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Temperature dependence of vibrational relaxation of the OH bending excitation in liquid H$_2$O

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ABSTRACT

Mid-infrared pump–probe spectroscopy measurements of the OH bending vibration in pure liquid water were performed at different temperatures. The population lifetime increases from 170 ± 15 fs at $T = 295$ K to 250 ± 15 fs at $T = 348$ K. This temperature dependence can be explained by the decrease in the spectral overlap between the OH bending and the high-frequency librational modes, supporting the relaxation scenario that the bend vibrational energy is dominantly transferred to librational motions. It was also found that the temperature dependence becomes absent below room temperature, the possible origin for which is discussed.

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1. Introduction

In the liquid phase, water molecules form the disordered three-dimensional (3D) hydrogen bond (HB) network which is continually changing in time [1]. The physical and chemical processes in liquid water are intimately connected with dynamics of the HB network. In particular, vibrational energy relaxation is a fundamental process that governs the dynamics in which this liquid thermalizes. It also plays a practically important role, acting as energy dissipation channel during chemical reactions in aqueous environments.

In the last decade, mid-infrared third-order spectroscopy has been applied to unravelling the vibrational relaxation dynamics of liquid water [2,3]. The ultrafast processes of population relaxation [4,5], resonant energy transfer [6], and spectral diffusion [7,8] of the OH stretching excitation have been investigated. It has been shown that the population relaxation of the OH stretch vibration for HOD dissolved in D$_2$O shows anomalous temperature dependence; it becomes slower with increasing temperature [4]. The same trend was found for the OH stretch vibration in pure H$_2$O [5,8]. In general, the vibrational relaxation of a solute–solvent system is accelerated with increasing temperature. This is because the occupation in the low-frequency accepting modes increases with temperature, causing stronger anharmonic interaction between the donor and acceptor modes. The anomalous temperature dependence found for HOD in D$_2$O has been ascribed to the weakening of the anharmonic coupling strength between the OH stretch

vibration and the intermolecular stretching modes [4]. In pure H$_2$O, the slower relaxation at higher temperature was explained from the decrease in overlap resonance between the OH stretching vibration and the overtone of the OH bending mode [5].

Compared with the OH stretching vibration, only a limited number of studies have been devoted to the relaxation dynamics of the other intramolecular mode, the OH bending vibration. The OH bending vibration has the lowest frequency among the intramolecular modes, and therefore, energy relaxation of this mode should involve librations and other intermolecular vibrations. As a result, the bending mode serves for initiating thermalization in the liquid. Furthermore, its lifetime can be a sensitive probe of the intermolecular interactions. The population lifetime of the OH bend vibration in pure H$_2$O at room temperature has been measured to be about 170 fs [9,10] and 250 fs [11] by the mid-infrared pump–probe spectroscopy. Recently, Ingrosso et al. [12] studied the decay of the bend vibration in neat H$_2$O by the classical molecular dynamics (MD) simulations and found a time constant of 270 fs. Bastida et al. [13] used hybrid quantum/classical simulations to obtain 120 fs time constant. These values are in reasonable agreement with the experimental ones [9–11]. Rey et al. [14] studied the pathway for the bend vibrational relaxation by the classical MD simulations, and showed that the relaxation is dominated by energy flow to the hindered rotation of the bend excited water molecule. A promising way to get insight into the relaxation mechanism and to verify the role of the HBs in the relaxation experimentally is measuring the temperature dependence, because the average HB strengths and the spectral overlaps change with temperature.

In this Letter, we study the temperature dependence of the population relaxation of the OH bending excitation in pure H$_2$O by the mid-infrared pump–probe spectroscopy. The population lifetime

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increased from 170 ± 15 fs at T = 295 K to 250 ± 15 fs at T = 348 K. This temperature dependence supports the relaxation scheme that the bend vibrational energy is mainly transferred to the librational motion and sheds light on the role of the HBs for rapid energy transfer to the surrounding molecules. It was also found that the temperature dependence becomes absent below room temperature, the possible origin for which is discussed.

