that the spectral diffusion time is shorter than the durations of the pulses used in the experiment. There is no lower limit to the spectral diffusion time constant: Equation 7.5 can be used even if the spectral diffusion is so fast that the spectrum would be significantly homogeneously broadened.

From measurements on many hydrogen bonded O–H groups the following empirical relation was derived [59]:

$$T_1(\omega) = a(\omega - \omega_{\text{OH},g})^{-1.8}, \quad (7.6)$$

with $a$ a constant, $\omega$ the O–H stretch vibrational frequency of the hydrogen-bonded O–H group, and $\omega_{\text{OH},g}$ the vibrational frequency of the same group in the gas phase. Equation 7.6 is also valid for aqueous systems. For a solution of HDO in D$_2$O the value of $T_1$ of the O–H stretch vibration was observed to increase from 750 fs at 273 K to 950 fs at 373 K, and to decrease to 380 fs when the HDO:D$_2$O liquid solution was frozen to ice [108]. For pure liquid H$_2$O, $T_1$ was observed to increase from 260 fs at 293 K to 320 fs at 353 K [51], see Chapter 4. These changes in $T_1$ are all accurately described by the combination of Equations 7.5 and 7.6.

The coupled Equations 7.1-6 cannot be solved analytically because $T_1$ depends on temperature, and thus on time. Hence, we solve these equations numerically using a fourth-order Runge-Kutta scheme. In addition, because the absorption spectrum, the Raman spectrum, and $T_1$ all depend on temperature, the shape of the focus of the infrared pump pulse should be accounted for. Therefore, Equations 7.1-6 are solved for a Gaussian distribution of pump pulse intensities $I_p(t)$. The final calculated result is the sum of all responses within this distribution. The results of the model are fitted to the experimental results of Chapter 4 and Ref. [69]. Most of the parameters
entering the model are obtained from independent experimental results. In calculating $T_1$ at different temperatures, we use for $\omega_{OH,g}$ the average frequency of the symmetric and the antisymmetric O-H stretch vibration of water in the gas phase: $\omega_{OH,g} = 3706 \text{ cm}^{-1}$. The Raman spectra $R(\omega, T)$ at different temperatures are obtained from an interpolation of cw (Stokes) Raman spectra reported in the literature. In this interpolation, we used the Raman spectra measured at 30°C and 90°C of Ref. [83]. These spectra are shown in Fig. 7.1b. The parameter $a$ that enters Equation 7.6 is chosen such that $T_1 = 0.3 \text{ ps}$ at 298 K, and the equilibration time $\tau_{eq}$ is set to a temperature independent value of 0.55 ps.

### 7.3 Results and comparison with experiments

In the studies on the vibrational relaxation of liquid water, the O–H stretch vibrations (3000-3600 cm$^{-1}$) were resonantly excited with an intense mid-infrared pulse. This pulse had different parameters in the different studies reported. In Chapters 4 and 5, the pulse had a duration of $\sim 200$ fs and an energy of $\sim 10 \mu J$ [51, 52]. In the mid-infrared pump anti-Stokes Raman probe studies the pulse had a duration of $\sim 1.4$ ps and an energy of 40-50 $\mu J$ [12, 69], or a duration of $\sim 0.7$ ps and an energy of $\sim 25 \mu J$ [101]. The excitation by the intense infrared pulse results in a bleaching of the fundamental $v = 0 \to 1$ transition and in an induced absorption of the $v = 1 \to 2$ transition. This $v = 1 \to 2$ transition is redshifted by $\sim 250 \text{ cm}^{-1}$ with respect to the $v = 0 \to 1$ transition [104]. The reported experiments differed in their method of probing. In the Chapters 4 and 5, the infrared transmission changes were probed with a weak, time-delayed probing pulse with a duration of $\sim 200$ fs. In the mid-infrared pump anti-Stokes probe experiments of Refs. [12, 69, 101] the residual population of the $v = 1$ state of the O–H stretch vibration was probed by measuring the anti-Stokes Raman spectrum with an intense delayed visible pulse with a duration of $\sim 1.4$ ps [12, 69] or $\sim 0.7$ ps [101].

To enable a comparison between the model and the results of the mid-infrared pump-probe experiments, the calculated populations $n_0$ and $n_1$ should be transferred into transient changes in the infrared absorption $\Delta \alpha(\omega, t)$:

$$
\Delta \alpha(\omega, t) = n_1(t)\{\sigma_{1 \to 2}(\omega, T(t)) - \sigma_{0 \to 1}(\omega, T(t))\} + n_0(t)\sigma_{0 \to 1}(\omega, T(t)) - n_0(-\infty)\sigma_{0 \to 1}(\omega, T = 298K). \quad (7.7)
$$

The terms at the right hand side represent the induced excited state $v = 1 \to 2$ absorption, the $v = 1 \to 0$ stimulated emission, the modified ground state $v = 0 \to 1$ absorption, and the reference ground state absorption, respectively.

