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Librational substructure of the OH-stretching band of an H-bonded dimer observed by time-resolved spectroscopy

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Abstract

The stretching mode of OH-groups with a proton donor function of an alcohol associating to open hydrogen-bonded dimers is investigated in the liquid phase. Spectral holes with a frequency spacing of $\approx 35 \text{ cm}^{-1}$ in the fundamental OH-transition and of $\approx 45 \text{ cm}^{-1}$ in the excited state-absorption are determined. This gives strong evidence for combination tones with the bending vibration of the hydrogen bridge bond governing the dynamics and the shape of the proton donor OH-stretching band. The combination modes display additional relaxation channels for the excited OH-stretching mode resulting in a lifetime shortening from 8 ps (monomer) down to 3.6 ps (proton donor, 260 K). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: OH-stretching band; H-bonded dimer; Time-resolved spectroscopy

The investigation of hydrogen-bonding is an important topic of science since this intermolecular interaction governs abundant structures from the double helix of the DNA to the three-dimensional network present in water. The OH-stretching mode can be utilized as a spectroscopic probe for a hydrogen bond due to the red-shift and broadening of the vibration with increasing H-bond strength. The explanation of the prominent broadening of this band due to H-bonding in, for example, water is an important but yet unsolved problem. Evidence for discrete structures, i.e. molecules in different preferred environments, has been obtained for polymer-matrices [1], diluted alcohols [2], and water [3,4]. On the other hand, in several theoretical papers a pronounced anharmonic

coupling to a bridge bond vibration was considered as the dominant mechanism [5–7] but this has been, however, not proved by respective experiments.

A powerful method to tackle these problems is time-resolved infrared spectroscopy [3,8,9] that has made significant progress in recent years, with the time resolution now extended to the fs-domain [10–12]. The underlying difficulties for the interpretation of experimental data taken on the OH-band are related to the complexity of structures, e.g. the disordered hydrogen-bonded network of water or the distributions of cyclic or linear oligomers in alcohols. Results on a structurally more simple system are highly desirable to investigate this fundamental question into detail.

In this article we investigate a dilute solution of 2,2-dimethyl-3-ethyl-3-pentanol ($\text{C}_9\text{H}_{19}\text{OH}$, abbreviated with DMEP) in CCl_4 . It is proposed that the alcohol associates to open dimers only, because of sterical hindrance [13]. This specific association, even in the

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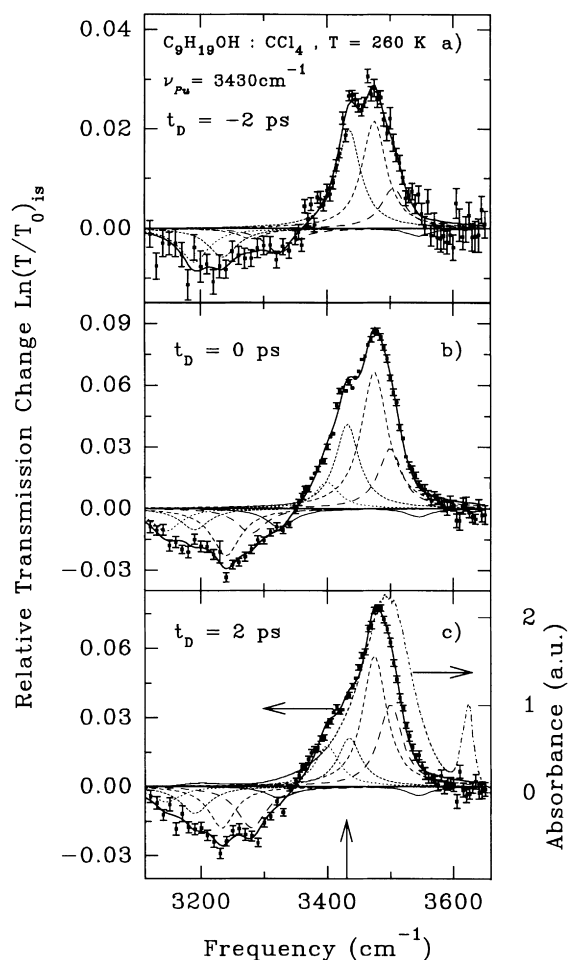


