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Reorientation dynamics in liquid alcohols from Raman spectroscopy

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Polarized Raman spectroscopy has been employed to study the reorientational, or more specifically the translational relaxation dynamics, of alcohol molecules in pure liquids and aqueous solutions. It is found from the spectral width measurements that alcohol molecules in pure liquids have typically translational relaxation times on the order of picoseconds, following the order methanol < ethanol < *i*-propanol < *n*-propanol. Temperature-dependent measurements show that hydrogen-bonding (HB) and hydrophobic interactions control the translational motion. The hydrophobic interaction reduces the relaxation time more apparently in view of the $-CH_3$ group than the skeleton motion. For alcohol–water mixtures, the increase of water concentration generally slows down the relaxation process in a non-monotonic behavior. However, the trend stops at a certain point and the motion of alcohol molecules becomes faster when the alcohol concentration further drops. Different mechanisms have been proposed to interpret these observations, which might be helpful to gain deeper insight into the HB networks of alcohols with water. Our study strongly illustrates that Raman spectroscopy can be applied to the study of fast translational motion of molecules in HB systems. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: translational relaxation; alcohol–water mixtures; hydrophobic interaction; hydrogen bonding; polarized Raman spectroscopy

Introduction

The reorientational movement of molecules in condensed phase is generally believed to be due to the combined effect of translational and rotational motions, whereas the translational motion at the molecular level is related to the diffusion at the macroscopic level. Both the translational and rotational motions are the most basic movements of molecules in liquids. They play a major role in many important processes, such as the electronic energy transfer,[1] proton transport,[2] and water polarization under thermal gradients.[3] The dynamics of these motions has been extensively studied in many practical situations, which has helped in understanding the ion effect on the architecture of liquid water,[4] quantum effects in molecular liquids,[5] Stokes–Einstein relation in supercooled aqueous glycerol,[6] fragile-to-strong transitions of water[7] and protein hydration water,[8] as well as the hydrophobic effect between water molecules and hydrophobic groups.[9]

Special attention has been paid to the translational and rotational dynamics in hydrogen-bonding (HB) systems, such as liquid water, short-chain alcohols, and alcohol–water mixtures, which are the fundamental solutions for many chemical processes and model systems for biological molecules. Several experimental techniques, such as Raman spectroscopy,[10] nuclear magnetic resonance (NMR),[11] dielectric spectroscopy (DS),[12] and optical Kerr effect (OKE),[13,14] as well as the theoretical method of molecular dynamics (MD) simulations,[15,16] have been employed in the last two decades to characterize the translational and/or rotational relaxation times in these HB systems. Among these HB systems, extensive dynamic studies have been performed on the simplest alcohol, i.e. liquid methanol,[11,13–21] even though no consensus has been achieved for this system. These studies have generally demonstrated that methanol molecules in liquids rotate within a time scale of picoseconds and translate in sub-picoseconds. However, compared to liquid methanol, fewer studies have been carried out on more complex liquid alcohols.

Among the methods of relaxation time measurements, the ultrafast OKE experiment[13,14,18,22–26] has been demonstrated to be a powerful tool in the studies of reorientation dynamics. It can measure the translational and the rotational relaxation times simultaneously and precisely, since these two types of motions are in different regions of the time-dependent behavior of the OKE signals.

In the present work, we tried to use Raman spectroscopy, instead of the relatively complex OKE technique, to systematically study the reorientation, or more specifically the translational motions, of several liquid alcohols such as methanol, ethanol, *n*-propanol, and *i*-propanol. Since the molecular motions in liquids, either translational or rotational, can introduce spectral broadening, the corresponding relaxation times may be obtained from Raman spectroscopy by measuring the line widths of a well-defined spectral profile.[10,27–29] By taking advantage of the polarization-dependent Raman spectra, one can obtain the relaxation time τ from the line width difference[10,29,30]:

$$\tau = \frac{1}{2\pi c(\omega_{\text{aniso}} - \omega_{\text{iso}})} \quad (1)$$

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where c, ω_{aniso}, and ω_{iso} are, respectively, the velocity of light and the full width at half-maximum (FWHM) of anisotropic and isotropic components of a polarized Raman spectral peak. Generally, the thus obtained relaxation time τ corresponds to the overall time of translational and rotational motions of molecules in liquids. For a non-HB system, one may imagine that the intermolecular interactions are so weak that the translational relaxation time should be much longer than the rotational motion. Therefore, the spectral broadening is caused mainly by the fast rotational motion, indicating that the obtained τ from Eqn (1) should correspond mainly to the rotational relaxation time.[10,29,30] However, the situation may be different for the HB systems in which strong intermolecular interactions exist, such as in water, alcohols, and their mixtures. In these systems, the translational relaxation times of molecules are generally shorter than the rotational motion, and the obtained time τ from Eqn (1) should mainly refer to the fast translational motion. Previous studies on the low wavenumber Raman spectra of water and methanol[18] have demonstrated that it is possible to obtain the translational and the rotational relaxation times from the spectral broadening measurements. In the present work, we found that the measured relaxation time in liquid methanol agrees reasonably well with the translational times obtained from OKE and other experiments.[13,14,17–19] This prompted us to extend our study of translational relaxation dynamics from the simplest liquid methanol to more complex liquid alcohols.

