Ultrafast vibrational dynamics of water

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Temperature Dependence of Vibrational Relaxation in Liquid $\text{H}_2\text{O}$

We have determined the lifetime of the OH-stretch vibration in pure liquid water as a function of temperature using femtosecond mid-infrared pump-probe spectroscopy. The lifetime $T_1$ increases from $260 \pm 18$ fs at $T = 298$ K to $320 \pm 18$ fs at $T = 358$ K. The increase in lifetime with temperature can be quantitatively explained from the decrease in overlap between the OH-stretch vibration and the overtone of the H-O-H bending mode.
Figure 4.1. The linear absorption spectrum of liquid water in the mid-infrared region showing three peaks: the symmetric and antisymmetric stretch bands around 3400 cm$^{-1}$ ($\nu_{OH}$), the bending mode ($\delta_{OH}$) at about 1640 cm$^{-1}$, and a small combination band of the bending mode with the librational mode ($\delta_{OH}+\nu_L$) at 2150 cm$^{-1}$.

4.1 Introduction

Infrared spectroscopy is a key tool in understanding the structure and composition of gas phase molecules, liquids, biomolecules and peptides. An additional tool is the use of isotopic substitution, which allows for a separation of groups that are otherwise very similar. For the study of the vibrations in liquid water, for example, an often used isotopic variation is HDO molecules dissolved in D$_2$O(HDO:D$_2$O) [17, 18, 100]. At low HDO concentrations, this system makes it possible to observe the behavior of an isolated OH-group, because the normal mode vibrations of the surroundings do not have spectral overlap with that of the OH-group.

As shown in Chapter 1, the H$_2$O molecule has three normal mode vibrations [35]: for an isolated molecule in the gas phase the asymmetric stretch vibration $\nu_3$ has a frequency of 3756 cm$^{-1}$, the symmetric stretch vibration $\nu_1$ has a frequency of 3657 cm$^{-1}$ and the bending mode $\nu_2$ has a frequency of 1595 cm$^{-1}$. The positions and shapes of the vibrational bands change when going from the gas to the liquid phase, mainly due to hydrogen bonding. The mid-infrared absorption spectrum of liquid H$_2$O is depicted in Figure 4.1. The spectral position of these bands changes due to hydrogen bonding: the two stretch modes undergo a red shift and overlap to form a band centered around 3400 cm$^{-1}$ with a FWHM of about 400 cm$^{-1}$. The bending mode undergoes a blue shift towards 1643.5 cm$^{-1}$. Due to the broad distribution of hydrogen bond lengths in liquid water, the lines become bands. In Figure 4.1, there
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is a third band centered around 2150 cm\(^{-1}\) that has been assigned to a combination tone of the bend mode and the librational band (500 cm\(^{-1}\)) [55, 56]. For HDO:D\(_2\)O the situation is completely different: there is no symmetric and antisymmetric normal mode, but an OH-stretch and an OD-stretch mode. The OH-stretch band lies at 3400 cm\(^{-1}\), the OD-stretch band at 2500 cm\(^{-1}\), and the HOD bending mode at 1450 cm\(^{-1}\).

Information on the mechanism of vibrational relaxation can be obtained by studying its temperature dependence. The general trend for the temperature dependence of the vibrational relaxation rate is that the rate increases with temperature, i.e. the lifetime gets shorter as the temperature gets higher. This has been theoretically described for the so-called vibron-phonon system, for which a distinction is made between the excited high frequency vibrational mode and the accepting low-frequency phonon modes [50]. Raising the temperature leads to an increase of the occupation in the low-frequency accepting modes, causing a stronger anharmonic interaction between the donor and acceptor modes, which results in a shorter lifetime. The predicted decrease of the lifetime has experimentally been confirmed for various systems. The OH-groups in fused silica [34] show a decrease in relaxation time from 110 ps at 100 K to about 15 ps for 1450 K. For liquid hydrogen chloride [8] the lifetimes are 2.1 and 1.0 ns at \(T = 173\) and 248 K, respectively. The lifetime of the SH-stretch mode in an As\(_2\)S\(_3\) glass [32] decreases from 2.0 to about 0.58 ps when going from 5 to 300 K.

