Hydrogen Bond in Liquid Water as a Brownian Oscillator

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We present the first experimental observation of a vibrational dynamic Stokes shift. This dynamic Stokes shift is observed in a femtosecond pump-probe study on the OH-stretch vibration of HDO dissolved in D_2O. We find that the Stokes shift has a value of approximately 70 cm^{-1} and occurs with a time constant of approximately 500 femtoseconds. The measurements can be accurately described by modeling the hydrogen bond in liquid water as a Brownian oscillator.

For hydrogen-bonded O—H$\cdots$O systems, the OH-stretch frequency ν_{OH} is strongly correlated to the hydrogen-bond length $R_{O-H\cdots O}$ [1,2]. In isolated (gas-phase) hydrogen-bonded complexes, the difference between the hydrogen-bond potentials in the $\nu_{OH} = 0$ and $\nu_{OH} = 1$ states leads to Franck-Condon progressions in the ν_{OH} spectra with a typical value for ν_{OH} of 3600 cm^{-1} and a typical spacing $\nu_{O\cdots H}$ of 200 cm^{-1} [3,4]. In the condensed phase, the hydrogen-bond mode is strongly damped by interaction with bath modes, resulting in a smooth and broad ν_{OH} absorption band. If the hydrogen-bond mode can still be described with displaced potential-energy curves, excitation of the OH-stretch mode will be followed by relaxation (contraction) of the hydrogen bond to its equilibrium position in the $\nu_{OH} = 1$ state. This should lead to a dynamic Stokes shift of the ν_{OH} frequency of the excited molecule, in close analogy with the dynamic Stokes shift observed in electronic transitions of fluorescent probe molecules in liquid solution [5].

For displaced harmonic hydrogen-bond potentials, the relation between the Stokes shift 2λ (in units of angular frequency) and the absorption line shape $e^{-\omega^2/2\Delta^2}$ is relatively simple [6]:

$$2\lambda = \hbar\Delta^2/k_B T, \qquad (1)$$

where $\hbar$ is Planck's constant, k_B is Boltzmann's constant, and T is the temperature. For the ν_{OH} mode of HDO dissolved in D_2O, the width (FWHM) of the absorption band of 260 cm^{-1} should correspond to a Stokes shift of approximately 60 cm^{-1}. However, a vibrational Stokes shift has never been experimentally observed and thus it is not clear whether the above equation can indeed be used.

It is experimentally quite difficult to observe a vibrational dynamic Stokes shift because, for strongly hydrogen-bonded systems in the condensed phase, the vibrational lifetime is extremely short. As a result, the quantum yield of the fluorescence will be extremely low. Hence, it is not possible to find evidence for a vibrational dynamic Stokes shift by measuring the fluorescence spectrum. The short vibrational lifetime also makes it difficult to observe a Stokes shift using transient absorption spectroscopy [6]. However, the recent development of (sub)picosecond mid-infrared laser systems has made

it possible to measure transient absorption spectra even for hydrogen-bonded systems that show extremely fast vibrational relaxation [7–9]. Unfortunately, for an OH-stretch vibration, the shape of the transient spectrum is not only determined by the bleaching of the $\nu_{OH} = 0 \rightarrow 1$ transition but also by the broad $\nu_{OH} = 1 \rightarrow 2$ excited-state absorption that overlaps with the red side of the $\nu_{OH} = 0 \rightarrow 1$ bleaching. The interplay between the bleaching and the excited-state absorption [10,11] makes it difficult to infer a dynamic Stokes shift from the first moment of the transient spectrum.

In this Letter, we present the first experimental evidence for the presence of a vibrational dynamic Stokes shift. This Stokes shift is observed for the ν_{OH} mode of HDO dissolved in deuterated water (D_2O) by measuring the ultrafast dynamics in different regions of the transient spectrum with two-color femtosecond pump-probe spectroscopy.

Our laser setup has been reported on previously [12,13]. It consists of a Ti:sapphire laser system that delivers pulses of $\sim$100 fs (energy 1 mJ, wavelength 800 nm), which are used to pump an optical parametric device based on BBO and KTP crystals. With this device, two independently tunable 200 fs mid-infrared pulses are generated. One of these pulses has an energy of $\sim$25 μJ and is used as a pump, the other has an energy of less than 1 μJ and is used as a probe. The bandwidths of pump and probe are approximately 70 cm^{-1}. The pump pulse is tuned to a specific frequency in the broad $\nu_{OH} = 0 \rightarrow 1$ absorption band, and the probe frequency is either redshifted or blueshifted with respect to the pump. The pump pulse induces a significant population of the $\nu_{OH} = 1$ level. This results in transient absorption changes, which are monitored by the probe pulse. The probe polarization is at the magic angle with respect to the pump polarization, ensuring that the observed signals are not influenced by orientational dynamics [14]. The sample consists of a 500 μm layer of dilute ($\sim$1:200) solution of HDO in D_2O kept between two CaF_2 windows at room temperature (298 K). At this concentration, Förster energy transfer between the OH groups is negligible. The water is circulated to avoid steady-state heating effects.

