

Ultrafast Vibrational Dephasing of Liquid Water

Jens Stenger, Dorte Madsen, Peter Hamm, Erik T.J. Nibbering, and Thomas Elsaesser

Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany

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We present the first infrared photon echo study of liquid water. For the O-H stretch vibration of HDO in D₂O, femtosecond four-wave mixing experiments reveal an extraordinary short pure dephasing time T_2^* on the order of 90 fs. This unusually fast time scale of dephasing is rationalized by taking into account the large anharmonicity of the hydrogen bonded O-H stretching mode.

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The microscopic structure of liquid water is determined by intermolecular O-H...O hydrogen bonds between the hydroxy (O-H) groups and the oxygen (O) atoms of neighboring water molecules. This results in extended hydrogen bonded networks of water molecules which undergo complex structural changes on ultrafast time scales [1]. Nuclear motions of the hydrogen bonded molecules play a central role for such ultrafast structural dynamics which—vice versa—is reflected in the line shape of vibrational bands. In particular, the stretching band of hydrogen bonded O-H groups displays a pronounced redshift and a strong broadening (FWHM 235 cm⁻¹, Fig. 1) compared to free O-H groups. The cause of this extreme spectral broadening, however, is not obvious. On the one hand, it is widely believed that different spectral positions within the band correspond to different hydrogen bond lengths $R_{\text{OH}\cdots\text{O}}$ [2]. Different models of discrete substructures in water have been proposed as well, which assume an inhomogeneous distribution of intermolecular configurations [3,4]. On the other hand, the appearance of sidebands due to anharmonic coupling of low frequency modes is a known broadening mechanism in hydrogen bonded systems [5,6]. Moreover, one expects a substantial homogeneous broadening by the fast dephasing of coherent optical polarizations on the vibrational transition. Such different contributions to the overall broadening cannot be distinguished in linear vibrational absorption spectra. Nonlinear vibrational spectroscopy using femtosecond infrared pulses has the potential to separate the different broadening mechanisms [3,4,6–11], and to determine the underlying ultrafast dynamics.

Recent ultrafast studies of the nonlinear O-H stretching absorption of HDO in D₂O in the femtosecond time domain have led to conflicting results [3,4,7–11]. Spectral holes of 45 cm⁻¹ width which have been observed in two-color pump-probe experiments with a time resolution of 1 ps [4] have been analyzed with a model [12] involving three different hydrogen bonded local structures. It has been argued [7] that these data might as well be interpreted as effects caused by coherent coupling of pump and probe pulses. Recent hole burning experiments with much shorter pulses of 150 fs duration reveal a time dependent spectral shift of the first moment of the transient spectrum towards the center of the O-H stretching band and a fre-

quency shift correlation time of 700 fs [8]. Assuming a roughly linear blueshift of the O-H stretching frequency with increasing hydrogen bond length $R_{\text{OH}\cdots\text{O}}$, the spectral shift of the first moment was attributed to a motion of the mean hydrogen bond length within the excited ensemble towards its equilibrium position. A dynamic Stokes shift of O-H stretching frequencies within the overall O-H band has been derived from pump-probe data with distinctly different pump and probe frequencies [9]. The results are well described by a Brownian oscillator model for the low frequency motion which changes the hydrogen bond length $R_{\text{OH}\cdots\text{O}}$ and is coupled to the excited O-H stretching mode. In addition to the transient spectral features of nonlinear vibrational absorption, the lifetime T_1 of the $\nu = 1$ level of the O-H stretching mode of 0.5 to 1 ps [10,11] and the rotational reorientation dynamics of excited O-H dipoles [3] have been studied.

So far, the homogeneous broadening of the O-H stretching band and the underlying dephasing processes are not understood. Femtosecond photon echo spectroscopy is a background-free technique which allows the separation of homogeneous and inhomogeneous broadening and—thus—is the method of choice to get insight into such phenomena. In this Letter, we report the first infrared photon

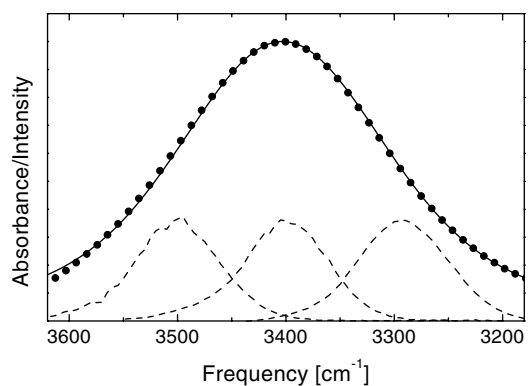


FIG. 1. Absorption spectrum of the O-H stretch vibration of HDO in D₂O corrected for D₂O background (●). The solid line is the absorption spectrum obtained from the global fit (see text). The power spectra of the laser pulses are represented by dashed lines.

echo study of dephasing processes in water. The measurements yield a pure dephasing time of 90 fs. This very fast vibrational dephasing can be accounted for by the large anharmonicity of the hydrogen bonded O-H stretching mode.