2. Experimental methods

Figure 1 shows the linear absorption spectrum of liquid water at room temperature, reproduced from Ref. [15]. The OH bending absorption band exhibits the maximum at 1645 cm^{-1} with the FWHM width of about 90 cm^{-1} and displays a pronounced asymmetry towards low frequencies. The asymmetry of the band has been attributed to a superposition of the absorption of fully and partially hydrogen bonded molecules [16]. A weak band centered at 2150 cm^{-1} is the combination tone of the OH bending and librational modes. The librational modes have their main L2 band centered at 700 cm^{-1} and their high-frequency components, extending up to the OH bending fundamental transition frequency. Compared with the gas phase spectrum peaked at 1594.7 cm^{-1}, the absorption peak of the OH bending vibration is blue-shifted by about 50 cm^{-1}. This is because the HB increases the force constant of the OH bend oscillator. Assuming that the absorption linewidth Δv of 90 cm^{-1} is dominated by the population relaxation of the OH bending excitation, the lifetime would be $T_1 = 1/(2\pi\Delta v) \sim 60$ fs. This is much shorter than the measured values [9–11] and therefore the linewidth should be dominated by the spectral diffusion due to the fluctuating force constant.

We have performed single-color pump–probe experiments with mid-infrared femtosecond pulses. Ti:sapphire regenerative amplifier (Spitfire 40, SpectraPhysics) generated 1 mJ, sub-50-fs pulses at a 1-kHz repetition rate. Then the optical parametric amplification (2-mm thick β-BaB$_2$O$_4$, type II) and the difference frequency generation (0.5-mm thick AgGaS$_2$, type II) produced mid-infrared pulses of 3–5 μJ energy with their center frequency tunable around 3–7 μm. The spectrum of the pump and probe pulses, shown as a dashed line in Figure 1, were centered at the OH bending transition frequency of 1645 cm^{-1}, with a FWHM bandwidth of about 200 cm^{-1}. The spectra fully covered the OH bending absorption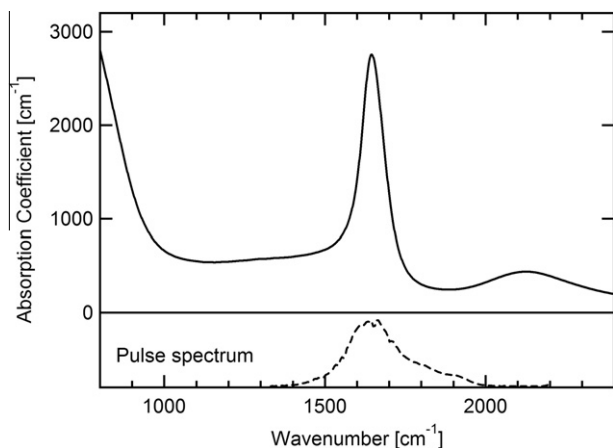 and excited a portion of the librational background. A small fraction of the mid-infrared pulses was split off with a wedged BaF$_2$ window to obtain probe and reference pulses, and the remainder was used as the pump. The linearly polarized pump and probe pulses were focused and overlapped in a sample by means of an off-axis parabolic mirror with an effective focal length of 108.9 mm. The focal diameter was 200 and 120 μm for the pump and probe, respectively. The residual chirp of the mid-infrared pulses was compensated by an 1-mm-thick germanium window. The resulting time resolution of the pump–probe measurements was 100 fs in FWHM, which was verified by the intensity cross-correlation measurement. The water layer (ultrapure water H$_2$O, Wako pure chemical industries Ltd.) was sandwiched between two 270-nm-thick Si$_3$N$_4$ windows (NTT Advanced Technology Corp.), which were temperature-controlled by a Peltier device with an accuracy of ±1 K. The thin window not only eliminated the cross-phase modulation signal originating from the window materials but also avoided the dispersive broadening of the pulses. Pump pulses with 3-μJ energy at the sample excited the water molecules within a 4.2 μm thick layer (optical thickness of 0.5 at 1645 cm^{-1}). The temperature rise after thermalization within the excitation volume of 1.3×10^{-7} mm^3 was estimated to be ~2 K. The spectra of probe and reference pulses transmitted through the sample were acquired by a monochromator and a 32×2 HgCdTe detector array, with the spectral resolution of 4 cm^{-1}. The whole path of the mid-infrared beams was purged with the dried and CO$_2$-reduced nitrogen gas.

