IR Spectroscopy of Hydrogen-Bonded Methanol: Vibrational and Structural Relaxation on the Femtosecond Time Scale

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Two-color pump−probe spectroscopy is performed with femtosecond time resolution in the OH-stretching region of methanol oligomers in a CCl_4 mixture at room temperature. The measured isotropic component of the probe transmission signal gives direct access to the lifetime of the OH-stretching vibration. It varies between 0.45 and 0.6 ps, increasing with excitation frequency from 3280 to 3400 cm^{-1}. After vibrational excitation of the OH-mode, fast spectral relaxation and/or vibrational energy migration with subsequent breaking of the excited oligomers is noticed. Recombination proceeds with a time constant of 9 ps. Comparison to earlier work on water and related alcohols is also made.

Introduction

The investigation of vibrational and structural relaxation in molecular systems is of special interest, as, for example, biologically important dynamics such as protein folding is strongly influenced by hydrogen bonds and the structural relaxation present in such systems. Direct, time-resolved observation of structural relaxation is possible by the help of laser systems emitting pulses in the infrared spectral region, where molecular vibrations exhibit their absorption. The first time-resolved investigations in the infrared were performed by Chesnoy et al.[1] and Heilweil and co-workers,[2] the latter one in liquids, but with only one tuneable IR pulse. The more elaborate first two-color experiments with independently tuneable pump and probe pulses in extented frequency ranges on liquid samples were demonstrated by Graener and co-workers.[3] With the help of two-color IR spectroscopy it was possible to obtain a detailed knowledge of intra- and intermolecular energy relaxation of molecules. This technique was first applied to simple molecules such as $CHBr_3$ in different solvents in the liquid phase.[4,5] Utilizing a polarization resolution for the determination of the change in sample transmission, Graener and co-workers could also measure for the first time directly reorientation time constants for excited vibrational modes of molecules in the liquid phase.[6] Furthermore, the impact of an H-bond on the lifetime of the OH-stretching mode of hydrogen-bonded dimers was demonstrated by the Heilweil group.[8] With increasing performance of laser systems, subpicosecond[9,10] to femtosecond[11−14] pulses are now accessible in the infrared spectral region. This enabled investigations on molecular vibrations on for example partially deuterated water[15−17] with the possibility to perform a real-time study[17] of the dynamics of an H-bonded system. In all of the experiments mentioned above, the OH-stretching mode is utilized as an ultrafast spectroscopic probe for H-bonding, as it exhibits a remarkable broadening, an increase in its absorption cross section, and shift toward lower frequencies with increasing strength of the H-bond.[18]

In this contribution we want to demonstrate an application of this technique to associated methanol. Methanol, as the simplest alcohol, has been of special interest in theoretical investigations,[19] as it represents a hydrogen-bonded system associating to more simple structures in comparison to water, for example.

Experimental Section

Our experimental system was described in detail elsewhere.[13] We start with an amplified Ti:S laser working at a 1 kHz repetition rate and emitting pulses of 130 fs duration and 1 mJ energy at 800 nm. Via amplification of a white-light continuum in nonlinear crystals and subsequent down-conversion we derive an IR pump pulse, tuneable from 2800 to 3800 cm^{-1} with energy of $\simeq$10 μJ. The independently tuneable probe pulse has a maximum energy of 1.5 μJ and exhibits tuneability inbetween 2300 and 4000 cm^{-1}. A duration of 190 fs and a spectral width of $\simeq$120 cm^{-1} determined experimentally for both IR pulses results in time−bandwidth products of 0.7, respectively, a factor of 1.6 above the limitation for the Gaussian-shaped pulses. For this reason coherent effects should only play a minor role in the measured transients.[20] Time-resolved measurements are performed at 12 different frequency positions ranging from 3020 cm^{-1} up to 3570 cm^{-1} at $T = 300$ K. Delay time zero and the temporal response function of the apparatus were determined in independent cross correlation measurements between the pump and the probe pulse.

The sample cell was 100 μm thick and contained a 1.2 M mixture of commercially available spectral grade methanol ("uvasol") and CCl_4 ("HPLC"). This results in a minimum transmission of the sample of 12% at 3330 cm^{-1}. The sample was circulated in order to avoid cumulative thermal effects.

