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Frequency-dependent vibrational population relaxation time of the OH stretching mode in liquid water

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Abstract

The vibrational population relaxation time has been measured across the inhomogeneously broadened OH stretching mode (ν_3) of a 0.5% solution of HDO in D_2O. Relaxation times vary from 0.5 ps at low frequency (3270 cm^{-1}) to 1.0 ps at high frequency (3600 cm^{-1}). This variation is attributed to a V–V transfer mechanism between ν_3 and $2\nu_2$. © 1999 Elsevier Science B.V. All rights reserved.

The study of hydrogen bond dynamics in the ground electronic state of liquids is important as many chemical reactions and most biochemical reactions involve hydrogen bonds. However, the direct study of these dynamics is difficult as they are expected to be rapid [1] and very little information is available in this field. Published work on the dynamics of thermally activated processes mainly refer to a dilute solution of HDO in D_2O. Midinfrared pump/probe experiments with 1 ps pulses were realized by Laenen et al. on the asymmetric OH stretching vibration of HDO and a population relaxation time (T_1) of 1.5 ps was inferred [2]. A similar experiment was performed by Woutersen et al. using 250 fs pulses and a T_1 of 750 fs was measured at band center (3420 cm^{-1}) at room temperature [3]. No indication of a frequency dependence of T_1 was seen in the above work. Woutersen et al. also explored the orientation relaxation of the OH stretch and found a pump-frequency-independent relaxation

time of 13 ps beyond 1 ps after excitation [4]. Time-resolved spectroscopy of holes burnt in the inhomogeneous OH band of the same isotopic mixture was performed by Gale et al. and a spectral relaxation time constant of 700 fs was observed [5].

The purpose of the present Letter is to explore in detail the frequency-dependence of T_1 inside the inhomogeneous OH stretching band of a 0.5% solution of HDO in D_2O. The experimental set-up consists of a 1 kHz Ti:sapphire amplifier which drives an optical parametric amplifier system producing a 10 μJ pump pulse and a 1 μJ probe pulse, both tunable from 2800 to 3800 cm^{-1} and having a duration of 150 fs and a spectral width of 65 cm^{-1} [6]. This set-up allows one to perform pump/probe spectroscopy with a time-resolution of ∼ 200 fs. Chopping the pump pulse at 500 Hz permits differential spectroscopy (with and without the pump).

The T_1 is measured by employing two different techniques. The first technique consists of burning a hole in the OH distribution, which is centered at 3420 cm^{-1}, with the intense pump pulse and then following the evolution of the hole by time-resolved

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differential spectroscopy using the attenuated probe pulse. This results in a series of differential spectra (see Ref. [5]) at different time delays from −100 fs to 10 ps. After minor correction for excited state absorption ($V = 1 \rightarrow V = 2$) the experimental area of the induced transmission spectra may be computed. The result of this computation for a pump at 3600 cm^{-1} is shown in Fig. 1 (points). The theoretical area of these curves is related to the population relaxation time by the following expression [5],

$$A(t) = C \left\{ 1 + \mathrm{erf} \left[\sqrt{\gamma} \left(t - \frac{1}{2\gamma\tau_1} \right) \right] \right\} $$
$$\times \exp \left[\frac{1}{\tau_1} \left(t - \frac{1}{4\gamma\tau_1} \right) \right], \qquad (1)$$

where $\gamma = 4\ln(2)/\tau_{\mathrm{IR}}^2$, τ_{IR} being the temporal half-width of the incoming midinfrared pulses and $1/\tau_1 = 1/T_1 + 1/\tau_0$, where τ_0 is the orientation relaxation time. Note that this expression is independent of spectral relaxation. Taking a value for τ_1 of 900 fs in the above expression yields the full curve in Fig. 1 in excellent agreement with experiment and allows one to deduce a T_1 of 970 fs at this pump frequency. The variation of T_1 with pump frequency, using this method, is shown in Fig. 2 (full squares). One notices a quite strong frequency dependence of T_1 even over this limited frequency range.