In view of the above, it is surprising that the OH–stretch vibration of HDO:D\(_2\)O shows a different behavior [108]. Below the solid-liquid phase transition, there is no significant temperature dependence of the lifetime. At the transition, the lifetime \(T_1\) jumps from 384 ± 16 to 745 ± 47 fs. Increasing the temperature in the liquid phase leads to a further increase of the lifetime to 900 fs. The explanation for this anomalous behavior is that the average hydrogen bond strength decreases with temperature. Staib and Hynes made a theoretical study on the vibrational relaxation of the OH–stretch vibration of an O–H⋯O group [88]. They calculated the anharmonic interaction between the OH–stretch mode and the hydrogen bond stretch mode (200 cm\(^{-1}\)), as a result of which the energy is transferred to the hydrogen bond mode. With increasing temperature, the hydrogen bonds become weaker, which leads to a decrease of the anharmonic interaction and thus to an increase of the vibrational lifetime.

Another method to unravel the relaxation scheme is the detection of the intermediate level directly, as has been done by Deàk et al. [12] Using time-resolved anti-Stokes Raman scattering on the OH–stretch vibration of HDO:D\(_2\)O and of pure H\(_2\)O, a strong response of the bending mode for pure H\(_2\)O was observed and a weaker response of the same mode for HDO:D\(_2\)O. These observations do not exclude, however, that the hydrogen bond stretch mode still plays a role in the relaxation. It is therefore interesting to measure the lifetime of the OH–stretch vibration in liquid H\(_2\)O as a function of temperature, in addition to the study performed by Deàk et al. [12], in which all experiments were performed at room temperature and the time resolution
was insufficient to extract the time scale of the relaxation.

4.2 Experimental

In the experiment, the OH-stretch vibration of a subset of water molecules is excited to the $\nu_{OH} = 1$ state with an intense femtosecond mid-infrared pulse. This excitation leads to a bleaching of the $0 \rightarrow 1$ transition and to an induced absorption of the $1 \rightarrow 2$ transition, which is red-shifted by about 300 cm$^{-1}$ with respect to the $0 \rightarrow 1$ transition [25]. The dynamics of the excitation are measured with time-delayed probe pulses by measuring the transmission change as a function of time.

The experimental setup is described in Chapter 3, here we just focus on the aspects that are important for the results obtained. The probe polarization was set at the magic angle with respect to the polarization of the pump pulse by means of a zero-order $\lambda/2$ plate, to rule out the effects of orientational relaxation [24]. To avoid thermal lensing effects, we collimate and focus the probe beam on the PbSe-detector. The sample used was a thin layer of pure liquid water (Aldrich, HPLC grade) in between two sapphire windows. The transmission at the center of the OH-stretch absorption band was a few percent typically. The transmission through a pinhole with a 100 $\mu$m diameter was 80% for the probe and 50% for the pump. The excitation by the pump eventually leads to a local increase in temperature. From the linear absorption spectrum and from the measured relative change in transmission, $\ln(T/T_0) = 0.1$ typically, we deduce a value for the single-pulse temperature increase of approximately 30 K. In order to avoid the accumulation of heat, the sample is rotated.

4.3 Results

Pump-probe scans for a pump frequency of 3250 cm$^{-1}$ and eight different probe frequencies are displayed in Figure 4.2. In these scans, the final level of transmission is observed to be increased or decreased, depending on the probe frequency. This observation can be explained from the increase in temperature that results after the thermalization of the excitation. The behavior at short delay times also depends on the probe frequency. When probing at the red side of the absorption band (upper two curves in the left panel of Figure 4.2), an induced $\nu_{OH} = 1 \rightarrow 2$ absorption is observed. When probing at the blue side of the absorption band (upper two curves in the right panel), a clear bleaching peak around $t = 0$ is observed. Near the center of the absorption band (lower two curves in the left panel), this peak is hidden under the thermalization effect. Next to these two effects, i.e. the long-time transmission increase or decrease and the bleaching or induced absorption peak around $t = 0$, there is a coherent interaction. This effect is most clearly observed at the two most blue probing wavelengths. Around $t = 0$ the transmission change shows a wiggle, which is negative for $t < 0$ and positive for $t > 0$. At a wavelength of 3200 cm$^{-1}$ the
situation is reversed: positive for $t < 0$ and negative for $t > 0$. This coherent effect results from induced phase modulation [13]. The pump pulse changes the phase of the probe pulse, and can thus affect its frequency spectrum. As a result, this pulse comes into better or worse resonance with the OH–stretch vibration, which causes an additional change in transmission.

