Evidence for Cooperative Vibrational Relaxation of the NH-, OH-, and OD-Stretching Modes in Hydrogen-Bonded Liquids Using Infrared Pump-Probe Spectroscopy

D. J. Shaw, M. R. Panman, and S. Woutersen
Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The Netherlands

(Received 29 September 2008; published 25 November 2009)

Vibrational energy relaxation of the NH-, OH-, and OD-stretching modes in hydrogen-bonded liquids has been investigated by means of infrared pump-probe spectroscopy. The relaxation rates have been determined both in neat liquids and in isotopic mixtures with systematically varied isotope fractions. In all liquids, the vibrational relaxation rate increases as the isotope fraction is increased and reaches a maximum in the neat liquid. The dependence of the relaxation rate on the isotope fraction suggests a relaxation channel in which the vibrational energy is partitioned between accepting modes of two neighboring molecules.

DOI: 10.1103/PhysRevLett.103.227401 PACS numbers: 78.30.Cp, 61.20.Lc, 78.47.J−, 82.37.Vb

For many processes taking place in liquids, vibrational energy relaxation is an essential dissipation channel. Consequently, the development of techniques capable of resolving this relaxation in time has motivated extensive subsequent studies [1,2]. These studies have generally focused on molecules in solution and on dilute isotopic mixtures. Here, we show that vibrational relaxation in neat hydrogen-bonded liquids occurs significantly faster than in such dilute isotopic mixtures. We find evidence that in neat liquids, the relaxation involves a cooperative mechanism that becomes possible only at the high concentrations characteristic of these systems.

We investigate the vibrational relaxation of the NH-, OH- and OD-stretch modes in a number of common hydrogen-bonded liquids: *N*-methylacetamide (CH_3-CO-NH-CH_3, NMA), ethanol, and methanol. By measuring the relaxation rates in mixtures of these molecules with their N- or O-deuterated isotopomers, we can continuously vary from isotopically dilute to neat liquid without changing the liquid structure. Vibrational relaxation is investigated using a pump-probe setup in which the stretching modes are resonantly excited using an intense infrared pump pulse and the subsequent population changes observed with a delayed probing pulse. The pump and probe pulses (duration 160 fs, energies 3 and 0.1 μJ, respectively, polarizations at the magic angle) are focused (focal diameter $\sim$200 μm) and overlapped in the sample, and transient-absorption changes are measured by frequency-dispersed detection of the probe and a reference pulse. The sample thickness is adjusted to keep the samples sufficiently transparent (ranging from 4 to 50 μm). All samples are at 295 K, except for NMA which is held at 308 K.

The absorption spectra of the neat liquids are very similar to those of the isotopically diluted liquids, as can be seen for NMA in Fig. 1(a). Changing x (the molar fraction of nondeuterated NMA) from 0.1 to 1 (neat liquid) results in a blueshift of the NH-stretch band of 10 cm^{-1}, much less than its width of $\sim$100 cm^{-1}. For the other liquids studied, the shifts are similar or smaller [3].

In contrast to the frequency, the vibrational relaxation is found to change strongly with x. Figures 1(b) and 1(c) show the absorption change upon resonant excitation of the NH-stretch mode of NMA/NMA-d_1 mixtures with $x = 0.1$ and $x = 1$ for several delays with respect to the excitation pulse. At short delays, the transient-absorption change is negative at the $v_{NH} = 0 \rightarrow 1$ transition frequency due to bleaching of $v_{NH} = 0 \rightarrow 1$ transition and $1 \rightarrow 0$ stimulated emission and positive at lower frequencies due to $v_{NH} = 1 \rightarrow 2$ excited-state absorption. Within less than a picosecond, vibrational relaxation causes these features to vanish. At longer delay times, a residual signal is observed, which is due to the increase in temperature that occurs after vibrational relaxation. From the focal size and pulse energy, we calculate temperature increases of 1.3 and 0.1 K for $x = 1$ and $x = 0.1$, respectively. These estimates are confirmed by comparison of the residual $\Delta\alpha$ spectrum with a temperature-difference spectrum of the sample [3].

The decay of the NH-stretch transient-absorption change at 3300 cm^{-1} is shown for $x = 0.1$, 0.2, and 1 in Fig. 2(a). We find that vibrational relaxation occurs much faster in neat than in isotopically diluted NMA. The same is observed for the OH-stretch modes of EtOH and MeOH and for the OD-stretch mode of EtOD (in EtOD/EtOH mixtures) [3]. In all cases, vibrational relaxation takes place much faster in the neat liquid than in the corresponding dilute isotopic mixtures.