Measurements were performed with parallel linear polarization of the pump and probe pulses, in order not to degrade the time resolution by inserting any dispersive element like a quarter-wave plate for the magic-angle geometry. This should not matter in evaluating the lifetime, since polarization-resolved experiments [9] indicated a constant pump–probe anisotropy during the bend lifetime, ruling out any important contribution from the intermolecular bend-to-bend vibrational energy transfer route. Furthermore, a bend-to-bend energy transfer time was estimated [12] to be much longer than the OH bending lifetime, by assuming that the dipole–dipole interaction is the dominant coupling in the bend-to-bend intermolecular energy transfer and by scaling the 100 fs vibrational energy transfer of the OH stretch [8] with the ratio of the bend to stretch transition dipole squared.

3. Experimental results

Figure 2 shows the linear absorption spectrum of liquid H$_2$O for different temperatures, measured by an FTIR spectrometer. Upon temperature elevation, the OH bending fundamental transition band slightly shifts to lower frequency with its linewidth narrowed [16]. A librational absorption background extending up to the OH bending band decreases with temperature. Here we note that the data were collected in transmission geometry with a water film sandwiched by the Si$_3$N$_4$ membranes. The observed features agree well with the ones obtained by the attenuated total reflection (ATR) technique [17,18], which provides more reliable quantitative information.

Figure 3a–d shows transient absorption spectra for different time-delays after OH bending excitation, measured at the temperature of 277 K (4 °C), 295 K (22 °C), 323 K (50 °C), and 348 K (75 °C), respectively. General features observed for each data are same as those in Refs. [9,10]. The strong bleaching around 1645 cm^{-1} is caused by the depletion of the $v = 0$ state of the OH bending oscillator and stimulated emission from the $v = 1$ state. The fast decay of the bleaching is due to the depopulation of the $v = 1$ state. The broad enhanced absorption observed at frequencies below 1610 cm^{-1} is due to the excited-state transition ($v = 1$–2). The redistribution of energy among all degrees of freedom results

Figure 1. Linear absorption spectrum of pure H$_2$O in a frequency range of 800–2400 cm^{-1}. The spectrum around the OH bending band consists of the absorption band of the OH bending vibration with the maximum at 1645 cm^{-1} and a broad librational absorption background. A weaker band centered at 2150 cm^{-1} is the combination tone of the bending vibration and the libration. Dashed line in a lower panel shows the pump and probe pulse spectrum.
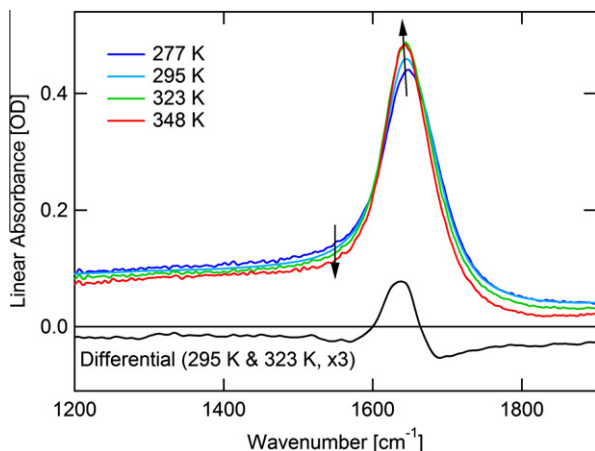
Figure 2. Linear absorption spectrum of liquid H_2O measured at the temperature of 277, 295, 323, and 348 K. The black line shows the differential absorbance obtained by subtracting the absorbance for 295 K from that for 323 K, and by multiplying a factor of three. Upon temperature elevation, the OH bending band slightly shifts to lower frequency with its bandwidth narrowed. The librational absorption background monotonically decreases with temperature.

in a macroscopically heated ground state. The absorbance change due to this thermalization, evolving at sub-picosecond time scale, has the spectral shape similar to the differential absorption shown in Figure 2.