Intense mid-infrared pulses which are tunable throughout the O-H stretching band of HDO in D₂O are generated by parametric frequency conversion of amplified pulses from a Ti:sapphire laser. An 800 nm pulse of 90 fs duration and 300 μ J energy pumps a two stage parametric KTiOPO₄ amplifier seeded with a white light continuum. The generated mid-infrared pulses have an energy of 3–5 μ J, a bandwidth of ~ 100 cm⁻¹, and a duration of 130 fs duration and thus are close to the transform limit. Photon echo measurements were performed at the three different spectral positions indicated by the pulse spectra in Fig. 1.

In the photon echo experiment, the infrared pulses are split into three parts with wave vectors k_1 , k_2 , and k_3 , parallel polarization and approximately the same energy. The three beams are focused onto the sample (focal diameter ~ 80 μ m) in the so-called box configuration, which allows the spatial separation of the third order polarization in the phase matching direction $-k_1 + k_2 + k_3$. For identical arrival time of pulses 2 and 3 in the sample a temporal scan of the first pulse yields a signal identical to the conventional two pulse photon echo in the $-k_1 + k_2 + k_3$ direction. The time integrated echo signal is then recorded by an InSb detector.

The sample consists of a diluted solution of HDO in D₂O (optical density ≈ 0.4) and was kept at room temperature between two CaF₂ windows with a spacing of 300 μ m. The solution was circulated rapidly to avoid local heating effects.

Figure 2 shows photon echo data for HDO in D₂O recorded at the three spectral positions indicated in Fig. 1 (solid circles) and for a 1 mm thick CaF₂ window (open circles) measured under exactly the same experimental conditions. The intensity diffracted into the $-k_1 + k_2 + k_3$ direction is plotted on a logarithmic scale as a function of delay time between pulse 1 and pulses 2 and 3. The CaF₂ signal is due to a nonresonant electronic third order nonlinearity and—thus—represents an instantaneous response reflecting the third order correlation function of the infrared pulses. The CaF₂ data in Fig. 2(a) display a slight asymmetry with an exponential rise at negative delay times and a Gaussian decay for positive delays. This asymmetry is attributed to the asymmetric pulse envelope and simulations of the generation process in optical parametrical amplifiers show that such asymmetric pulse shapes are to be expected; see, e.g., [13].

The signal from the HDO sample shows an instantaneous rise for negative delay times and reaches a maximum at a positive delay of +45 fs. This so-called peak shift with respect to delay zero points to the generation of a photon echo caused by inhomogeneous broadening of the O-H stretching transition. At all spectral positions, the

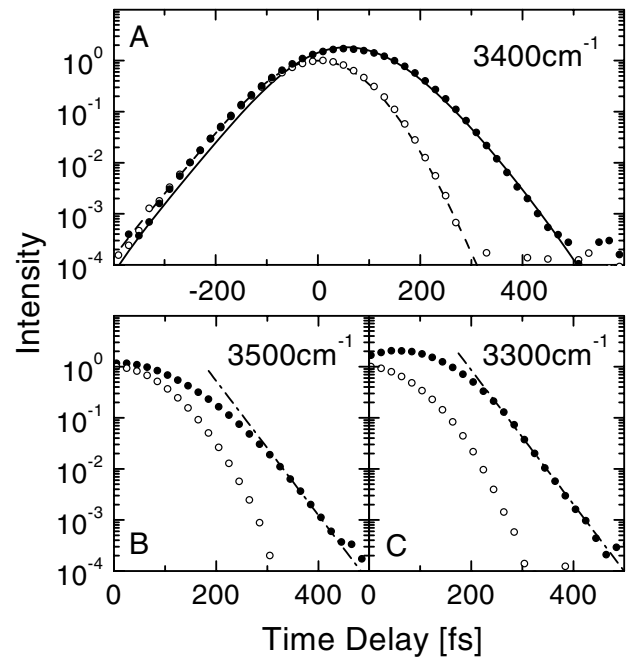


FIG. 2. Integrated four-wave mixing intensity as a function of delay time between pulse 1 and pulses 2 and 3 at three spectral positions (○: instantaneous response in CaF₂; ●: response of HDO in D₂O). The solid line in (a) represents the global fit of the water data, the dotted line the fit of the instantaneous response (see text). In (b) and (c) the slope of 33 fs is indicated by a dash-dotted line.