The data show that there are two time scales present in the relaxation. The first relaxation step is from the $\nu_{\text{OH}} = 1$ state to an intermediate state with a time constant $T_1$, the lifetime of the OH–stretch vibration. This first time scale is seen as the decay of the bleaching in Figure 4.2 (right panel), and as the decay of the induced absorption (left panel, upper two scans). The relaxation of this intermediate level leads to a complete equilibration and is characterized by a time constant $\tau_{\text{eq}}$. The equilibrated state represents a situation in which the excitation energy is thermally distributed over all degrees of freedom in the focus. This dumping of energy leads to a temperature increase in the sample, which will affect the linear absorption spectrum of the OH–stretch band. An increase in temperature leads to a decrease of the absorption cross section and a shift of the absorption maximum to the blue, as is illustrated in Figure 4.3. A blue shift of the OH–stretch band indicates that the hydrogen bonds have become weaker and longer [67, 28]. In this case, the excess energy is delivered on a
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![Absorption spectra at different temperatures](image)

**Figure 4.3.** The OH-stretch absorption band at different temperatures. With increasing temperature, the absorption cross section decreases and the maximum of the absorption band shifts to the blue.

Femtosecond time scale, so that there is no time for volume expansion. This means that the average oxygen-oxygen distance between the water molecules cannot increase. Hence, the blue shift cannot result from a lengthening of the average hydrogen bond length, but is likely caused by a change of the angle between the OH-bond and the hydrogen bond. An increased bending of the O–H···O system results in a weakening of the hydrogen bond interaction. The blue shift of the OH-stretch band means that a probe pulse in the red or center part of the band will see fewer molecules absorbing at that specific wavelength, which explains the higher final level of transmission. For probe pulses in the blue, the situation is reversed. Here, the pulse will see extra molecules at longer delay times, which gives rise to a lower final level of transmission, as can be seen in Figure 4.2 (right panel, lower two scans).

The temperature dependence of the thermalization process can best be determined in the red wing of the absorption band, i.e. near 3300 cm$^{-1}$, because at this frequency the thermalization effect completely dominates the observed dynamics. Transients of this frequency are shown in Figure 4.4, for three different temperatures. For comparison, the measured scans are scaled in such a way that at all temperatures, the final transmission change is the same. It is clear from Figure 4.4 that the equilibration time has no significant temperature dependence. For the lifetime of the OH-stretch vibration, however, we do find a temperature dependence, as is shown in Figure 4.5. Here, scans are shown at two temperatures: 298 and 358 K measured at a probe wavelength of 3000 cm$^{-1}$, which is resonant with the $\nu_{OH} = 1 \rightarrow 2$ absorption.
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**Figure 4.4.** Delay time scans at different temperatures measured with pump and probe frequencies of 3400 and 3300 cm\(^{-1}\), respectively.

**Figure 4.5.** Transmission change \(\ln(T/T_0)\) as a function of delay between pump and probe pulse at two different temperatures. The pump frequency was 3400 cm\(^{-1}\), the probe frequency 3000 cm\(^{-1}\).
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![Energy level scheme](image)

**Figure 4.6.** Energy level scheme used for fitting the data.

### 4.4 Kinetic modeling

To fit the data we use a model depicted in Figure 4.6 and fully described in Ref. [64]. It consists of the vibrational ground state (0), the first excited state (1), populated by the pump pulse, the second excited state (2) and the intermediate level 0* to which the population of state 1 relaxes with a time constant $T_1$. In this model, the decay of the intermediate 0*-state leads to a full thermalization of the system. The associated time scale $\tau_{eq}$ represents the equilibration or thermalization time. The absorption cross sections for the 0 $\rightarrow$ 1 and 0* $\rightarrow$ 1* transitions are $\sigma_{01}(\omega)$ and $\sigma_{01}^*(\omega)$, respectively.

