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Orientational dynamics of hydrogen-bonded phenol

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We use femtosecond mid-infrared pump-probe spectroscopy to study the effects of hydrogen bonding on the orientational dynamics of the OD-stretch vibration of phenol-*d*. We study two samples: phenol-*d* in chloroform and phenol-*d* in chloroform to which we added excess acetone. For phenol-*d* in chloroform, we observe rotational diffusion of the OD group around the CO bond, with a correlation time of 3.7 ps. For phenol-*d* hydrogen bonded to acetone, the reorientation time is strongly dependent on the probe frequency, varying from 3 ps on the blue side of the spectrum to more than 30 ps on the red side. © *2004 American Institute of Physics.*
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I. INTRODUCTION

Hydrogen bonds play a crucial role in the molecular dynamics of many complex systems, such as biomolecules, solute-solvent complexes, and hydrogen-bonded liquids (e.g., water). An elegant method for studying the dynamics of hydrogen-bonded systems is provided by probing the OH-stretch vibration, as its frequency is highly sensitive to the local geometry of the hydrogen bond. In general, hydrogen bonding leads to a strongly broadened OH absorption band that is redshifted with respect to the free OH absorption. The broadening of the absorption is a direct consequence of the large number of conformations present in hydrogen-bonded systems, differing in hydrogen-bond length and therefore absorbing at a different frequency; ''the shorter the hydrogen bond, the lower the OH-stretch frequency,'' is the rule of thumb by which this phenomenon is described.[1,2]

The correlation between hydrogen-bond length and OH-stretch frequency makes it possible to distinguish the different hydrogen-bonded conformations spectroscopically, which opens the way to study their dynamical properties. Unfortunately, *linear* infrared techniques cannot provide dynamical information about subensembles, as this requires the use of at least two light-matter interactions. *Nonlinear* infrared methods do have the ability to provide such information. In these methods one or more light pulses are used to label a subensemble, after which the evolution of the system is read out by a next pulse.

One of these nonlinear techniques is femtosecond mid-infrared pump-probe spectroscopy. This technique has been applied extensively to the investigation of the dynamics of hydrogen-bonded systems.[3–9] In addition to providing information about vibrational relaxation and spectral diffusion, the method can also be used to study reorientational processes in molecules. In the past reorientational measurements have thus provided insight into the dynamics of HDO molecules in liquid heavy water (D_2O)[10,11] and ionic solvation shells.[12] These studies suggest that the reorientation time of water molecules depends strongly on the hydrogen-bond strength. However, the rapid interconversion of conformations, which occurs in liquid water, makes it impossible to directly probe the orientational dynamics of a *unique* conformation for longer than about 1 ps. Therefore these studies have relied on models for extracting information about the frequency dependence of orientational processes. Structurally more complex molecules, such as alcohols, dissolved in apolar solvents display a much slower rate of interconversion, and it should therefore be possible to probe the reorientation of different conformations directly. However, only few papers have been published that study reorientation in these systems,[13–15] and none have presented a study of the influence of the hydrogen-bond interaction on reorientational processes.

Here we report on the use of polarization and frequency resolved mid-infrared pump-probe spectroscopy to investigate the influence of the O–D···O hydrogen-bond length on the orientational dynamics of the hydrogen-bond donating OD group.

II. EXPERIMENT

Laser system. The laser system we used for our experiments consists of a commercial Ti:sapphire regenerative amplifier that generates pulses with a duration of 100 fs and an energy of 1 mJ. Its output is used to pump a commercial two-stage optical parametric amplifier (OPA) based on β-barium borate (BBO), which we tuned such that the 800 nm pump light is split into signal and idler photons of 1.3 and 2 μm, respectively. The idler pulse is frequency-doubled in a second BBO crystal, and the resulting 1 μm light is used as a seed in a second OPA process in $KNbO_3$, pumped by the residual 800 nm light from the first OPA process. This process yields pulses that are resonant with the OD-stretch mode (4 μm), with an energy of 4 μJ and a duration of about 350 fs.