The local temperature increase of the sample due to the deposited energy via excitation is estimated to be only a few degrees Kelvin from the long time component of the sample bleaching (see Figures 3 and 4), indicating a minor effect.

By blocking every second pump pulse and proper signal averaging we are able to detect the induced, relative transmission change of the sample, $\ln(T/T_0)$, where T and T_0, respectively, denote the measured energy transmission of the probe pulse at a certain frequency position and delay time with and without excitation of the sample. A half-wave plate adjusts the polariza-

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tion of the probing pulse to 54.7° in respect to the linearly polarized pump. This detection scheme allows one to concentrate on the pure vibrational dynamics, as reorientation should not contribute to the measured transients.

All measurements were performed at a low excitation level with transmission changes of only a few percent, to reduce heating of the sample via the deposited vibrational energy. This results in an intensity level in the experiments which was as low as possible in order to prevent higher order nonlinear effects[21] for the intense infrared pump pulse.

The measured signal transients are compared with calculated curves by solving a rate equation system[22] describing a five-level relaxation scheme. Excitation promotes a few percent of the molecules from the vibrational ground state (0) into the first excited state (1). Spectral relaxation populates subsequently a further level (2) with similiar energy compared to level 1. In turn, breaking of the excited oligomers occurs resulting in additional broken methanol aggregates and corresponding missing longer oligomers (3). After recombination of the broken methanol aggregates, a new thermal equilibrium is obtained (4) due to the deposited energy. Subsequent relaxation to the ground state proceeds on a time scale much slower compared to the initial fast dynamics around delay time zero and will for this reason not be discussed in detail here. The excited oligomers are investigated in the vibrational ground state (bleaching of the sample) as well as in the first excited state (excited state absorption). The broken oligomers are exclusively seen in the vibrational ground state and show up as an induced absorption of the sample in the transient spectrum. As the two IR pulses are clearly not bandwidth-limited, coherent effects can be neglected in the model calculations[20] in the following.

Results and Discussion

To demonstrate the quality of our data, experimental results of our two-color pump−probe spectroscopy on associated methanol are depicted in Figures 1 and 2 with excitation adjusted to 3280 and 3400 cm^{-1}, respectively. For three different probing frequencies the temporal evolution of the isotropic component of the change in sample transmission is displayed: 3070 cm^{-1} (a), $\nu = \nu_{Pu}$ (b), and 3470 cm^{-1} (c). By probing in the red part of the spectrum (a) an induced absorption builds up within the time resolution of the experiment, which is explained via excited-state absorption (ESA). Vibrational excitation promotes a few percent of the methanol molecules into the first excited state. The $\nu = 1 \rightarrow 2$ transition starting from this level is red-shifted in comparison to the $\nu = 0 \rightarrow 1$ transition due to the pronounced anharmonicity of the OH-potential of methanol, present even without any H-bonding.[23] From comparison of the recovery of the signal transients with numerical calculations applying the model outlined in the Experimental Section, we can determine directly the averaged vibrational lifetime of the OH-stretching mode of associated methanol to vary between 0.45 ± 0.05 ps (ν_{Pu} = 3280 cm^{-1}) and 0.6 ± 0.05 ps (ν_{Pu} = 3400 cm^{-1}). The positive amplitude of the signal transient seen for late delay times (>2 ps) in the figures is due to missing molecules in the vibrational ground state via breaking of the excited methanol oligomers,[24] as will be discussed later in detail. The result of adjusting the probe frequency equal to ν_{Pu} is displayed in panel b of Figures 1 and 2 for the two different excitation frequencies mentioned already. In both cases we notice first a fast increase in sample transmission due to excitation within the temporal response function of the experiment. This is followed by a slower build up of the bleaching with a time constant of 0.5 ps (Figure 1b) or a decay within 0.6 ps (Figure 2b) for ν_{Pu} = 3400 cm^{-1}. The finite amplitude of the transients at late delay times is a result of heating of the excited volume which relaxes to the ground state with a time constant ≥30 ps, not resolved in our investigations.

