The Journal of Physical Chemistry A

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LETTERS

Vibrational Lifetime Shortening in a Hydrogen-Bonded Dimer Monitored by Transient Hole Burning in the Infrared

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Received: February 4, 1998; In Final Form: June 19, 1998

The stretching mode of OH-groups with proton donor function of open 2,2-dimethyl-3-ethyl-3-pentanol dimers is investigated in the solvent CCl_4 at 260 K. The lifetime of the OH-stretching vibration is determined to be 3.6 ± 0.2 ps, notably shorter as the one of the nonbonded molecules of 8 ps. The transient spectral holes and satellite holes in the measured sample transmission suggest that the bending vibration of the hydrogen bridge bond is involved in the dynamics offering additional relaxation channels for the OH-vibration of the proton donor group.

The investigation of vibrational lifetimes[1] is of particular interest as it offers insight into the dynamical properties of molecules. Intra- and intermolecular energy transfer is possible, depending on the excited vibration and the solvent. Of special interest are molecules that exhibit one or more hydrogen bonds, as these bonds are expected to significantly modify the dynamical properties of a molecule. The investigation of hydrogen bonding itselfs is an important topic of science since this intermolecular interaction governs abundant structures as the double helix of the DNA or the three-dimensional network of water. Structural and also dynamical properties of H-bonded systems have been extensively investigated during the past decades both experimentally and theoretically.[2] A powerful method to tackle these problems is time-resolved infrared spectroscopy,[3−5] which has made significant progress in recent years, with the time resolution now extended to the subpicosecond and femtosecond domain.[6−8] The technique is particularly useful in its two-color version as in this case the vibrational lifetime can be directly inferred from the temporal evolution of the population of the excited state, which shows up as a red-shifted induced absorption due to the anharmonicity of the vibration under interest. In the case of diluted ethanol, hydrogen bonding offers an additional relaxation channel for the excited OH-stretching mode as breaking of oligomers into shorter associates is possible and could be recently demonstrated.[9,10] For ethanol a vibrational lifetime shortening for the OH-mode from 8 ps (monomer)[11] down to approximately 1.5 ps (oligomer, depending slightly on the chain lengths)[10] was determined. As a broad variety of oligomers with different chain lengths are expected to be excited in these investigations[12] resulting in corresponding complicated transient spectra, results on simpler hydrogen-bonded alcohols in the liquid phase are highly desirable in order to investigate the influence of H-bonding on vibrational lifetimes. First investigations in this direction have been performed by the group of Heilweil[4] on acid:base complexes demonstrating vibrational lifetime shortening via H-bonding.

In this Letter we investigate a dilute solution of 2,2-dimethyl-3-ethyl-3-pentanol ($C_9H_{19}OH$, abbreviated with DMEP) in CCl_4. The alcohol is known to associate to open dimers, only, because of sterical hindrance.[13] This allows us for the first time to investigate the dynamics of singly hydrogen-bonded alcohol molecules with proton donor function in the liquid phase with ultrashort laser pulses in the infrared.

Our experimental system was described recently.[14] The pulses are derived from parametric oscillator-amplifier devices

S1089-5639(98)01012-3 CCC: $15.00

with duration of 1 ps (2 ps), spectral width 16 cm^{-1} (8 cm^{-1}), and typical energy of 10 nJ (10 μJ) in the range 1600−3700 cm^{-1} (numbers in parentheses refer to the pump). The energy transmission $T(\nu)$ of the probing pulse at frequency position ν through the excited sample is measured for parallel (||) and perpendicular (⊥) polarizations relative to the polarization plane of the pump and compared with the probe transmission $T_0(\nu)$ for blocked excitation beam. The resulting relative transmission changes $\ln(T/T_0)_{\|,\perp}$ for variable probe frequency and delay time t_D represent the relevant quantities from which an isotropic signal, $\ln(T/T_0)_{is} = (\ln(T/T_0)_{\|} + 2\ln(T/T_0)_{\perp})13$, and the induced dichroism are determined.[15] For negligible energy-transfer processes, the time evolution of the isotropic signal delivers direct information on the vibrational population dynamics. The time-dependent measurements are numerically calculated considering a three-level system with a long-living intermediate interacting with the two light pulses in the case of the monomer and a respective number of excited-states for the proton donor. Reorientational motion with one average time constant and coherent coupling between the electric fields and the induced polarization is included.[16] In the case of inhomogeneous broadening and phase relaxation T_2 comparable to the duration of the two pulses, a remarkable increase in the width of the spectral hole can be calculated with delay time due to a coherent interaction.[16] This coherent contributions to the spectral dynamics reduces, however, significantly with, for example, decrease of T_2 or even a slight phase modulation of the light pulses, as present here, and we found from our spectra no clear evidence for this. A coherence peak resulting from the nonresonant interaction between the two infrared pulses and the solvent can be definitely excluded from control measurements on the neat CCl_4.

