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Hydrogen bond and lifetime dynamics in diluted alcohols

The similarity in hydrogen bond dynamics, obtained for a broad range of primary alcohols led us to conclude that the dynamics are essentially independent of the hydrophobic tail. It further demonstrates that using an alcohol with different alkyl chains as a probe of solvation dynamics does not significantly change the outcome. This may prove true for other amphiphilic probes as well, thereby providing previously unforeseen flexibility for future studies of hydrophobic hydration.

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Hydrogen bond and lifetime dynamics in diluted alcohols†

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and Maxim S. Pshenichnikov[‡]*

Hydrogen-bonding plays a crucial role in many chemical and biochemical reactions. Alcohols, with their hydrophilic and hydrophobic groups, constitute an important class of hydrogen-bonding molecules with functional tuning possibilities through changes in the hydrophobic tails. Recent studies demonstrated that for solutions of alcohols changes in the hydrophobic tail significantly affect a broad range of dynamics properties of the liquid. Still, the understanding is lacking on the origin of such differences in terms of a solvent- versus a solute-dominated effect. Here we reveal this origin by studying hydrogen-bond dynamics in a number of alcohol molecules – from methanol to butanol – diluted in a hydrogen-bond accepting environment, acetonitrile. The dynamics were investigated by pump-probe and 2D infrared spectroscopy combined with molecular dynamics-spectral simulations, using the OH stretching mode as a reporter. For all the considered alcohols, the vibrational lifetime of the OH stretching mode was found to be ~ 3 ps. The hydrogen-bond dynamics exhibit similar behavior with a fast (~ 200 fs) initial relaxation dominated by librational motion and a slow (~ 4 ps) relaxation due to hydrogen-bond exchange dynamics. The similar dynamics over such a broad range of alcohols led us to conclude that the previously observed differences in dynamics in bulk alcohols originate from the dependence of the solvent properties on the hydrophobic tail, while the solute properties as found herein are essentially independent of the hydrophobic tail.

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1. Introduction

Hydrogen bonding¹ (HB) is one of the fundamental interactions in chemistry, biology and materials sciences, and as such has been extensively studied.^{2,3} Ultrafast two-dimensional (2D) IR spectroscopy^{4,5} has been proven to be a powerful tool for revealing the HB dynamics in water, liquids^{6,7} and interfaces^{8,9} alike. Alcohols present another example of a HB liquid, where the molecules form HBs *via* the hydroxyl group^{10–13} that is attached to a hydrophobic alkyl tail.

So far, most of the studies on alcohols have been devoted to alcohol clusters in a non-polar solvent such as CCl_4 .^{14–20} The primary alcohols as methanol and ethanol were in a particular

focus^{12,15,16,18–28} due to their simple structure. Woutersen *et al.*²⁰ demonstrated dependence of OH-stretching mode lifetime on the excitation frequency in ethanol clusters in CCl_4 with the timescales ranging from 250 to 900 fs. The HB recombination time was found to vary with the size of the alkyl chain group, from ~ 9 ps in methanol to ~ 15 ps in ethanol. Later, Laenen *et al.*¹⁸ reported a similar trend for methanol clusters. Gaffney *et al.*²⁹ implemented another approach, where the concentration of methanol-*d* diluted in CCl_4 was varied, and the relaxation dynamics of the methanol-*d* clusters were reported as ~ 500 fs for all molar ratios with a conclusion that the HB dynamics hardly change with changing alcohol concentration.

Similarly to alcohol clusters, recent experimental and theoretical studies on bulk alcohols showed the effect of the size of the alkyl-chain group on hydroxyl stretching dynamics.^{30–32} Mazur *et al.*³¹ explored such dynamics in bulk deuterated alcohols by monitoring vibrational and rotational dynamics of the OD stretching mode. The lifetime of the excited OD stretch was found in the sub-ps region and dependent on the alkyl chain size (0.75 ps for methanol and 0.9 ps for ethanol, 1-propanol and 1-butanol). In contrast to the lifetime, the structural relaxation time exhibited a strong correlation with the size of alcohol molecules, *i.e.* the larger alkyl chain group led to slower dynamics: ~ 5 ps for methanol, ~ 8 ps for ethanol,

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† Electronic supplementary information (ESI) available: Determination of the solution concentration range, linear absorption spectra of the OH-stretching region of eight studied alcohols dissolved in acetonitrile at different molar concentrations, linear spectra analysis: central frequency and full width at half maximum, isotropic pump-probe transient spectra at different delay times for all studied solutions, energy level diagram and calculation of OH-stretching mode lifetime, temperature jump of the solution focal volume, 2D IR spectra for all studied solutions, and center line slope analysis. See DOI: 10.1039/c7cp03222f

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~ 10.5 ps for 1-propanol, and ~ 11 ps for 1-butanol. Furthermore, the rotational dynamics possessed a similar correlation with the size of alcohol molecules, *i.e.* the increase of the alkyl chain led to slower dynamics.