Fig. 1. Conventional spectrum (c; dash-dotted line; right hand ordinate scale) and transient spectra of 2 M DMEP in CCl_4 (isotropic signal) in the OH-stretching region taken at 260 K for different delay times: (a) -2 ps; (b) 0 ps; and (c) 2 ps; excitation at 3430 cm^{-1} (vertical arrow); evidence for spectral subcomponents is obtained; experimental points, calculated curves.

neat liquid at room temperature, is confirmed by quantum statistical thermodynamics using ab initio calculated molecular clusters [14]. From these numerical investigations, which are partially verified by additional NMR-experiments on the neat DMEP, we can conclude that the dimers and monomers are present in the neat liquid only. In the 2 M DMEP: CCl_4 mixture with a smaller DMEP concentration present the contribution of dimers is supposed to be even less in comparison to the neat DMEP. This allows us for the first time to investigate the dynamics of singly

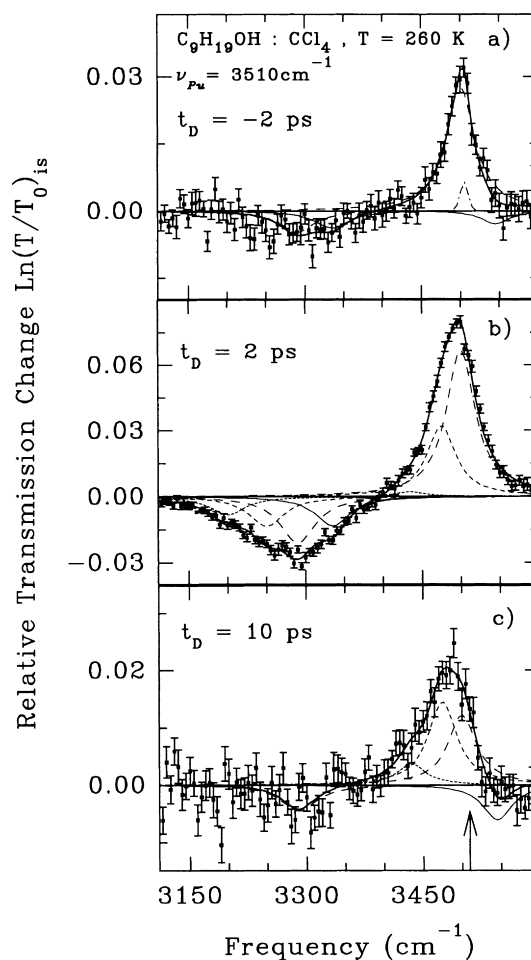


Fig. 2. Same as Fig. 1 but for the excitation at 3510 cm^{-1} (vertical arrow) and delay times of: (a) -2 ps; (b) 2 ps; and (c) 10 ps, respectively. Hole-burning can be clearly seen as well as a coherent contribution (a, dash-dotted line) at early delay times; experimental points, calculated lines.

hydrogen-bonded molecules with a proton donor function in the liquid phase with ultrashort laser pulses in the infrared.

Our experimental system was described recently [15]. The pulses are derived from parametric oscillator–amplifier devices with a duration of 1 ps (2 ps), spectral width 16 cm^{-1} (8 cm^{-1}) and a typical energy of 10 nJ ($10\text{ }\mu\text{J}$) in the range $1600\text{--}3700\text{ cm}^{-1}$ (numbers in brackets refer to the pump). Delay time zero (optimum overlap between pump and probe) and the cross correlation between the two IR-pulses are determined in independent measurements via two-photon

Table 1

Frequency positions of the transient holes and inverse holes as determined by fitting of the time-resolved spectra taken at various delay times and excitation frequencies. Discussion see text

	$\Delta n = 1$	$\Delta n = 0$	$\Delta n = -1$	$\Delta n = -2$	$\Delta n = -3$
ν_{01} (cm ⁻¹)	3545	3505	3475	3435	3400
ν_{12} (cm ⁻¹)	3325	3280	3240	3190	3145

absorption in Ge [16]. The energy transmission $T(\nu)$ of the probing pulse at frequency position ν through the excited sample is measured for parallel (\parallel) and perpendicular (\perp) polarizations relative to the polarization plane of the pump and compared with the probe transmission value $T_0(\nu)$ for blocked excitation beam. The resulting relative transmission changes $\ln(T/T_0)_{\parallel,\perp}$ for variable probe frequency and delay time t_D represent the relevant quantities, from which an isotropic signal, $\ln(T/T_0)_{\text{is}} = (\ln(T/T_0)_{\parallel} + 2\ln(T/T_0)_{\perp})/3$ is determined. For negligible energy transfer processes, the time evolution of the isotropic signal delivers direct information on the vibrational population dynamics. A DMEP concentration of 2 M is adjusted in CCl₄ at a temperature of 260 K. 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 Fig. 1c, dash-dotted line). This asymmetric, approximately 100 cm⁻¹ wide band represents absorption of molecules with the proton-donor function in dimers, as shown by comparison with other diluted alcohols [13].