Pump-probe setup. Figure 1 shows a schematic outline of the pump-probe setup. A small part of the mid-infrared light is split off by a wedged CaF_2 window to obtain probe and reference pulses. A $\lambda/2$ plate is used to turn the polarization of the pump pulse by 45° with respect to that of the probe light. The pump, probe, and reference beams are fo-

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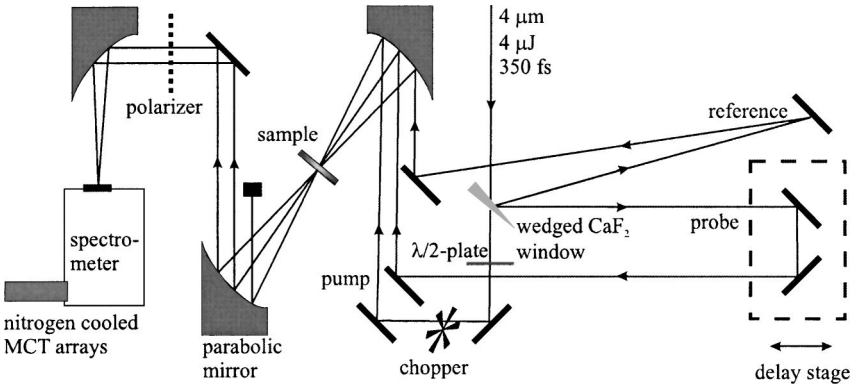

FIG. 1. Schematic outline of the pump-probe setup.

cused onto the sample by an off-axis parabolic mirror and recollimated by an identical mirror. The probe and reference pulses are focused onto the entrance slit of a spectrometer. In the spectrometer the pulses are spectrally dispersed onto a liquid-nitrogen cooled 2×32 MCT (mercury-cadnium-telluride) array. Behind the sample a polarizer is placed to select either the parallel or the perpendicular polarization component of the probe light with respect to the pump, which yields the transient absorptions $\Delta\alpha_{\parallel}$ and $\Delta\alpha_{\perp}$, respectively. From these signals the isotropic signal

$$\Delta\alpha_{\mathrm{iso}}=\frac{\Delta\alpha_{\parallel}+2\Delta\alpha_{\perp}}{3}, \tag{1}$$

which is independent of reorientational processes, and the anisotropy

$$R=\frac{\Delta\alpha_{\parallel}-\Delta\alpha_{\perp}}{3\Delta\alpha_{\mathrm{iso}}}, \tag{2}$$

which only reflects reorientation, are constructed.

Sample. In order to study the effect of hydrogen bonding on the orientational dynamics of the OD group of phenol-*d* we compared two samples: a solution of phenol-*d* in chloroform ($0.4M$) and a solution of phenol-*d* in chloroform ($0.6M$) to which an excess of acetone was added ($\sim 3M$). Phenol-*d* was obtained by dissolving 2 g of phenol-*h* (Aldrich) in 10 ml of D_2O and boiling the solution until all D_2O had evaporated. Chloroform (high performance liquid chromatography grade) was used as received. All measurements were performed in a static cell with an optical path length of 500 μm.

Figure 2 shows the linear IR absorption spectra of these two samples. Two OD-stretch absorption bands can be observed in the spectrum of phenol in chloroform; a narrow band at 2650 cm^{-1} (FWHM≃20 cm^{-1}) and a broad band at 2500 cm^{-1} (FWHM≃200 cm^{-1}), where FWHM stands for full width at half maximum. The narrow band is due to monomeric phenol molecules, whereas the broad band is caused by clusters of hydrogen-bonded phenol molecules.[16] When an excess of acetone ($\sim 3M$) is added, the band at 2650 cm^{-1} disappears while the band at 2500 cm^{-1} grows in intensity, which leads us to the conclusion that all phenol molecules in this sample are hydrogen bonded. As an excess of acetone is present, we can safely assume that acetone acts as the hydrogen-bond acceptor, rather than other phenol molecules.