In all liquids, the decay due to the vibrational relaxation is followed by a slower decay caused by thermalization [see inset of Fig. 2(a)]. This is because the energy of the stretching mode is not immediately thermalized after vibrational relaxation but is first redistributed over one or more accepting modes [4]. To derive accurate values for the vibrational relaxation rates from the experimental data, we account for the effect of thermalization in the data analysis. The pump-probe response is then given by [4]

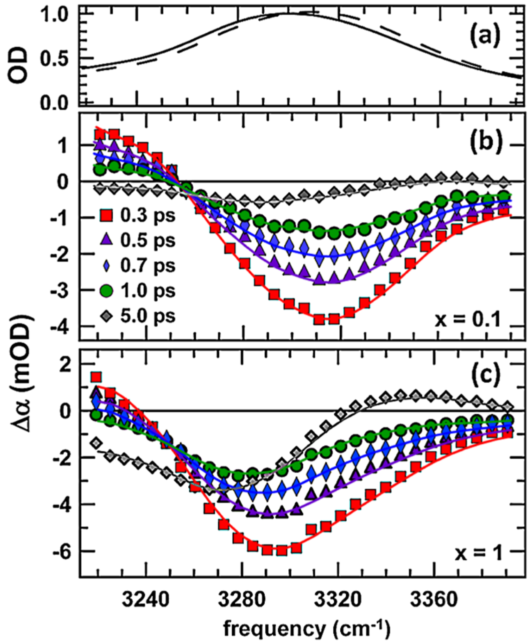

FIG. 1 (color online). (a) Absorption spectrum of NMA/NMA-d_1 for $x = 0.1$ (dotted curve) and $x = 1$ (solid curve). (b) Transient-absorption change upon excitation of the NH-stretching mode of an NMA/NMA-d_1 mixture with $x = 0.1$ for several pump-probe delays. (c) The same for neat NMA. The curves in (b) and (c) are the result of the global least-squares fit described in the text.

$$\Delta\alpha(\omega,t)/N_1(0) = [\sigma_{12}(\omega) - 2\sigma_{01}(\omega)]e^{-kt} + \Delta\sigma'_{01}(\omega)\left[\frac{ke^{-k_*t} - k_*e^{-kt}}{k_* - k} + 1\right] + \Delta\sigma^*_{01}(\omega)\frac{k(e^{-kt} - e^{-k_*t})}{k_* - k}, \tag{1}$$

where $N_1(0)$ is the initial fraction of excited-state molecules at $t = 0$, $k = 1/T_1$ is the vibrational relaxation rate, k_* is the thermalization rate, $\sigma_{12}(\omega) - 2\sigma_{01}(\omega)$ is the pure pump-probe spectrum, $\Delta\sigma'_{01}(\omega)$ is the steady-state temperature-difference spectrum, and $\Delta\sigma^*_{01}(\omega)$ is the difference spectrum between the ground state and intermediate state [4]. In order to determine k and k_* as accurately as possible, they are treated as global parameters in the least-squares fit to the observed $\Delta\alpha(\omega, t)$. To avoid the coherent-coupling contribution to the pump probe, we fit the data only for delays ≥ 0.24 ps. After fitting the model to the experimental data, the thermal contribution can be subtracted from the raw data and the excited-state decay contribution to the signal can be obtained [Fig. 2(d)]. The vibrational relaxation rates can still be accurately determined even when the thermal residual signal is large, as it is for MeOH [Figs. 2(b) and 2(c)], because the time scales of the vibrational relaxation and the subsequent thermalization differ by more than an order of magnitude (for MeOH, $k = 2.0\ \text{ps}^{-1}$ and $k_* = 0.15\ \text{ps}^{-1}$). In all liquids, the $v = 1 \rightarrow 2$ induced-absorption signals exhibit the same dynamics as the $v = 0 \rightarrow 1$ bleaching signals [3].

