Anomalous Temperature Dependence of Vibrational Lifetimes in Water and Ice

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We have used femtosecond two-color midinfrared spectroscopy to determine the temperature dependence of the OH-stretching lifetime in dilute HDO:D_2O solution, both in the liquid and solid (ice Ih) state. Like many other properties of water, the vibrational lifetime shows a remarkable temperature dependence: In liquid water the vibrational relaxation of the OH-stretching mode is twice as slow as in ice, and becomes even slower with increasing temperature. [S0031-9007(98)06669-1]

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Many physical properties of water exhibit a remarkable temperature dependence. The best known example is probably the density, which is larger in the liquid than in the solid phase. Other examples include the viscosity, the specific heat, and the static dielectric constant, all of which show temperature dependences that differ significantly from what is generally observed in liquids. In many cases the anomalous temperature dependence of these properties provided fundamental information on the dynamics and structure of water.

A better understanding of the physical properties of liquids can be obtained by studying the dynamics of the elastic and inelastic microscopic molecular interactions. Information on the inelastic molecular interactions can in turn be obtained by measuring the lifetime of molecular vibrations. Of special interest in this respect is the measurement of the vibrational lifetime as a function of temperature, since in many cases this allows the identification of the modes to which the energy of the excited mode is transferred. In most theories for vibrational relaxation [1–3] the vibrational lifetime strongly decreases with temperature, in most cases as a result of the increased occupation of the energy-accepting bath modes. Measuring the temperature dependence of the lifetime allows the determination of the frequencies of the coupled modes and thus may help in their identification. It is clear that measuring the lifetime of a vibration of the water molecule as a function of temperature might provide us with new insights in the microscopic molecular couplings in water, which eventually may lead to a better understanding of the anomalous macroscopic properties of this liquid. The OH-stretching mode of water is obviously the most suitable candidate, as it is a very sensitive probe for the hydrogen-bond structure [4]. Unfortunately, the time resolution in previous time-resolved midinfrared studies on ice and water was not sufficient to accurately determine the OH-stretching lifetimes [5–8]. Here we report on the determination of OH-stretching lifetime and its temperature dependence in dilute HDO:D_2O solution, both in the liquid and solid (ice Ih) phases.

The laser setup is a slightly extended version of the one reported in detail previously [9]. It consists of a Ti:sapphire laser system that delivers pulses of 100 fs (energy 1 mJ, wavelength 800 nm), which are used to pump an optical parametric generation and amplification (OPA) stage based on β-BaB_2O_4. By parametrically amplifying the broadband output of this OPA (center wavelength $\sim$1.1 μm) with the residual 800 nm pump in a $KTiOPO_4$ (KTP) crystal, we generate pulses of $\sim$200 fs with an energy of $\sim$25 μJ, which are continuously tunable from 3000 to 3600 cm^{-1} (bandwidth $\sim$100 cm^{-1}). These are used as the pump pulses in the infrared pump-probe experiments. The probe pulses (energy <1 μJ, also tunable from 3000 to 3600 cm^{-1}) are generated by parametric amplification in a second, independently tunable, KTP crystal, using the 800 nm and signal light available after the first KTP crystal.

In the pump-probe experiments, the pump and probe pulses are focused to a spot with a diameter of $\sim$300 μm and have spatial overlap in the sample. The pump pulse is tuned to the $\nu_{OH} = 0 \rightarrow 1$ frequency, and the probe pulse to either the $\nu_{OH} = 0 \rightarrow 1$ or the $\nu_{OH} = 1 \rightarrow 2$ frequency. The pump pulse induces a significant population of the $\nu_{OH} = 1$ level, which is monitored by the probe pulse. By measuring the excited state ($\nu_{OH} = 1 \rightarrow 2$) absorption as a function of delay between the pump and probe pulses, we determine the vibrational lifetime T_1. The probe polarization was at the magic angle with respect to the pump polarization, ensuring that the observed transients are determined by the vibrational relaxation only [10].

The sample consisted of a 500 μm layer of dilute ($\sim$1:500) solution of HDO in D_2O kept between two sapphire windows, and was mounted on the cold finger of a closed-cycle He cryostat equipped with a heater. This enabled us to continuously tune the temperature of the sample from 30 to 363 K with an accuracy of 0.2 K. We lowered the pump pulse repetition rate to 70 Hz to avoid heating of the sample in the focus. Using the differential equation for diffusion of heat, an upper bound can be obtained for the steady-state heating in the focus, which is 2.5 K for water and 1 K for ice. These values represent the uncertainty in the reported temperature values.

