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**Anomalous temperature dependence of the vibrational lifetime of the OD stretch vibration in ice and liquid water**

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The temperature dependence of the vibrational  $T_1$  lifetime of the OD stretch vibration of HDO in H<sub>2</sub>O ice was measured with femtosecond mid-IR pump-probe spectroscopy. We found an increase of  $T_1$  from  $480 \pm 40$  fs at 25 K to  $860 \pm 60$  fs at 265 K. These lifetimes are remarkably shorter than the vibrational lifetime of the OD stretch vibration of HDO in H<sub>2</sub>O in the liquid phase, which has a value of  $1.7 \pm 0.1$  ps at 274 K and increases to  $2.24 \pm 0.09$  at 343 K. The observed temperature dependence of  $T_1$  can be well explained from a relaxation mechanism in which the OD vibration relaxes via energy transfer to the bend–libration combination tones of H<sub>2</sub>O and HDO.

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## I. INTRODUCTION

Water exhibits many remarkable temperature dependencies. For instance, water expands on freezing and it possesses an unusually high heat capacity. Most of these anomalies are rationalized by the presence of intermolecular hydrogen bonds.<sup>1</sup> The IR spectrum of water is strongly influenced by the formation of these hydrogen bonds, which makes IR spectroscopy a powerful tool to study the properties of water molecules. The position, width, and intensity of the vibrational bands all depend on hydrogen bond strength.<sup>2</sup> Especially the OH stretching vibrations of the water molecule are particularly sensitive to the local environment.<sup>3</sup>

In neat water, the two OH stretch modes within the water molecule are strongly coupled. In addition, these vibrations are coupled to the OH stretch modes located on other water molecules. These strong interactions make the OH stretch vibrations of pure water a far from ideal system to study the dynamics of individual water molecules. This study can best be performed with isotopically diluted water, i.e. dilute HDO in H<sub>2</sub>O or D<sub>2</sub>O, as the OH(OD) vibration of HDO will only be weakly coupled to the surrounding OD(OH) vibrations.<sup>4</sup>

The temperature dependence of the vibrational relaxation of the OH stretch vibration of HDO in D<sub>2</sub>O water and ice has been studied both experimentally<sup>5</sup> and theoretically<sup>6</sup>, and an anomalous increase of the vibrational lifetime with temperature was observed. The temperature dependence of the OD stretch of HDO in H<sub>2</sub>O in the liquid phase has also been investigated<sup>7-9</sup>, and again an increase of the vibrational lifetime was found from  $1.7 \pm 0.1$  ps at 274 K to  $2.2 \pm 0.1$  ps at 343 K<sup>7</sup>. Recently, the vibrational relaxation of this system has been studied in the ice phase at 80 and 258 K,<sup>10,11</sup> but its temperature dependence has not yet been studied.

In this work we present a study on the temperature dependency of the OD stretch vibration of the HDO molecule in H<sub>2</sub>O in the solid (ice Ih) phase. Combined with the results for the water regime obtained by Tielrooij et al.<sup>7</sup>, we present and discuss the temperature dependence of the OD relaxation over the temperature range from 25 to 343 K. We also present a relaxation model that can explain the observations.

## II. EXPERIMENT

Linear spectra are collected with a PerkinElmer 881 double beam IR spectrometer.

Infrared pump-probe spectroscopy measurements are performed on the OD stretch vibration of HDO in H<sub>2</sub>O in the temperature range 25–265 K. In this technique, a pump pulse excites the OD stretch vibration, and the transient changes in absorption resulting from this excitation are monitored with a second (probe) pulse. The transient spectrum typically consists of two parts: a bleaching and stimulated emission at the 0 → 1 transition, and an induced absorption at the 1 → 2 transition. The latter signal has a lower frequency than the fundamental transition due to the anharmonicity of the vibrational potential of the OD stretch vibration.

The ice samples are prepared as follows. Isotopic diluted water of 2% D<sub>2</sub>O in H<sub>2</sub>O ( $\cong$  4% HDO:H<sub>2</sub>O) is inserted between two sapphire windows with a spacer of 10  $\mu$ m. This dilution is low enough to prevent diffusion by resonant Föster energy transfer<sup>12</sup> and the samples show a desired transmission of about 10%. The samples are frozen using a closed cycle cryostat (CTI-Cryogenics) with a stability of 0.5 K.