Examples for time-resolved spectra taken at different delay times and excitation frequencies are presented in Figs. 1 and 2. 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 Fig. 1 for three different delay times. It is interesting to see the double-peak structure at early times (Fig. 1a) that has already relaxed to a single maximum at $t_D = 0$ (Fig. 1b) followed by a shift of the transient band towards 3500 cm⁻¹ (see Fig. 1c). The bleaching of the sample for $\nu > 3350$ cm⁻¹ reflects the depletion of the vibrational ground state $\nu = 0$ 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. The time-resolved spectrum can be well described by a discrete substructure of the transient band as suggested by the multiple maxima of the bleaching and ESA (see below).

Changing the pump frequency to 3510 cm⁻¹ yields transient spectra depicted in Fig. 2. A narrow bleaching occurs around the excitation frequency at early times (Fig. 2a) representing a transient spectral hole together with a minor coherent coupling effect between pump and probe pulses (induced population grating, dash-dotted line). At later times the bleaching structure broadens (Fig. 2b and c) and survives over time intervals > 10 ps; the latter finding may be related to the heating of the molecules in the relaxation (see below). Excited state population of the OH-mode is again visible via ESA below 3400 cm⁻¹ (Fig. 2b), but has almost disappeared at $t_D = 10$ ps (Fig. 2c).

The transient spectra can be well described by a time dependent spectral hole at the excitation frequency with an approximate Lorentzian shape and width of 45 ± 5 cm⁻¹ as well as additional components assigned to satellite holes with different time evolutions to account for the complex, rapidly changing band shape [17]. The data suggest and are well described by an approximately constant frequency spacing of 35 ± 5 cm⁻¹ between the subcomponents. Satellite maxima are also seen in the induced absorption (see Fig. 1) and assigned to inverse spectral holes, but with a different frequency distance of 45 ± 5 cm⁻¹. The decomposition of the spectra is indicated in Figs. 1 and 2 by calculated curves. Corresponding spectral holes (inverse holes) are plotted with the same line style.

We have investigated the transient spectra in the delay time interval -2 to 10 ps for excitation at four frequencies in the range 3430–3555 cm⁻¹ (data shown only in part). The time-resolved spectra are fitted consistently with a fixed set of Lorentzian shaped spectral lines (transient holes and inverse holes) by determining the minimum deviation numerically [18] via variation of the amplitudes. Some results are summarized in Table 1. The transition frequency of holes ($\nu = 0 \rightarrow \nu = 1$) is denoted by ν_{01} , while ν_{12} is that of inverse holes ($\nu = 1 \rightarrow \nu = 2$). A spectral width of 45 ± 5 cm⁻¹ and 55 ± 5 cm⁻¹

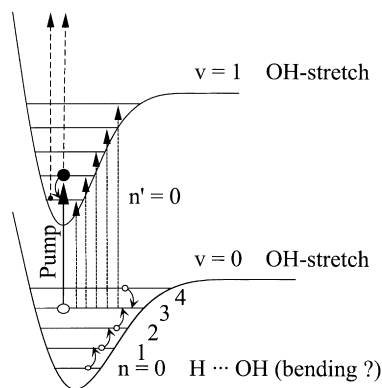


Fig. 3. A simplified energy level scheme that accounts for the spectral observations with librational substructure (horizontal lines, n , n') of the OH-stretching levels (solid curves, v); the thick vertical arrow represents an example for the excitation process with $\Delta n = -2$; thin solid and dashed vertical arrows denote possible probing transitions for different Δn for ν_{01} - and ν_{12} -transitions, respectively; the distribution of transitions due to the thermal population is not indicated for better visibility.

for the holes and inverse holes, respectively, accounts for the data.