Shinokita *et al.*³⁰ explored the OH stretch dynamics of methanol, ethanol and 2-propanol molecules diluted in respective deuterated solutions to avoid intermolecular vibrational couplings. It was found that the lifetime of the OH-stretching mode exhibits a strong dependence on the size of the alkyl chain (630 fs, 720 fs and 990 fs for methanol, ethanol and 2-propanol, respectively). OH-stretch dynamics occurred at two prime time scales: fast (~ 150 fs) and long (> 4 ps), with both the components slowing down with the increase of the molecule size. The rotational dynamics of the OH group, obtained by Shinokita *et al.*³⁰ using ultrafast IR spectroscopy and by Ludwig *et al.*³³ using NMR also possessed the dependence on the size: the larger the molecule, the slower the rotational dynamics. The timescales of the HB exchange dynamics, obtained experimentally, showed an increase from 5 ps for methanol^{30,31,33} to ~ 90 ps in 1-hexanol.³³

All the aforementioned studies came to the unanimous conclusion: increasing the size of the alkyl chain leads to slowing down the hydroxyl stretching mode as well as HB dynamics. The dynamics, however, depends on both inter- and intra-molecular interactions. This raises the question: which one is dominant on the observed time scales?

Here we address this issue by eliminating the differences in the interaction of the excited OH-stretch and the bulk solvent by studying alcohols diluted in acetonitrile, where the intermolecular interactions between the alcohol molecules are negligibly weak. A series of primary alcohol molecules (methanol, ethanol, two isomers of propanol, and four isomers of butanol) were studied by linear, pump-probe and 2D IR spectroscopy, with the OH-stretching mode (~ 3535 cm^{-1}) acting as a reporter for HB dynamics. We show that the lifetime of the OH-stretching mode (~ 3 ps) and two timescales of HB dynamics (~ 200 fs and ~ 4 ps) are similar in all alcohols in sharp contrast to the observations in bulk alcohols. The latter finding is also confirmed by theoretical work, which uses response function based calculations to predict the linear and 2D IR spectra. The obtained results strongly suggest that in diluted alcohols the alkyl groups play a minor role in solvation and therefore the differences in the vibrational lifetimes and solvation dynamics in the bulk alcohols originate from the intermolecular interactions.

2. Methods

2.1. Experimental

Eight alcohol molecules (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and *tert*-butanol) and acetonitrile (MeCN) were obtained from Sigma-Aldrich and used without any further purification. Acetonitrile was used as a solvent due to its HB properties³⁴ and low absorption in the region of OH-stretch frequency. Alcohol molecules were dissolved in MeCN at pre-calculated molar ratios.

The linear absorption spectra were recorded using an FTIR-spectrometer Bruker IFS 88 at room temperature (295 ± 5 K), with 4 cm^{-1} spectral resolution in a 100 μm thickness CaF_2 cuvette. Due to the hygroscopic properties of the chemicals used, all the measurements were performed within one day of preparation.

The molar ratio between alcohol and MeCN was varied from 0.01 to 0.09 to determine the molar ratio at which the alcohol molecules do not cluster (see the ESI,† Fig. S1 and S2). For further experiments, solutions with a molar ratio of 0.03 were used as a compromise between alcohol molecules clustering and the signal-to-noise ratio.

The IR pulses at a central wavelength of 3540 cm^{-1} and 75 fs in duration were generated by a home-built optical parametric amplification (OPA).³⁵ For the 2D IR measurements, a pump-probe geometry was used³⁶ for which the OPA output was split into two collinear pump pulses (~ 3 μJ per pulse) and a probe pulse (~ 3 μJ per pulse). The polarization between the two pump pulses and the probe pulse was set at a magic angle of $\sim 54.7^\circ$. The prepared solutions were pumped through a 50 μm thick sapphire nozzle to create a free-standing jet. To minimize water vapor adsorption from air, the circulatory pump system and the 2D IR setup were constantly purged with dry nitrogen.