The thermalization signal is less pronounced for higher temperature, as is observed in Figure 3a–d. Because the temperature

dependence of the linear absorption is moderate (Figure 2), the total pulse energy absorbed by the resonant excitation depends only weakly on temperature. Then the observed tendency indicates that the differential absorption upon constant temperature rise of $\sim$2 K is smaller at higher temperature. The same tendency was found in the ATR measurements [17,18]. Here the factor analyses on the infrared spectra suggested the existence of two species and indicated the suppressed temperature dependence of the two principal factors at higher temperature.

The kinetic data for the probe frequencies of 1650 and 1570 cm^{-1} measured at different temperatures are presented in Figure 4a and b, respectively. Each trace was normalized for its amplitude at early time-delay. At probe frequency of 1650 cm^{-1}, the bleaching signals decay within 500 fs, followed by picosecond evolution due to thermalization. At probe frequency of 1570 cm^{-1}, the excited-state absorptions disappear well within 500 fs. The absorbance decrease at this frequency after 500 fs is again due to thermalization. At each of the probe frequencies, the transient signal for different temperature deviates from each other after the time delay of 150 fs.

The transients were analyzed by a rate-equation model. In the model, the pump pulse resonantly excites the molecule from the ground state into the first excited state of the OH bend vibration. The population of the excited state (I) relaxes with a time constant T_1 to the intermediate level (II), and then to the hot-ground state (III). The intermediate level and its time constant τ_{int} were introduced to phenomenologically describe the thermalization dynamics after the energy is deposit into the intermolecular modes. The hot-ground state is a thermalized state where the OH bend excitation has been relaxed and its energy has been distributed evenly
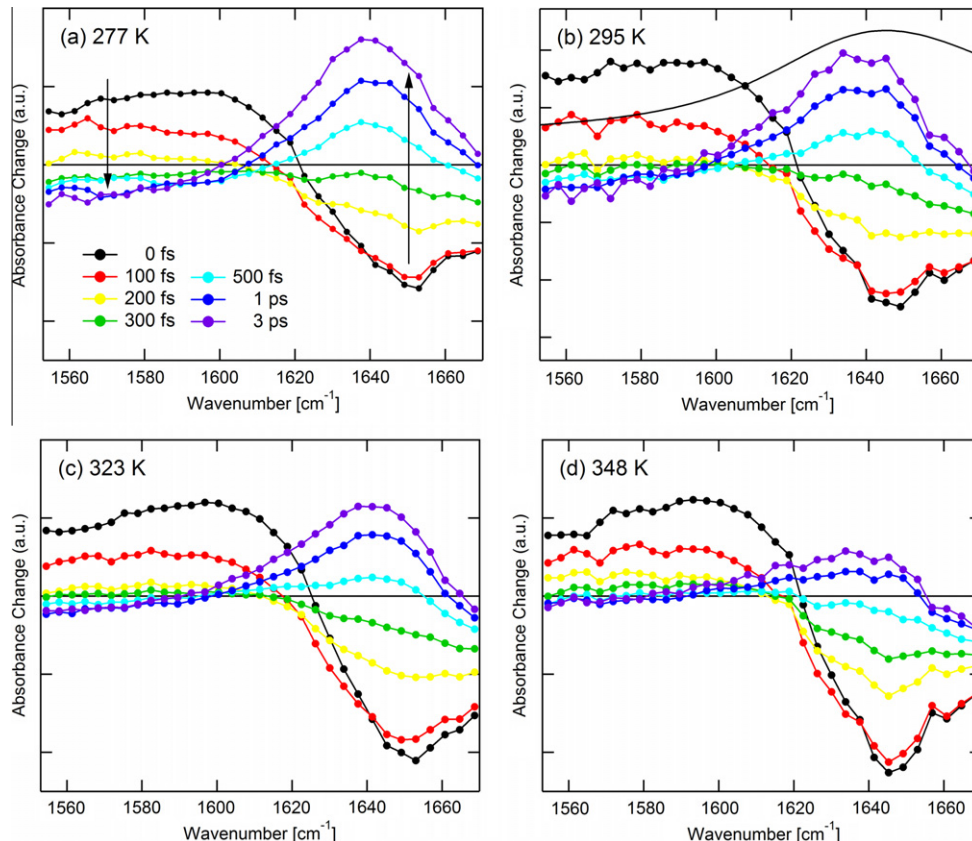