The absorption of a probe beam by the sample can be denoted as follows

$$\alpha(\omega) \propto \sigma_{01}(\omega)(n_0 - n_1) + \sigma_{01}^*(\omega)(n_0^* - n_1^*)$$  

(4.1)

where $n_i$ denotes the population of state $i$. We can set $n_1^*(t) = 0$ because there is no thermal population of 0* and excitation by the probe beam will be negligible. When we substitute $n_0 = N - n_1 - n_0^*$, with $N$ the total number of molecules and subtract the absorption of the probe without excitation by the pump pulse ($\alpha \propto \sigma N$), we get for the absorption change

$$-\Delta\alpha_{01}(\omega, t) \propto \sigma_{01}(\omega)[2n_1(t) + (1 - \frac{\sigma_{01}^*(\omega)}{\sigma_{01}(\omega)})n_0^*(t)] + N\delta\sigma_{01}(\omega, t)$$  

(4.2)

The $\delta\sigma_{01}(\omega)$ in the last term of Equation (2) represents the change in cross section due to the temperature increase that results after the thermalization. Depending on the probe frequency this change will be positive (at the blue side of the absorption band) or negative (at the red side of the absorption band). Because the cross section change is proportional to the number of molecules relaxed from 0*, the last term can be written as:

$$N\delta\sigma_{01}(\omega, t) \propto \int_{-\infty}^{t} \frac{n_0^*(t')}{\tau_{eq}} dt'$$  

(4.3)
If the probe pulse only probes the $1 \to 2$ transition, the absorption change reads as follows:

$$\Delta \alpha_{12}(\omega, t) \propto \sigma_{12}(\omega)n_1(t) + N\delta\sigma_{01}(\omega, t) \quad (4.4)$$

We have neglected $n_2(t)$ in the above equation, which is a good approximation since the excitation fraction of $\nu_{\mathrm{OH}} = 1$ is only about 1%. The last term again represents the effect of the change of the absorption band due to thermalization. The population numbers for the different states satisfy the following rate equations:

$$\frac{dn_1}{dt} = \frac{n_1}{T_1} \quad (4.5)$$

$$\frac{dn_0^*}{dt} = \frac{n_1}{\tau_1} - \frac{n_0^*}{\tau_{\mathrm{eq}}} \quad (4.6)$$

$$\frac{dn_0}{dt} = \frac{n_0^*}{\tau_{\mathrm{eq}}} \quad (4.7)$$

$$N = n_0 + n_1 + n_0^* \quad (4.8)$$

The rate equations can be solved leading to

$$n_1(t) = n_1(0)e^{-t/T_1} \quad (4.9)$$

$$n_0^*(t) = \frac{1}{\tau_1} - \frac{1}{\tau_{\mathrm{eq}}} \left( e^{-t/T_1} - e^{-t/\tau_{\mathrm{eq}}} \right) n_1(0) \quad (4.10)$$

$$n_0(t) = N - n_1(t) - n_0^* \quad (4.11)$$

These functions are convolved with the measured cross correlation function of the pump and probe beam to account for the nonzero pulse widths. This gives us the full expressions for $-\Delta \alpha_{01}(\omega, t)$ and $\Delta \alpha_{12}(\omega, t)$ which can be compared to the measured $\ln(T/T_0)$. Fitting these functions to the actual data gives us the time constants $T_1$ and $\tau_{\mathrm{eq}}$, as well as the ratio $\sigma_{01}^*/\sigma_{01}$ at the probe frequency.

At some specific pump/probe combinations, an extra wiggle around $t = 0$ is observed, the induced phase modulation artifact [13] (see Section 4.3). We account for this effect by adding the derivative of the cross correlation function to the fit function, as an approximation.

A difficulty in fitting $T_1$ is the overwhelming contribution of the thermalization effect to the measured transmission change. This makes it impossible to get a reasonable $T_1$ value from the fits for probe frequencies larger than $3200 \text{ cm}^{-1}$. The best way to get an accurate value for $T_1$ is by fitting the scans which probe the $1 \to 2$ transition (Figure 4.2, upper scans of left panel). We take the value for the equilibration time $\tau_{\mathrm{eq}}$ from the measurements at $3300 \text{ cm}^{-1}$ where the temperature effect is so large that a precise determination of this value is possible. Using this value as a constant in the fit for the $1 \to 2$ transition, we obtain the value for $T_1$. 
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Figure 4.7. The lifetime of the OH–stretch vibration of H₂O as a function of temperature. The drawn curve represents the calculated behavior according to the Fermi's Golden rule expression of Equation 4.12 (see text).