III. RESULTS AND DISCUSSION

Transient spectra and vibrational relaxation. Figure 3 shows the transient spectrum of phenol in chloroform. The ground state bleach (2650 cm^{-1}) and the excited state absorption (2550 cm^{-1}) are clearly separated. Apparently the OD potential has an anharmonicity of 100 cm^{-1}. In addition to the bleach and the excited state absorption, a rather broad shoulder is observed on the red side of the bleach (~2625 cm^{-1}). This shoulder decays much faster (~1 ps) than the bleach and the excited state absorption (~10 ps), and can be attributed to clusters of hydrogen-bonded phenol molecules. This assignment is supported by the linear spectrum, which shows that the tail of the cluster band lies in the region where the shoulder is observed.

The decay of the transient absorption (Fig. 4) is faster on the red side of the spectrum than on the blue side. We have used biexponentials to fit these measurements, thereby accounting for the transient bleaching of the tail of the cluster band, which overlaps with the monomer band and contributes weakly to the total transient signal (~15% at 2650 cm^{-1}). In Fig. 5 the two derived time constants are plotted as a function of the probe wavelength. The slow decay time, which we interpret as the lifetime of the OD-stretch vibration

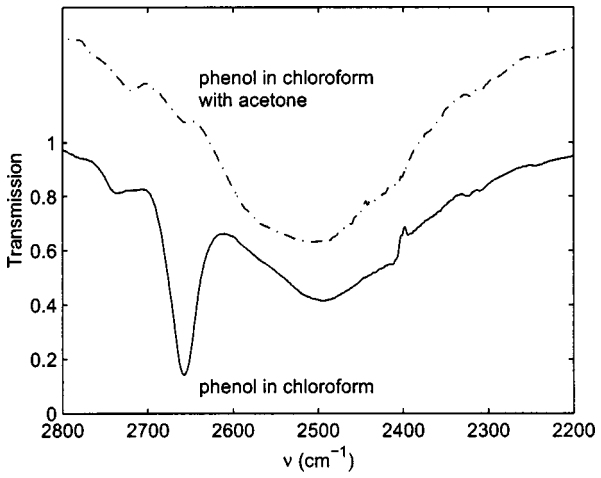

FIG. 2. Linear IR absorption spectra of phenol-*d* in chloroform ($0.4M$) and phenol-*d* in chloroform ($0.4M$) with acetone ($\sim 3M$). For clarity the latter spectrum has been shifted upwards by 0.4. The sample thickness was 500 μm.

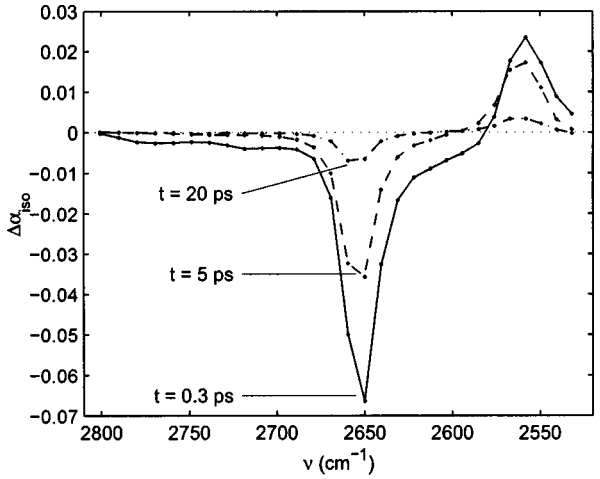

FIG. 3. Transient spectra of phenol in chloroform (0.4*M*) at delays of 0.3, 5, and 20 ps. The pump pulse was centered at 2650 cm^{-1}.