In Fig. 7.2 femtosecond pump-probe data are shown obtained for a sample of pure H$_2$O at four different probe frequencies. The pump pulses had a central frequency of 3250 cm$^{-1}$. The solid curves are calculated with the model of the previous section. At a probe frequency of 3100 cm$^{-1}$, the signal is initially dominated by the induced
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Figure 7.2. Femtosecond mid-infrared pump-probe scans of liquid water at 298 K. Shown is the absorption change as a function of delay at four different probe frequencies. The central frequency of the pump is 3250 cm$^{-1}$. The solid curves are calculated with the model described in the text.

Figure 7.3. Calculated populations $n_1$ of the excited $v = 1$ state and $n_0^*$ of the intermediate state as a function of delay. These populations are calculated with the pulse parameters of the femtosecond mid-infrared pump-probe experiments shown in Fig. 7.2. Also shown is the increase in temperature that results from the relaxation of the intermediate level.
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\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_4.png}
\caption{Calculated anti-Stokes Raman scattering spectra at different delays. The spectra are calculated using the model described in the text and the pulse parameters of the experiments of Ref. [69].}
\end{figure}

$v = 1 \rightarrow 2$ absorption that decays to zero with $T_1$. At longer delays, the signal further decays to a decreased absorption due to the temperature increase that results from the thermalization process. At 3400 cm$^{-1}$, the signal is dominated by the thermalization process that at this frequency leads to a large decrease in absorption. The initial bleaching of the $v = 0 \rightarrow 1$ transition is only observed as a small shoulder. The signal at 3500 cm$^{-1}$ most clearly shows that the relaxation involves two subsequent processes. First there the bleaching of the $v = 0 \rightarrow 1$ decays with $T_1$, then there is again a decrease in absorption due to the thermalization with $\tau_{eq}$. At 3620 cm$^{-1}$ the signal is dominated by the thermalization effect that at this frequency leads to a final induced absorption. It is clear that the model provides a quantitative description of all thermally induced transmission changes. In Fig. 7.3 the time-dependent populations $n_1$ and $n_0$ are shown together with the time-dependent change in temperature at the maximum intensity of the pump focus.

In Fig. 7.4 calculated anti-Stokes Raman scattering spectra $I_A(\omega, t)$ at different delays are presented. These spectra are calculated using $I_A(\omega, t) \sim n_1(t)R(\omega, T)$. The anti-Stokes Raman spectrum is constructed from an interpolation of the continuous wave Raman spectra shown in Fig. 7.1b. In this calculation we used the pulse parameters used in the experiments described in Ref. [69]. To get an accurate description of the shape of the spectra measured by Pakoulev et al. [69], we had to shift the Raman spectrum at 90°C by 70 cm$^{-1}$ to higher frequencies (see next section). As in Ref. [69], all spectra were normalized to constant area. The calculated spectral dynamics show
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great similarity with the transient spectra shown in Fig. 5b of Ref. [69]. The spectra clearly shift to the blue with increasing delay. In Refs. [69] and [101] this blue shift was interpreted as a single spectral diffusion process with a time constant of \( \sim 0.4 \) ps. However, here we find that this blue shift is in fact not a single process but the result of the consecutive action of the vibrational relaxation of room temperature water and the thermalization. It should be realized that the cross-correlations of 1.8 ps [69] and 1.1 ps [101] of the infrared pump pulse and the visible probing used in Refs. [69, 101] are too long to resolve these two processes. Therefore, the vibrational relaxation and thermalization are observed as a single process giving rise to a blue shift. This also means that the blue shift is not the result of a vibrational Stokes shift within the excited \( v = 1 \) state [69, 101], but rather a shift of the complete spectrum to higher frequencies. This mechanism for the blue shift also explains the observation reported in Ref. [101] that the magnitude of the blue shift depends on the excitation intensity, i.e. on the amount of energy dissipated. In the case of a vibrational Stokes shift, the magnitude of the shift should not depend on the excitation intensity, whereas in the case of a thermal shift such a dependence is obvious.

The rate limiting step of the blue shift is the thermalization process. Indeed, the value of \( \tau_\text{eq} \) of 0.55\( \pm 0.05 \) ps of this process is similar to the time constant of the blue shift of \( \sim 0.4 \) ps reported in Ref. [69]. It is even strikingly similar to the time constant of 0.55 ps reported for the rise of a blue-shifted absorption component in Ref. [101]. In Ref. [101] this blue-shifted component is interpreted as being a sub-band of the absorption spectrum of water. From our calculations we find that the apparent rise of a blue-shifted component with \( \tau \sim 0.55 \) ps can be very well explained from a thermally induced blue shift of the complete O-H spectrum. Moreover, if there really would exist a blue-shifted sub-band, then pumping of this band should inevitably lead to population transfer to red-shifted sub-bands, which is not observed in Ref. [101].

