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### Structure and dynamics of complex hydrogen-bonded systems

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# Concentration and temperature dependence of the bending-mode lifetime of H<sub>2</sub>O in liquid D<sub>2</sub>O

## 9.1 Introduction

As discussed in previous Chapter, ultrafast nonlinear vibrational spectroscopy has contributed significantly to a better understanding of both structural and dynamical aspects of water. However, only recently the relaxation pathway of the OH-stretching mode has been established,<sup>26</sup> in terms of a relaxation mechanism via the H<sub>2</sub>O-bending mode. Subsequent studies on the H<sub>2</sub>O bending-mode dynamics suggest that the libration mode plays an important role in the bending-mode relaxation.<sup>26, 154, 157</sup> However, the direct observation of the energy transfer from the bending to the libration mode is not possible due to the sub-100 fs lifetime of the libration mode.<sup>158</sup> Here, we use alternative experiments to investigate the bending-mode lifetime as a different way to confirm whether the libration acts as an accepting mode in the bending-mode vibrational relaxation.

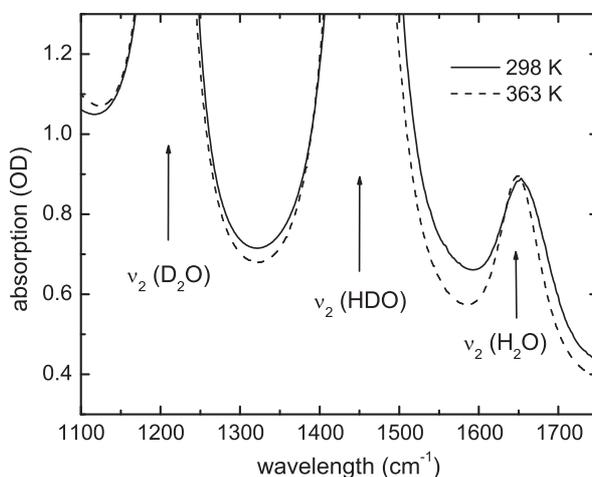
Temperature dependence of the lifetime is one of methods that has helped in the past to elucidate the relaxation mechanism of the vibrational transitions.<sup>159</sup> In the present work, we have measured the lifetime of the H<sub>2</sub>O-bending mode in H<sub>2</sub>O:HDO:D<sub>2</sub>O isotopic mixtures as a function of temperature. We find that the relaxation rate decreases with increasing temperature. We will show that this confirms that the libration mode is involved in the bending-mode relaxation dynamics.

## 9.2 Materials and methods

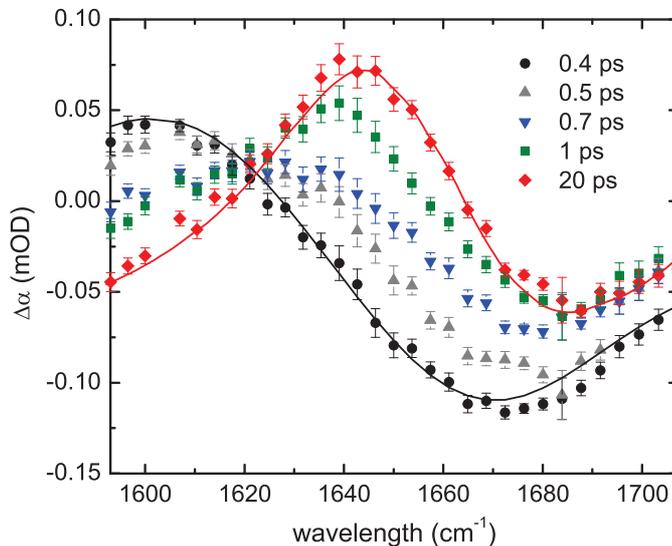
In our experiment, we resonantly excite the H<sub>2</sub>O-bending mode, and monitor the subsequent vibrational relaxation process by measuring the frequency-dependent absorption change as a function of delay time. Our optical setup is based on the design reported by Hamm *et al*<sup>45</sup> and has been described in 2.3.3. Isotopic H<sub>2</sub>O:D<sub>2</sub>O solutions are prepared by mixing appropriate amounts of H<sub>2</sub>O and D<sub>2</sub>O. All experiments were carried out at temperatures between 278 K and 363 K.