A DMEP concentration of 2 M is adjusted in CCl_4 at a temperature of 260 K, while the sample length amounts to 60 μm. This results in a minimum sample transmission of ≃10% at 3505 cm^{-1}. All experiments were performed with moderate pump energies of 1−2 μ J to prevent extended thermal effects. The conventional spectrum of the sample in the OH-stretching region consists of a narrow line at 3625 cm^{-1} attributed to monomers and proton acceptor groups and a second band at 3505 cm^{-1} (see Figure 1c, dash−dotted line). This asymmetric, approximately 100 cm^{-1} wide band represents absorption of molecules with proton-donor function in dimers, as shown by comparison with other diluted alcohols.[13]

Examples for time-resolved spectra taken at different delay times are presented in Figure 1. The isotropic signal component is plotted, i.e., information on population dynamics without a contribution by reorientational motion. Excitation of OH-groups at 3430 cm^{-1} in the red wing of the dimer band is shown in Figure 1 for three different delay times. It is interesting to see the structure in the spectrum at delay time zero (Figure 1a, determined in independent measurement via two-photon absorption in Ge[17]) with different temporal evolution of the spectral components at the peak position and the red-edge of the OH-band monitored at $t_D = 5$ ps (b) and 10 ps (c), respectively. The bleaching of the sample for $\nu > 3350$ cm^{-1} reflects the depletion of the vibrational ground-state $v = 0$ upon excitation. Correspondingly, induced absorption of molecules in the first excited state (ESA) is observed at frequencies <3350 cm^{-1}, red-shifted via the anharmonicity of the OH mode. At $t_D = 10$ ps (c) a shift in the distribution of the spectral components is indicated by the long living bleaching peaked at ≈3480 cm^{-1} and the induced absorption in the blue part of the transient spectrum. Excitation at the peak position of the band at 3510 cm^{-1} is depicted in Figure 2 in the same way as introduced in Figure 1. In this case clearly one bleaching component at 3510 cm^{-1} can be seen at $t_D = 0$ ps (a), which dominates the spectrum, while the same component represents only a minor contribution to the spectra in the case of $\nu_{Pu} = 3430$ cm^{-1} (Figure 1). A correspondingly broad ESA is noticed below 3400 cm^{-1}. The bleaching of the sample increases in width at a delay time of 5 ps (b), and finally the energy thermalizes as can be seen at $t_D = 10$ ps (c). The time-resolved spectra can be well described by a discrete substructure of the transient band as suggested by the multiple maxima of the bleaching and ESA. This decomposition of the time-resolved spectra is supported by consistently fitting of all measurements taken at eight different delay times and four excitation frequencies within the full width of the OH-band with one set of spectral components (data shown only in part).