In Fig. 7.5, the calculated delay dependence of the anti-Stokes Raman scattering signal \( I_A(\omega, t) \) at particular frequencies \( \omega \) is shown. These delay curves are also calculated with the pulse parameters of the experiments reported in Ref. [69]. The decays represent the combined action of vibrational relaxation of the \( v = 1 \) state of the O-H stretch vibration and of the thermally induced spectral shift to the blue. The calculated curves are in excellent agreement with the experimental results of Fig. 3b of Ref. [69]. In Fig. 7.6 the time-dependent populations \( n_1 \) and \( n_0^* \) are shown together with the time-dependent change in temperature at the maximum intensity of the pump focus. The final calculated increase in temperature amounts to 78 K which is in excellent agreement with the estimated experimental temperature increase of the experiments of Ref. [69].

The solid lines in Fig. 7.5 represent exponential fits to the points that are calculated with the model of the previous section. At 3200 cm\(^{-1}\) the decay obtained with the model can be quite well fitted with an exponential decay with a time constant of 0.7 picoseconds. At 3520 cm\(^{-1}\), the best fit is obtained with an exponential with a time constant of 1.1 picoseconds. These values are surprisingly long in comparison to the
Figure 7.5. Calculated anti-Stokes Raman scattering signal at 3200 cm\(^{-1}\) (solid squares) and 3520 cm\(^{-1}\) (open squares) as a function of delay between an exciting infrared pulse and a probing visible pulse. The calculation is performed using the pulse parameters of Ref. [69]. Also shown is the cross-correlation of the infrared pump and visible probe with a full-width-at-half-maximum of 1.8 ps (dashed line). The calculated signals can be well described by convolutions (solid lines) of the cross-correlation function and exponential decays with time constants of 0.7 and 1.1 ps for the signals at 3200 and 3520 cm\(^{-1}\), respectively.

Figure 7.6. As Fig. 7.3, but calculated for the pulse parameters used in the time-resolved anti-Stokes Raman spectra of Ref. [69].
value of $T_1$ of 0.3 ps at 298 K. This slowing down is largely due to the increase of $T_1$ that results from the strong increase in temperature. This increase of $T_1$ also explains the observation in Ref. [101] that a doubling of the pump pulse energy led to an increase of the observed vibrational lifetimes with 15%. This directly shows that the claim in Ref. [69] that the dynamics observed in the anti-Stokes Raman experiments would be insensitive to the thermalization process, is not correct. In fact, the dynamics observed are very sensitive to the thermalization and the negative feedback effect: the negative feedback can lead to an increase of $T_1$ by a factor of four.

The effect of the thermalization on $T_1$ will be much smaller in the femtosecond mid-infrared pump-probe experiments shown in Chapters 4 and 5, because the pulses were significantly shorter than the thermalization time. In Fig. 7.3 it is seen that there is indeed very little population $n_1$ left at the delay at which the temperature rise becomes significant and starts to affect the spectrum and $T_1$ time constant. In contrast, in the anti-Stokes Raman scattering experiments of Refs. [69] and [101] the used infrared pump pulses are longer (1.4 and 0.7 ps) than the thermalization time (0.55 ps), so that many O-H stretch vibrations are excited for which the rate of vibrational relaxation has been changed due to the relaxation of excitations by the front wing of the pump pulse. In Fig. 7.6 it is indeed clearly seen that the population $n_1$ is still significant at delay times at which there already is a substantial increase in temperature.

At the blue side (3520 cm$^{-1}$), the decay of the anti-Stokes Raman signal is slower (1.1 ps) than at the centre and at the red side of the spectrum. This frequency dependence seems to be in conflict with the concept of a rapid spectral equilibration of the O-H stretch excitation and a frequency-independent effective $T_1$. However, the frequency dependence of the decay time of the calculated results of Fig. 7.5 and the experimental results of Refs. [69, 101] does not result from the inhomogeneous character of the O-H absorption spectrum, but from another type of inhomogeneity. The excitation by the infrared pump pulse leads to a spatial distribution of dissipated energies and thus of temperature increases in the focus. At the highest intensities, the temperature increase, the spectral blue shift, and the time constant $T_1$, all have the largest values. Hence, the signal at 3520 cm$^{-1}$ is dominated by the part of the focus where the infrared pump pulse is most intense, whereas the signal at 3200 cm$^{-1}$ represents the regions of the focus where the pump is less intense. In the experiments of Refs. [69] and [101] the probe focus (400 μm) was of about the same size as the pump focus (370 μm) so that the measured signal indeed contains contributions from regions with strongly different pump intensities. An additional minor effect that contributes to the frequency dependence of the decay is the dynamics of the spectral blue shift. In the experiments reported in Refs. [69] and [101] the vibrational relaxation is significantly slowed down due to the increase in temperature. Hence, the spectral blue shift takes place on the same time scale as the vibrational relaxation and thus leads to an apparent faster decay at the red side and a slower decay at the blue side of the spectrum. In the femtosecond mid-infrared pump-probe experiments the effect
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of the blue shift on the observed decay times is much smaller, because in those experiments the vibrational relaxation is almost finished before the blue shift due to the thermalization occurs (Fig. 7.3).