Figure 3. Transient absorbance changes for different pump–probe delays after excitation measured for the sample temperatures of (a) 277 K, (b) 295 K, (c) 323 K, and (b) 353 K, respectively. A black solid line in (b) shows the linear absorption spectrum of H_2O. The bleaching signal around 1645 cm^{-1} is caused by the depletion of the $v = 0$ state of the OH bending oscillator and stimulated emission from the $v = 1$ state. The broad enhanced absorption observed at frequencies below 1610 cm^{-1} are the $v = 1$–2 transition. The absorbance change due to thermalization evolves at sub-picosecond time scale.
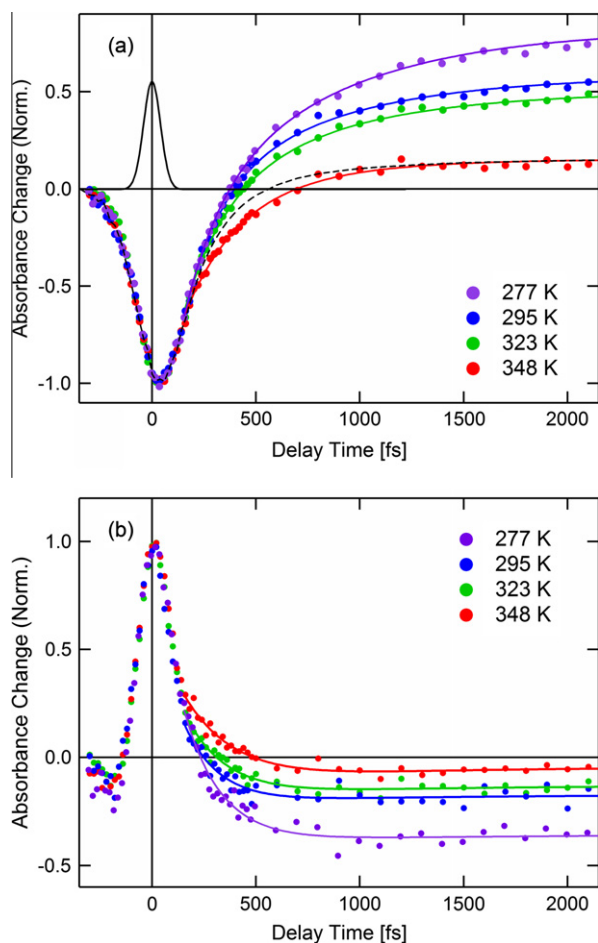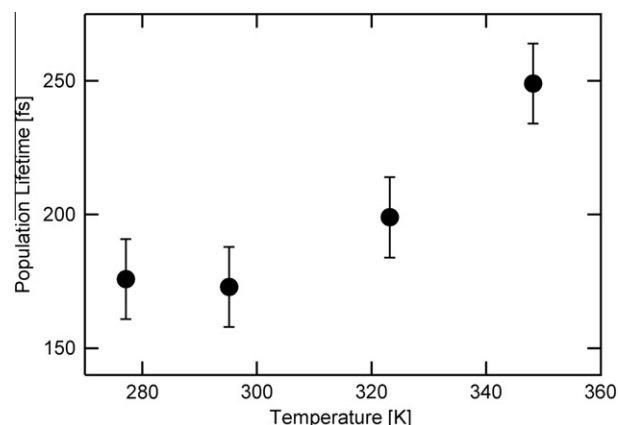
Figure 5. Temperature dependence of the measured population lifetime of the OH bending excitation. The lifetime monotonically increases with temperature above 295 K but such dependence is absent below 295 K.