It has been shown recently that in inhomogeneously broadened bands of hydrogen-bonded OH groups the vibrational lifetime can be strongly dependent on the

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excitation frequency [11,12]. In addition, there can be spectral diffusion effects [8,13]. To investigate if such effects occur, we have recorded pump-probe scans in liquid water at room temperature, with a fixed pump frequency of 3500 cm^{-1}, which is at the high-frequency side of the ν_{OH} band, and three different probe frequencies within the broad $\nu_{OH} = 0 \rightarrow 1$ band (Fig. 1). If the probe pulse is tuned to the same frequency as the pump, the decay rate of the bleaching is initially larger than the value approached for large delays, which is clearly suggestive of spectral diffusion [14]: the spectral diffusion of the excited OH groups out of the spectral window of the probe pulse gives rise to an extra contribution to the decay of the bleaching, which adds to that of the vibrational relaxation. At probe frequencies away from the pump frequency, the decay rate is initially slower due to spectral diffusion of the excited OH groups into the spectral window of the probe, a process that competes with the vibrational relaxation. The spectral diffusion also causes the bleaching at these frequencies to rise to a maximum at larger delay values than at the pump frequency. After approximately 1 ps, the decay rate has become equal at all probing frequencies, indicating that no more spectral diffusion takes place. Similar results are obtained when the pump is tuned to the low-frequency side of the absorption band.

Typical pump-probe scans recorded in ice and in water, showing the excited state ($\nu_{OH} = 1 \rightarrow 2$) absorption versus the delay between pump and probe, are presented in Fig. 2. These scans show that in water at 353 K the vibrational lifetime is significantly *longer* than at 298 K, in striking contrast with the generally observed decrease of vibrational lifetimes with temperature [15–17]. Figure 2 also shows that the vibrational relaxation takes place approximately *twice as fast* in ice as in water.

We have recorded pump-probe scans in a broad range of temperatures, keeping the pump frequency fixed at 3400 cm^{-1} for water and 3330 cm^{-1} for ice (the center frequencies of the ν_{OH} band at room temperature and 260 K, respectively). The probe was always tuned to the $\nu_{OH} = 1 \rightarrow 2$ frequency (3150 cm^{-1} for water, 3090 cm^{-1} for ice). By fitting monoexponential decays to the pump-probe scans, we have determined the vibrational lifetime as a function of temperature. Even though the observed transients can be well described by a convolution of a Gaussian with a monoexponential decay (Fig. 2), it cannot be excluded that for small values of the delay the decay of the absorption at the $\nu_{OH} = 1 \rightarrow 2$ frequency might be partly determined by effects of spectral diffusion, similar to the decay of the bleaching at the $\nu_{OH} = 0 \rightarrow 1$ frequency (see above). For this reason, only the data points for delay values larger than 1 ps were used in the fit to the measurements on liquid water.

Figure 3 presents T_1 as a function of temperature. In ice, no significant temperature dependence is observed all the way from 30 K up to the melting point. At the transition from the solid to the liquid phase, T_1 suddenly increases from 384 ± 16 to 745 ± 47 fs. Note that in undercooled water at 270 K the vibrational lifetime is close to the value at room temperature, and roughly twice that measured in ice at 270 K. As the temperature of the water increases, the vibrational lifetime becomes significantly longer.

In describing the temperature dependence of vibrational relaxation in the condensed phase, it is often assumed that the accepting modes are harmonic oscillators, either phonons (in solids) or instantaneous normal modes (in liquids) [3]. For a single accepting mode the matrix element that describes the relaxation is typically of the form $\langle 1_q n_Q | q Q^m | 0_q n_Q + m \rangle$, where q and Q are the normal coordinates of the high-frequency and phonon modes,

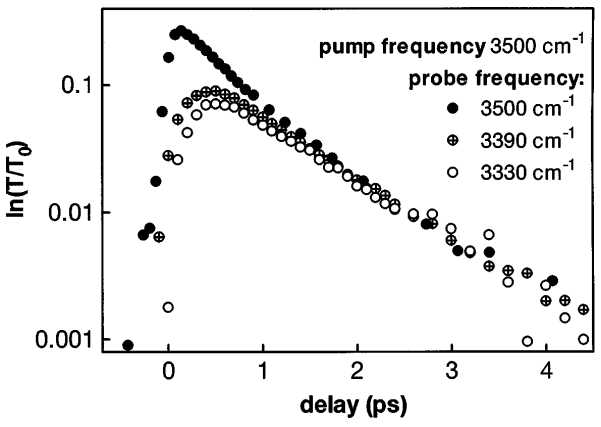

FIG. 1. Pump-probe scans recorded in dilute HDO:D_2O at room temperature, showing the transmission change $\ln(T/T_0)$ of the probe pulse as a function of the delay between pump and probe, at three different $\nu_{OH} = 0 \rightarrow 1$ probing frequencies and with $\nu_{pump} = 3500$ cm^{-1}.