The infrared pulses are generated using a commercial Ti:Sapphire laser system (Coherent Evolution) that delivers 3.5 mJ pulses at a wavelength of 800 nm and a repetition rate of 1 kHz. The 800 nm light is converted into mid-infrared light using non-linear crystals. This is done using two independent Optical Parametric Amplifiers (OPAs) pumped by the 800 nm light. The infrared pump is produced by differential frequency mixing of a part of the 800 nm light with the doubled idler output (995 nm) produced by a commercial OPA (TOPAS Light Conversion). This process yields 10  $\mu$ J pulses at 4.1  $\mu$ m (2450 cm<sup>-1</sup>) with a bandwidth of 200 nm (110 cm<sup>-1</sup>). The infrared probe is generated with a home-built OPA, consisting of two BBO ( $\beta$ -barium borate) based amplification stages. The resulting signal and idler pulses are used in a difference frequency mixing process in a AgGaS<sub>2</sub> crystal to produce pulses at 4.4  $\mu$ m (2250 cm<sup>-1</sup>) with a bandwidth of 300 nm (150 cm<sup>-1</sup>). From this beam two 100 nJ pulses are split off by ZnSe plates (8% reflection). One of these pulses is overlapped with the pump beam in the sample, the other is used as a reference to correct for pulse-to-pulse fluctuations. The probe is sent over a delay stage with a resolution of 0.03 ps to vary the time delay between the pump and the probe. After the sample the probe and reference pulses are dispersed with an Oriel monochromator and detected with a 2 × 32 pixel liquid-nitrogen-cooled MCT (mercury cadmium telluride) detector array. The width of the cross-correlation of pump and probe is determined by a germanium plate to be 200 fs.

Every second pump pulse is blocked by a chopper wheel to determine the pump-induced

absorption changes  $\Delta\alpha$ . After the sample the probe beam passes through a rotating polarization filter which allows the selection of either the parallel or perpendicular component of the transient absorption,  $\Delta\alpha_{\parallel}$  and  $\Delta\alpha_{\perp}$ , respectively. From these two signals we construct the isotropic signal:<sup>13</sup>

$$\Delta\alpha_{\text{iso}}(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)}{3}. \quad (1)$$

The pump pulse is resonant with the  $v_1 = 0 \rightarrow 1$  transition of the OD stretch vibration and excites a significant fraction (a few percent) to  $v_1 = 1$ . The population dynamics of the first excited state are probed with a probe pulse that covers the  $v_1 = 1 \rightarrow 2$  transition. As a result, the measurements are not affected by scattered pump light falling on the probe array of the MCT detector, because the probe and pump pulse are dispersed differently by the monochromator. In addition, the population of the first excited state ( $v_1 = 1$ ) is directly probed, without a contribution of the ground state recovery which would be the case when the transient signal at the  $v_1 = 0 \rightarrow 1$  transition would be probed.<sup>14</sup>

### III. RESULTS

#### A. Linear absorption spectra

In Figure 1 the linear spectrum of HDO in  $\text{H}_2\text{O}$  is shown at seven different temperatures. The spectrum shows two absorption peaks: a broad band centred at  $\sim 2200 \text{ cm}^{-1}$  that can be assigned to a combination of the bend and libration (frustrated rotation) mode of  $\text{H}_2\text{O}$  (Fig. 1b), and a more narrow peak centred at  $\sim 2450 \text{ cm}^{-1}$  that is assigned to the OD stretch band of HDO (Fig. 1c).

The absorption strength and the centre frequency of the  $\text{H}_2\text{O}$  bend–libration combination both increase with decreasing temperature.<sup>15–17</sup> The absorption band of the OD stretch becomes narrower and its peak intensity becomes larger in the transition from the liquid to the solid phase. The narrowing results from the transition from the disordered liquid phase to the much more ordered and less inhomogeneous crystalline phase. The centre frequency of the OD stretch absorption band shifts to lower frequencies when the temperature is decreased. In addition, we observe an increase in the total absorption cross section  $\sigma_{\text{tot}}$  with decreasing temperature.