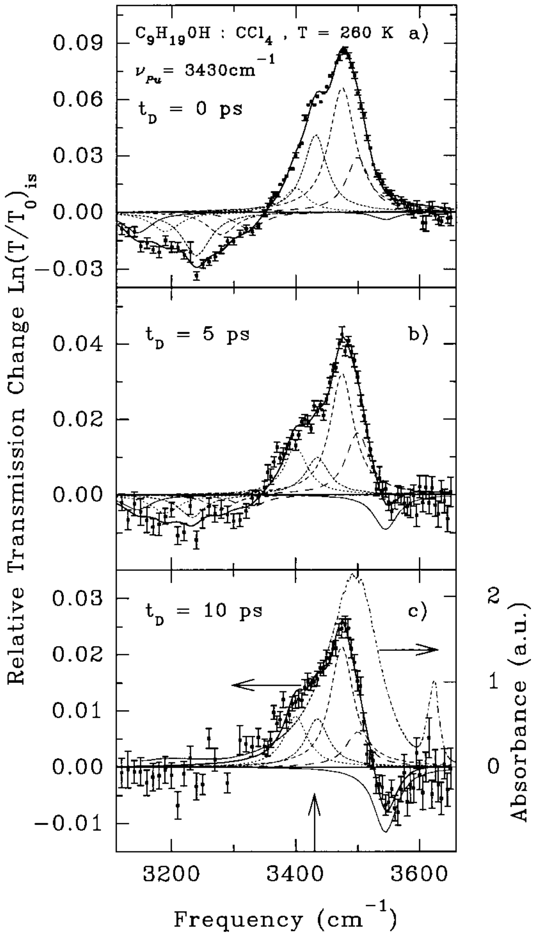

Figure 1. Conventional spectrum (c; dash−dotted line; right-hand ordinate scale) and transient spectra of 2 M DMEP in CCl_4 (isotropic signal) in the OH-stretching region taken at 260 K for different delay times: 0 ps (a), 5 ps (b), and 10 ps (c); excitation at 3430 cm^{-1} (vertical arrow); spectral holes and satellite holes are denoted by different line styles; experimental points, calculated curves.

The temporal evolution of the absorbance change of the sample for excitation at the peak position of the OH-band at 3510 cm^{-1} is shown in Figure 3. Probing is performed at the frequency position of excitation (a, c) and within the excited-state absorption at 3330 cm^{-1} (b). The isotropic signal contribution (a, b) is depicted to monitor the population dynamics solely. In both cases an increase of the absolute amount of the respective signals within the time resolution of the experiment is monitored, while the short-time relaxation taken at $\nu = \nu_{Pu}$ (a) and the dynamics of the excited-state

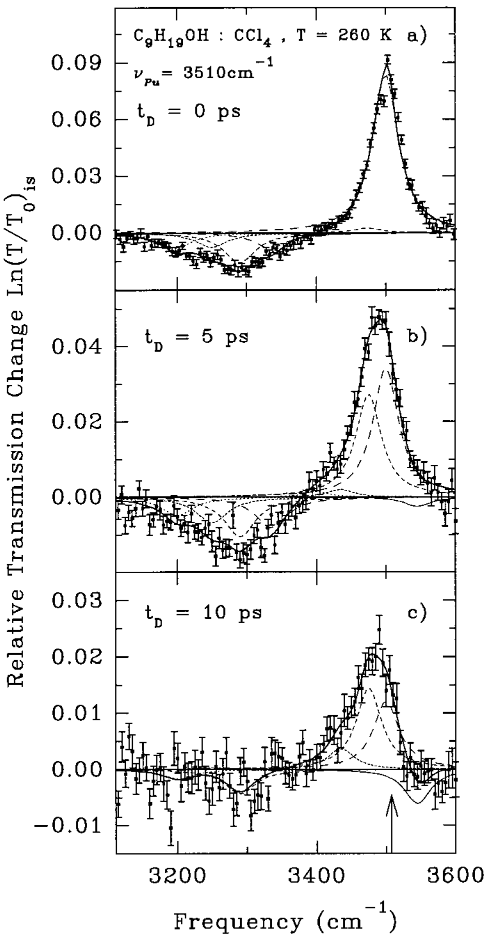

Figure 2. Same as depicted in Figure 1; excitation is, however, adjusted to the peak absorption of the OH-band at 3510 cm^{-1} (vertical arrow); different delay times of 0 ps (a), 5 ps (b), and 10 ps (c).