Figure 1 presents pump-probe scans recorded with a pump frequency of 3450 cm^{-1} and redshifted probe
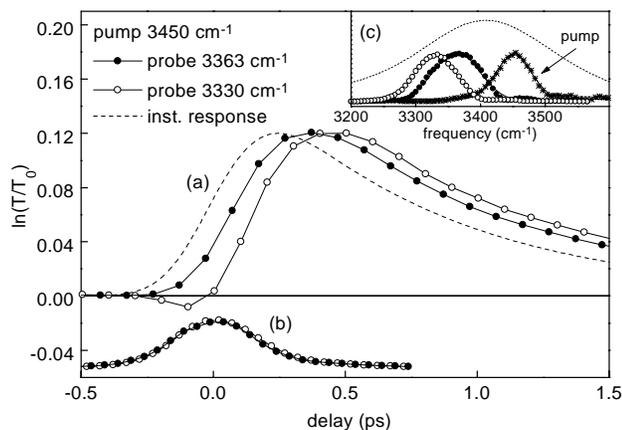
FIG. 1. (a) Pump-probe scans recorded in dilute HDO:D_2O at room temperature, showing the transmission change $\ln(T/T_0)$ of the probe pulse as a function of the delay between pump and probe, with a pump frequency of 3450 cm^{-1} and probe frequencies of 3363 and 3330 cm^{-1}. The open points have been scaled by a factor of 1.85 for better comparison. The dashed curve represents the convolution of the cross correlation with an exponential decay e^{-t/T_1}, with $T_1 = 740$ fs [13]. (b) Cross-correlation traces of the pump and probe pulses. (c) Power spectra of the pump and probe pulses (represented as stars and circles, respectively), and the OH-stretch absorption band (dashed curve).

frequencies of 3363 (solid circles) and 3330 cm^{-1} (open circles). We took care that the pump and the probe have negligible spectral overlap to avoid coherent artifacts [Fig. 1(c)]. Also shown is a convolution of the cross correlation of pump and probe with an exponential decay e^{-t/T_1} ($T_1 = 740$ fs [13]) (dashed curve), which represents the pump-probe signal for instantaneous response that would be observed if no spectral relaxation would take place on the time scale of the experiment. At a probe frequency of 3363 cm^{-1}, the pump-probe signal rises significantly more slowly than this calculated convolution. At a probe frequency of 3330 cm^{-1}, the pump-probe signal rises even more slowly. Figure 2 shows pump-probe scans recorded with a pump frequency of 3320 cm^{-1} and blueshifted probe frequencies of 3445 (solid circles) and 3500 cm^{-1} (open circles). If the probe is tuned to 3445 cm^{-1}, the measurement can be quite well described by a convolution of the cross correlation with e^{-t/T_1} (dashed curve). Only if the probe is tuned to 3500 cm^{-1}, the pump-probe signal is slightly delayed with respect to the instantaneous signal. It is also observed that the bleaching signals are much smaller than in Fig. 1. From the difference between the measurements presented in Figs. 1 and 2, it is clear that with increasing delay the bleaching signal broadens much stronger towards lower frequencies than towards higher frequencies. This observation shows that a dynamic Stokes shift of the ν_{OH} frequency indeed occurs in liquid HDO:D_2O.