In a semiclassical approach, with a classical treatment of the light, the integrated cross

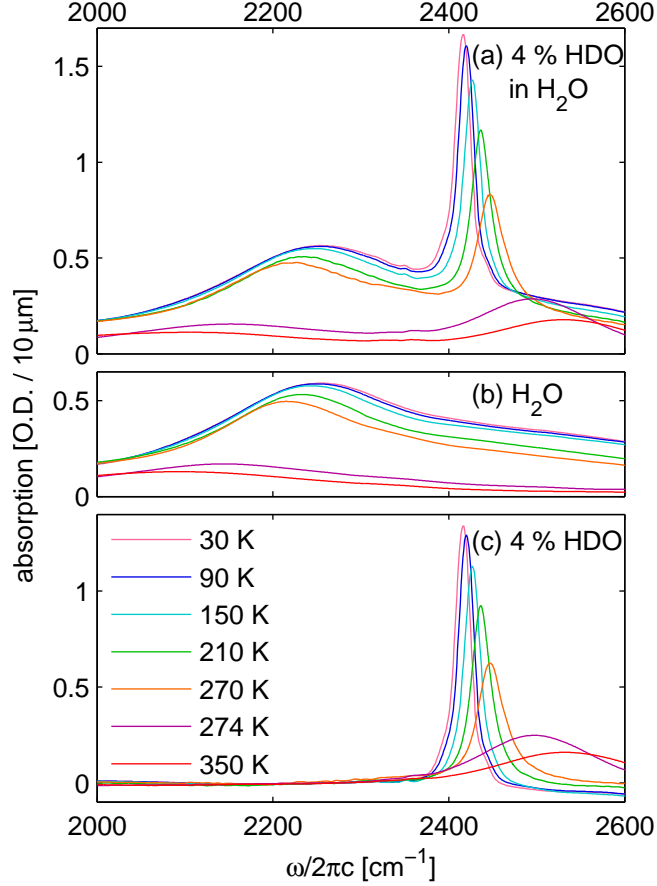


FIG. 1. Linear absorption spectra of 4% HDO in H<sub>2</sub>O (a) and of H<sub>2</sub>O (b) at seven different temperatures. The HDO spectrum (c) is obtained by subtracting the H<sub>2</sub>O spectrum (b) from the HDO:H<sub>2</sub>O spectrum (a). The H<sub>2</sub>O spectrum contains the H<sub>2</sub>O bend-libration combination (b) and the HDO spectrum gives sign of the OD stretch band of HDO (c).

section  $\sigma_{\text{tot}}$  can be expressed as:<sup>18</sup>

$$\sigma_{\text{tot}} \equiv \int d\omega \sigma(\omega) = \frac{\pi}{3\hbar c \epsilon_0} \int d\omega \left| \frac{\partial \bar{\mu}}{\partial q} \right|_{q=q_e}^2 | \langle 1 | \hat{q} | 0 \rangle |^2 \omega g(\omega), \quad (2)$$

where  $q$  is the vibrational coordinate,  $\bar{\mu}$  the electric dipole moment, and  $g(\omega)$  the distribution function that describes the initial spectral distribution of the vibrations ( $\int d\omega g(\omega) = 1$ ). The hydrogen bonding strength is temperature dependent and therefore the spectral shape and magnitude of the cross section also depend on temperature. The dipole moment derivative  $\partial \bar{\mu} / \partial q$  exhibits a strong non-Condon effect, meaning that its value strongly depends on the equilibrium position  $q_e$  and thus on the strength of the local hydrogen bond.<sup>15,19–22</sup> Because of the increase in charge flux associated with the vibration, i.e.  $\partial \bar{\mu} / \partial q$ , the integrated cross

section increases with increasing hydrogen bond strength and thus decreasing temperature. For the OD stretch vibration, this increase is close to linear within the liquid and solid phase.<sup>19,21</sup>

## B. Vibrational energy relaxation dynamics

In Figure 2 a typical transient spectrum is shown. We observe an induced absorption that