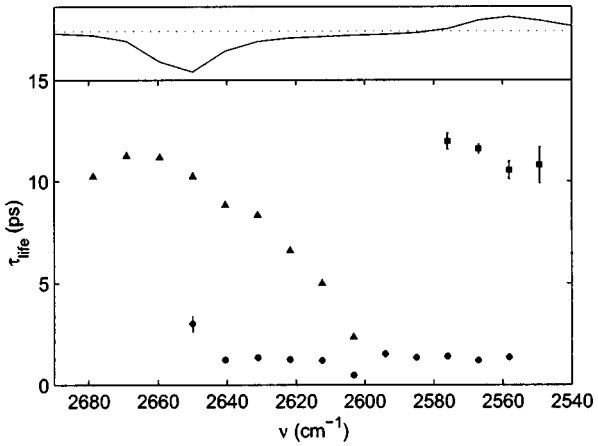

FIG. 5. Time constants obtained from biexponential fits to the transient spectrum (top panel) of phenol-*d* in chloroform as a function of the probe wavelength ($\nu_{pump}=2650\,cm^{-1}$). The triangles correspond to the bleaching of the OD band of monomeric phenol, the squares to its induced absorption and the circles to the bleaching of the cluster band.

of monomeric phenol, varies smoothly from about 5 to 11 ps going from the red to the blue side of the spectrum. This behavior contrasts with that of the cluster band, which shows a remarkably constant lifetime of about 1 ps over the entire probe range.

The strong variation in vibrational lifetime as a function of frequency suggests that the (monomeric) phenol molecules are hydrogen bonded to the solvent chloroform molecules. Furthermore, it suggests that the phenol-chloroform conformations do not interconvert within ~10 ps (for else a frequency independent lifetime would have been observed).

Figure 6 shows the transient spectra of phenol in chloroform with excess acetone. We observe a broad bleaching signal and the high-frequency wing of the excited state absorption on the red side of the probe spectrum. The bleach decays monoexponentially with a time constant of about 1 ps, which is an order of magnitude faster than for phenol hydrogen-bonded to chloroform. This time constant is very similar, however, to that of phenol clusters. Figure 7 shows a plot of the lifetime of phenol hydrogen-bonded to acetone as a function of the probe wavelength. Remarkably, hardly any variation in lifetime can be observed, only at the very blue edge the lifetime increases.

The role of the hydrogen bond in vibrational relaxation. The above results show that the hydrogen bond provides, either directly or indirectly, a very efficient vibrational relaxation pathway. For weakly hydrogen-bonded phenol, we observe that the lifetime decreases from 11 to 5 ps as the hydrogen-bond strength increases. When the hydrogen-bond strength is further increased, i.e., by adding the strong hydrogen-bond acceptor acetone, the lifetime decreases down to 1 ps. At this point the lifetime seems to reach its minimum value, and a further increase in hydrogen-bond strength no longer results in a decrease of the lifetime.

When seeking an explanation for the frequency independence of the lifetime of phenol hydrogen-bonded to acetone, the first thing that comes to mind is that the strongly hydrogen-bonded conformations may interconvert rapidly, so that in fact, an average lifetime is observed. However we will see below that there is no rapid spectral diffusion, which

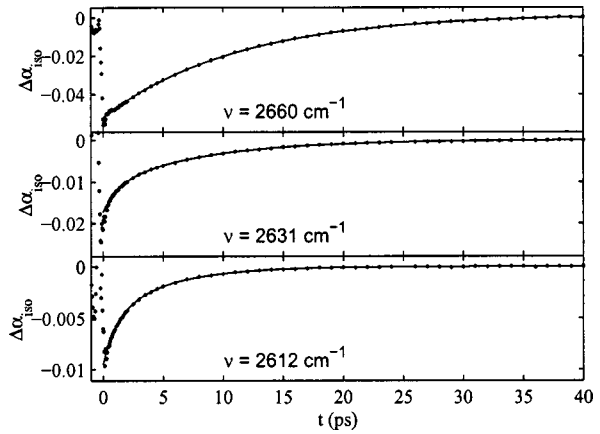

FIG. 4. Delay scans at three different probe frequencies in the bleaching region of the transient spectrum of phenol-*d* in chloroform ($\nu_{pump}=2650\,cm^{-1}$).