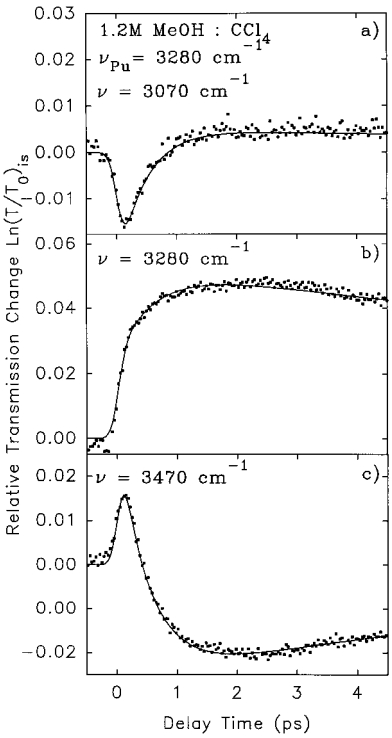

Figure 1. Isotropic time dependent measurements taken at 300 K and excitation within the red part of the OH-band of associated methanol at ν_{Pu} = 3280 cm^{-1} are shown in this figure. The probe frequency is adjusted to 3070 cm^{-1} (a), 3280 cm^{-1} (b), and 3470 cm^{-1} (c); calculated, solid line; measured, filled squares.

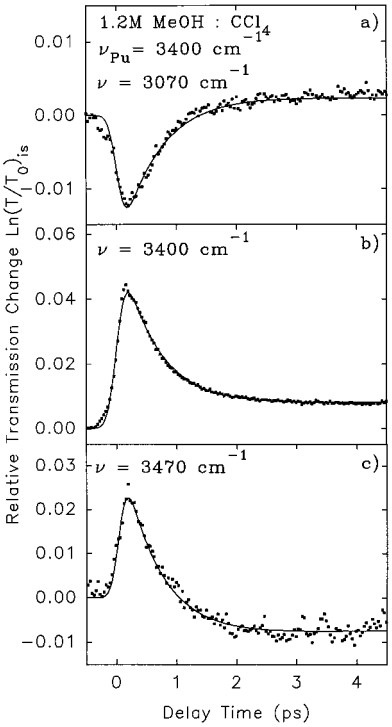

Figure 2. The same as shown in Figure 1, this time for ν_{Pu} = 3400 cm^{-1}, however.

Probing in the blue part of the OH-band of oligomeric methanol is depicted in Figures 1c and 2c. A first, fast increase

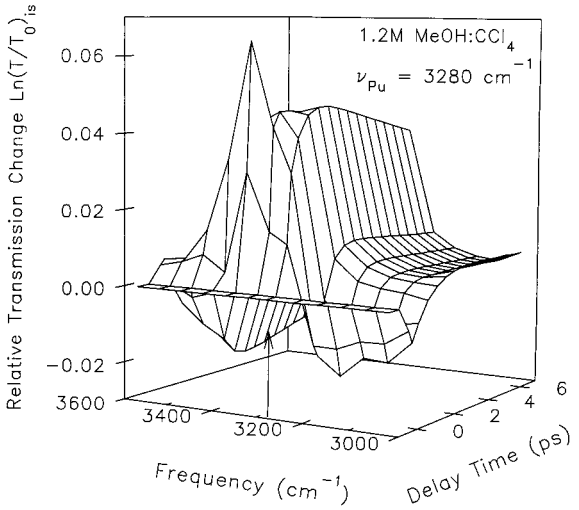

Figure 3. Three-dimensional plot of the experimentally determined change in sample transmission versus delay time and frequency for $\nu_{Pu} = 3280$ cm^{-1}. The data are taken from time-dependent measurements at the respective frequencies and are corrected for the dispersion in the probe branch, which results in a frequency dependent delay time zero. Note that the maximum bleaching around $t_D = 0$ ps is $\simeq$80 cm^{-1} red-shifted in respect to ν_{Pu}.

in sample transmission is seen, which decays with the lifetime of the OH-mode and subsequently turns into an induced sample absorption. This induced absorption is related to an increased number of shorter methanol aggregates, generated by breaking of the excited longer methanol oligomers. This induced absorption subsequently returns to zero with a time constant of 9 ps for an excitation frequency of 3280 cm^{-1}.