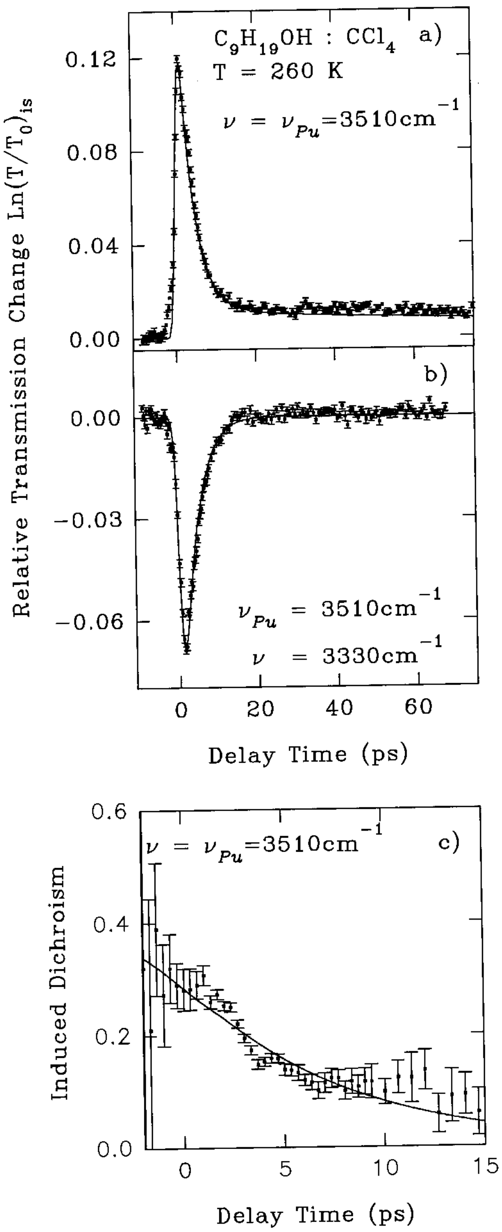

Figure 3. Temporal evolution of the isotropic signal (a, b) and the induced dichroism (c) with excitation at the peak position of the OH-stretching band (3510 cm^{-1}). Probing is performed at the frequency position of excitation (a, c) and within the excited-state absorption (b) at 3330 cm^{-1} delivering a lifetime of this vibration of 3.6 ± 0.2 ps. From the induced dichroism we infer $\tau_{\mathrm{anis}} = 8 \pm 2$ ps; experimental points, calculated lines.

absorption (b) allows for determining the average lifetime of the proton donor OH-mode to be 3.6 ± 0.2 ps. The long-time component in (a) is attributed to heating of the molecule via the deposited energy (see Figure 1c, 2c). In Figure 3c we show the induced dichroism of the sample deduced from the same data as depicted in Figure 3a. A time constant $\tau_{\mathrm{anis}} = 8 \pm 2$ ps is deduced. As the proton donor cannot be described as a two-level system, τ_{anis} may be shorter as the time constant for reorientational motion due to spectral relaxation.

From the transient spectra shown in Figure 1 and similiar ones taken at other excitation frequencies within the OH-band, we infer a spectral redistribution within this band notably faster than the lifetime of the OH-stretching mode of the monomeric species of 8 ps (data not shown). The H-bond enables in addition to intramolecular energy transfer three further relaxation processes past excitation of the proton donor OH-stretch: (i) structural relaxation involving reorientation of the molecules with subsequent modification of H-bond length and angle, (ii) breaking of the dimer into two monomers, and (iii) excitation of combination tones between the OH and hydrogen bridge bond vibrations. From the induced dichroism shown in Figure 3c, we infer a lower limit for reorientational motion of the proton donor (i) of 8 ps, much too slow to account for the fast redistribution depicted in Figure 1a. In addition it should be noted that the DMEP molecule looks like half-spheres with the OH-group located in the approximately flat plane. Therefore, the possibilities for variation of, for example, the H-bond angle are strongly reduced, and structural relaxation is not expected to play an important role. Furthermore, we found from the transient spectra no indication of H-bond breaking (ii) after vibrational excitation occurs, as was demonstrated for associated ethanol.[10] A corresponding induced absorption at 3625 cm^{-1} due to an increasing number of monomers is not measured. In this context one should, however, keep in mind the notably different masses of the respective molecules. For this reason, we attribute the spectral components indicated in Figure 1 by different line styles to combination tones between the OH-stretching and a low-lying vibration, which is most probably directy connected to the hydrogen bond (iii). The frequency spacing of 35 ± 5 cm^{-1} for the 0−1 transition (OH, bleaching of the sample) and 45 ± 5 cm^{-1} in the induced absorption (1−2, OH) supports a contribution of the bending mode of the H-bond to the dynamics.[19] For comparison, in water a band located at 50 cm^{-1} was proposed to represent the bridge bending