## 9.3 Results and discussion

Figure 9.1 shows the linear absorption spectrum of 6 M solution of H<sub>2</sub>O in D<sub>2</sub>O at 298 K and 363 K, with the H<sub>2</sub>O, HDO and D<sub>2</sub>O-bending modes indicated by arrows. All three bands are well separated, so specific excitation of the H<sub>2</sub>O-bending mode is possible. The frequency of the H<sub>2</sub>O-bending mode shifts slightly from 1645 cm<sup>-1</sup> to 1642.5 cm<sup>-1</sup> for 298 K and 363 K respectively, in agreement with values published before.<sup>148,150,159</sup> The change of about 2.5 cm<sup>-1</sup> is very small compared to the shift of about 50 cm<sup>-1</sup> observed for the OH-stretching mode,<sup>160</sup> which suggests that coupling between the bending mode and the hydrogen-bond is not significantly influenced by temperature.



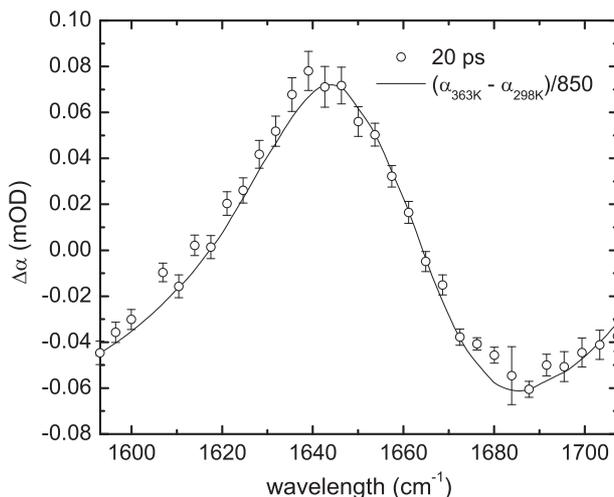
**Figure 9.1:** Linear absorption spectrum of 6 M H<sub>2</sub>O in HDO/D<sub>2</sub>O for 298 K and 363 K. The arrows indicate the position of H<sub>2</sub>O, HDO and D<sub>2</sub>O-bending modes.



**Figure 9.2:** Transient absorption spectrum of a 6 M solution of  $\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$  at 298 K for several delays of the pump with respect to the probe. The points are the experiment and the curves for the delays of 0.4 ps and 20 ps are the fits based on Eq. 9.1 and scaled thermal difference spectrum, respectively.

Transient absorption spectra upon resonantly exciting the bending mode of 6 M solution of  $\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$  at 298 K for several time delays are shown in Fig. 9.2. Since the power spectrum of the pump pulse is much broader than the absorption band of the  $\text{H}_2\text{O}$ -bending mode, no hole burning occurs. At short delays, the transient absorption spectrum is negative for the  $\nu = 0 \rightarrow 1$  frequency due to bleaching of the vibrational ground state and  $\nu = 1 \rightarrow 0$  stimulated emission, and positive for lower frequencies due to  $\nu = 1 \rightarrow 2$  excited-state absorption. After a few ps the excited molecules return to the vibrational ground state and the corresponding bleaching and excited-state absorption diminish. The features of the transient absorption spectrum gradually change due to population relaxation and subsequent thermal equilibration. The signal that remains for delays longer than 5 ps can be assigned to the temperature increase that occurs after vibrational relaxation.<sup>147,161</sup> This can be shown by comparing the pump-probe spectrum at 20 ps delay and the linear difference spectrum (Fig. 9.3), which also allows us to estimate the temperature change induced by the pump pulse. To fit the transient spectrum at 20 ps delay we use the thermal difference spectrum described by  $\alpha_0(363 \text{ K}) - \alpha_0(298 \text{ K})$ , where  $\alpha_0(T)$  represent the linear absorption spectrum for 363 K and 298 K, respec-

tively. To a good approximation, the linear absorption spectrum changes linearly with increasing temperature. Thus by proportionally scaling the thermal difference spectrum we estimate that the temperature increase caused by the pump pulse in the time-resolved experiments is about 0.1 K, see Fig. 9.2.