Figure 4. (a) Transient absorbance changes at 1650 cm^{-1} for varied temperatures reflect the bleaching signal of $v = 0$–1 transition and the stimulated emission of $v = 1$–0 transition at time delay of <500 fs and the thermalization signal at picoseconds delays. The numerical fitting to each data is shown as a solid line. The dashed line which simulates the transient absorption with the time constants of 295 K clearly deviates from the data for 348 K. The instrumental response function measured by the intensity cross-correlation measurement is shown as black solid line. (b) Transient absorbance changes at 1570 cm^{-1} for varied temperatures reflect the excited-state absorption of $v = 1$–2 transition, the librational response, and the thermalization signal. The solid lines are the numerical fittings with the time constants obtained from the global analysis on the frequencies which probe $v = 0$–1 transition.

into all degrees of freedom. The time constant of this hot-ground state was taken as 100 ps, much longer than the maximum measured time delay of 3 ps. We assumed that the absorption changes are induced upon population at the excited state (I) and at the thermalized state (III), and deduced T_1 and τ_{int} by numerically fitting the measured transients.

The fittings were performed for the time delay larger than 150 fs in order to exclude the coherent artifacts. At the probe frequencies below 1600 cm^{-1}, the concomitant librational response contributes to the absorbance change, in addition to the excited-state absorption signal. In fact, the simultaneously excited high-frequency librations decays within 100 fs, followed by the spectral reshaping of sub-picosecond time scale [9,10]. This makes it difficult to obtain reasonable T_1 value from the fits. In order to get a reliable value for T_1, we performed the global numerical fittings to the transients between 1630 and 1660 cm^{-1}, which probe the $v = 0$–1 transition. The fitted curves for the probe frequency of 1650 cm^{-1} are shown in Figure 4a as solid lines. The population lifetime T_1 was obtained as 176 ± 15, 174 ± 15, 200 ± 15 and

250 ± 15 fs for the measured temperature of 277, 295, 323, and 348 K, respectively. The time constant for thermalization has much less temperature dependence; the obtained time constant τ_{int} was 750 ± 30, 700 ± 30, 700 ± 30 and 670 ± 90 fs for 277, 295, 323, and 348 K, respectively. Here we note that the errors were determined as the standard deviations of the fitting parameters. In addition, the obtained time constants varied well within the presented errors, when the earliest time delay of the fitting range was varied between 120 and 200 fs (while keeping the latest time delay as 3 ps). The dashed line in Figure 4a was obtained by simulating the transient signal with the time constants for 295 K, so as to match the measured transient for 348 K at early and late time-delays. The simulated curve deviates from the measured one, which clearly indicates that the population decay is slower for 348 K than for 295 K. Solid curves shown in Figure 4b were obtained by fitting the transients for 1570 cm^{-1} with the same time constants as listed above and by taking into account the spectral reshaping at the intermediate state (II).

The temperature dependence of the measured OH bending lifetime is summarized in Figure 5. Above room temperature, the population lifetime showed anomalous temperature dependence, i.e., the lifetime gets longer with increasing temperature. Interestingly, such temperature dependence fades away below room temperature within the liquid phase. We have performed another sets of measurements and confirmed that the results shown in Figure 5 are reproducible, well within the indicated errors.

4. Discussions

We now discuss the relaxation scheme of the OH bend excitation and the role of the HBs for the rapid energy transfer based on our experimental findings.