The time and frequency dependence of the experimentally determined change in sample absorption are depicted in Figure 3 for $\nu_{Pu} = 3280$ cm^{-1} and in Figure 4a,b for $\nu_{Pu} = 3340$ and 3400 cm^{-1}, respectively. As delay time zero (optimum temporal overlap between pump and probe pulse) is changing with varying probe frequency due to dispersion, we have corrected all transients for this. With the help of additional cross correlation measurements with the sample cell substituted by a thin nonlinear crystal, we have determined the delay time zero versus probing frequency (data not shown).

Excitation in the red part of the OH-band of associated methanol yields complicated spectral dynamics. It is clearly seen that at early delay times of 0 and 0.2 ps (see Figure 3) the maximum of the sample bleaching is notably blue-shifted by $\simeq$80 cm^{-1} in comparison to ν_{Pu}. Subsequently the sample bleaching broadens and shifts toward lower frequencies. This is accompanied by the build up of an induced absorption for $\nu > 3400$ cm^{-1} and a decrease of the excited-state absorption which changes to a bleaching of the sample. These spectral dynamics are further illustrated in Figure 5a, where we plotted the same data as time-resolved spectra at delay times of 0 ps (dotted line), 0.2 ps (solid line), 0.5 ps (dashed line), and 2 ps (dash−dotted line). From fitting of the latter data with a set of three Gaussians we obtain the following line parameters, which are listed in Table 1. At early delay times of 0 ps, the spectral feature at the maximum of the sample bleaching is obviously limited by the spectral width of the probing pulse (90 cm^{-1}).

In the case of excitation at the maximum of the OH-band at 3340 cm^{-1} (see Figures 4a and 5), the transient spectrum consists of a bleaching close to the excitation frequency and the corresponding ESA centered at 3140 cm^{-1}. The induced absorption at early delay times (ESA) changes time delayed to an induced bleaching of the sample while simultaneously an induced absorption builds up for $\nu > 3400$ cm^{-1}. Both spectral components are again related to missing and broken oligomers via excitation, respectively. Similiar spectral dynamics are noticed for $\nu_{Pu} = 3400$ cm^{-1} (see Figures 4b and 5c). It is noteworthy, however, that in comparison to the situation of excitation at the center of the OH-band, the ESA is higher in amplitude while the induced absorption in the blue part of the spectrum is lower. This may be a result of the longer T_1 determined in the latter case as well as the closer spectral distance between the bleaching at the excitation and the induced absorption in the blue part of the transient spectrum, which may partly cancel due to the spectral width of the probe pulse. The spectral components determined at the three excitation frequencies are at variance for late delay times of 2 ps, as can be seen from Table 1.