Figure 3 shows schematically what happens after excitation at a specific ν_{OH} frequency. The bleaching is caused by both the depletion of the $\nu_{OH} = 0$ state (usually re-
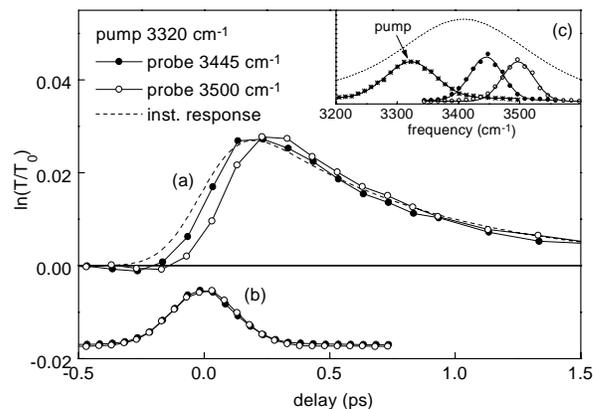
FIG. 2. (a) Pump-probe scans recorded in dilute HDO:D_2O at room temperature, with a pump frequency of 3320 cm^{-1} and probe frequencies of 3445 and 3500 cm^{-1}. The open points have been scaled by a factor of 1.5 for better comparison. (b) Cross-correlation traces of the pump and probe pulses. (c) Power spectra of the pump and probe pulses, and the OH-stretch absorption band.

ferred to as the "hole" contribution [6]) and the population of the $\nu_{OH} = 1$ state (the "particle" contribution [6]). After excitation from the $\nu_{OH} = 0$ to the $\nu_{OH} = 1$ state, the hydrogen bond is initially in a nonequilibrium state. Subsequent relaxation of the hydrogen bond to its new equilibrium position leads to a redshift of the $\nu_{OH} = 0 \rightarrow 1$
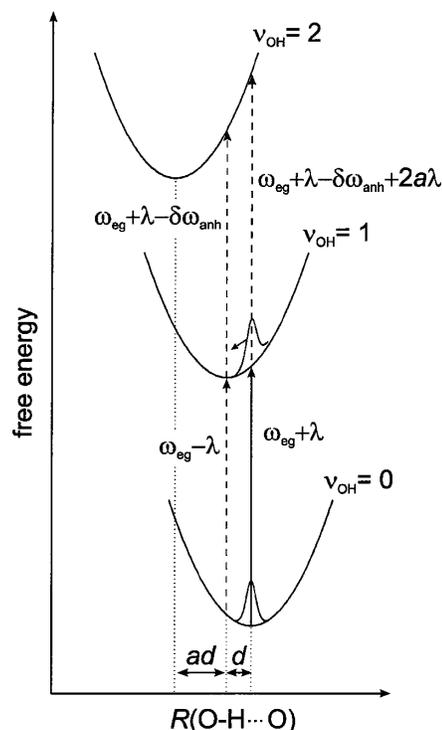
FIG. 3. Schematic picture of the potential-energy functions of the $\nu_{O-H\cdots O}$ mode in the $\nu_{OH} = 0$, $\nu_{OH} = 1$, and $\nu_{OH} = 2$ states. The linear displacement of the $\nu_{OH} = 2$ potential with respect to the $\nu_{OH} = 1$ potential is a times that of the $\nu_{OH} = 1$ potential with respect to the $\nu_{OH} = 0$ potential.

frequency of the excited molecule, and, hence, to a red-shift of the particle contribution to the bleaching. This relaxation corresponds to a contraction of the hydrogen bond. Simultaneously, the depletion in the $\nu_{OH} = 0$ state at the excitation frequency is gradually filled up due to the modulation of $R_{O-H\cdots O}$ of the remaining molecules in the $\nu_{OH} = 0$ state, causing the hole contribution to broaden towards the linear absorption band. The total bleaching signal is the sum of the particle and the hole contributions, and therefore broadens mainly towards the red side of the absorption band. In a previous theoretical study of the dynamics of the OH-stretch mode in HDO:D_2O, only the hole contribution was taken into account, and, hence, only a broadening of the spectral hole towards the linear ν_{OH} absorption spectrum was predicted [15].

In a recent study it was found that the first spectral moment of the transient spectrum of the OH-stretch mode in HDO:D_2O does not shift to a Stokes-shifted value [9]. In view of the present experimental observations this result may seem surprising, but it should be realized that the transient spectrum is not only affected by the Stokes shift but also by two other effects that counteract a redshift of the first spectral moment. First, the transient spectrum will be strongly influenced by the transient $\nu_{OH} = 1 \rightarrow 2$ absorption, which is redshifted by ~ 270 cm^{-1} with respect to the $\nu_{OH} = 0 \rightarrow 1$ transition frequency [7]. The $\nu_{OH} = 1 \rightarrow 2$ absorption is extremely broad (approximately 500 cm^{-1} [7]) and strongly overlaps with the red side of the $\nu_{OH} = 0 \rightarrow 1$ bleaching. Second, it is well known that the vibrational lifetime strongly decreases with decreasing ν_{OH} [16]. In the absence of the dynamic Stokes shift, both effects would lead to a significant blueshift of the first spectral moment. Hence, the first spectral moment, which averages over the whole transient spectrum, will not reveal the Stokes shift. In contrast, by comparing the dynamics at short delay times in different spectral regions of the transient spectrum, as is done in the two-color pump-probe scans of Figs. 1 and 2, the Stokes shift can be clearly observed.