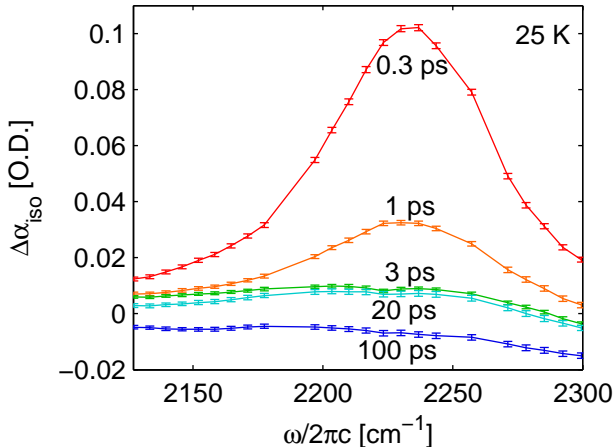


FIG. 2. Transient absorption spectrum for different delay times at 25 K.

decays with increasing delay time. The subsequent thermalization of the vibrational energy leads to an absorption spectrum that differs from that of the initial state. The  $\nu_1 = 1 \rightarrow 2$  transition of the OD stretch at  $2230 \text{ cm}^{-1}$  overlaps with the  $\text{H}_2\text{O}$  bend–libration combination (see Fig. 1(b)). However, this band is not observed in the transient spectrum because the (non-linear) transient absorption response scales approximately with the square of the cross section and the cross section of the  $\text{H}_2\text{O}$  bend–libration combination is much lower than that of the OD stretch vibration.

The transient spectra are fitted with a population relaxation model where the vibration decays exponentially and the heating effect grows in with the same rate. Up to 0.3 ps, the overlap between the pump and the probe pulses gives rise to artifacts due to coherent coupling and cross-phase modulation. After the vibrational relaxation is complete (after  $\sim 3$  ps), we observe additional dynamics at timescales of 20–100 ps, which can be attributed to a thermally induced reorganization of the ice lattice.<sup>23</sup> Therefore, we fit the relaxation dynamics to the data in the time interval 0.3–3 ps. A typical fit result is shown in Fig. 3.

Based on linear difference spectra we estimate the local heating caused by energy deposition of the pump pulse to be maximally 10 K. The temperature jump due to the relaxation of the OD stretch vibration only takes place after the relaxation of the vibration, and therefore does not affect the lifetime. The direct excitation of the H<sub>2</sub>O bend–libration combination by the pump pulse might lead to an early heating of a few degrees.

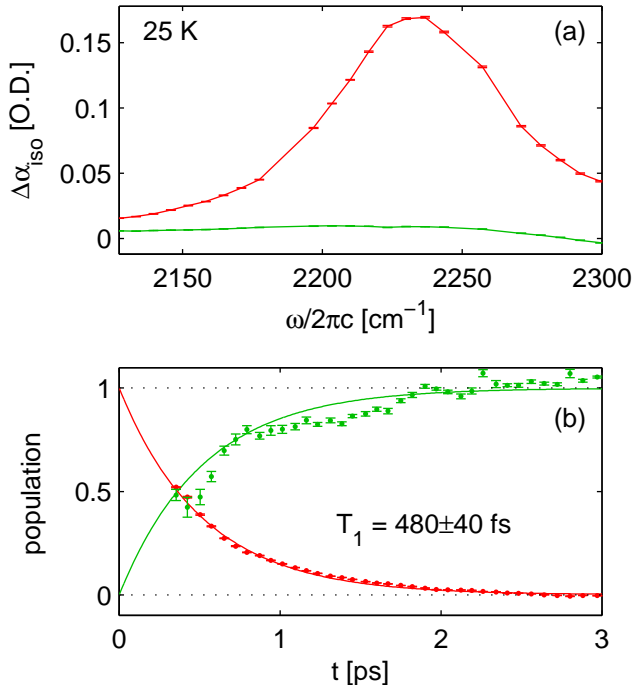


FIG. 3. Spectral decomposition (a) and population dynamics (b) of the  $v_1 = 1 \rightarrow 2$  transition of the OD stretch vibration (red) and the heated ground state (green) at 25 K.

We performed measurements at different temperatures between 25–265 K. A selection of delay traces with corresponding fits are shown in Fig. 4. In this figure both uncorrected (Fig. 4a) and heat-subtracted delay traces (Fig. 4b) are shown.