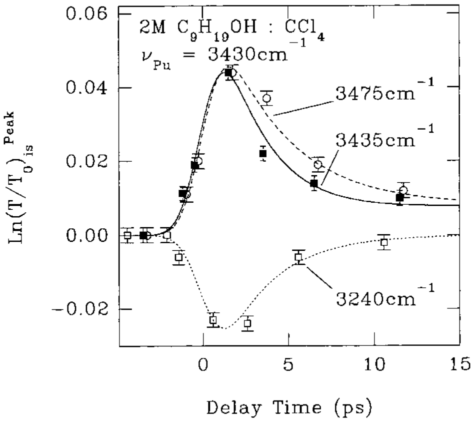

Figure 4. Time evolution of the spectral components at 3475 cm^{-1} (hollow circles), 3435 cm^{-1} (filled squares), and 3240 cm^{-1} (hollow squares); calculated curves; see text.

mode.[18] With regard to the notably weaker H-bond of the present dimers, our interpretation appears reasonable.

The different holes and satellite holes are related within this picture to transitions between the ground and excited state of the OH-mode, while the quantum number n of the low-frequency mode may change by 0, ±1, ±2, ... owing to the enhanced anharmonic character. In this context it is pointed out that, for example, for the OH-stretching mode of HDO a strong anharmonic shift of approximately 8% is deduced from transient spectroscopy.[20] An even higher anharmonicity of up to ≈15% is possible from the accuracy of our data for the proposed bending mode of the H-bond. An interpretation of the spectral features in terms of stretching modes of the H-bond is not very likely as these modes are expected to show up around 100 cm^{-1} and the frequency spacing of 35 cm^{-1} would consequently equal an anharmonic shift of 35%. The interpretation of the spectral dynamics via combination tones is supported by the temporal evolution of the different spectral holes. Experimental results on the time evolution of the subcomponents are presented in Figure 4. The amplitudes of the contributions at 3475 cm^{-1} ($\Delta n = -1$, hollow circles) and 3435 cm^{-1} ($\Delta n = -2$, filled squares) as derived from a decomposition of the measured transient spectra are plotted versus delay time. The decay times of these two components are determined to 4.5 ± 0.5 and 3 ± 0.5 ps, respectively. Two mechanisms could contribute to the time constants: population decay of the OH-stretching mode and population redistribution among the bridge bond vibrations. Since the excess population of the lower n-levels is transferred to larger n, probing with $\Delta n = -2$ yields a faster decay compared to $\Delta n = -1$, as indicated by the data. For larger delay times the system does not return exactly to its initial situation, since the deposited OH-excitation energy thermalizes. In fact, the nonvanishing amplitudes of the bleaching curves in Figure 4 (solid and dashed lines) for large t_D may be related to a temperature increase of the sample of ≈1 K from comparison with temperature-dependent IR-absorption spectra of the same sample. From the ESA component at 3240 cm^{-1} (hollow squares) also shown in the figure we determine a relaxation time of 3 ± 0.5 ps. This time constant is slightly shorter than the lifetime of the proton donor OH-stretch derived from fitting of the time evolution of the complete area of the excited-state absorption yielding a number of 3.5 ± 0.5 ps. This value is in correspondence to the one obtained by the measurement at 3330 cm^{-1} of 3.6 ± 0.2 ps (see Figure 3b). This indicates additional dynamics within the low-frequency sublevels of the $v = 1$ state of the OH-mode. A similiar vibrational lifetime shortening via a H-bond has recently been demonstrated[21] for acid:base complexes from 183 ps (monomer) down to 70 ps (complex, depending on the base strength and the concentration).