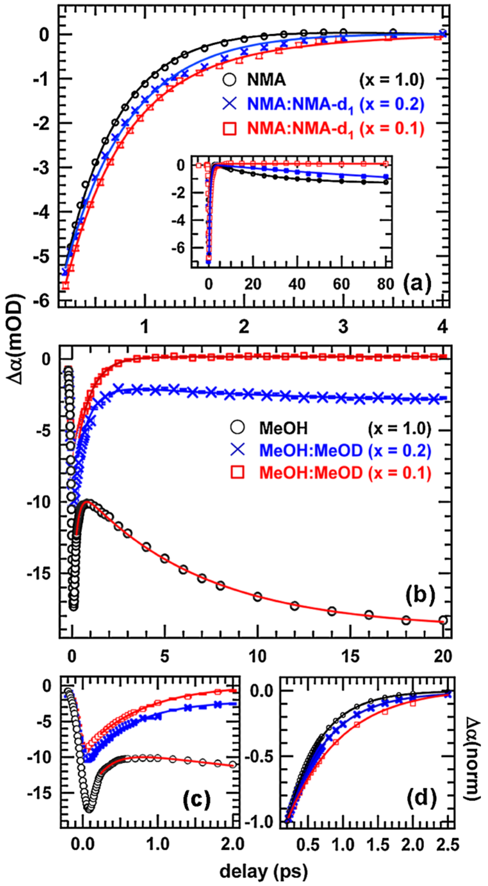

FIG. 2 (color online). (a) Transient-absorption change versus pump-probe delay at a frequency of $3300\ \text{cm}^{-1}$ for NMA/NMA-d_1 mixtures with different x. The inset displays the absorption change at long delays due to thermalization. (b) The same for MeOH. (c) Close-up showing vibrational relaxation in MeOH. (d) Pure pump-probe signals in MeOH, obtained after subtraction of the thermalization using the procedure of Ref. [4] and normalized to the value at $t = 0.24$ ps. In all graphs, the curves show the result of the global least-squares fit described in the text.

By least-squares fitting Eq. (1) to the experimental data (see supporting material and Figs. 1 and 2), we obtain the relaxation rates of all mixtures and neat liquids. The result is shown in Fig. 3. In all cases, vibrational relaxation occurs significantly faster in the neat liquid than in the isotopically dilute mixtures, with a similar functional dependence on x. In the following, we show that our data suggest the existence of a cooperative relaxation channel in neat liquids, in which the vibrational energy is distributed over intramolecular accepting modes of two neighboring molecules. Several other mechanisms to explain the x dependence of the vibrational relaxation can first be ruled out:

(1) Feedback effect.—In neat liquids, relaxation of high-frequency modes can lead to significant excitation of low-

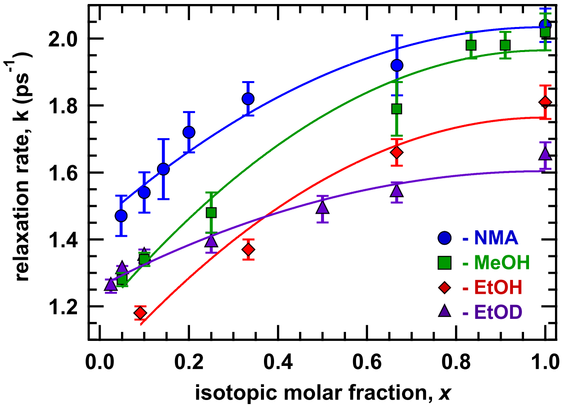

FIG. 3 (color online). (a) Relaxation rate versus x for the NH-stretch of NMA/NMA-d_1, the OH-stretch mode of MeOH/MeOD and EtOH/EtOD, and the OD-stretch mode of EtOD/EtOH. The curves are least-squares fits of Eq. (2).

frequency modes. This can, in turn, influence the relaxation rate of the remaining fraction of vibrationally excited molecules. To verify that this feedback effect [5] is not responsible for the observed increase in relaxation rate with x, we measured the relaxation at higher temperature, where low-frequency modes are more populated. We find that at higher temperatures, the vibrational relaxation becomes slower [3]. Hence a feedback effect, if present, should lead to a slowing down of the vibrational relaxation with increasing x.