**Figure 9.3:** Comparison of the transient spectrum of 6 M H<sub>2</sub>O in D<sub>2</sub>O at 20 ps delay (○) and the scaled difference spectrum of the steady-state spectra at 363 and 298 K (—).

We have also determined the anharmonic shifts of the H<sub>2</sub>O-bending mode by fitting the experimental data at short delays using the simple model used in the previous chapter. The shapes of both bleaching and excited-state absorption are described by the linear absorption spectrum  $\alpha_0(\nu)$  with opposite signs, where the spectrum of the excited-state absorption is red-shifted by the anharmonicity  $\delta$  (see eq. 9.1).

$$\Delta\alpha(\nu) = \alpha_0(\nu + \delta) - \alpha_0(\nu) \quad (9.1)$$

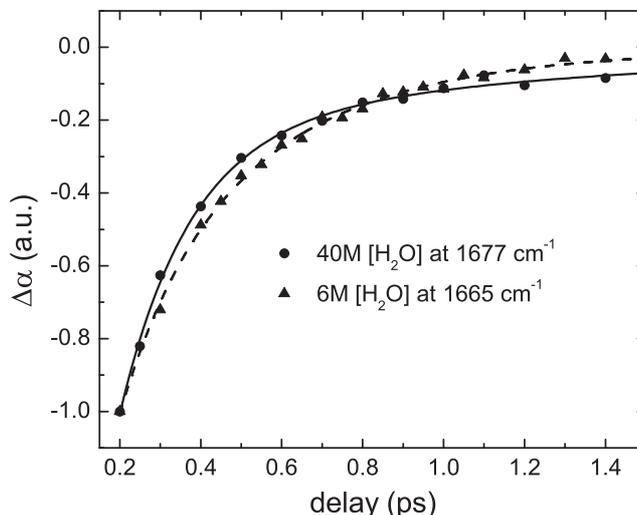
We find the anharmonic shift to be  $54 \pm 5 \text{ cm}^{-1}$  for 363 K.

In a previous study, Huse and coworkers<sup>154</sup> have determined the lifetime of the H<sub>2</sub>O-bending mode for pure water to be 170 fs. In the case of a 6 M H<sub>2</sub>O in D<sub>2</sub>O solution, the lifetime is approximately twice as long.<sup>147</sup> Possibly, the population relaxation decay via the H<sub>2</sub>O libration is determined by the concentration of H<sub>2</sub>O, which would limit this relaxation channel in isotopically diluted H<sub>2</sub>O. Additionally, the D<sub>2</sub>O libration does not serve as an efficient relaxation pathway due to its red-shifted frequency compared to the H<sub>2</sub>O libration which subsequently causes a

longer lifetime for a more diluted H<sub>2</sub>O solution. To confirm the isotopic dilution is sufficient to ensure that the relaxation dynamics of the H<sub>2</sub>O-bending mode is not governed by the concentration of the H<sub>2</sub>O we have measured the lifetime of the H<sub>2</sub>O-bending mode as a function of H<sub>2</sub>O concentration. Figure 9.4 shows the normalized absorption changes as a function of delay between the pump and the probe pulse for the high and low concentration of H<sub>2</sub>O in D<sub>2</sub>O, where the symbols and lines represent the data points and fits, respectively. We plot data for bleaching frequencies with a small contribution of the thermalization effect for better comparison. To determine the rate constants of the relaxation dynamics we have performed a least-squares fit of the whole data set using the convolution of a Gaussian and a double exponential function plus another Gaussian to model the non-linear effects that occur at zero time delay. The rate constants represent the lifetime of the H<sub>2</sub>O-bending mode and the thermalization effect, respectively. In the case of the most dilute solution (6M H<sub>2</sub>O in D<sub>2</sub>O), the fit converged to a single exponential decay due to the very small amplitude of the thermalization effect. A least-squares fit of the data using a simple single exponential decay function for the delays longer than 0.4 ps shows the same relaxation rate. Figure 9.4 shows that the population decay is a double and a single exponential for the high and low concentration, respectively. This is due to the absence of the thermalization effect at low concentrations.