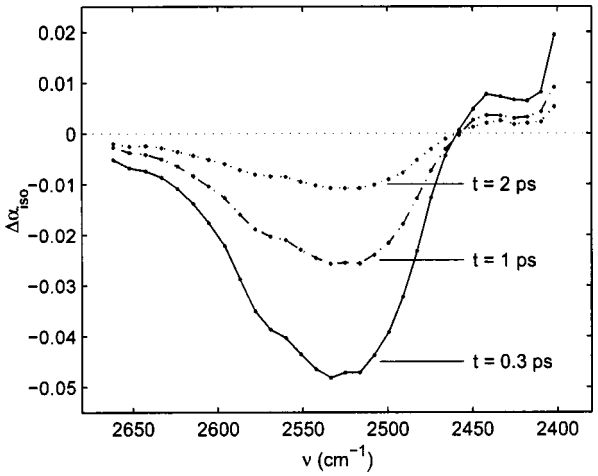

FIG. 6. Transient spectra of phenol-*d* hydrogen-bonded to acetone in chloroform measured at 0.3, 1, and 2 ps. The pump pulse was centered at 2525 cm^{-1}.

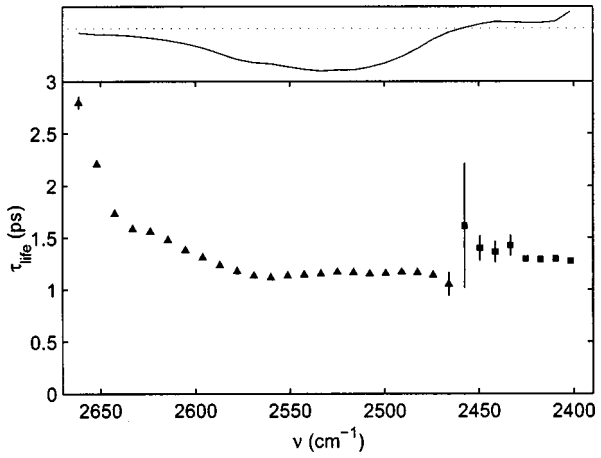

FIG. 7. Lifetime of the OD vibration of phenol-*d* hydrogen-bonded to acetone as a function of probe wavelength ($\nu_{pump}=2525\ cm^{-1}$). The transient spectrum is shown in the top panel. The triangles correspond to the bleaching region of the spectrum, the squares to the excited state absorption.

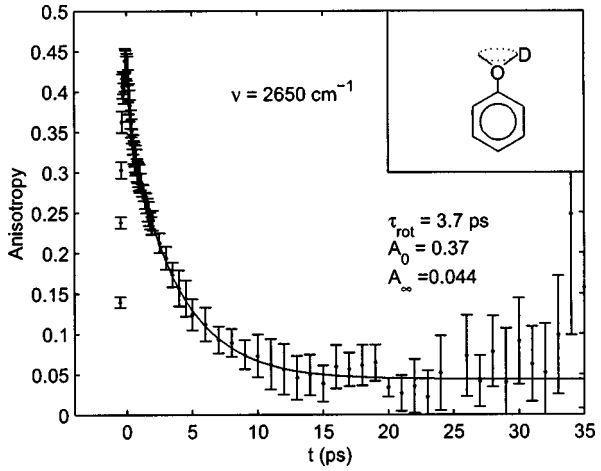

FIG. 8. Anisotropy decay of phenol-*d* in chloroform at 2650 cm^{-1}. The solid line represents a fit to the data of the form $R=(A_0-A_\infty)e^{-t/\tau_{rot}}+A_\infty$. The inset illustrates the orientational dynamics that lead to the decay of the anisotropy.

means that this explanation cannot be correct. Therefore we conclude that the relaxation involves a mechanism that speeds up with increasing strength of the hydrogen bond, but only up to a certain limiting rate. Of course this leads to the question what the exact nature of this relaxation channel could be. Even though it is impossible to provide a conclusive answer based on the experiments described in this paper, it is unlikely that the hydrogen bond is one of the accepting modes, since then the relaxation rate is expected to keep increasing with the hydrogen-bond strength. Instead, the role of the hydrogen bond may be indirect in matching the energy of the excited OD-stretch vibration to that of the combination of (other) accepting modes.