As will be shown in the next chapter, for liquid water $\tau_{eq} = 0.55 \pm 0.05$ ps, independent of probe wavelength and of the amount of energy to be equilibrated [52]. All data of Fig. 4.2 can be well fitted with a $\tau_{eq}$ of $0.55 \pm 0.05$ ps and a lifetime $T_1$ of $260 \pm 18$ fs. The results displayed in Figure 4.4 can all be well described with a $\tau_{eq}$ of $0.55 \pm 0.05$ ps for all temperatures. The measured lifetimes $T_1$ are depicted in Figure 4.7 as a function of temperature. The increase of 20% is comparable with the increase measured in HDO:D₂O dilutions [108]. The relaxation in liquid water is three times faster than that of HDO:D₂O, where a lifetime of 740 fs was measured at room temperature [108].

4.5 Relaxation mechanism for the OH-stretch vibration

Deák et al. found that the relaxation of the OH–stretch vibration of H₂O results in a significant response of the H–O–H bending mode ($\delta$) [12]. If the bending mode would be the main accepting mode, normally a decrease of the lifetime $T_1$ is expected as a function of temperature, because this mode has nearly harmonic character [36, 65]. This expectation is based on a theory that assumes that the excited mode is resonant with a large number of excitations in low-frequency accepting modes. However, the bending mode has a high frequency of about 1650 cm⁻¹, so that this mode can accept only one or two quanta. Hence, if the bending mode is one of the accepting modes, the relaxation rate will also strongly depend on the energy mismatch between donor
Relaxation mechanism for the OH-stretch vibration

The energy mismatch can be accounted for by calculating the following overlap integral, which results from Fermi's Golden Rule, and which gives an expression for the relaxation rate ($\propto 1/T_1$):

$$\frac{1}{T_1} \propto 2\pi/h \int \frac{e^{\frac{E}{kT}} - 1}{\prod[e^{\frac{E}{kT}} - 1]} |\langle 1_\nu|0_\delta|R_\nu R_\delta^2|0_\nu 2_\delta\rangle|^2 \delta(E_\nu - E_{2\delta})\rho(E_\nu = E_{2\delta})dE \quad (4.12)$$

where $R_\nu$ is the OH-stretch coordinate, $R_\delta$ the bending coordinate, $|0_\nu\rangle$ and $\langle 1_\nu|\,$ the wave functions of the ground and excited state of the OH-stretch vibration, and $|2_\delta\rangle$ and $\langle 0_\delta|\,$ the wave functions of the ground and second excited state of the bending mode. $\rho(E_\nu = E_{2\delta})$ is the density of states. The term preceding the anharmonic coupling matrix element represents the effect of the thermal population of the accepting mode on the relaxation [66]. This term assumes the transfer of one OH-stretch quantum to two quanta of the bending mode. Raising the temperature from 298 to 358 K, this term increases by 0.1%, which means that this term has a negligible effect on the relaxation rate.

The anharmonic coupling matrix element $|\langle 1_\nu|0_\delta|R_\nu R_\delta^2|0_\nu 2_\delta\rangle|^2$ can be written as $|\langle 1_\nu|0_\delta|0_\nu\rangle|^2 |\langle 0_\delta|2_\delta\rangle|^2$. The spectral dependence of $|\langle 1_\nu|R_\nu|0_\nu\rangle|^2$ can be approximated by the linear absorption spectrum of the OH-stretch, provided that the spectral diffusion within this band is very rapid. Similarly, the spectral dependence of $|\langle 0_\delta|2_\delta\rangle|^2$ can be approximated by the absorption or Raman spectrum of the overtone of the bending mode. The presence of the function $\delta(E_\nu - E_{2\delta})$ implies that the integral in Eq. 4.12 will only be nonzero if the absorption bands of the OH-stretch and the overtone of the bending mode overlap. The temperature dependence of Eq. 4.12 can thus be approximated by calculating the overlap as a function of temperature [1].