As mentioned in the introductory part, the recent classical MD simulations examined the pathway for H_2O bend vibrational relaxation in liquid water [14]. The relaxation was found to be dominated by energy flow to the librational motion of the bend excited water molecule. This energy transfer represented approximately 2/3 of the transferred energy. The remaining energy flow (~1/3) was dominated by transfer to the librational energy of the first hydration shell. The authors pointed out that the librational motion around the x-axis (parallel to the straight line connecting two hydrogen atoms of a water molecule) has the nearly maximal vibrational–rotational coupling with the OH bend vibration via the centrifugal coupling. It was also shown that the hindered rotational

motion around the *x*-axis represents the overtone spectrum which extends well above the OH bending frequency. It is in fact observed that the librational absorption background extends up to the bending frequency (Figure 1).

Cho et al. [19] theoretically showed that librational modes have a collective character in general, involving 10–100 water molecules over the majority of the librational spectrum. In the frequency range higher than 800 cm^{-1}, however, the librational mode is fairly localized and the number of the involved molecules drops below 10 molecules [19]. Therefore we can expect that the librational overtone or combination band beyond 1600 cm^{-1} is rather localized, even though not to a single molecule. Then we can interpret the relaxation picture suggested by Ref. [14] in terms of the Fermi's golden rule at least for qualitative discussions: *the energy transfer from an excited OH bend vibration proceeds via ahnarmonic couplings to the combination tones and overtones of the librational modes.* Here we note that the bending fundamental has almost twice the frequency for librational L2 band. Furthermore, the librational motion around the *x*-axis has the same symmetry as the bending vibration. Therefore the dominant energy transfer should be caused by this 2:1 Fermi resonance. Coming back to the linear absorption spectra shown in Figure 2, the librational absorption at 1200–1600 cm^{-1} decreases upon temperature elevation, while the OH bending band shifts to lower frequency only slightly. Therefore the spectral density of the librational overtones at the OH bending frequency decreases with increasing temperature. This fact explains the observed trend that the relaxation becomes slower with increasing temperature. In this regard, our experimental results support the relaxation scheme that the bend vibrational energy is dominantly transferred to librational modes. The linear absorption spectrum of the librational L2 band peaked at 700 cm^{-1} is red-shifted with increasing temperature, which has been observed in an ATR measurement [18], the pump–probe experiment [20], and an MD simulation [21]. This is consistent with the picture that the librational overtones become confined to lower frequency at higher temperature.

The difference in the spectral density of accepting (librational) modes at the bending frequency explains the relaxation rate of the H$_2$O bending excitation among different situations. The population relaxation time of the bending mode of H$_2$O molecules diluted in non-polar solvents was reported to be between 4.8 and 40.5 ps [22]. The relaxation rates were nicely correlated with frequency distance between the OH bending mode and the nearest vibrational solvent modes. Here the thermal bath of the non-polar solvents offers a considerable density of states of non-vibrational modes only at frequencies below 200 cm^{-1}. When H$_2$O molecules are diluted in D$_2$O, the lifetime of the bending mode becomes ~400 fs [23]. In liquid D$_2$O, the HB network produces the librational modes whose density of states extends up to the OH bending frequency. This drastically accelerates the OH bending relaxation. Even faster relaxation found in neat H$_2$O [9,10] can be explained by the more pronounced density of states for librational modes at the bending frequency.

The Fermi's golden rule tells that the relaxation rate is affected by the thermal population of the accepting modes and the anharmonic coupling strength, as well as the spectral density of the accepting modes at the resonance frequencies of the relaxing modes [24]. The thermal occupations at librational modes lead to pronounced fluctuations required for deactivation of the bending vibration. For the energy transfer from one OH bend quantum to two quanta of the librational mode, the effect of the thermal population on relaxation is described as a multiplication factor of $[\exp(h\nu_\delta/kT) - 1]/[\exp(h\nu_L/kT) - 1]^2$ [5]. Here ν_δ and ν_L denote the bending and librational frequencies, respectively. The temperature rise from 277 to 348 K, however, increases this term by only 4%. For the intramolecular relaxation process where the bending energy