We describe the data quantitatively assuming that the hydrogen bond is a Brownian oscillator coupled to the optically excited OH-stretch mode [6]. The Brownian oscillator model assumes harmonic potential-energy functions for the low-frequency (hydrogen-bond) mode, which are linearly displaced by a distance d with respect to each other in the ground and first excited state of the optically excited (OH-stretch) mode (see Fig. 3). Because of the approximately Gaussian shape of the OH-stretch absorption band, we assume that the hydrogen-bond mode is a strongly overdamped mode (SOM) [6]. The motion of the Brownian oscillator is then diffusive, and the dynamics can be described in terms of three parameters: Λ, the inverse of the correlation time of the diffusive motion; 2λ, the Stokes shift in units of angular frequency; and Δ, the linewidth parameter [6]. An explicit expression for the pump-probe signal S_{PP} in terms of Λ, λ, Δ, and the pulse parameters can be found in the literature [Eq. (13.32) of Ref. [6]]. In addition to the $\nu_{OH} = 0 \rightarrow 1$ bleaching, the transient spectral response is also affected by the broad, redshifted $\nu_{OH} = 1 \rightarrow 2$ induced absorption. The effect of this absorption can be seen from the delay scan with a probe frequency of 3330 cm^{-1} (Fig. 1), which shows an initial decrease of the transmission due to this absorption. For later delay times, this transmission decrease evolves into a bleaching signal due to the Stokes shift of both the $\nu_{OH} = 1 \rightarrow 0$ stimulated emission and the $\nu_{OH} = 1 \rightarrow 2$ induced absorption. The $\nu_{OH} = 1 \rightarrow 2$ absorption can easily be included by adding an extra term to the expression of Ref. [6]:

$$S_{PP}(\omega_1, \omega_2, \tau) = \frac{2\pi e^{-\tau/T_1}}{\sqrt{(\Delta^2 + w_1^2)\alpha^2(\tau)}} e^{-(\omega_1 - \omega_{eg}^0 - \lambda)^2/2(\Delta^2 + w_1^2)}$$
$$\times \{ e^{-[\omega_2 - \omega_e(\tau)]^2/2\alpha(\tau)^2} + e^{-[\omega_2 - \omega_g(\tau)]^2/2\alpha(\tau)^2} - \sigma_{ea} e^{-[\omega_2 - \omega_{ea}(\tau)]^2/2a^2\alpha(\tau)^2} \}, \qquad (2)$$

with

$$\omega_e(\tau) = \omega_{eg}^0 - \lambda + e^{-\Lambda\tau}(\omega_0 - \omega_{eg}^0 + \lambda), \qquad (3)$$

$$\omega_g(\tau) = \omega_{eg}^0 + \lambda + e^{-\Lambda\tau}(\omega_0 - \omega_{eg}^0 - \lambda), \qquad (4)$$

$$\omega_{ea}(\tau) = \omega_{eg}^0 + \lambda - \delta\omega_{anh} + ae^{-\Lambda\tau}(\omega_0 - \omega_{eg}^0 + \lambda), \qquad (5)$$

$$\omega_0 = \omega_1 \frac{\Delta^2}{\Delta^2 + w_1^2} + (\omega_{eg}^0 + \lambda)\frac{w_1^2}{\Delta^2 + w_1^2}, \qquad (6)$$

$$\alpha^2(\tau) = \Delta^2 \left[1 - \frac{\Delta^2}{\Delta^2 + w_1^2} e^{-2\Lambda\tau} \right] + w_2^2, \qquad (7)$$