The 2D IR spectra were obtained by the following algorithm: at a given waiting time between the pump and probe pulses, one of the pump pulses was scanned from -400 to 400 fs with respect to the second one to create the coherence time interval. The exact delay between the two pump pulses was calculated from the interference pattern obtained from a backstage Michelson interferometer referenced to a 3.39 μm CW He-Ne laser. The zero delay between the pump pulses was determined by fitting their interference patterns by a cosine function modulated by a Gaussian. For each OPA pulse (1 kHz repetition rate), the spectrum of the probe pulse was measured using a 64 element MCT detector providing the ω_3 (probe frequency) dimension. The real part of the Fourier transformation over the coherence time provided the ω_1 (excitation frequency) dimension in the 2D IR spectrum. To avoid the situation when the probe pulse appears between pump pulses during the coherence time scan, the spectrum with the positive coherence time was mirrored to the negative coherence time. For measuring a frequency-resolved pump-probe spectrum, only one pump pulse was used, with a synchronous chopper inserted into the pump beam path.

All the experiments were performed at room temperature of 295 ± 0.5 K. The presence of water content was controlled by measuring the absorption spectrum of the solution before and after each experimental session (~ 8 – 10 hours); it appeared to stay negligibly low during the session. The blank pump-probe experiments were performed on the solvent (MeCN) alone, with the obtained signal being lower by a factor of at least 10 than that for alcohol solutions, even in the region of the pulse overlap. Therefore, this signal can be safely disregarded.

2.2. Molecular dynamics simulations

Molecular dynamics (MD) simulations of diluted methanol, 1-butanol, and *tert*-butanol (as representative alcohols) in MeCN

Fig. 1 Illustration of the molecular dynamics simulations boxes for (a) methanol, (b) 1-butanol, (c) *tert*-butanol in MeCN. The HBs are depicted by the dashed white line. The oxygen atoms are represented in red, the hydrogen in white, the carbons in light blue, and the nitrogen in yellow.

were performed, using the GROMACS 4.6.1 suite.³⁷ The simulation boxes were composed of 1 molecule of the respective alcohol and 200 molecules of MeCN (Fig. 1). The interactions between the molecules were described by using the Optimized Potential for Liquid Simulations all-atom (OPLS-AA) force field³⁸ for both the solvent and the solute. The Lennard-Jones and Coulombic interactions were truncated at 1.1 nm cutoff. The long range Coulombic interaction was accounted using the Particle Mesh Ewald (PME) scheme.³⁹ After initial equilibration, a 5 ns constant volume and temperature of 298.15 K production run was obtained using the Berendsen thermostat.⁴⁰ The snapshots were stored at 10 fs intervals, and all the bonds were constrained using the LINCS algorithm.⁴¹

2.3. Spectral calculations

The time-dependent vibrational Hamiltonian for the OH stretch^{5,42} was generated from the production run, and has the form:

$$H(t) = \omega_{10}(t)B^\dagger B - \Delta/2B^\dagger B^\dagger BB - \vec{\mu}(t)\vec{E}(t)(B^\dagger + B) \quad (1)$$

Here, $B^\dagger$ and B are the bosonic creation and annihilation operators, $\vec{E}(t)$ is the external electric field used to excite the OH oscillator, and Δ is the anharmonicity (fixed at an experimental value of 200 cm^{-1}). This form of the Hamiltonian implies that the harmonic rule is applied for the $|1\rangle \rightarrow |2\rangle$ transition dipoles.⁵

The site frequency of the OH stretch $\omega_{10}(t)$ and the transition dipole, $\vec{\mu}(t)$, were calculated for all the stored snapshots of the production run, making use of the existing electrostatic maps for the OH stretch.^{42,43} These relate the electrostatic field E_{OH} created by the force field point charges on the hydrogen atom of the hydroxyl group in the direction along the OH bond, with the site frequency and the transition dipole. We used the electrostatic map developed for the OH stretch of water,^{42,43} which was built using electronic structure calculations (DFT) of water clusters. Even though this mapping was developed for the OH stretch of water, such an approach has previously been successfully applied to alcohols.^{30,44}

$$\omega_{10}(t) = 3761.6 - 5060.4E_{\text{OH}}(t) - 86.225(E_{\text{OH}}(t))^2 \quad (2)$$

$$x_{10}(t) = 0.1024 - 1.29 \times 10^{-5}\omega_{10}(t) \quad (3)$$

$$\vec{\mu}(t) = (0.71116 - 75.591E_{\text{OH}}(t))\mu_g'\vec{u}_{\text{OH}}(t)x_{10}(t) \quad (4)$$

Here, the frequency $\omega_{10}(t)$, OH oscillator displacement $x_{10}(t)$, and electric field $E_{\text{OH}}(t)$ have units of wavenumbers, Ångström

and E_{H}/a_0e , respectively. μ_g' is equal to $0.18749e$, and $\vec{u}_{\text{OH}}$ is a unit vector along the OH bond in the direction of hydrogen.