Effect of hydrogen bonding on reorientation. In order to obtain the reorientation time of the OD group of phenol in chloroform, we have measured the anisotropy of the transient absorption. In Fig. 8 the anisotropy is shown for the peak position of the bleach. By fitting this anisotropy to a single exponential we obtained a rotational correlation time of 3.7 ps. Interestingly, whereas the vibrational relaxation showed a strong frequency dependence for phenol in chloroform, the reorientation time is fairly frequency independent.

A point worth mentioning is that the anisotropy does not decay to zero as one would expect in the case of free rotational diffusion, but to a value of ~0.04. This nonzero end level can be explained by considering the two motions that play a role in the reorientation of the OD group; the first is the rotation of the OD group around the CO-bond axis, and the second is the rotation of the phenol molecule as a whole, which of course also contributes to the reorientation of the OD group. We assume that the first process occurs much faster than the second, so that on the time scale of our experiment, we essentially only observe the rotation of the OD group around the CO-bond axis (see inset to Fig. 8). As this rotation restricts the reorientation of the OD group to a limited portion of the unit sphere, a nonzero anisotropy will be measured at long delays. The end level of the anisotropy is determined by the solid angle that can be covered by the OD group and therefore by the C–O–D angle.

This reasoning leads us towards attributing the reorientation time of 3.7 ps to the rotational diffusion of the OD-group around the CO bond. The fact that this time constant does not depend on frequency shows that the orientational mobility is negligibly affected by the weak hydrogen bond to chloroform. In principle, the anisotropy should further decay to zero if we would measure up to longer delays, at which the molecular reorientation of phenol becomes important. Unfortunately, because of the finite relaxation time of the OD vibration, we were only able to accurately determine the anisotropy for delays up to 15 ps.

We compare these results with those obtained for strongly hydrogen-bonded phenol. Figure 9 shows the anisotropy decay of strongly hydrogen-bonded phenol at four distinct positions in the transient spectrum. Interestingly, while the lifetime showed no variation over the absorption

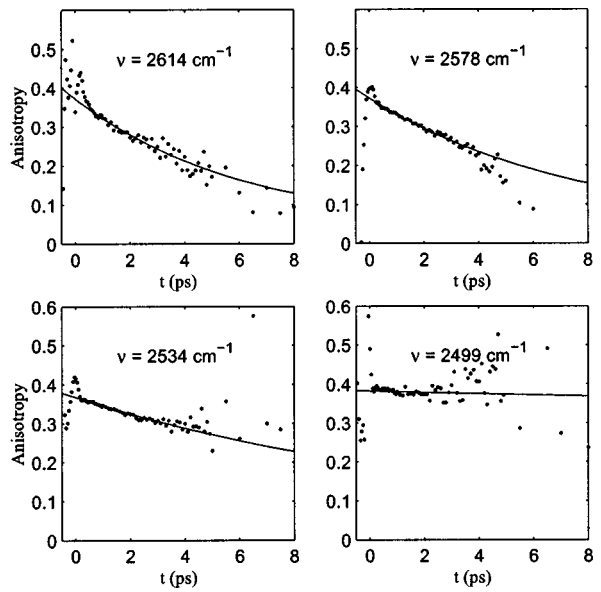

FIG. 9. Anisotropy decay at different frequencies in the transient spectrum of phenol-*d* hydrogen-bonded to acetone. The solid curves are monoexponential fits with an end level of 0.04.