The decay rates as a function of H<sub>2</sub>O concentration are shown in Fig. 9.5. The symbols represent the data points, where the square for pure H<sub>2</sub>O is taken from Huse *et al.*<sup>154</sup> The data shows an initial sharp decrease of the relaxation rate from 5.8 ps<sup>-1</sup> for pure water down to 3 ps<sup>-1</sup> for 25 M solution of H<sub>2</sub>O in D<sub>2</sub>O. The rate levels off at 2.8 ps<sup>-1</sup> for 6 M solution of H<sub>2</sub>O in D<sub>2</sub>O. This behavior suggests that the interaction between neighboring H<sub>2</sub>O molecules is at this concentration negligible for H<sub>2</sub>O relaxation dynamics. Hence, in a sample with a concentration smaller than 6 M, the observed temperature dependence of the H<sub>2</sub>O bending-mode relaxation will be representative of that at infinite dilution.

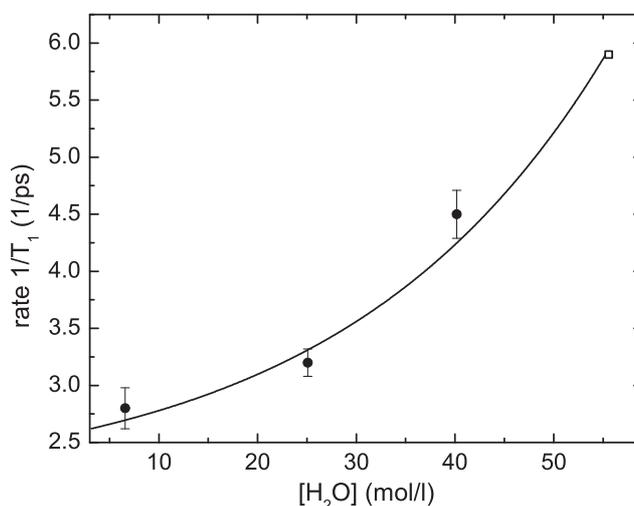
Figure 9.6 shows the absorption change of the H<sub>2</sub>O-bending mode as a function of delay between the pump and the probe pulse at 298 K and 363 K. To improve the signal-to-noise the data was averaged over 6 frequencies in the bleaching part of the spectrum (1660 – 1680 cm<sup>-1</sup>). For better comparison we have subtracted the thermalization effect and scaled the data (the inset shows the unmodified data). The decay of the pump-probe signal can be described by a single exponential decay. Using a least-squares fit, we determined the lifetime to be 340±15 fs and 422±8 fs for 298 K and 363 K, respectively. In order to avoid contributions from coherent coupling<sup>152</sup> and cross-phase modulation,<sup>153</sup> only data points with a delay longer than 0.4 ps were used. Compared to our previous study<sup>147</sup> the lifetime of 6 M H<sub>2</sub>O in D<sub>2</sub>O at 298 K was determined more accurately due a better signal-to-noise ratio.



**Figure 9.4:** The pump-probe transient absorption signal as a function of delay for 40 M and 6 M solution of H<sub>2</sub>O in D<sub>2</sub>O. The symbols represent the data and the lines the fitted model.

The experimentally determined and calculated relaxation rates of the H<sub>2</sub>O-bending mode are depicted in Fig. 9.7. The relaxation rate decreases as a function of temperature from  $3.6 \pm 0.18 \text{ ps}^{-1}$  to  $2.35 \pm 0.05 \text{ ps}^{-1}$  for 278 K and 363 K, respectively.