All spectra were calculated using the Numerical Integration of Schrödinger Equation (NISE) method,⁴⁵ in which the time-dependent Schrödinger equation is numerically propagated for the OH stretch time-dependent Hamiltonian thus allowing the calculation of both the linear and third-order response functions. An *ad hoc* vibrational lifetime for the OH stretch of 1 ps was used for apodization. The coherence times were varied from 0 to 640 fs. The response functions were Fourier transformed to obtain the FTIR and 2D IR spectra. Sampling was done at 1 ps intervals along the 5 ns trajectories, giving a total number of 5000 realizations.

3. Results and discussion

3.1. Linear absorption

The absorption spectra of methanol, 1-butanol and *tert*-butanol dissolved in MeCN in the region of the OH-stretching mode are shown in Fig. 2, together with their simulated counterparts (for the spectra of other alcohols, see the ESI,† Fig. S3). The absorption peak of the OH stretch situated near $\sim 3535 \text{ cm}^{-1}$ slightly red-shifts and becomes $\sim 10\%$ narrower as the alcohol size increases (see the ESI,† Fig. S4). The simulated spectra are wider than the experimental ones (especially for *tert*-butanol) and do not possess any size-dependence which is attributed to the fact that the classical force fields are not fully optimized for this type of modelling.

3.2. Pump-probe

The pump-probe transients are shown in Fig. 3 (for the pump-probe transients and the transient spectra of all alcohols, see the ESI,† Fig. S5 and S6, respectively) at the frequency of maximum bleaching (3535 cm^{-1}) and induced absorption (3370 cm^{-1}). After the initial relaxation at the ps time scale, the transients level off which is attributed to population relaxation to the hot ground state.⁶ To account for this effect, the transients were fit with the three-state kinetic model (see the ESI,† Fig. S7); the temperature jump was estimated as $\sim 0.5 \text{ K}$ (see the ESI,† Fig. S8).

Lifetimes T_1 of the OH stretch for all alcohols are about 3 ps (Fig. 4) with a weak trend to increase with the increase of the molecule size. The obtained results are in good agreement with the lifetime of the hydrogen bonded OH-stretching mode previously reported as $3.5 \pm 0.4 \text{ ps}$.⁴⁶ Nonetheless, the trend obtained also suggests partial energy relaxation *via* intramolecular channels, to be consistent with the finite lifetime of $7.5 \pm 0.5 \text{ ps}$ of free OH-stretch vibrations.⁴⁶

In contrast with diluted alcohol molecules, the lifetimes of hydroxyl stretching mode in bulk alcohols are shorter than 1 ps.^{30,31} Furthermore, the lifetimes of bulk alcohols show a prominent increase (by a factor of ~ 2) from methanol to 2-propanol.³⁰ These are clear signatures of the fact that in bulk alcohols the OH stretch vibrational relaxation is mediated by collective intermolecular rather than intramolecular modes.

Fig. 2 Experimental (dots) and simulated (solid lines) linear absorption spectra of (a) methanol, (b) 1-butanol and (c) *tert*-butanol dissolved in MeCN. The simulated spectra are blue-shifted by 50 cm⁻¹ for the ease of comparison.

Fig. 3 Experimental transients (symbols) at bleaching/stimulated emission (3535 cm⁻¹, open circles) and induced absorption (3370 cm⁻¹, filled circles, the sign is inverted) regions for (a) methanol, (b) 1-butanol, (c) *tert*-butanol, diluted in MeCN. The fits obtained from a kinetic model (ESI,† Fig. S7) are shown by the lines with the corresponding lifetimes T_1 indicated.

Fig. 4 Lifetime of the OH-stretching mode T_1 , calculated from the three-state kinetic model (ESI,† Fig. S6) for all the studied alcohol/MeCN samples (open violet diamonds) in comparison to the bulk alcohol lifetimes (filled olive circles; the data are taken from ref. 30).