(2) Hopping of the excitation to an energy sink or delocalization of the excitation.—Because of inhomogeneity of the liquid, there might be particular XH groups ($X = N, O$) for which relaxation occurs very efficiently. By resonant transfer of the vibrational excitation [6] between XH groups, the vibrational excitation might be transferred to an oscillator for which the relaxation is fast, leading to an effectively faster decay (this would require that the averaging out of the T_1 inhomogeneity due to dynamic structural rearrangements in the liquid occurs slower than T_1 itself, since otherwise the additional averaging out due to hopping of the excitation would have no effect). The delocalization of the XH-stretch excitation [7] could result in a similar effect. It can be shown that delocalization of the XH-stretch mode leads to a relaxation rate that is the average of the local relaxation rates [8], so if there would exist a wide distribution of local relaxation rates, the increased delocalization at high x might lead to a speeding up of the relaxation. However, for the effective rate to increase with x by either mechanism, the distribution of relaxation rates should span at least the difference between the observed limiting rates for high and low x. As a consequence, in the measurements at low x, where no hopping or delocalization can occur, so that the observed decay is a sum over the distribution of relaxation rates, a strongly nonexponential decay should be observed. Since this is not the case, neither hopping nor delocalization can account for our observations.

(3) Change in low-frequency spectrum.—The vibrational relaxation might involve low-frequency intermolecular modes to compensate for a possible energy mismatch between the initially excited and the intramolecular accepting modes. If changing x would influence the frequencies of these intermolecular modes, this might change the effectiveness with which they compensate for the energy mismatch, thus changing the relaxation rate (note that since we always excite the same isotopomer, the frequencies of the intramolecular accepting modes do not change with x). However, the low-frequency spectrum of the liquids investigated here hardly changes upon N or O deuteration. The hydrogen-bond stretching frequencies of liquid MeOH and MeOD are 280 and 262 cm^{-1}, respectively [9]. In the vitreous phase, the OH-libration frequency of MeOH changes from 730 cm^{-1} to 708 cm^{-1} in going from neat CD_3OH to dilute $CD_3OH : CD_3OD$ (the values in liquid isotopic mixtures have not been reported) [10]. For NMA, the effect of deuteration on the low-frequency modes has not been investigated, but for the similar compound formamide the hydrogen-bond related low-frequency bands change from 190 to 182 cm^{-1} and from 99.8 to 94.7 cm^{-1} upon deuteration [11]. To estimate the effect of these shifts on the above-mentioned energy mismatch, they should be compared to the convolution of the XH-stretch and low-frequency bands. One finds that for NMA and the alcohols the shifts are 4%–6% of the width of this convolution. The change in the low-frequency spectrum therefore cannot explain the observed increase in relaxation rate in the neat liquid as compared to the isotopic mixtures.

Based on the observed dependence of T_1 on the isotope fraction, we propose that the enhanced relaxation involves an additional relaxation channel in which the XH-stretch vibrational energy is redistributed over intramolecular accepting modes in two neighboring XH-isotopomer molecules (or XD isotopomers when the XD-stretching mode is excited), one of them being the initially excited molecule. Using some simplifying assumptions, we can predict the dependence on x that the rate of such a bimolecular relaxation channel should have. The liquids studied here are known to form hydrogen-bonded chains [12,13], and the interaction between an excited XH group and its nearest neighbors will be stronger than that with the other molecules in the liquid. We therefore assume that the bimolecular relaxation occurs only for pairs of molecules that are neighbors in a hydrogen-bonded chain. For a given excited XH-stretching mode, the probability that at least one of its neighbors in the chain is also an XH group is $2x - x^2$. Because of fast delocalization of the XH-stretch excitation [7], the effective rate of bimolecular relaxation will thus be proportional to $2x - x^2$ [8]. Assuming that the intramolecular rate k_0 changes negligibly with x, the total relaxation rate becomes

$$k = k_0 + k_1(2x - x^2). \tag{2}$$

We find that this equation describes the experimental data well for all four liquids, see Fig. 3. The ratio k_1/k_0 ranges from 0.3 (EtOD) to 0.7 (EtOH and MeOH), which implies a significant contribution of the additional relaxation channel to the overall vibrational relaxation in neat liquids.