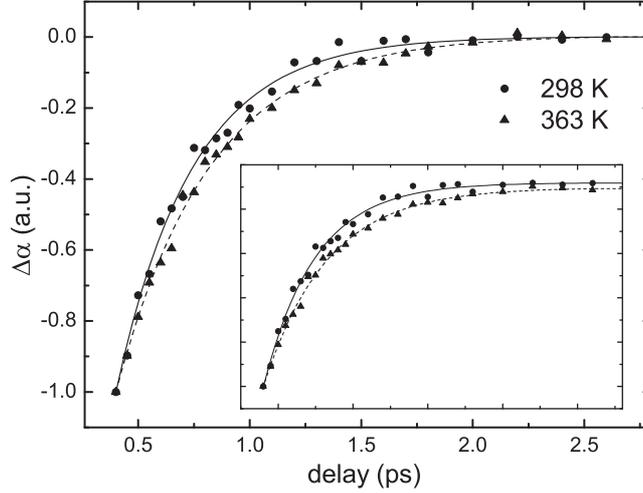
In the vibrational relaxation of the H<sub>2</sub>O-bending mode the accepting modes cannot be intra-molecular modes because the bending mode itself is energetically the lowest intra-molecular mode. The vibrational relaxation must therefore occur via inter-molecular modes. Energetically the highest of these modes are the libration mode at  $\sim 680 \text{ cm}^{-1}$  and the hydrogen-bond stretching and bending modes at  $\sim 185 \text{ cm}^{-1}$  and  $\sim 50 \text{ cm}^{-1}$ , respectively.<sup>162</sup> The study of vibrational predissociation of an OH $\cdots$ O complex describes a model which was used to describe the temperature dependence of the relaxation lifetime in water. The authors suggest that direct relaxation of the bending mode to translational motion would be two orders of magnitude slower than the relaxation of the OH-stretching mode.<sup>163</sup> However, the lifetime of the H<sub>2</sub>O-bending mode is actually found to be twice as short as the lifetime of the OH-stretching mode. We can therefore conclude that the complete energy transfer from the bending mode to the hydrogen-bond stretch is very unlikely. In addition, the bending-mode vibrations are more likely to be



**Figure 9.5:** The relaxation rate of the H<sub>2</sub>O-bending mode as a function of H<sub>2</sub>O concentration. The square at [H<sub>2</sub>O]=55 M is an experiment from work published by Huse and coworkers.<sup>154</sup> The line is a guide to the eye.

coupled to rotational rather than to translational motion.

It has been previously suggested that librations and/or the hydrogen bond stretch and bend can act as the accepting modes. To explore the possible involvement of the libration modes in the relaxation dynamics of the H<sub>2</sub>O-bending mode we have measured the linear absorption spectrum of pure H<sub>2</sub>O at several temperatures (see Fig. 9.8). The maximum of the H<sub>2</sub>O libration band shifts from 685 cm<sup>-1</sup> to 650 cm<sup>-1</sup> and broadens from 180 cm<sup>-1</sup> to 195 cm<sup>-1</sup> when going from 288 K to 348 K. In contrast, the H<sub>2</sub>O bending-mode frequency blueshifts from 1642.5 cm<sup>-1</sup> to 1645 cm<sup>-1</sup>. Both the redshift of the libration and blueshift of the bending mode are direct consequences of the weakened hydrogen-bond network. It should be noticed that the shape of the bending-mode absorption spectrum is asymmetric with a large baseline at the low-frequency side. This absorption has been previously assigned to the overtone of the libration<sup>164</sup> and to the combination band.<sup>155</sup> However, later studies show that the origin of this absorption are fundamental high energy libration modes. Upon excitation of the H<sub>2</sub>O-bending mode the relatively large energy of the libration modes does not allow for accepting more than two energy quanta. The energy mismatch and the overlap integral between the excited and accepting mode will influence the relaxation dynamics. The libration spectrum

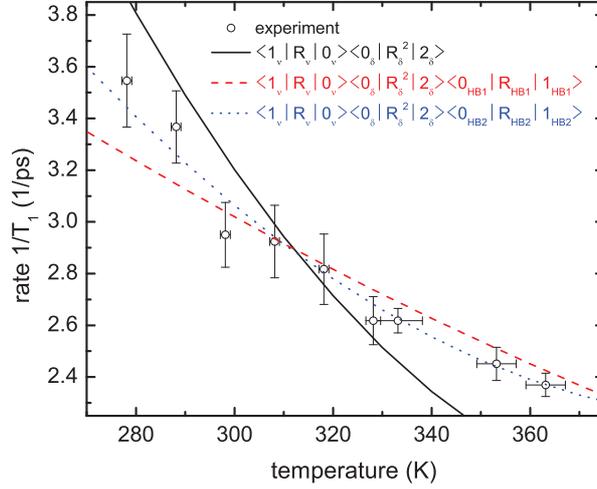


**Figure 9.6:** Transient absorption change as a function of pump-probe delay averaged for probing frequencies from  $1660\text{ cm}^{-1}$  to  $1680\text{ cm}^{-1}$  at 298 K (●) and 363 K (◐). The solid and dashed curves are single exponential decays with a time constants of 340 fs and 422 fs, respectively. The inset shows the same data without subtraction of the thermalization effect.