For an interpretation of the observed substructure of the dimer band two major mechanisms may be considered: (i) local disorder effecting the strength of the H-bond; (ii) anharmonic coupling between the OH-mode and the intermolecular H-bridge bond vibration(s) generating a discrete set of OH-transition frequencies. Our analysis suggests that mechanism (i) is of minor importance, as due to the sterical hindrance the proton donor OH-group seems to be well defined in respect to its orientation towards the surrounding CH_n -groups. Furthermore, reorientation of the proton donor OH-group along the CO-axis is determined to proceed with a time constant of 8 ps, a factor of 2 slower in comparison to the nonbonded monomeric OH-group [19]. For this reason reorientation or structural relaxation cannot account for the fast dynamics (see Fig. 1a). The experimental evidence for spectral subcomponents, on the other hand, immediately provokes the conclusion that mechanism (ii) is dominant with time-dependent bandshapes via transient population changes of the low-frequency vibration(s). The constant frequency spacing of the measured spectral holes indicates that one mode is dominant and is considered in our simplified physical picture in the following. A Franck–Condon-like situation,

illustrated by Fig. 3, is assumed with significant anharmonic coupling between the high-frequency OH-stretching vibration of the donor molecule and the low-frequency mode (quantum numbers v , n and frequencies ν_{OH} , ν_{bb} , respectively). Anharmonic frequency changes of ν_{bb} , on the other hand, with the quantum number n are considered to be small compared to the measured holewidths and are omitted. In addition to the selection rules of the harmonic case, $\Delta v = 1$, $\Delta n = 0$, transitions $\Delta n = \pm 1, \pm 2, \dots$ have to be included (see Fig. 3). Tentatively we assign the maximum of the conventional absorption band to a superposition of $\Delta n = 0$ transitions, suggesting the value $\nu_{\text{OH}} = 3505 \text{ cm}^{-1}$. In the time-resolved measurements, the pump pulse promotes a subensemble of molecules from thermally populated $(0, n)$ -levels to a modified set $(1, n')$, the population changes depending on the individual cross-sections. In Fig. 3 the situation for pumping at 3430 cm^{-1} is considered corresponding to $\Delta n = -2$ transitions (thick vertical arrow). Since the n' 's are lowered in the excitation step, excess population of the lower quantum numbers is generated compared to the Boltzmann distribution. The perturbed occupation of the low-frequency mode gives rise to subsequent relaxation and transient bandshape changes, i.e. spectral holes and, correspondingly, inverse holes for $v = 1 \rightarrow v = 2$ probing transitions (Figs. 1, 2b and c). In this picture the frequency spacing of the components is equal to the mode position in the $v = 1$ states (ν_{01} -transitions) and $v = 2$ levels (ν_{12} -transitions), respectively.

For this reason the depicted probing transitions in Fig. 3 have to be taken as an example. The measured induced transmission change at, for example, 3430 cm^{-1} is equal to the sum over all ν_{01} -probing transitions with $\Delta n = -2$ within this picture. The physical situation is supported by a comparison of computed bandshapes with the measured conventional dimer absorption, the temperature dependence of which is well described (see below).

Tentatively we assign the low-frequency mode to the bending vibration of the hydrogen bridge bond, the frequency value $\nu_{\text{bb}} \approx 35 \text{ cm}^{-1}$ referring to the OH-level $v = 1$. In the low-frequency Raman spectrum of neat DMEP a band around 27 cm^{-1} with a width of approximately, 50 cm^{-1} shows up which may be attributed to the OH \cdots H-bending mode in

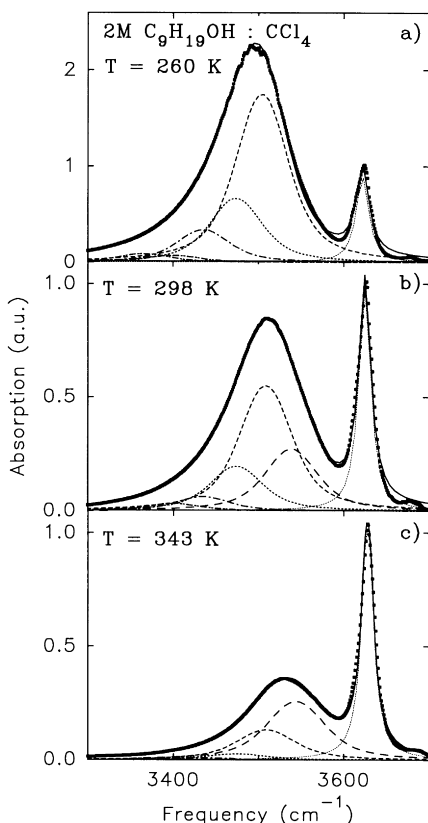


Fig. 4. Here we show conventional absorption spectra of the 2 M DMEP and CCl_4 mixture in the OH-stretching region at the three indicated temperatures of (a) 260 K; (b) 298 K; and (c) 343 K. The spectral components derived from time-resolved spectroscopy and denoted by different line styles account well for the measured data.