The efficiency of the proposed bimolecular relaxation mechanism depends on the anharmonic interaction between intramolecular modes in neighboring molecules and on the availability of suitable accepting modes within the molecules. Since the intramolecular accepting modes available in two neighboring molecules of the same isotopic species are identical, the energy mismatches for an intramolecular and a bimolecular relaxation channel that involve the same type of accepting modes (but located in the same and in two neighboring molecules, respectively) are comparable. The energy mismatch of the bimolecular channel differs from that of the intramolecular channel by an amount equal to the anharmonic shift of the accepting mode, which is small compared to the linewidth of the stretching mode. Hence the fact that comparable efficiencies are observed for the two relaxation channels suggests that the anharmonic interactions that couple the excited and accepting modes should be of comparable magnitude for the two relaxation channels; that is, the intermolecular anharmonic potential-energy terms of type $Q_{A,\mathrm{stretch}}Q_{A,\mathrm{accept}}Q_{B,\mathrm{accept}}$ (with Q normal-mode coordinates and A, B indicating different molecules) should be comparable to the intramolecular anharmonic terms of type $Q_{A,\mathrm{stretch}}Q^2_{A,\mathrm{accept}}$. Such high intermolecular anharmonicities might arise from the strong intermolecular interactions in hydrogen-bonded liquids, as seems to be confirmed by the observation that in neat liquid $CHBr_3$ and $CDBr_3$, the CH- and CD-stretch relaxation rates are the same as in a 1:1 isotopic mixture [14]. It cannot be determined from our data which specific intramolecular accepting modes are involved in the proposed bimolecular relaxation mechanism. In MeOH, an important relaxation channel of the OH-stretch mode is energy transfer to the OH-bending overtone [15,16], which suggests that a potential bimolecular relaxation channel could be the transfer of one stretching-mode quantum to two bending-mode quanta in neighboring molecules.

Although the type of experiment reported here cannot be done on water (because of fast $2HDO \rightleftharpoons H_2O + D_2O$ exchange), it is tempting to speculate whether a similar mechanism might play a role in this liquid, too. In fact, a bimolecular relaxation mechanism for the OH-stretch relaxation in H_2O has been suggested as an explanation for the fact that no population of the $v = 2$ state of the H_2O-bending mode is observed upon OH-stretch relaxation [17]. It was thus proposed that energy transfer to the bending-mode fundamentals of two neighboring H_2O molecules is the dominant relaxation channel, which would make water a special case with $k_1 \gg k_0$. It should be noted, however, that comparable experiments by Ashihara *et al.* [18] are at odds with such a scenario.

We kindly thank Wybren Jan Buma and Yves Rezus for valuable discussions. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

[1] A. Laubereau and W. Kaiser, Rev. Mod. Phys. **50**, 607 (1978).
[2] J. C. Owrutsky, D. Raftery, and R. M. Hochstrasser, Annu. Rev. Phys. Chem. **45**, 519 (1994).
[3] See EPAPS Document No. E-PRLTAO-103-052947 for additional information. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[4] Y. L. A. Rezus and H. J. Bakker, J. Phys. Chem. A **112**, 2355 (2008).
[5] H. J. Bakker, A. J. Lock, and D. Madsen, Chem. Phys. Lett. **384**, 236 (2004).
[6] M. L. Cowan, B. D. Bruner, N. Huse, J. R. Dwyer, B. Chugh, E. T. J. Nibbering, T. Elsaesser, and R. J. D. Miller, Nature (London) **434**, 199 (2005).
[7] B. M. Auer and J. L. Skinner, J. Chem. Phys. **128**, 224511 (2008).
[8] See section A7 of the EPAPS document (Ref. [3]).
[9] H. G. M. Edwards and D. W. Farwell, J. Mol. Struct. **220**, 217 (1990).
[10] M. Falk and E. Whalley, J. Chem. Phys. **34**, 1554 (1961).
[11] Y. J. Chang and W. Castner, Jr., J. Phys. Chem. B **98**, 9712 (1994).
[12] J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. K. Shuh, H. Ågren, and J. Nordgren, Phys. Rev. Lett. **91**, 157401 (2003).
[13] N. T. Hunt and K. Wynne, Chem. Phys. Lett. **431**, 155 (2006).
[14] G. Seifert, R. Zürl, T. Patzlaff, and H. Graener, J. Chem. Phys. **112**, 6349 (2000).
[15] L. K. Iwaki and D. D. Dlott, J. Phys. Chem. A **104**, 9101 (2000).
[16] T. S. Gulmen and E. L. Sibert, J. Phys. Chem. A **108**, 2389 (2004).
[17] J. Lindner, P. Vöhringer, M. S. Pshenichnikov, D. Cringus, D. A. Wiersma, and M. Mostovoy, Chem. Phys. Lett. **421**, 329 (2006).
[18] S. Ashihara, N. Huse, A. Espagne, E. T. J. Nibbering, and T. Elsaesser, J. Phys. Chem. A **111**, 743 (2007).