In Table I we present the fitted vibrational lifetimes  $T_1$  at different temperatures, supplemented with the results in the liquid phase measured by Tielrooij et al.<sup>7</sup> These lifetimes are plotted as a function of temperature in Fig. 5.

The lifetime increases from  $480 \pm 40$  fs to  $860 \pm 60$  fs in the temperature range from 25 K to 265 K. At the solid-liquid transition, the lifetime increases by a factor of two to  $1.7 \pm 0.1$  ps at 274 K. The vibrational lifetime at 80 K of  $480 \pm 40$  fs is somewhat longer than the value previously found by Perakis et al.<sup>10</sup> In this study vibrational lifetimes of  $410 \pm 20$  fs for the

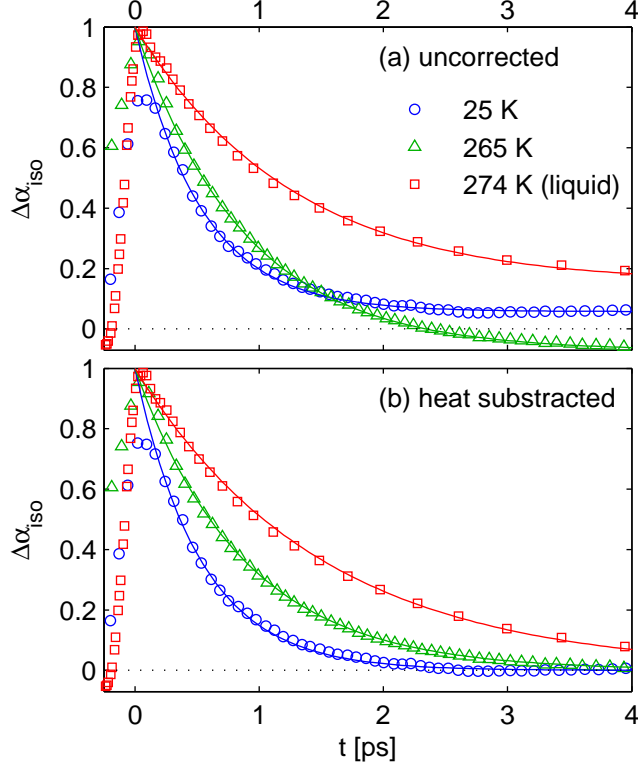


FIG. 4. Uncorrected (a) and heat subtracted (b) normalized absorption changes as a function of delay time. The signals are at the centre frequency of the  $\nu_1 = 1 \rightarrow 2$  transition of the OD stretch vibration of HDO at 25 K and 265 K. For comparison a measurement at 274 K in the liquid phase measured by Tielrooij et al.<sup>7</sup> is included. The data are fitted with a monoexponential decay and heat ingrowth (see text). The fits yield lifetimes of  $0.48 \pm 0.04$ ,  $0.86 \pm 0.06$ , and  $1.7 \pm 0.1$  ps, respectively.

$\nu_1 = 0 \rightarrow 1$  transition and  $360 \pm 40$  fs for the  $\nu_1 = 1 \rightarrow 2$  transition were reported at this temperature. This difference could be due to a difference in the modeling of the rise of the thermal effect on the transient spectrum. We find that the relaxation does not slow down with decreasing temperature, as most theories for vibrational relaxation would predict.<sup>24,25</sup> In fact even the reverse is observed; the lower the temperature, the faster the vibrational decay. A similar anomalous temperature dependence of  $T_1$  has been observed for the OH vibration of HDO in D<sub>2</sub>O.<sup>5,6</sup>