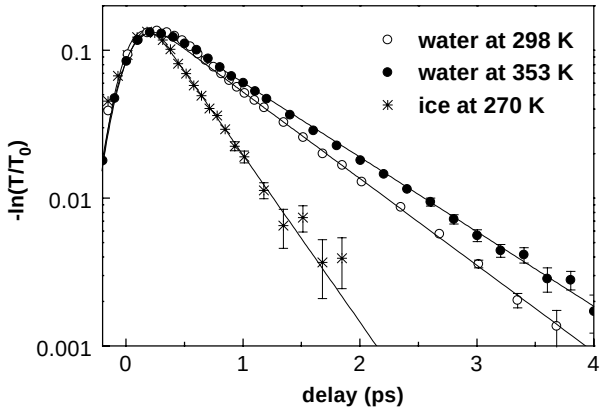

FIG. 2. Pump-probe scans recorded in HDO:D_2O in the liquid ($\nu_{pu} = 3400$ cm^{-1}, $\nu_{pr} = 3150$ cm^{-1}) and solid phases ($\nu_{pu} = 3330$ cm^{-1}, $\nu_{pr} = 3090$ cm^{-1}), showing the absorption increase at the probe frequency vs the delay between the pump and probe pulses. The drawn curves are convolutions of a Gaussian with monoexponential decays with time constants of 740 fs (298 K), 861 fs (353 K), and 385 fs (270 K), respectively.

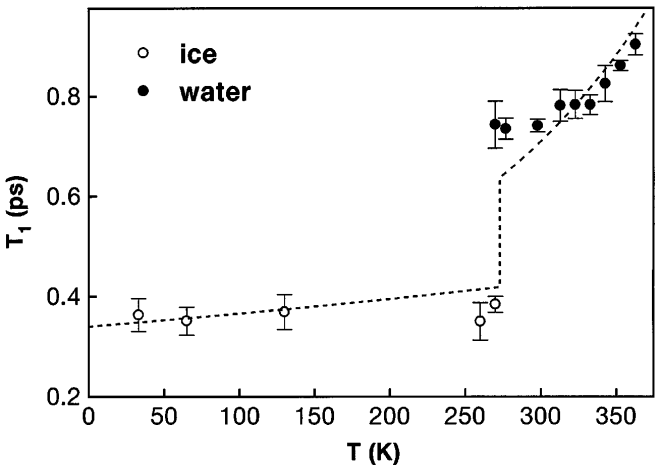

FIG. 3. Vibrational lifetime T_1 of the OH-stretching mode of dilute HDO:D_2O as a function of temperature. Note that the lifetime at $T = 270$ K has been measured both in the solid and (undercooled) liquid phases. The dashed curve has been calculated using a power-law dependence of T_1 on the hydrogen-bond induced redshift of the OH-stretch frequency: $T_1 \propto (\delta\nu_{\mathrm{OH}})^{-1.8}$ [29].

respectively, and m is the number of phonons involved [2]. The value of this matrix element strongly depends on the overlap of the q and Q wave functions, and increases with n_Q, since for a harmonic oscillator the corresponding $|n_Q\rangle$ and $|n_Q + m\rangle$ wave functions are more extended. With increasing temperature, higher levels of the Q mode will be occupied, and the thermally averaged value of the coupling matrix element increases. Hence, the vibrational lifetime is predicted to decrease with temperature. A similar argument holds when more than one accepting mode is involved.

Previous studies have shown that in the vibrational relaxation of the $\nu_{\mathrm{OH}} = 1$ state of a hydrogen-bonded OH group a large part of the energy is transferred to the hydrogen-bond (O—H $\cdots$ O) mode [12,18], which typically has a frequency of $\sim$200 cm^{-1}. Therefore, one would expect a strong decrease of the vibrational lifetime with temperature, both in ice and in water. The observation that in ice the relaxation is nevertheless temperature independent might be due to the fact that the hydrogen bond is a strongly anharmonic oscillator, the potential function probably containing two minima separated by a barrier and/or strong quartic contributions [19,20]. As a result, the wave functions of the excited hydrogen-bond states are probably not much more extended than that of the ground state. Therefore, the matrix element $\langle 1_q n_Q | q Q^m | 0_q n_Q + m\rangle$ will be virtually independent of n_Q. Consequently, the thermal average of this matrix element, and therefore the vibrational lifetime, may be expected to depend only weakly on the temperature, as is indeed observed in ice.