7.4 Discussion

The negative feedback effect is not a minor effect and can lead to an increase of $T_1$ from $\sim 300$ fs to $\sim 1.1$ ps. The effect is so strong because of the large blue shift of the spectrum that results from the thermalization of the excitation energy. It should be noted that the experimentally observed blue shift [69, 101] is in fact larger than one would expect from the temperature dependence of the cw Raman spectrum of water [83]. For an increase in temperature of $\sim 80$ K, the anti-Stokes Raman spectra measured by Pakoulev et al. shifts $\sim 70$ cm$^{-1}$ more to the blue than the ordinary cw Raman spectra. The authors of Ref. [69] suggest that the large blue shift could result from the excitation of specific other modes like bending and torsion vibrations. However, in general the excitation of anharmonically coupled modes leads to a red shift of the O-H stretch vibrational frequency and not to a blue shift (the hydrogen bond is an exception). In addition, the subsequent relaxation of these modes is expected to lead to spectral redshifts on a picosecond time scale, which are not observed. A more likely origin of the large thermal blue shift is that the water has not yet completely equilibrated after the dissipation of the infrared pump energy. The frequency of the O-H stretch vibration is determined by the length and angle of the O-H • • • O hydrogen bond, and increases with increasing O•••O distance and angle between the O-H and O•••O coordinates [58, 67, 77]. In the case of heat dissipation on a picosecond time scale, the volume, and thus the average oxygen-oxygen distance cannot change. Hence, dissipation of heat in a constant volume likely will lead to a very strong bending of the hydrogen bonds. At longer time scales, the oxygen-oxygen distance can expand, and the O-H and O•••O coordinates will get better aligned again. Hence, the strongly bent hydrogen bonds that are generated in the first picoseconds after heat dissipation, are likely weaker than the lengthened, but only slightly bent hydrogen bonds that result after volume expansion. In a recent molecular dynamics study it was shown that the strength of the hydrogen-bond interaction is indeed strongly dependent on the angle of the hydrogen bond [77]. The strong relation between hydrogen-bond angle and the strength of the hydrogen bonds can also be illustrated by comparing water to ice. Going from ice to water, the volume gets less, which implies that the average O•••O distance decreases, but in addition the almost perfect alignment of the O-H bond and the O•••O coordinate of ice is lost. The overall effect is a weakening of the hydrogen-interaction, which results in a blue shift of the O-H frequency of $\sim 150$ cm$^{-1}$. Hence, the anomalously large blue shift of the anti-Stokes Raman spectra observed in Ref. [69] is likely caused by the strong bending of the hydrogen bonds that in turn results from the dissipation of a large amount of energy in a constant volume.
7.5 Conclusions

The O–H stretch vibrations of liquid water are delocalized as a result of the strong intermolecular coupling and high density of the water molecules. An important consequence of this delocalization and high density is that there is a strong negative feedback effect on the relaxation of the O–H stretch vibrations. The heat dissipated in the vibrational relaxation and subsequent thermalization leads to a deceleration of the relaxation and a blue shift of other, still excited O–H stretch vibrations. This effect can lead to an increase of $T_1$ by a factor of four. We present a model for the vibrational relaxation of liquid water that includes this negative feedback effect.

In recently reported mid-infrared pump anti-Stokes Raman probe experiments [69, 101], the pulses used were longer than the time constants of the vibrational relaxation ($T_1 = 0.3\pm0.05$ ps at 298 K) and the thermalization ($\tau_{eq} = 0.55\pm0.05$ ps), leading to a strong negative feedback effect on the relaxation rate. We also find that the fast and large spectral blue shift of the anti-Stokes Raman spectrum reported in Refs. [69, 101] can be well explained from the subsequent action of the vibrational relaxation and the thermalization process. This explanation is confirmed by the observations that both the blue shift and $T_1$ increase with increasing energy of the excitation pulse [101]. The dependence of the blue shift and relaxation rate on the excitation energy also leads to a frequency dependence of the vibrational relaxation, because of the inhomogeneity of the dissipated energy in the focus of the pump pulse.