of  $\text{H}_2\text{O}$  redshifts with increasing temperature, so the energy mismatch and overlap integral will decrease. Consequently the rate of the vibrational relaxation should decrease at higher temperatures. Based on far-IR<sup>165–167</sup> and low-frequency Raman spectra,<sup>168</sup> we can say that the hydrogen bond vibrations are not influenced by temperature as much as the libration band and so the libration modes are the best candidates for the accepting modes in the  $\text{H}_2\text{O}$ -bending mode relaxation mechanism. There is also the possibility of energy relaxation via the bending mode of HDO and/or  $\text{D}_2\text{O}$ . However, we believe that the energy relaxation via the libration mode is more probable because the energy is more likely transferred via the vibrational mode in which the excited molecule is directly involved.

We have used a semi-quantitative approach to estimate the relaxation rate from the bending to the libration mode by applying Fermi's golden rule as described by Nitzan *et al.*<sup>159,169</sup> The relaxation rate  $1/T_1$  is then given by:

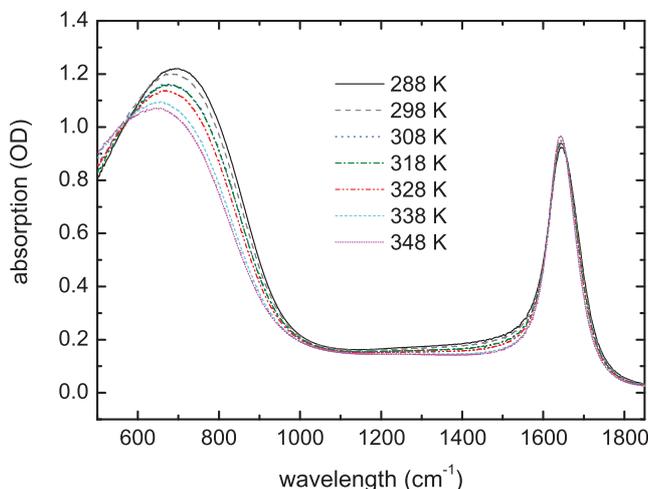
$$1/T_1 \propto 2\pi/h \int \frac{e^{E_v/kT} - 1}{\prod [e^{E_\delta/kT} - 1]} |\langle 1_v 0_\delta | R_v R_\delta^2 | 0_v 2_\delta \rangle|^2 \times \rho(E_v) dE, \quad (9.2)$$



**Figure 9.7:** Rate of the vibrational relaxation  $1/T_1$  of  $\text{H}_2\text{O}$ -bending mode as a function of temperature. Points are the measured data and lines are the scaled calculations according to the Fermi's golden rule, see Eq. 9.2. The solid, dashed and dotted lines represent the calculations where the accepting mode is purely the overtone of the libration, the overtone of the libration and the hydrogen-bond stretch - HB1 ( $\sim 185 \text{ cm}^{-1}$ ) and the overtone of the libration and the hydrogen-bond bend - HB2 ( $\sim 50 \text{ cm}^{-1}$ ), respectively.