TABLE I.  $T_1$  lifetime of the OD stretch vibration of HDO in H<sub>2</sub>O for different temperatures

solid phase		liquid phase <sup>7</sup>	
Temperature (K)	$T_1$ (ps)	Temperature (K)	$T_1$ (ps)
25	$0.48 \pm 0.04$	274	$1.71 \pm 0.10$
35	$0.49 \pm 0.07$	278	$1.81 \pm 0.10$
40	$0.48 \pm 0.06$	283	$1.81 \pm 0.10$
80	$0.48 \pm 0.05$	288	$1.79 \pm 0.03$
130	$0.56 \pm 0.05$	293	$1.80 \pm 0.02$
160	$0.59 \pm 0.05$	298	$1.86 \pm 0.03$
180	$0.66 \pm 0.06$	303	$1.90 \pm 0.06$
200	$0.71 \pm 0.06$	313	$1.96 \pm 0.08$
225	$0.75 \pm 0.05$	323	$2.07 \pm 0.13$
250	$0.80 \pm 0.07$	333	$2.14 \pm 0.04$
265	$0.86 \pm 0.06$	343	$2.24 \pm 0.09$

### C. Vibrational energy relaxation pathways

The vibrational lifetime is largely determined by non-radiative decay channels. Radiative spontaneous emission is very slow in the mid-infrared regime owing to the  $\omega^3$  dependence of the Einstein coefficient<sup>18</sup>. The transfer probability to a specific channel depends both on its spectral overlap, the amount of accepting modes, and the coupling strength with the initial vibration.

The OD stretch vibration is resonant with the H<sub>2</sub>O bend–libration combination tone (see Fig. 1), and energy transfer to this combination tone forms a possible relaxation pathway. Another, similar relaxation channel is formed by energy transfer to the combination tone of the HDO bend vibration and a librational mode. This combination tone is red shifted by about 300 cm<sup>-1</sup> with respect to the H<sub>2</sub>O bend–libration combination<sup>26</sup>. Yet another relaxation channel is formed by energy transfer to the OD···O hydrogen bond.<sup>27</sup> We do not have quantitative information about the specific coupling strengths of these three possible relaxation channels. However, we can determine the temperature dependencies of the three channels, and by comparing these to the experimental data we can get more information on

their likeliness.

For the two relaxation channels to the H<sub>2</sub>O and HDO bend–libration combination tones we can determine the temperature dependence of the relaxation rate from the effect of temperature on the spectral overlap of their respective absorption bands and the absorption band of the OD stretch vibration. Following Fermi’s golden rule, the relaxation rate of the OD stretch vibration ( $v_1$ ) to a bend–libration combination ( $v_2 + L_2$ ) can be expressed in the following manner:

$$1/T_1 = 2\pi/\hbar \int d\omega |\langle 0_{v_1} 1_{v_2} 1_{L_2} | V_{v_1, v_2 + L_2} | 1_{v_1} 0_{v_2} 0_{L_2} \rangle|^2 \rho_{v_2 + L_2}(\omega) g_v(\omega), \quad (3)$$

where  $g_{v_1}(\omega)$  is the spectral distribution of the OD stretch vibration ( $\int d\omega g_{v_1}(\omega) = 1$ ) and  $\rho_{v_2 + L_2}(\omega)$  is the density of states of the bend–libration combination. In this expression we assume rapid spectral diffusion over the stretch band. This clearly is an approximation as the OD stretch vibration shows slow spectral diffusion components both in the liquid phase and the ice phase. However, the homogeneous linewidth is relatively large, especially in the ice phase.<sup>28</sup>

We assume the density of states of the H<sub>2</sub>O  $v_2 + L_2$  combination to be proportional to its spectral distribution, i.e.  $\rho_{v_2 + L_2}(\omega) \propto g_{v_2 + L_2}(\omega)$ . For the HDO  $v_2 + L_2$  combination we take the spectral shape of the H<sub>2</sub>O  $v_2 + L_2$  combination band redshifted by 300 cm<sup>-1</sup>. Furthermore, we assume the interaction potential responsible for the coupling to be proportional to the product of the local mode coordinates of the vibrations,

$$V_{v_1, v_2 + L_2} \propto \hat{q}_{v_1} \hat{q}_{v_2} \hat{q}_{L_2}. \quad (4)$$

Because the coordinate operators act on the corresponding states only, we can decompose the coupling matrix as follows,

$$\langle 0_{v_1} 1_{v_2} 1_{L_2} | \hat{q}_{v_1} \hat{q}_{v_2} \hat{q}_{L_2} | 1_{v_1} 0_{v_2} 0_{L_2} \rangle = \langle 0_{v_1} | \hat{q}_{v_1} | 1_{v_1} \rangle \langle 1_{v_2} 1_{L_2} | \hat{q}_{v_2} \hat{q}_{L_2} | 0_{v_2} 0_{L_2} \rangle. \quad (5)$$