where ω_1, w_1 and ω_2, w_2 are the center frequency and spectral width of the pump and probe pulse, respectively, and $\omega_{eg}^0 + \lambda$ is the center frequency of the absorption band. In Eq. (2), the first and second terms in the braces correspond to the particle and hole contributions to the bleaching, which have delay-dependent center frequencies $\omega_e(\tau)$ and $\omega_g(\tau)$, respectively. The third term represents the excited-state absorption, with center frequency $\omega_{ea}(\tau)$. The excited-state absorption is characterized by the $\nu_{OH} = 1 \rightarrow 2$ cross section σ_{ea} (relative to the $\nu_{OH} = 0 \rightarrow 1$ cross section), the anharmonicity $\delta\omega_{anh}$, and the ratio a of the displacement between the $\nu_{OH} = 2$ and $\nu_{OH} = 1$ potentials and the displacement between the $\nu_{OH} = 1$ and $\nu_{OH} = 0$ potentials (see Fig. 3). We added a factor $e^{-\tau/T_1}$ to account for the finite excited-state lifetime. We found better agreement between theory and data if a small homogeneous broadening (FWHM of 33 cm^{-1}) in addition to the broadening caused by the Brownian oscillator was assumed.
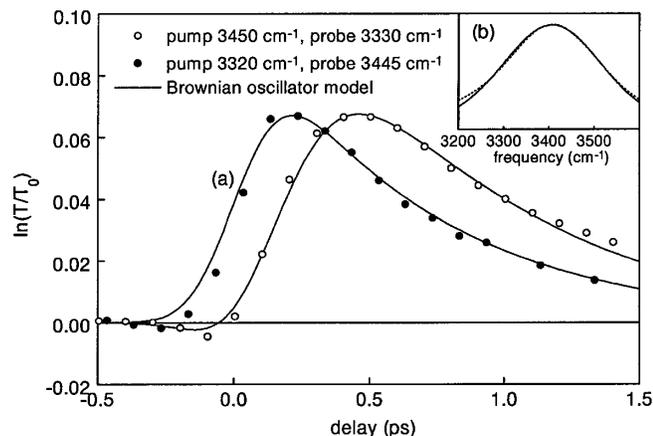
FIG. 4.   (a) Experimental pump-probe delay scans (solid and open points), and delay scans calculated using the Brownian oscillator model (solid curves). The vertical scale of the solid points has been scaled by a factor of 2.35 for better comparison. (b) Experimental OH-stretch absorption spectrum (dashed curve) and the absorption spectrum calculated using the Brownian oscillator model (solid curve).

Convolution of the result of Eq. (2) with the experimentally determined cross-correlation trace [Figs. 1(b) and 2(b)] yields theoretical pump-probe delay scans. To describe the data, the spectral widths and center frequencies of pump and probe were determined from least-squares fits to the power spectra [Figs. 1(c) and 2(c)]. We used $\delta\omega_{anh} = 270$ cm^{-1} [7], a relative excited-state cross section $\sigma_{ea} = 1.54$, and a scale factor $a = 2$. This value for a implies that the $\nu_{OH} = 1 \rightarrow 2$ and $\nu_{OH} = 0 \rightarrow 2$ absorption bands are much broader than the $\nu_{OH} = 0 \rightarrow 1$ band, in agreement with experiment [7,17]. With $T_1 = 650$ fs, $\Lambda = 2$ THz, $\lambda = 7$ THz, and $\Delta = 19$ THz, we found good agreement between data and theory [Fig. 4(a)]. With the same parameter values we could also describe the linear absorption spectrum [Fig. 4(b)]. The value for λ corresponds to a Stokes shift of 74 cm^{-1}, and the value of 2 THz for Λ corresponds to a correlation time of 500 fs for the diffusive motion of the hydrogen bond.

It is clear that the Brownian oscillator model provides a quantitative description of the observed broadening of the bleaching signal towards lower frequencies. This redshift results from the Stokes shift of both the stimulated emission of the $\nu_{OH} = 1 \rightarrow 0$ transition and the $\nu_{OH} = 1 \rightarrow 2$ induced absorption, that is a times as large. The fact that λ does not exactly correspond to the Stokes shift of 60 cm^{-1} obtained from Eq. (1), and the fact that $T_1 = 650$ fs instead of 740 fs leads to a better description of our data, both suggest that the Brownian oscillator model does not accurately describe the spectral relaxation for large delay times. It is quite likely that the hydrogen-bond potentials contain anharmonic contributions [13,18] and have different shapes in the $\nu_{OH} = 0$ and $\nu_{OH} = 1$ states

[19]. Both effects will lead to more complicated spectral dynamics than is described by the Brownian oscillator model.

In conclusion, we have observed a transient dynamic Stokes shift for the OH-stretch vibration in liquid water. The value of this Stokes shift agrees quite well with the value that is predicted by describing the hydrogen-bond mode with displaced harmonic potentials. This constitutes strong evidence that the hydrogen bond in liquid water behaves as a Brownian oscillator with near-harmonic vibrational potentials.

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