where  $R_v$  and  $R_\delta$  are the bending and libration coordinates,  $|0_v\rangle$ ,  $|1_v\rangle$ ,  $|2_\delta\rangle$  and  $|0_\delta\rangle$  are the wave functions of the ground and excited states of the  $\text{H}_2\text{O}$  bending  $v$  and libration  $\delta$  modes. The anharmonic coupling matrix element  $|\langle 1_v 0_\delta | R_v R_\delta^2 | 0_v 2_\delta \rangle|^2$  can be split into  $|\langle 1_v | R_v | 0_v \rangle|^2$  and  $|\langle 0_\delta | R_\delta^2 | 2_\delta \rangle|^2$ , where the frequency dependence of the first term can be approximated by the linear spectrum of the  $\text{H}_2\text{O}$ -bending mode. By inserting the unity operator  $|i\rangle\langle i|$  into the term  $|\langle 0_\delta | R_\delta^2 | 2_\delta \rangle|^2$  and using harmonic oscillator selection rules we obtain  $|\langle 0_\delta | R_\delta | 1_\delta \rangle \langle 1_\delta | R_\delta | 2_\delta \rangle|^2$ , which is the square of the absorption spectrum of the libration mode if we assume the same spectral shape for the fundamental and  $1 \rightarrow 2$  transitions. The term preceding the anharmonic coupling matrix element is determined by the thermal population of excited and accepting modes.  $E_v$  and  $E_\delta$  represent the energies of the excited and accepting modes, respectively. The density of states  $\rho(E_v)$  is assumed to be independent of temperature and constant over the range where the integrand is nonzero.

To calculate the overlap integral we use the square of the linear spectrum of pure  $\text{H}_2\text{O}$  for the librations between  $500 \text{ cm}^{-1}$  and  $1200 \text{ cm}^{-1}$  (Fig. 9.7) and the



**Figure 9.8:** Linear absorption spectrum of pure H<sub>2</sub>O for temperatures from 288 K to 348 K. The libration band shifts from 685 cm<sup>-1</sup> to 650 cm<sup>-1</sup> going from 288 K to 348 K, while the bending mode shifts to the blue by 2.5 cm<sup>-1</sup> (from 1645 cm<sup>-1</sup> to 1642.5 cm<sup>-1</sup>).

linear spectrum of 6 M H<sub>2</sub>O in D<sub>2</sub>O for the bending spectral region (Fig. 9.1). The results of the pump probe experiments are influenced by the presence of H<sub>2</sub>O, HDO and D<sub>2</sub>O libration bands. However, to use the absorption spectrum of the 6 M H<sub>2</sub>O solution in D<sub>2</sub>O would not be correct because it consists of three different contributions coming from all present species (H<sub>2</sub>O, HDO and D<sub>2</sub>O). The actual libration spectrum of a H<sub>2</sub>O molecule in the mixture of HDO and D<sub>2</sub>O is only slightly red-shifted with respect to the libration band in pure H<sub>2</sub>O. Because of the similar shifts of H<sub>2</sub>O and D<sub>2</sub>O libration bands as a function of temperature we can assume that the H<sub>2</sub>O libration in pure water is a good approximation of the libration spectrum of a H<sub>2</sub>O molecule in the HDO/D<sub>2</sub>O mixture.

As shown in Fig. 9.7, the predicted relaxation rate decreases with temperature. We have also estimated the relaxation rate in case the energy is partly transferred to the other intermolecular modes, in particular the hydrogen-bond stretching and bending modes. The solid, dashed and dotted lines represent the calculations where the accepting mode is the overtone of the libration,<sup>170</sup> the overtone of the libration and one quantum of the hydrogen-bond stretch (HB1), and the overtone of the libration and one quantum of the hydrogen-bond bend (HB2), respectively. With increasing number of phonon states involved in the relaxation mechanism the relaxation rate decreases less steeply with increasing temperature.

All calculated relaxation pathways show reasonable quantitative agreement with the experimental data.

Our model is largely oversimplified and does not allow us to fully describe the relaxation mechanism of the H<sub>2</sub>O-bending mode. We hope that our study will stimulate more theoretical work to better understand relaxation processes for the H<sub>2</sub>O-bending mode, as it already has done for the OH-stretching mode.<sup>144, 146, 171</sup> We believe, though, that the strong correlation between the relaxation rate and the overlap integral between the bending mode and libration overtone agrees with a mechanism in which the libration mode acts as an accepting mode.

## 9.4 Conclusions

To summarize, we have performed femtosecond pump-probe experiments of the H<sub>2</sub>O-bending mode in H<sub>2</sub>O:HDO:D<sub>2</sub>O isotopic mixtures as a function of temperature and have shown that the relaxation rate decreases with rising temperature. Our results confirm previous suggestions that the librations are as important to the H<sub>2</sub>O bending-mode relaxation as the bending mode is to the OH-stretch vibrational dynamics.<sup>26, 154, 158, 171</sup>