Inserting this expression for Fermi’s golden rule (Eq. (3)), we find that the relaxation rate is proportional to

$$1/T_1 \propto \int d\omega |\langle 1_{v_1} | \hat{q}_{v_1} | 0_{v_1} \rangle|^2 g_{v_1}(\omega) |\langle 1_{v_2} 1_{L_2} | \hat{q}_{v_2} \hat{q}_{L_2} | 0_{v_2} 0_{L_2} \rangle|^2 g_{v_2 + L_2}(\omega). \quad (6)$$

This equation can be rearranged to an expression for the spectral overlap of the cross sections of the OD stretch and the bend–libration combination bands, using Eq. (2)

$$1/T_1 \propto \int d\omega \sigma_{v_1}(\omega) \sigma_{v_2 + L_2}(\omega) \left( \omega^2 \left\langle \left| \frac{\partial \bar{\mu}}{\partial q_{v_1}} \right|^2 \right\rangle_{\omega} \left\langle \left| \frac{\partial \bar{\mu}}{\partial q_{v_2 + L_2}} \right|^2 \right\rangle_{\omega} \right)^{-1}. \quad (7)$$

We take the spectral average of the squared dipole moment derivative  $\langle |\partial\tilde{\mu}/\partial q|^2 \rangle_\omega$  proportional to the integrated cross section at each temperature. We fit this expression for both the H<sub>2</sub>O  $v_2 + L_2$  and HDO  $v_2 + L_2$  bands to the measured lifetimes. The only free parameter in these fits is an overall scaling parameter, which is chosen to fit the data in the ice regime. The result of the fits is depicted by the red (HDO  $v_2 + L_2$ ) and blue (H<sub>2</sub>O  $v_2 + L_2$ ) lines in Fig. 5.

For the relaxation channel to the OD...O hydrogen bond the vibrational lifetime is highly correlated to the hydrogen bond induced frequency shift  $\delta\omega_{v_1}$  of the OD stretch vibration with respect to its gas phase value. This dependence has been described with a power law relation  $T_1 \propto (\delta\omega_{v_1})^{-1.8}$ .<sup>27</sup> To determine the hydrogen bond induced frequency shift  $\delta\omega_{v_1}$  we used the maximal value of the linear absorption spectrum (Fig. 1) and 2723.7 cm<sup>-1</sup> as the gas phase OD frequency<sup>29</sup>. The proportionality constant was again chosen to obtain the best fit to the data in the ice regime (green line in Fig. 5).

The results of Fig. 5 show that relaxation to the HDO  $v_2 + L_2$  band yields a temperature dependence of  $T_1$  that agrees surprisingly well with the experimental data in the ice phase. The relaxation channel to the H<sub>2</sub>O  $v_2 + L_2$  band provides a lower quality description of the temperature dependence of  $T_1$  in the ice phase, but is superior in describing the change of  $T_1$  at the phase transition from ice to water. Finally, the relaxation channel to the hydrogen bond does not provide a quantitative description in either the ice or the water phase or at the transition between these phases.

#### IV. DISCUSSION

We considered three possible decay channels for the excited OD stretch vibration of HDO. The relaxation channel to the HDO bending + libration combination tone probably involves the strongest anharmonic coupling, as the HDO bending mode is located in the same molecule as the excited OD stretch vibration. On the other hand, the HDO bending + libration combination tone is redshifted by  $\sim 300$  cm<sup>-1</sup> with respect to the H<sub>2</sub>O bending + libration combination tone, thereby introducing a significant energy gap with the OD stretch vibration and a spectral overlap that is  $\sim 3$  times smaller. In addition, as the HDO molecule is surrounded by H<sub>2</sub>O molecules, the density of possible accepting HDO bending modes is obviously lower than that of H<sub>2</sub>O bending modes, which will also favor relaxation