photon echo signal decreases by several orders of magnitude on a time scale of several hundreds of femtoseconds. For times larger than 250 fs the echo decay at 3400 cm⁻¹ follows a monoexponential function with a time constant of $\tau = 33 \pm 5$ fs [Fig. 2(a)]. This slope is clearly smaller than that of the third order pulse correlation (open circles). Within the experimental accuracy, the photon echo decay times at 3500 and 3300 cm⁻¹ are the same [Figs. 2(b), 2(c)], in contrast to the variation of the $\nu = 1$ lifetime [10] and the reorientation time [3]. It is important to note that the photon echo decay is much faster than the population relaxation of the $\nu = 1$ level of the O-H stretching mode which occurs with characteristic time constants of 0.5–1 ps [10]. Hence, population relaxation does not contribute significantly to the photon echo decay and dephasing is dominated by the pure dephasing time T_2^* .

In the following, we first derive the dephasing time of the O-H stretching transition from the measured decay of the photon echo signals. We then discuss the mechanisms underlying such an unusually fast vibrational dephasing. In the simplest approximation, the decay time of the photon echo signal of $\tau = 33$ fs would correspond to $T_2^* = 2\tau = 66$ fs for a purely homogeneously broadened ensemble of independent two level systems, and to $T_2^* = 4\tau = 132$ fs for an inhomogeneously broadened ensemble. In our case, both homogeneous and inhomogeneous broadening are present so that $66 \leq T_2^* \leq 132$ fs. As the line

shape function should self-consistently describe both the photon echo signal *and* the absorption spectrum [14], the information contained in both can be used to narrow this interval. To extract this information, we performed a global fit of both using the following simplified (Bloch) model for the frequency fluctuation correlation function [14]:

$$\langle \delta\omega(t)\delta\omega(0) \rangle = \delta(t)/T_2^* + \Delta_{\text{inh}}^2. \quad (1)$$

Here, the first term describes homogeneous broadening with an infinitely short correlation time, and the second term describes (static) inhomogeneous broadening with width Δ_{inh} . Of course, inhomogeneity in the liquid phase will not be static, and it has been shown that a spectral diffusion process on a time scale of 700 fs is the dominant inhomogeneous broadening mechanism [8]. The two-pulse photon echo experiment performed here, however, is expected to not be particularly sensitive to such spectral diffusion processes [15]. These would come into view as a function of the so-called population time (i.e., the time between the 2nd and the 3rd field interaction), which is zero in this type of experiment.

When calculating the photon echo signal, the asymmetry of the pulse shape is taken into account by modeling it by a sech^2 function for $t < 0$ and a Gaussian function for $t > 0$. They were adjusted to reproduce the slopes of the instantaneous 3rd order response [Fig. 2(a), dashed line]. To calculate the system response, all time orderings were taken into account during pulse overlap, and all three-level Feynman diagrams were included [16,17]. The fit self-consistently explains the photon echo signal [Fig. 2(a), solid line] and the absorption spectrum (Fig. 1, solid line) with a vibrational dephasing time of $T_2^* = 90$ fs and an inhomogeneous width of $\Delta_{\text{inh}} = 66 \text{ cm}^{-1}$. From a variation of these two parameters in the calculation, one estimates an error of T_2^* on the order of ± 20 fs.

To justify the use of the simplified frequency fluctuation correlation function of Eq. (1), we have also performed fits using as an ansatz for the frequency fluctuation correlation function $\langle \delta\omega(t)\delta\omega(0) \rangle = \Delta_h^2 \exp(t/\tau_c) + \Delta_{\text{inh}}^2$, and $\langle \delta\omega(t)\delta\omega(0) \rangle = \delta(t)/T_2^* + \Delta_{\text{inh}}^2 \exp(-t/700 \text{ fs})$. In the first case, the homogeneous process is described by a finite correlation time τ_c , which, when varied freely in the fit procedure, converges towards $\tau_c = 30$ fs. This means that $\tau_c < T_2^*$, i.e., this term is in the motional narrowing limit. In this limit, only the product $T_2^* = (\Delta_h^2 \tau_c)^{-1}$ is determined while the correlation time τ_c and the fluctuation amplitude Δ_h cannot be separated. With the second ansatz, we include the spectral diffusion process observed before by dynamic hole burning experiments [8]. This modification, however, does not affect the result for T_2^* and the inhomogeneous width Δ_{inh} , as this inhomogeneity is quasistatic on the time scale of our experiment. The quality of the fit is only insignificantly modified in both cases compared to the ansatz of Eq. (1).