3.3. 2D IR spectra

Fig. 5 shows the 2D IR spectra of methanol, 1-butanol and *tert*-butanol solutions at waiting times of $T = 0.1$ ps and $T = 1$ ps (see the ESI,† Fig. S9, for the complete set of 2D IR spectra). At short waiting times, the 2D spectra are diagonally elongated which corresponds to a high correlation between excitation and probe frequencies. By $T = 1$ ps, the diagonal elongation decreases virtually to zero which signifies complete loss of the phase memory. Although the simulated 2D spectra (bottom panel) are slightly broader (see Fig. 2 and discussion therein), they nonetheless show a reasonable agreement with the experimental ones.

To extract quantitative information on the frequency-frequency correlation function⁴⁷ we applied the center line slope (CLS) analysis⁴⁸ in the frequency range of 3485–3580 cm⁻¹ (Fig. 5, black lines). The center lines are not perfectly straight as was also previously reported for other hydrogen bonding systems.^{49–52} This is interpreted as a frequency-dependent correlation function, *i.e.*, in other words, the dynamics are non-Gaussian.⁵¹ Without performing any further analysis (which requires a low noise level) we note that the dynamics on the red side of the spectra are generally faster than that on the blue side in accordance with the previous observations for the OH-stretch mode. The averaged slope values for the systems with non-Gaussian dynamics have larger error bars,⁵¹ which we accounted for in our analysis.

The dependences of the CLS values on the waiting time T are summarized in Fig. 6 (for all CLS data, see the ESI,† Fig. S10 and S11). The dynamics are essentially identical for all alcohols: the fast (~ 200 – 300 fs, share of $\sim 80\%$) decay in the beginning followed by an ~ 4 ps tail identical for all alcohols (within the error bars). The relatively large uncertainties in the slow dynamics originate from the following. First, their share in the correlation function is low ($\sim 20\%$); second, the lifetime of the OH stretch is shorter as compared to the timescale of slow dynamics (which provides a narrow observation window), and finally, the temperature response begins to rise at a similar timescale. The obtained dynamics have a reasonable match with the previously reported values for the MeCN bath, using a chromophore⁵³ (150 fs and ~ 3 ps, respectively), water⁵² and HDO⁵⁴ (150–200 fs and 2 ps, respectively) as the solutes. The obtained results on CLS analysis are again in a sharp contrast to those for the bulk alcohols,³⁰ where both the fast and long

Fig. 5 Experimental absorption spectra (top panels), experimental (middle panels) and simulated (bottom panels) 2D IR spectra in the OH-stretching mode region for the MeCN solution of (a) methanol, (b) 1-butanol and (c) *tert*-butanol at $T = 0.1$ ps and $T = 1$ ps. The 2D spectra are normalized to the maximal amplitude; only the bleaching region is shown. The equidistant contours are drawn with a 10% step of the maximal amplitude. The results of the CLS analysis are depicted by black lines. The simulated spectra are blue-shifted by 50 cm^{-1} along both the axes for the ease of comparison.

Fig. 6 Comparison of the results of the CLS analysis obtained from experimental (open symbols) and simulated (filled symbols) for (a) methanol, (b) 1-butanol and (c) *tert*-butanol. Biexponential fits to the experimental data are shown by the solid lines, with the parameters (decay time and the amplitude) indicated in the legends.

components slowed down with an increase in the size of the alcohol molecule. This provides another hint that the diluted alcohol dynamics are governed by the bath rather than by a particular alcohol molecule.

In the theoretical calculations, the fast component of the CLS functions is underrepresented (Fig. 6, filled symbols), most probably because of underestimation of the time scale of the librational contribution to the frequency fluctuations. This originates either from inaccuracies in the interaction between the MeCN and the hydroxyl groups in the applied force field combination or from the fact that the water mapping was employed to model alcohols.

3.4. Discussion

The frequency–frequency correlation functions derived from MD simulations are shown in Fig. 7. They are similar for all alcohols (the strongly damped short-time oscillations notwithstanding): the fast component (~ 50 fs) originates from the OH librations (Fig. 8) while the slow component (~ 1 ps) is due to spectral diffusion as the result of rearrangement of HBs: breaking and forming new ones (Fig. 8). The experimental CLS values are slower, most probably due to the fact that the MD simulations underestimate damping of the OH librations. The simulated frequency–frequency correlation functions are also very similar to those previously reported for water in MeCN.⁴⁷ The tail

Fig. 7 Normalized frequency–frequency correlation functions for the three simulated alcohols. The share of each exponent is indicated next to the lifetime in the parentheses.

observed for water is slower, which may be caused by stronger HB and slower HB exchanges; however, this conclusion should be taken with caution as the water simulations were performed with a different force field.