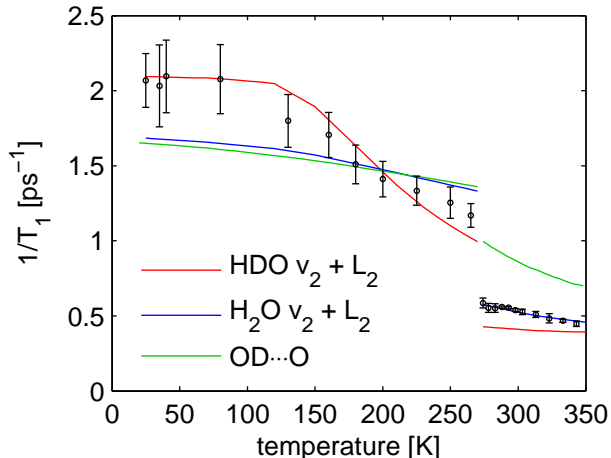


FIG. 5. The lifetime of the OD stretch vibration of HDO as function of temperature. The data in the liquid water range (274–348 K) were published previously by Tielrooij et al.<sup>7</sup> The solid curves represent calculated lifetimes according to different theoretical models (explained in the text). Red: a decay via HDO bend–libration combination. Blue: a decay via the H<sub>2</sub>O bend–libration combination. Green: a decay via the hydrogen bond mode.

to the H<sub>2</sub>O bending + libration combination tone.

We found the experimentally observed temperature dependence of  $T_1$  to be in excellent agreement with the temperature dependence of the relaxation channel to the HDO bend–libration combination, while the large change in  $T_1$  at the phase transition from ice to water is best described by the relaxation channel to the H<sub>2</sub>O bending + libration combination tone. These findings suggest that both relaxation channels may be important. It is even possible that relaxation to the HDO combination tone dominates in the ice phase, while relaxation to the H<sub>2</sub>O combination tone is more important in the water phase. We think that relaxation to the hydrogen bond mode can be excluded as a significant relaxation channel, as the temperature dependence of this relaxation channel poorly agrees with the experimental observations. We hope that the present results will initiate theoretical work that fully reveal the relaxation mechanism of the OD stretch vibration of HDO in H<sub>2</sub>O ice and water.

It is striking that the temperature dependence of the lifetime of the OD stretch of HDO in H<sub>2</sub>O shows many similarities with the OH stretch lifetime of HDO in D<sub>2</sub>O. In the solid phase, the OH stretch lifetime is about a factor of two shorter than in the liquid phase. In

the liquid regime,  $T_1$  increases further from  $745 \pm 47$  fs at 270 K to  $910 \pm 20$  ps at 360 K.<sup>5</sup> The vibrational lifetime is determined by the available decay channels. Since a deuterium atom has twice the mass of a hydrogen atom, the OD stretch frequency is about a factor of  $\sqrt{2}$  lower than the OH stretch frequency. Therefore, the vibrational relaxation channels of the OH and the OD vibration will likely differ. Whereas the OD stretch vibration probably decays via the H<sub>2</sub>O or HDO bend–librational combination, the dominant relaxation pathway of the OH stretch vibration likely involves the bend overtone ( $\nu_2 = 0 \rightarrow 2$ ) of HDO<sup>30–32</sup>. Both mechanisms have in common that they become less probable with increasing temperature owing to the red shift of the bending modes and a corresponding increase in energy gap with the stretching modes. As a result, both relaxation mechanisms show an analog (anomalous) temperature dependence.

## V. CONCLUSIONS

We measured the vibrational energy relaxation dynamics of the OD stretch vibration of HDO in ice Ih at different temperatures. We observed an increase in lifetime from  $480 \pm 40$  fs at 25 K to  $860 \pm 60$  fs at 265 K, which is remarkably faster than the  $1.7 \pm 0.1$  ps at 274 K in the water phase. The temperature dependence of the  $T_1$  lifetime of the OD stretch vibration of HDO in H<sub>2</sub>O is thus anomalous in both its condensed phases. This anomalous behavior can be near-quantitatively explained from the decrease in spectral overlap of the OD stretch and the bend–libration combinations of H<sub>2</sub>O and HDO vibration with increasing temperature. This result suggests that these modes form the main accepting modes of the energy of the OD stretch vibration.

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