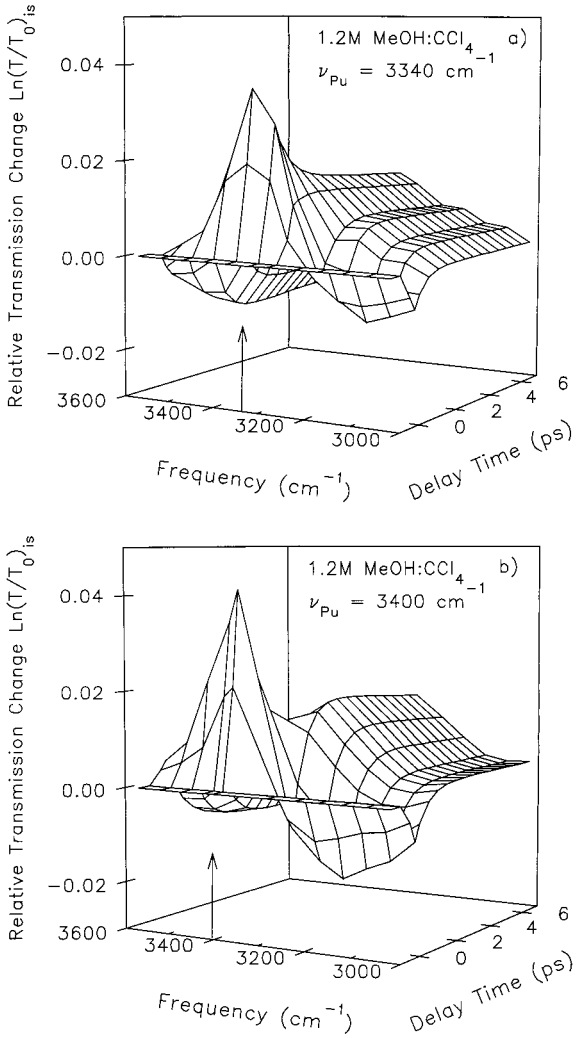

Figure 4. The same as shown in Figure 3, but the excitation frequency is adjusted to 3340 cm^{-1} (a) and 3400 cm^{-1} (b), respectively.

In the following we will discuss the different dynamics observed in our femtosecond-experiments on the OH-mode of hydrogen-bonded methanol.

(i) Vibrational Lifetime Shortening. First of all we conclude that there is a prominent lifetime shortening of the OH-stretching mode in the presence of an H-bond. In comparison to the number for monomeric methanol in a CCl_4 mixture of 9 ps,[23] a shortening down to 0.45 ps in the case of strong H-bonds, which are selected preferably by excitation at 3280 cm^{-1}, is noted. This shortening of T_1 by a factor of 20 is most probably related to excitation of H-bonds with subsequent breaking of the excited methanol oligomers. The broken oligomers show up in the

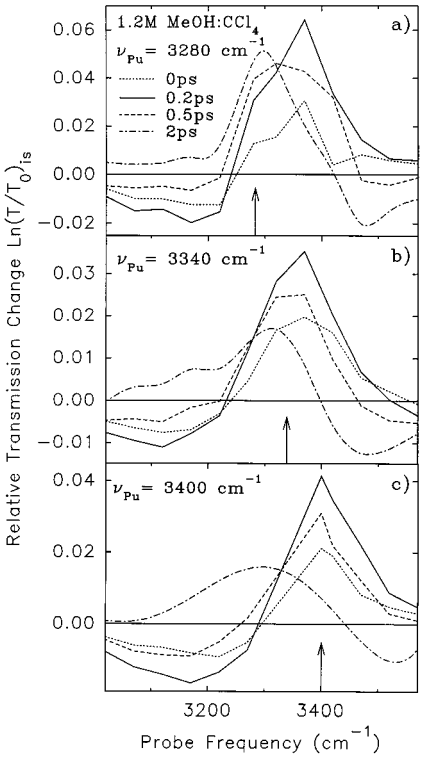

Figure 5. Isotropic transient spectra obtained from the delay time zero corrected time dependent measurements at four prominent delay times of 0 ps (dotted line), 0.2 ps (solid line), 0.5 ps (dashed line), and 2 ps (dash−dotted line). Data are taken at excitation frequencies of 3280 cm^{-1} (a), 3340 cm^{-1} (b), and 3400 cm^{-1} (c), respectively, marked with an arrow.

TABLE 1: Parameters of the Gaussians, Fitted to the Transient Spectra Shown in Figure 5 at Delay Times of 0 and 2 ps[a]

	ν_{Pu}	ESA	missing oligomers	bleaching 0 ps/2 ps	broken oligomers
ν_G (cm^{-1})	3280	3140	3120	3360/3320	3460
$\Delta\nu_G$ (cm^{-1})	3280	170	170	90[b]/110	170
ν_G (cm^{-1})	3340	3140	3130	3370/3340	3460
$\Delta\nu_G$ (cm^{-1})	3340	230	150	150/120	170
ν_G (cm^{-1})	3400	3220	3100	3400/3340	3480
$\Delta\nu_G$ (cm^{-1})	3400	250	170	120/170	170

[a] All numbers have an accuracy of ±20 cm^{-1}. [b] Spectral widths are calculated by deconvoluting the Gaussians with the respective probe pulse spectrum, with the exception of this value.

transient spectra as an induced absorption for $\nu > 3400$ cm^{-1}. An additional relaxation channel for the excited OH is energy transfer to, for example, the neighboring CH-stretching vibrations, as concluded earlier already from time-resolved spectroscopy of ethanol monomers[25] and ethanol oligomers[26] in solution. This relaxation channel could, however, not be inspected directly in the present investigation, as the spectral width of the femtosecond pulses exceeds notably that of the CH-stretching modes. But this will be a point to be investigated in detail in future experiments with higher spectral resolution.