the $\nu = 0$ state [20]. The difference between the two numbers may be related to the different OH-levels. For comparison, in water a band located at 50 cm^{-1} was proposed to represent the bridge bending mode [21]. With regard to the notably weaker H-bond of the present dimers, our interpretation appears reasonable.

At an elevated temperature the low frequency mode should be already populated to higher quantum numbers. This shift of the population numbers by increasing the sample temperature should, of course, be reflected by the conventional absorption spectrum of our DMEP sample. For this reason we have performed a fitting, of the proton donor OH-stretch absorption band with the spectral components listed

in Table 1. The result of this is shown in Fig. 4 for three prominent temperatures of 260 K (a), 298 K (b), and 343 K (c) for the 2 M DMEP sample diluted with CCl_4 . The conventional spectra of the sample are taken with a commercial FT-IR spectrometer. The spectral components are denoted in the figure by different line styles in correspondence to the one chosen in Figs. 1 and 2. To account for the measured conventional IR-absorption of the sample we have taken Voigt profiles with a width of the Lorentzian and Gaussian contributions of $45 \pm 5 \text{ cm}^{-1}$ each. There is an excellent agreement between the measured data (thick solid line) and the sum of the spectral components (thin solid line). Especially a shift of the peak of the distribution is noted from the component at 3505 cm^{-1} (260 K, a) to the one at 3545 cm^{-1} for $T = 343 \text{ K}$ (c).

Of course, it is interesting to compare the number of transitions starting from different low-frequency modes with the total energy of the hydrogen bond in the DMEP dimer. From a simple model for a hydrogen bonded system the energy of an H-bond can be determined from the frequency shift of the OH-stretching vibration which results from the presence of an H-bond [22]. For the proton donor OH-peak absorption of 3530 cm^{-1} at 343 K a shift of 95 cm^{-1} compared to the monomer OH-absorption is related to a H-bond energy of $\approx 240 \text{ cm}^{-1}$. On the other hand, the spectral holes cover a frequency range of $\approx 175 \text{ cm}^{-1}$ at 343 K (see Table 1), close to the H-bond energy. As the thermal energy is of the same order of magnitude as the H-bond energy even a slight temperature increase from 260 to 343 K results in a significant decrease of the number of dimers and a shift of the frequency position of the proton donor OH (see Fig. 4). As a consequence, an H-bonded associate is even less probable. From our conventional absorption spectra of the sample we estimate that only 10% of the DMEP molecules are associated at 343 K.

Finally, we comment briefly on the variation of the bridge bond frequency observed in the excited state absorption. From the ν_{12} numbers in Table 1 the value of approximately 45 cm^{-1} is suggested for the $\nu = 2$ level, i.e. a strengthening of the H-bond with the quantum number ν . An anharmonic shift of the OH-vibration of $215 \pm 15 \text{ cm}^{-1}$ is estimated that favorably compares with the result of $213 \pm 5 \text{ cm}^{-1}$ for

dimers in the solid PVB matrix [1]. The numbers are also consistent with the anharmonic shift of $220 \pm 10 \text{ cm}^{-1}$ derived for ethanol oligomers in a solution of CCl_4 [2].

In conclusion, we have found strong evidence for a librational substructure in the OH-stretching band of the proton donor molecule of H-bonded dimers in the liquid phase. The observed transient spectral holes with a spacing of approximately 35 cm^{-1} are interpreted as combination tones involving the $\text{OH}\cdots\text{H}$ -bending vibration. Corresponding satellite holes are observed in excited-state absorption with frequency separations of $\approx 45 \text{ cm}^{-1}$. The different frequencies suggest a tightening of the hydrogen bond with an increasing occupation number of the OH-vibration. With the experimentally determined spectral holes we are able to fit the temperature dependent conventional absorption spectra of the 2 M DMEP sample perfectly in the OH-stretching region.

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