At first sight, in liquid water a similar independence of temperature could be expected as in ice. However, the vibrational lifetime in water actually *increases* with temperature. To our knowledge, up to now such an increase of the vibrational lifetime with temperature has been observed only for the T_{1u} stretching mode of $W(CO)_6$ dissolved in some organic solvents and in supercritical C_2H_6 [21–23]. For the latter system, the increase of T_1 with temperature could be explained from the strong temperature dependence of the properties of the solvent just above the critical point. At temperatures sufficiently far above the critical point, the lifetime exhibited the usual decrease with increasing temperature. In the case of $W(CO)_6$ in some organic solvents, it was found that the increase of T_1 with temperature must result from a strong decrease of the coupling to the accepting modes with temperature, but the reason for this decrease could not be identified [24].

There are two temperature dependent parameters that in principle could lead to a decrease of the coupling between the OH-stretching mode and the accepting bath mode with temperature (and thus to a decrease in vibrational lifetime), namely, the density and the average hydrogen-bond strength.

Above 277 K, the density of liquid water decreases with increasing temperature, which in principle could lead to a lengthening of the vibrational lifetime [24]. Although it cannot be excluded that for liquid water the increase of T_1 with temperature partly results from the decrease in density, it is clear that the density in itself is not an important parameter since the T_1 of liquid water is much longer than that of the less dense ice.

A much more important effect is that the average hydrogen-bond strength decreases with increasing temperature, as can be derived from the redshift of the hydrogen-bond (O—H $\cdots$ O) stretching frequency observed in the far-infrared and low-frequency Raman spectra of water [25,26], and from the blueshift of the OH-stretching mode in the Raman and infrared spectra [27,28]. In ice, the OH-stretch frequency varies much more slowly with temperature [27], which indicates that the effects mentioned below will be less relevant for ice.

A decrease of the hydrogen-bond strength will lead to a decrease of the anharmonic interaction between the OH-stretching mode and the hydrogen bond. If the hydrogen bond forms one of the accepting modes of the vibrational energy, this will lead to an increase of the vibrational lifetime. To see if such a mechanism could explain the observed temperature dependence of T_1(OH), we tried to describe our data with a previously developed model for the vibrational relaxation of hydrogen-bonded OH groups [29]. This model describes the vibrational relaxation of an isolated OH group hydrogen bonded to an oxygen atom, and assumes that all vibrational energy initially present in the OH-stretching mode flows to the hydrogen-bond (O—H $\cdots$ O) mode. It shows that the vibrational lifetime T_1(OH) strongly depends on the hydrogen-bond induced redshift $\delta\nu_{\mathrm{OH}}$ of the OH-stretching frequency with respect to the gas-phase value, and predicts the

power-law relation $T_1(\mathrm{OH}) \propto (\delta\nu_{\mathrm{OH}})^{-1.8}$, which has been observed experimentally for a wide range of hydrogen-bonded complexes [30]. We used this relation and the experimentally observed temperature dependence of $\delta\nu_{\mathrm{OH}}$ in dilute HDO:D_2O [27] to calculate the vibrational lifetime $T_1(\mathrm{OH})$ as a function of temperature. The proportionality constant was chosen such that the calculated T_1 at 323 K equals the experimentally observed value. Since the thermal occupation of the hydrogen-bond mode is not expected to influence the temperature dependence of T_1 (see above), it was not incorporated in the analysis. The calculated T_1 is shown as the dashed curve in Fig. 3. The agreement between the calculated and observed values is reasonably good over the entire temperature range from 30 to 363 K, especially in view of the fact that the model of Ref. [29], which describes an isolated O—H $\cdots$ O unit, is surely a strong oversimplification of the actual situation in liquid water.

It thus seems likely that the origin of the strong correlation between $T_1(\mathrm{OH})$ and the hydrogen-bond strength lies in the anharmonic coupling between the OH-stretch and the hydrogen-bond modes, although it cannot be excluded that the hydrogen-bond strength and $T_1(\mathrm{OH})$ are related in a different manner. For instance, the decrease of the hydrogen-bond induced redshift of the OH-stretch frequency with temperature might lead to an increase of the energy gap between the OH-stretch and *other* accepting modes, thereby decreasing the rate of vibrational energy transfer to these other modes. We think that as yet it is not possible to determine the precise mechanism behind the correlation between the lifetime and the hydrogen-bond strength, but we hope that our data will stimulate theoretical work to elucidate this mechanism.