These results clearly show that a significant contribution, i.e., $1/(\pi T_2^*) = 120 \text{ cm}^{-1}$, to the total linewidth of

235 cm^{-1} (FWHM) originates from homogeneous broadening. Thus, the often used correlation of O-H stretching frequency with hydrogen bond length is, if valid at all, not extremely sharp. The lifetime of such heterogeneous distributions of hydrogen bond structures is comparably long [8] and gives rise to a quasistatic inhomogeneous broadening.

Dephasing times of vibrational transitions of polar molecules dissolved in polar solvents have been studied extensively [16,18]. At room temperature, pure dephasing times typically vary in a relatively narrow range between ca. 1 to 4 ps, revealing a typical linewidth of some 10 cm^{-1} . In particular, the stretching band of free O-H groups of H_2O monomers in organic solvents shows a spectral width of $\leq 35 \text{ cm}^{-1}$ (FWHM), corresponding to dephasing times ≥ 300 fs [19]. In view of this discussion, it is a central question why dephasing is so much faster in the case of an O-H stretching mode in a hydrogen bond.

Vibrational pure dephasing has been studied theoretically with the help of classical molecular dynamic simulations [20]. Typically, one is expanding the interaction potential between the solute and the solvent

$$\begin{aligned} V &= \left[\frac{dV}{dQ} \right]_{Q=0} Q + \frac{1}{2} \left[\frac{d^2V}{dQ^2} \right]_{Q=0} Q^2 + \dots \\ &\equiv F_1 Q + F_2 Q^2 + \dots \end{aligned} \quad (2)$$

which reveals two terms for the fluctuating transition frequency shift $\delta\omega(t)$:

$$\begin{aligned} \hbar\delta\omega(t) &= (Q_{11} - Q_{00})F_1(t) \\ &+ [(Q^2)_{11} - (Q^2)_{00}]F_2(t) + \dots, \end{aligned} \quad (3)$$

where Q_{ii} is the expectation value of the O-H bond length in the vibrational state $\nu = i$. The first term, which describes the (linear) force exerted by the solvent on the solute oscillator coordinate, vanishes for a harmonic oscillator [21]. When taking into account intramolecular anharmonicity of the solute, however, it has been found for two very different systems (weakly interacting neat N_2 [22] and strongly interacting CN^- in H_2O [20]) that this term dominates the total pure dephasing rate. Expressing $(Q_{11} - Q_{00})$ in terms of experimentally available parameters, we obtain for the (pure) dephasing rate [23]

$$(T_2^*)^{-1} \propto \frac{\Delta}{\hbar^2 \omega^2 \mu} \int_0^\infty \langle F_1(t)F_1(0) \rangle dt, \quad (4)$$

where Δ is the intramolecular anharmonicity of the solute transition (i.e., the difference between the $\nu = 1 \rightarrow \nu = 2$ and the $\nu = 0 \rightarrow \nu = 1$ transition frequency), μ the reduced mass of the vibration, and ω its mean oscillation frequency. Hence, we see that vibrational pure dephasing scales linearly with the anharmonicity Δ . It is interesting to compare this scaling with experimental numbers: For hydrogen bonded O-H groups, one finds an uncommonly large anharmonicity of $\Delta \approx 270 \text{ cm}^{-1}$ [12] of the O-H stretching mode and a dephasing time of approximately 100 fs. In contrast, the stretching modes of free

O-H groups display a much smaller anharmonicity on the order of 100 cm^{-1} or less [19] and comparably long dephasing times $\geq 300 \text{ fs}$. In a microscopic picture of solute-solvent coupling, the solvent forces exerted on the solute molecule do not affect a harmonic oscillator. Increasing its intramolecular anharmonicity as a consequence of hydrogen bonding, however, makes the oscillator attackable and gives rise to extremely fast dephasing. It should be noted that it is still the fluctuating force F_1 , which is responsible for this dissipative process.

Though such arguments are of a qualitative nature, they clearly stress that one can indeed expect enhanced dephasing rates for O-H stretching excitations in hydrogen bonds, even when the fluctuating forces $F_1(t)$ are in the usual range of intermolecular interactions.

In conclusion, we have presented the first four-wave mixing study on the ultrafast dynamics of liquid water. An unusual fast dephasing time T_2 on the order of 90 fs is reported and we show that homogeneous dephasing is a major contribution to the broadening of the O-H stretching absorption band. Furthermore, we can explain our results by considering the strong anharmonicity of the vibration in a perturbative approach. Recent *ab initio* molecular dynamics simulations gave a realistic width of the O-D stretching band in D_2O [24], so that it seems conceivable to quantitatively model the dynamics observed here for HDO in D_2O .

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