The second technique for measuring T_1 is simply to pump and probe at the same frequency. This method has the advantage of being more sensitive
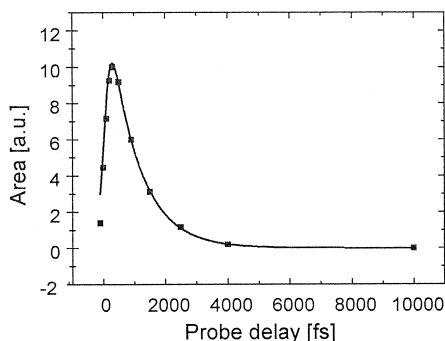

Fig. 1. The area of the induced transmission spectra (filled squares) with the pump at 3600 cm^{-1}, as a function of probe delay in fs. The full curve is calculated using Eq. (1) yielding $\tau_1 = 900$ fs.
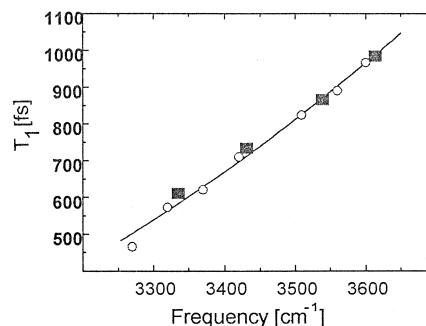

Fig. 2. Experimental results for T_1 in fs) as a function of excitation frequency in cm^{-1}. The filled squares are obtained from the area of the induced transmission spectra and the open circles by pumping and probing at the same frequency. The full curve is calculated using Eqs. (2) and (3).

than the precedent but the complication of depending both on τ_1 (exponential decay) and spectral relaxation (non-exponential decay). It is observed that 2 ps after excitation the signal always decays exponentially and we identify the final time constant with τ_1. The results of this second technique are shown in Fig. 2 (open circles). It is to be noted that the two methods give essentially the same behavior for T_1 which exhibits a variation from 0.47 ps at 3270 cm^{-1} to 0.97 ps at 3600 cm^{-1}.

These results may be interpreted in terms of an intramolecular V–V transfer process between the OH stretching mode ν_3 and the overtone of the bending mode $2\nu_2$ at 2960 cm^{-1}.

Qualitatively, the nearer the excitation of ν_3 is close to $2\nu_2$ the faster is the relaxation. The probability of this process is extremely high in the gas phase at room temperature (11% per gas kinetic collision [7]) and hence is expected to be very efficient in the liquid phase. Quantitatively, we determine the probability of relaxation of ν_3 to $2\nu_2$ by a simple model based on SSH theory [8] in the condensed phase. One obtains the following coupling probability per collision [8],

$$P_{\mathrm{SSH}} = \exp \left\{ -\frac{3}{2} \left(\frac{4\pi^2\mu\omega^2 L^2}{kT} \right)^{1/3} \right\}, \qquad (2)$$

where μ is the reduced collision mass, ω is the difference between the frequency of ν_3 excited and $2\nu_2$, kT is the thermal energy and L is a scaling

parameter obtained from the potential. In the gas phase all the parameters, except L, are known which enables a determination of L. Assuming that L is similar in the liquid and gas phase we may use the above formula to calculate the dependence of P_{SSH} on the frequency difference ω.

The relaxation time in the liquid T_1 is then related to P_{SSH} by multiplying it by an appropriate collision frequency,

$$1/T_1 = \xi P_{SSH}(\omega) \nu_{LP} , \tag{3}$$

where ν_{LP} is the O–O stretch local phonon frequency which we take to be the speed of light times 220 cm^{-1} [9] and ξ is an eventual correction factor which might take account, for example, for any difference of L between gas and liquid. Note that a similar order of magnitude may be obtained with a hard-sphere collision frequency. The result of this calculation with $\xi = 1$ is shown in Fig. 2 (full line) and it can be seen that agreement between experiment and this model is excellent.

In conclusion, we have measured a strongly frequency-dependent vibrational population relaxation time across the inhomogeneously broadened OH stretching band in a 0.5% solution of HDO in D$_2$O. The results may be explained in terms of a simple model for V–V transfer between ν_3 and $2\nu_2$.

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