Summarizing, we have found that the vibrational lifetime of the OH-stretching mode dramatically increases at the phase transition from ice to water, and shows a highly anomalous temperature dependence in the liquid phase. In ice, $T_1(\mathrm{OH})$ is independent of temperature, probably due to the strong anharmonicity of the hydrogen-bond mode, which causes the coupling between the OH-stretch and hydrogen-bond modes to depend only weakly on the thermal occupation of the excited levels of the latter modes. It is quite likely that the strong increase of T_1 at the phase transition from ice to water, and the increase of T_1 with temperature in the liquid both result from the concomitant decrease of the average hydrogen-bond strength, but as yet the precise mechanism of this effect is not known.

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[1] A. Nitzan and J. Jortner, Mol. Phys. **25**, 713 (1973).
[2] S. H. Lin, J. Chem. Phys. **65**, 1053 (1975).
[3] V. M. Kenkre, A. Tokmakoff, and M. D. Fayer, J. Chem. Phys. **101**, 10 618 (1994).
[4] G. Walrafen, in *Water, A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972), Vol. I, Chap. 5.
[5] K. L. Vodopyanov, J. Chem. Phys. **94**, 5389 (1991).
[6] H. Graener, G. Seifert, and A. Laubereau, Phys. Rev. Lett. **66**, 2092 (1991).
[7] G. Seifert, K. Weidlich, and H. Graener, Phys. Rev. B **56**, R14 231 (1997).
[8] R. Laenen, C. Rauscher, and A. Laubereau, Phys. Rev. Lett. **80**, 2622 (1998).
[9] U. Emmerichs, S. Woutersen, and H. J. Bakker, J. Opt. Soc. Am. B **14**, 1480 (1997).
[10] H. Graener, G. Seifert, and A. Laubereau, Chem. Phys. Lett. **172**, 435 (1990).
[11] M. Bonn, M. J. P. Brugmans, A. W. Kleyn, and R. A. van Santen, Chem. Phys. Lett. **223**, 309 (1995).
[12] S. Woutersen, U. Emmerichs, and H. J. Bakker, J. Chem. Phys. **107**, 1483 (1997).
[13] S. Bratos and J.-C. Leicknam, J. Chem. Phys. **101**, 4536 (1994).
[14] A. Tokmakoff *et al.*, J. Chem. Phys. **102**, 3919 (1995).
[15] J. Chesnoy and D. Ricard, Chem. Phys. Lett. **73**, 433 (1980).
[16] E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, Chem. Phys. Lett. **117**, 185 (1985).
[17] U. Happek, J. R. Engholm, and A. J. Sievers, Chem. Phys. Lett. **221**, 279 (1994).
[18] H. Graener, T. Q. Ye, and A. Laubereau, J. Chem. Phys. **90**, 3413 (1989).
[19] D. Hadži and S. Bratos, in *The Hydrogen Bond*, edited by P. Schuster, G. Zundel, and C. Sandorfy (Elsevier, Amsterdam, 1976), Vol. II, Chap. 12.
[20] C. N. R. Rao, in *Water, A Comprehensive Treatise* (Ref. [4]), Vol. I, Chap. 3.
[21] A. Tokmakoff and M. D. Fayer, J. Chem. Phys. **103**, 2810 (1995).
[22] A. Tokmakoff, B. Sauter, and M. D. Fayer, J. Chem. Phys. **100**, 9035 (1994).
[23] D. J. Myers, R. S. Urdahl, B. J. Cherayil, and M. D. Fayer, J. Chem. Phys. **107**, 9741 (1997).
[24] P. Moore, A. Tokmakoff, T. Keyes, and M. D. Fayer, J. Chem. Phys. **103**, 3325 (1995).
[25] H. R. Zelsmann, J. Mol. Struct. **350**, 95 (1995).
[26] K. Mizoguchi, Y. Hori, and Y. Tominaga, J. Chem. Phys. **97**, 1961 (1992).
[27] T. A. Ford and M. Falk, Can. J. Chem. **46**, 3579 (1968).
[28] D. E. Hare and C. M. Sorensen, J. Chem. Phys. **93**, 25 (1990).
[29] A. Staib and J. T. Hynes, Chem. Phys. Lett. **204**, 197 (1993).
[30] R. E. Miller, Science **240**, 447 (1988).