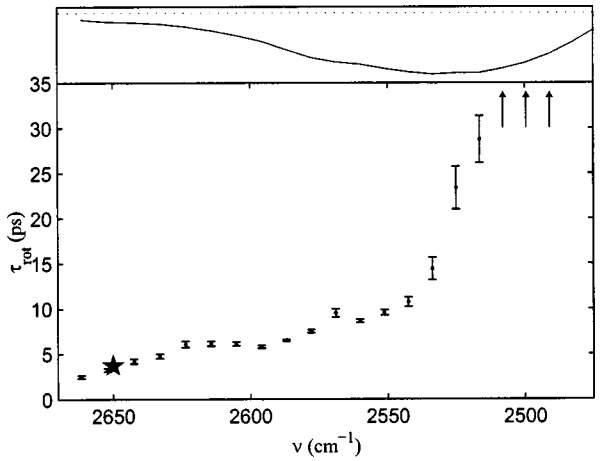

FIG. 10. Reorientation time of the OD group of phenol-*d* hydrogen-bonded to acetone as a function of the probe wavelength ($\nu_{\text{pump}}=2525\ \text{cm}^{-1}$). The arrows indicate reorientation times that greatly exceed 30 ps, but that could not be fitted accurately. The top panel shows the transient spectrum. The star corresponds to the reorientation time measurement for phenol-*d* in chloroform.

band, we now see that the reorientation proceeds much faster on the blue side of the spectrum than on the red side. As the anisotropy decays more or less linearly over the range that we can measure, it is impossible to unambiguously fit these curves with monoexponentials including a nonzero end level. In order to be able to assign a decay time to these curves, we have fitted them to monoexponentials with an end level that is the same as the one we found for phenol hydrogen-bonded to chloroform (0.04). The reasoning underlying this choice is that hydrogen bonding may affect the reorientation time of the OD group, but not the solid angle over which it can reorient, so that the final anisotropy should be the same.

Figure 10 shows the reorientation time as a function of probe wavelength for the entire probe range. On the blue side of the band the anisotropy decays with a time constant that is comparable to that of phenol hydrogen-bonded to chloroform (3 ps), suggesting that also for these molecules the rotation of the OD group is not hindered by the hydrogen bond. On the red side of the band however, the reorientation time increases dramatically to over 30 ps.

These results show that hydrogen bonds hinder the rotation of the donating hydroxyl group, and that the strongest hydrogen bonds are most effective at doing so. The fact that we were actually able to probe the orientational dynamics of unique conformations, implies that these conformations live for a relatively long time. The rate of interconversion must be slower than about 5 ps, for else we would not have observed different values of the anisotropy at this delay.

The time scales that have been identified in this paper can be placed in a broader perspective by making a comparison with the study by Nienhuys, Van Santen, and Bakker on the reorientation of HDO molecules in liquid heavy water.[10] In this study HDO molecules were found to reorient with a time constant of 2.6 ps, which seems extremely rapid compared to the time constant of >30 ps observed for the strongly hydrogen-bonded OD group of phenol-*d*. This is particularly true considering that an HDO molecule is embedded in a *network* of hydrogen bonds, contrary to phenol that forms a complex with only a single acetone molecule. The paradox is resolved, when one realizes that the reorientation of water molecules is assisted by the rapid breaking and reformation of hydrogen bonds that occurs in liquid water. It is more difficult to understand however that the reorientation of the OD group of phenol, when it is weakly hydrogen bonded to chloroform, proceeds slower (3.7 ps) than that of hydrogen-bonded HDO molecules (2.6 ps). A tentative explanation may be that the rotation of the OD group is considerably hindered by the phenyl ring, as gas phase studies and quantum chemical calculations[17] indicate that the OD group lies preferentially in the plane of the phenyl ring, leading to a significant barrier for internal rotation around the CO-bond axis.

IV. CONCLUSION

We studied the influence of hydrogen bonding on the orientational dynamics of the OD group of phenol-*d*. These dynamics are measured by probing the anisotropy of the excitation of the OD-stretch vibration. For weakly hydrogen-bonded phenol molecules dissolved in chloroform, the anisotropy decays with a time constant of 3.7 ps to a nonzero value. This partial decay of the anisotropy results from the rotational motion of the OD group around the CO-bond axis. The molecular reorientation of phenol that would lead to a complete decay of the anisotropy takes place on a much slower time scale. The rotational diffusion of the OD group is observed to slow down with increasing hydrogen-bond strength, resulting in an increase of its time constant to values >30 ps. Hydrogen bonding also affects the vibrational relaxation. The vibrational lifetime τ_{life} decreases with increasing hydrogen-bond strength but only down to a limiting value of ~ 1 ps.

ACKNOWLEDGMENTS

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