flows to the librational energy of the bend excited molecule through centrifugal coupling [14], the coupling strength is independent of the HB strength or the temperature. On the other hand, the coupling for the intermolecular relaxation process where the accepting librational modes delocalize over several molecules, can be weakened at higher temperatures, correlated with the weakening of the HBs. In both cases, the spectral overlap with the OH bend vibration is degraded at higher temperature, since the resonant frequency of a librational mode is red-shifted when the average HB strength is reduced. It is therefore concluded that the spectral density diminishes with increasing temperature, decelerating the relaxation rate more strongly than the thermal population increase in the librational modes accelerates. It cannot be excluded that the weakening in the coupling strength for the intermolecular relaxation process also contributes to slow down the relaxation at higher temperatures.

As is observed in Figure 5, the relaxation rate becomes almost temperature independent below room temperature of 295 K. This fact may be understood as a saturation effect, i.e., the trend that the spectral density of the accepting librational modes increases with decreasing temperature gets saturated as the temperature approaches the freezing point, where the average HB strength is maximal. Another possibility is that there is a mechanism which leads to an opposite temperature dependence. Even though the major relaxation channel would be the transfer from the OH bending vibration to the librational overtones, there would also be sub-channels which involve the excitations of low frequency modes, such as the HB stretching vibration (~200 cm^{-1}), the HB bending vibration (~50 cm^{-1}) and the structural relaxation. These modes can compensate the residual energy mismatch to enable the energy transfer to the librational components, whose frequencies are apart from the OH bending frequency. Thermal depopulations of these low frequency modes decelerate the relaxations through the sub-channels. Here we note that the structural relaxation slows down at lower temperatures; the time constant varies from 0.22 ps at 314 K to 0.74 ps for 273 K [25]. Correspondingly, the spectral density at 2–50 cm^{-1} drastically drops, as was confirmed in a classical MD simulation [26]. This fact would make the relaxations via the sub-channels inefficient and reduce the total relaxation rate of the OH bending excitation.

It is, however, not yet possible to determine the origin for the observed temperature independence, but we hope that our data will stimulate theoretical works to elucidate it. It is worth noting that similar trend that the temperature dependence of the relaxation rate becomes weaker below room temperature has been observed for the OH stretch vibration of a HOD in D$_2$O as well as that of an H$_2$O molecule in neat H$_2$O [4,5,8]. Further experimental studies on the relaxations of these intramolecular modes at even lower temperatures of a supercooled state will clarify whether the observed level-off is a simple saturation or an indication of a mechanism leading to an opposite temperature dependence.

5. Conclusions

In conclusion, mid-infrared pump–probe spectroscopy has revealed that the vibrational relaxation of the OH bend excitation in neat H$_2$O exhibits anomalous temperature dependence, similar to the OH stretching excitation. Above room temperature, the population lifetime monotonically increased from 170 ± 15 fs at T = 295 K to 250 ± 15 fs at T = 348 K. This temperature dependence can be explained by the decrease in the spectral overlap between the OH bending vibration and the librational modes at higher frequencies. In this regard, our results support the relaxation scenario that the bend vibrational energy is dominantly transferred to high-frequency librations. The ultra-rapid vibrational energy transfer

from the bending excitation can be ascribed to the important roles of HBs in establishing the large spectral density of the (high frequency) librations at the bending frequency and, probably, in inducing strong anharmonic couplings to the librational modes.

The relaxation rate becomes almost temperature independent below room temperature within the liquid phase. This may be due to that the enhancement in the spectral density of the accepting librational modes at the bending frequency with decreasing temperature is saturated as it approaches the freezing point. It is also possible that there is a mechanism which slows down the relaxation at lower temperature against the major trend of accelerated relaxation with decreasing temperature. Further theoretical and experimental works are required to elucidate the physics underlying the diminished temperature dependence.

Acknowledgments

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