The lifetime shortening of the OH-mode of associated methanol may be compared with the one determined previously for associated ethanol. In the latter case, a shortening of T_1 due to the presence of H-bonds is determined from 8 ps (monomer)[25] down to 1.4 ps (oligomer).[27] On the other hand, from femtosecond-investigations of associated ethanol predissociation, time constants ranging from 250 to 870 fs were reported[31] on the same order as the numbers for T_1 presented here. These time constants are, however, mainly concluded from ground-state dynamics, whereas our numbers for T_1 are directly determined from monitoring the population of the first excited-state of the OH. Comparing the T_1^{OH} of diluted alcohols with increasing strength of the H-bond, the following picture is derived: The alcohol 2,2-dimethyl-3-ethyl-3-pentanol (DMEP) exhibits the weakest H-bond, as it associates to an open H-bonded dimer, only. For the proton donor, $T_1^{OH} = 3.6$ ps is determined from time-resolved spectroscopy.[28] Diluted ethanol is in respect to its H-bond properties between this open dimer and the even simpler methanol, while associated methanol shows the shortest numbers for T_1^{OH}; i.e., with increasing strength of the H-bonds, the lifetime of the OH of hydrogen-bonded alcohols decreases notably.

A similiar trend has been reported recently for an HDO:D_2O mixture:[15] the authors concluded an increase of T_1^{OH} with temperature from 0.75 to 0.9 ps with heating of the sample from 273 to 353 K while the H-bonds are expected to weaken with increasing sample temperature.

The width of the ESA and the anharmonic shift observed between the $\nu = 0 \rightarrow 1$ and the $\nu = 1 \rightarrow 2$ transition is comparable to the respective numbers determined for associated ethanol[24] and an HDO:D_2O mixture:[16] in the latter case numbers of 160/230 and 180/230 cm^{-1}, respectively, are reported. Here the corresponding ones can be found in Table 1. The width of the ESA varies between 170 and 250 cm^{-1}, while the anharmonic shift ranges from 180 to 230 cm^{-1}. The number 180 cm^{-1} is derived for excitation in the blue part of the OH-band and the corresponding weakest H-bonds; i.e., the anharmonic shift of the OH-vibration increases with strengthening of the H-bond. These numbers are typical numbers, however, as the corresponding sample bleaching related to the missing molecules in the vibrational ground state exhibit a time dependent red shift. The width of the ESA exceeds in all cases discussed here that of the corresponding bleaching, which is related to missing molecules in the vibrational ground state at early delay times as concluded from Table 1. Consequently, the T_1 values stated here are averaged over all aggregates which are initially excited. In addition, they may be influenced by fast spectral relaxation, which is discussed in the following.

(ii) Spectral Relaxation. During the presence of the pump pulse, two fast dynamical features are derived from our time-resolved spectroscopy on methanol oligomers. The first one is related to an initial bleaching of the sample, which is noticed with a decreasing amplitude for increasing frequencies $\nu > 3400$ cm^{-1} (see Figures 1c, 2c, and 5). This fast spectral dynamics can be interpreted in two ways. In the case of diluted ethanol[29] or the special alcohol DMEP,[30] similiar fast spectral dynamics has been noticed from time-resolved vibrational spectroscopy and were interpreted in terms of energy migration along the chain of associated molecules. Due to the similiar vibrational energies of neighboring molecules, the excitation of the OH-mode is proposed to migrate toward molecules with weaker H-bonds, e.g. toward higher frequencies, within the excited oligomers. Following this argument, we have evidence for the same dynamics taking place in associated methanol, too. As this spectral dynamics is not resolved by our pulses, we estimate an upper limit for this of ≈300 fs. A complication of resolving this dynamics is the spectral width of our pulses, ≃120 cm^{-1}, covering part of the transient spectrum where this spectral relaxation proceeds.