In conclusion, we have demonstrated a notable lifetime shortening of the OH-stretching mode of a proton donor in comparison to the monomeric species from 8 ps down to 3.6 ± 0.2 ps. The additional relaxation path opened for the hydrogen-bonded dimer is most probably via excitation of bending vibrations of the hydrogen bridge bond. This is indicated by spectral holes and satellite holes in the transient spectra, which exhibit distinguishable dynamics.

Acknowledgment. Stimulating discussions and continuous support of this investigation by Prof. A. Laubereau are gratefully acknowledged.

References and Notes

(1) Spanner, K.; Laubereau, A.; Kaiser, W. *Chem. Phys. Lett.* **1976**, *44*, 88. Heilweil, E. J.; Casassa, M. P.; Cavangh, R. R.; Stephenson, J. C. *J. Chem. Phys.* **1986**, *85*, 5004. Li, M.; Owrutsky, J.; Sarisky, M.; Culver, J. P.; Yodh, A.; Hochstrasser, R. M. *J. Chem. Phys.* **1993**, *98*, 5499. Tokmakoff, A.; Zimdars, D.; Urdahl, R. S.; Francis, R. S.; Kwok, A. S.; Fayer, M. D. *J. Phys. Chem.* **1995**, *99*, 13310.

(2) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond*; North-Holland: Amsterdam, 1976; Vols. I−III.

(3) Graener, H.; Seifert, G.; Laubereau, A. *Phys. Rev. Lett.* **1991**, *66*, 2092.

(4) Arrivo, S. M.; Heilweil, E. J. *J. Phys. Chem.* **1996**, *100*, 11975.

(5) Laenen, R.; Rauscher, C.; Laubereau, A. *J. Phys. Chem.* **1997**, *A101*, 3201.

(6) Woutersen, S.; Emmerichs, U.; Bakker, H. J. *J. Chem. Phys.* **1997**, *107*, 1483.

(7) Hamm, P.; Lim, M.; Hochstrasser, R. M. *J. Chem. Phys.* **1977**, *107* 10523.

(8) Laenen, R.; Simeonidis, K.; Laubereau, A. *J. Opt. Soc. Am.*, **1998**, *B15*, 1213.

(9) Graener, H.; Ye, T.-Q.; Laubereau, A. *J. Chem. Phys.* **1989**, *90*, 3413.

(10) Laenen, R.; Rauscher, C. *J. Chem. Phys.* **1997**, *106*, 8974.

(11) Laenen, R.; Rauscher, C. *Chem. Phys. Lett.* **1997**, *274*, 63.

(12) Laenen, R.; Rauscher, C. *J. Chem. Phys.* **1997**, *107*, 9759.

(13) Smith, F. A.; Creitz, E. C. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 145.

(14) Laenen, R.; Simeonidis, K.; Rauscher, C. *IEEE J. Sel. Top. Quantum Electron.* **1996**, *2*, 487.

(15) Graener, H.; Seifert, G.; Laubereau, A. *Chem. Phys. Lett.* **1990**, *172*, 435.

(16) Laenen, R.; Rauscher, C. *Chem. Phys.*, in press.

(17) Rauscher, C.; Laenen, R. *J. Appl. Phys.* **1997**, *81*, 2818.

(18) Walrafen, G. E.; Hokmabadi, M. S.; Yang, W.-H. *J. Phys. Chem.* **1988**, *92*, 2433.

(19) Laenen, R.; Simeonidis, K. Submitted for publication.

(20) Laenen, R.; Rauscher, C.; Laubereau, A. *Phys. Rev. Lett.* **1998**, *80*, 2622.

(21) Grubbs, W. T.; Dougherty, T. P.; Heilweil, E. J. *J. Am. Chem. Soc.* **1995**, *117*, 11989.