To understand the vanishing difference between the dynamics of the different alcohols dissolved in MeCN, we analyzed the HB between the alcohols and the nitrogen atoms of the MeCN molecules. Using a standard HB criterion,⁵⁵ we found an average of 0.827, 0.802, and 0.806 of such HBs formed for methanol,

Fig. 8 Illustration of (a) OH-librations and (b) diffusion of a methanol molecule dissolved in MeCN (adapted from MD simulations). A blur represents the previous positions of the OH-stretching mode (a) and the prior positions of the methanol molecule (b). The final HBs between alcohols and MeCN are depicted by the dashed white lines.

Fig. 9 The HB (*i.e.* O–N) distance distribution obtained from MD simulations.

1-butanol, and *tert*-butanol, respectively, which already suggests very similar HB environments. In Fig. 9, the distributions of the HB distances are shown for solutions of the different alcohols; they again suggest analogous HB patterns. We further analyzed the HB lifetime dynamics as the duration between HB exchanges (Fig. 10). Because the definition of HB is somewhat arbitrary, briefly broken bonds may result in artificially short HB lifetimes; nevertheless, the HB dynamics are essentially identical.

Fig. 10 Histograms of the number of HB exchange events with a given time per alcohol molecule per picosecond for the three simulated alcohols according to the HB criterion of ref. 55.

A unified picture emerges that the experimentally observed dynamics of the alcohols depend predominantly on the HB dynamics of the OH group, and these HB dynamics are determined by the interaction of the OH group and the MeCN bath molecules. The hydrophobic tails affect the dynamics very little allowing the interaction of the OH group with the bath molecules and the nature of bath molecules the dominant factors. Despite the fact that the increase of the hydrophobic tail increases the moment of inertia and might therefore affect rotational relaxation, it appears to be a minor effect for the studied properties.

For bulk alcohols it was suggested²⁸ that different types of dynamics largely scale with the self-diffusion constant of the bath molecules. We found the diffusion constant of bulk MeCN to be $4.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is almost twice as fast as $2.57 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ reported for bulk methanol.³⁰ This suggests that the slow components of the observed dynamics of the alcohols in MeCN should be faster than for any bulk alcohol. For the CLSs, the predicted slowest timescale for a bath with a diffusion constant of $4.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (*i.e.* the MeCN bath) is about 2.3 ps, which is in qualitative agreement with the slowest timescale observed herein for the CLSs, and the slowest timescale found from the frequency–frequency correlation function decay. The qualitative agreement is, thus, consistent with the conclusion that the slow dynamics are essentially driven by the solvent diffusion. However, caution must be taken as the diffusion constants and HB dynamics are quite sensitive to the particular force field choice and MeCN and alcohols are molecules with different functional groups (CN vs. OH).

4. Conclusions

In this paper, we have studied dynamics and lifetimes of the OH-stretching mode of diluted alcohol molecules in the polar HB-accepting solvent, acetonitrile. Previous studies of bulk alcohols showed a large variation in the involved time scales depending on the size of the alkyl chain. This difference could originate from either inter- or intra-molecular interactions. In the present study, the intermolecular interactions between the alcohol molecules are eliminated by dilution; therefore, the obtained dynamics have solely intramolecular origin.

The lifetime of the OH-stretching mode, used as a reporter for HB dynamics in our study, was found to be ~ 3 ps for all eight studied alcohols. In a sharp contrast to bulk alcohols, there is no dependence on the size of alcohol molecules. From this we conclude that the intermolecular interactions must be the main reason for the observed differences in the bulk alcohols. The intramolecular vibrational relaxation must thus predominantly be directed to modes involving only the carbon and hydrogen atoms adjacent to the hydroxyl group under the test.

The OH stretch dynamics, deduced from the CLS analysis of the 2D IR spectra, revealed the following two timescales: a fast librational one (~ 200 – 300 fs) and a slow one (~ 4 ps) related to

the HB dynamics. The slow timescale was again essentially independent of the alkyl chain of the involved alcohol molecule in sharp contrast to the previous observations in bulk alcohols. This matches well with the supposition³⁰ that the HB exchange is correlated with the diffusion of the HB partners.

The present findings underline the importance of the solvent on the vibrational dynamics of HB groups such as the hydroxyl group of alcohols. It further demonstrates that using an alcohol with different alkyl chains as a probe of dynamics does not significantly change the outcome. This may prove true for other amphiphilic probes as well, thereby providing previously unforeseen flexibility for future studies of hydrophobic hydration.

Conflicts of interest

There are no conflicts to declare.

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