Another possibility to explain this initial fast spectral relaxation toward higher frequencies or corresponding methanol molecules with weaker H-bonds is related to the excitation of the OH-stretch in an associate. In the case of excitation of an

internal OH-group exhibiting slightly nonlinear hydrogen bonds, this vibrational excitation could result in a weakening of the hydrogen bonds toward the two neighbors of the pumped OH-group. Consequently, the potential of the excited OH is modified significantly, resulting in a shift of the absorption frequency of the excited OH-mode toward higher frequencies. Further experiments are needed to decide whether energy migration and/or modification of the OH-potential during vibrational excitation is responsible for the discussed dynamics. An additional fast spectral dynamics not reported previously is noticed at the excitation frequency around delay time zero. From the numbers summarized in Table 1 on the bleaching component nearby ν_{Pu} at 0 ps as well as the data depicted in Figures 1b and 2b, one concludes a systematic dependence of this spectral component on ν_{Pu}. It exhibits a red shift in comparison to ν_{Pu}, which decreases from 80 cm^{-1} ($\nu_{Pu} = 3280$ cm^{-1}) down to 30 cm^{-1} ($\nu_{Pu} = 3340$ cm^{-1}) and finally 0 at $\nu_{Pu} = 3400$ cm^{-1}; i.e., this shift of the maximum of the sample bleaching at early delay times seems to be related to the strength of the hydrogen bonds experienced by the excited molecules. Strong H-bonds result in a shift well resolved by our IR pulses while for excitation of predominantly weak H-bonded species this effect cannot be resolved. A detailed understanding of this spectral dynamics is still under investigation but again may be related to a modification of the OH-potential of the excited hydrogen-bonded methanol.

(iii) Dissociation of Excited Oligomers. Finally we conclude from our experiments that breaking of the excited methanol aggregates into shorter specimens occurs, which show up in the transient spectrum as an induced absorption for $\nu > 3400$ cm^{-1} at delay times $t_D > 0.5$ ps (see Figures 3−5). The corresponding missing, previously excited, longer oligomers are noticed as a time-delayed build up of sample bleaching for $\nu < 3280$ cm^{-1}. A predissociation of the excited oligomers is not supported by our data, as was previously noticed in the case of excitation of ethanol oligomers.[29,31,32] Concerning the question of dissociation or predissociation, it is interesting to compare again the different alcohols which have been already investigated by time-resolved IR spectroscopy. In the case of the DMEP dimer, no breaking of the excited H-bonded associate was determined, although the H-bond is the weakest one of the compared alcohols and the deposited energy exceeds the H-bond energy notably. This may be related to the heavy molecules and the slow reorientation of its OH-group in comparison to ethanol or methanol.[23] Hydrogen-bond vibrations are expected in this case to be excited, but as the whole molecule nor the OH-group can reorient sufficiently within T_1^{OH}, a breaking of the H-bond will not be noticed in this special case. For the substantially smaller ethanol molecule, reorientation of the OH-group proceeds on the same time scale as predissociation (2 ps),[24] allowing the molecule to reorient with a high probability of finding no new partner for H-bonding within a few picoseconds. Methanol is expected to exhibit even faster reorientation, as the molecule is composed of an even smaller number of atoms in comparison to ethanol, and perhaps for this reason predissociation is not seen in our investigations on associated methanol. Recombination of the broken oligomers is determined to proceed with a time constant of 9 ps for methanol, while comparable numbers are reported for diluted ethanol.[29]

Conclusions

With our two-color femtosecond spectroscopy in the infrared we are able to determine the lifetimes of the OH-stretching mode as well as structural relaxation of associated methanol dissolved in CCl_4. We measure values of T_1 from 0.45 ± 0.05 to 0.6 ± 0.05 ps with increasing excitation frequency from 3280 to 3400 cm^{-1}. For $\nu_{Pu} = 3280$ and 3340 cm^{-1}, first fast spectral relaxation is monitored below our time resolution, which is explained in terms of weakening of the H-bonds due to excitation of the high-frequency OH-mode and/or vibrational energy migration toward methanol groups exhibiting weaker H-bonds. The excitation of the OH-mode results subsequently in breaking of the methanol oligomers with generation of additional shorter aggregates and missing longer specimens. Recombination is monitored with a time constant of 9 ps.

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