For the calculation of the overlap of the spectra we have used the measured temperature dependent absorption spectra as displayed in Figure 4.3, where a decrease of the absorption cross section and a slight blue shift is observed. The reason for this change of the linear absorption spectra is that the hydrogen bonds get weaker [67]. With increasing temperature, the position of the bending mode slightly shifts to the red (from 1644.5 at $T = 298$ K to 1642.3 cm$^{-1}$ at $T = 348$ K) [16] and the band gets somewhat narrower (83 cm$^{-1}$ FWHM at $T = 348$ K instead of 88 cm$^{-1}$ FWHM at $T = 298$ K) [16]. The intensity of this band does not depend on temperature [55, 5, 4]. The spectrum of the bending mode can be well fitted with a Lorentzian line shape. We calculate the convolution of this spectrum with itself to estimate the absorption profile for the overtone.

The result of the calculation of the overlap of the spectrum of the OH-stretch and the overtone of the bending mode is displayed in Figure 4.7. The only free parameter in the comparison between experiment and theory is the absolute value of $T_1$. Clearly, the calculation gives a good description of the observed temperature dependence of
The increase in $T_1$ with temperature can thus be explained from the blue shift of the OH-stretch band, the red shift of the overtone of the H-O-H bend mode, and the decrease in cross section of the OH-stretch mode. These changes in the spectra all follow from the weakening of the hydrogen bonds with temperature. This means that, although practically all of the energy of the excited OH-stretch of the H$_2$O molecule is transferred to the bending mode, the hydrogen-bond interaction still plays an important role in determining the rate of energy transfer, since it influences the energy mismatch and the magnitude of the anharmonic coupling.

In the next chapter [52], we will show that the energy relaxation of the intermediate state likely forms the rate limiting step of the equilibration. The combination of that result with the present findings on the nature of the intermediate state, suggests that the vibrational lifetime of the bending mode is 550 fs. This value agrees quite well with the interval of $0.6 < T_\delta < 1.2$ ps (with $T_\delta$ the lifetime of the bending vibration) found by Deák et al. [12].

Based on the present findings for the relaxation mechanism of pure H$_2$O, one could ask the question whether the bending mode forms also the accepting mode in HDO:D$_2$O. Pure liquid water has the special feature that the overtone of the bending mode ($2\delta$) is in resonance with the OH-stretch vibration ($\nu$). For HDO:D$_2$O, however, the resonance frequency of the bending mode is 1450 cm$^{-1}$, which gives rise to a frequency mismatch of more than 500 cm$^{-1}$ between the OH-stretch and the overtone of the bending mode. Therefore extra excitation in other modes is needed to overcome this energy mismatch, a reasonable candidate is the hydrogen bond stretch mode (200 cm$^{-1}$). Hence, we must conclude that for HDO:D$_2$O the relaxation mechanism is still not completely clear. It is not possible yet to decide whether the accepting mode is a combination of the bending mode and the hydrogen bond stretch mode, or both this combination tone and a relaxation channel in which all the energy is transferred to the hydrogen bond mode.

4.6 Conclusions

We performed mid-infrared pump-probe spectroscopy to study the temperature dependence of the lifetime of the OH-stretch vibration in pure liquid water (H$_2$O). We observed two time scales in the relaxation process, the lifetime of the OH-stretch vibration $T_1$ and the equilibration time $\tau_{eq}$. For the equilibration time constant no temperature dependence of the equilibration time was observed. For the lifetime of the OH-stretch vibration, an increase is observed from 260 ± 18 (at 298 K) to 320 ± 18 fs (at 358 K). This means that the relaxation in pure H$_2$O is three times faster than in HDO:D$_2$O; the increase with temperature, however, is comparable, 20% in both cases. We were able to give an accurate description of the observed lifetime increase for pure H$_2$O by calculating the overlap integral between the overtone of the bending mode and the stretch mode as a function of temperature. The spectral positions and shapes
of both absorption bands alter as a function of temperature due to changes in the hydrogen bond interactions. This means that for H₂O the OH-stretch vibrations relax by energy transfer to the overtone of the bending mode, but the rate at which this transfer takes place strongly depends on the hydrogen-bond interaction, since this interaction determines the energy mismatch and the magnitude of the anharmonic coupling.