In addition to the study of MD in pure alcohol liquids, we were also interested in the dynamics in alcohol–water mixtures, since the aqueous alcohols have many abnormal properties and are often used as model systems for biological molecules in water. For these aqueous solutions, previous studies have paid much attention to the rotational dynamics[10–12,16,20,21,31,32] as well as to the translational motions.[11,16,31,33] In these studies, the translational motions were generally characterized by the diffusion coefficient in liquids, rather than the relaxation time which is a straightforward parameter to picture the translational motions. In this paper, we used the well-defined spectral fingerprints of individual functional groups of alcohol molecules to study the translational motion of alcohols in view of different directions of motion in aqueous solution as well as the effect of alcohol concentrations on the translational relaxation times.

Experimental

The experimental setup is similar to that used in our previous studies.[34–36] In this work, a backscattering geometry was employed to obtain the Raman spectra. All the experimental data were obtained with a triple monochromator system (Acton Research, TriplePro) coupled to a liquid-nitrogen-cooled charge coupled device (CCD) detector (Princeton Instruments, Spec-10 : 100B). The sample holder was a 10×10 mm quartz cell cuvette, which was thermally controlled at $25.0 \pm 0.1\,^{\circ}C$ by a heating bath (THD-2006, Ningbo). A stable cw laser (Coherent, Verdi-5 W, 532 nm) was employed as the excitation light source (power 1.0 W at the sample). During the experiments, the incident laser was linearly polarized with a Glan-laser prism, and its polarization direction was controlled vertically with a half-wave plate.

The Raman scattering light was collected at 180° relative to the incident laser beam with a pair of $f = 2.5$ and 10 cm quartz lenses, and imaged onto the entrance slit of the monochromator for spectral dispersion. In between the two lenses, a Glan-Taylor prism and an optical scrambler were inserted. The Glan-Taylor prism was used to select the polarization of the scattering light which could be parallel (I_V) and perpendicular (I_H) to that of the excitation laser, and the scrambler was used to depolarize the polarized scattering light in order to eliminate any polarization-dependent effect from the dispersion gratings. The isotropic and anisotropic components of a Raman spectral peak were obtained with the measured parallel and perpendicular Raman spectra from the relation[10,29,30]

$$I_{iso} = I_V - \frac{4}{3} I_H$$
$$I_{aniso} = I_H \qquad (2)$$

In the experiments, four kinds of alcohols (purity >99.5%) were studied, i.e. methanol (MeOH), ethanol (EtOH), *i*-propanol (*i*-PrOH), and *n*-propanol (*n*-PrOH). These alcohols, purchased from Sinopharm Chemical Reagent Co., were used without further purification. The liquid water, used as solvent, was purified with a Millipore Simplicity 185 (18.2 MΩ·cm) from triple distilled water. The isotropic and anisotropic Raman spectra were recorded in the C–C and C–O stretching as well as the $-CH_3$ rocking vibration regions (700–1280 cm^{-1}) for pure liquid and aqueous alcohols. For aqueous solutions, the alcohol concentrations were varied in a molar fraction range of $\chi = 0.01$–1 at intervals of 0.05.

Results and Discussion

Measurable range and precision of the relaxation time

The maximum measurable relaxation time and the measurement precision, according to Eqn (1), are governed by the minimum measurable difference between the FWHMs of the two spectral components and the spectral resolution. In a previous study of the dynamics of ethanol in aqueous solutions with Raman spectroscopy,[10] the relaxation time had a relatively large uncertainty of about 1 ps due to the instrumental limitations, which might bury some detailed dynamic information. To verify the ability and the reliability of our experiment, an isolated spectral line of a mercury lamp was used as standard. Thirty cycles of measurements were performed for the emission line, which is shown in Fig. 1(a) as an example. The widths, i.e. the instrumental resolution measured from the spectral fittings with a Gaussian profile, have been collected in Fig. 1(b). It can be seen that, with our Raman spectral system, the largest measurement inaccuracy of the line widths is about 0.07 cm^{-1}. The minimum difference between the widths of two spectral peaks measured with our system should be the double of 0.07 cm^{-1}. Therefore, the maximum measurable relaxation time is determined from Eqn (1) to be ~35 ps. In other words, any molecular motion that relaxes faster than ~35 ps can be reliably determined from our measurements, which demonstrates that our Raman system is suitable to the dynamic study of alcohols, as the relaxation time is usually below ~35 ps.[17–19,32]

To estimate the measurement precision of the relaxation time, we have recorded the isotropic and anisotropic components of the Raman spectra of liquid methanol in the C–O stretching and $-CH_3$ rocking vibration regions at room temperature, as shown respectively in Figs 1(c) and (d). The widths for the C–O stretching vibration, determined from spectral fittings with a Lorentzian profile and averaged over several independent measurements, are 19.63 ± 0.08 and 29.23 ± 0.06 cm^{-1}, respectively. Using the determined widths and errors, the relaxation time is deduced to be 0.553 ± 0.005 ps. The small error of the measured time, ~5 fs, enables us to study the relaxation dynamics of alcohol molecules in

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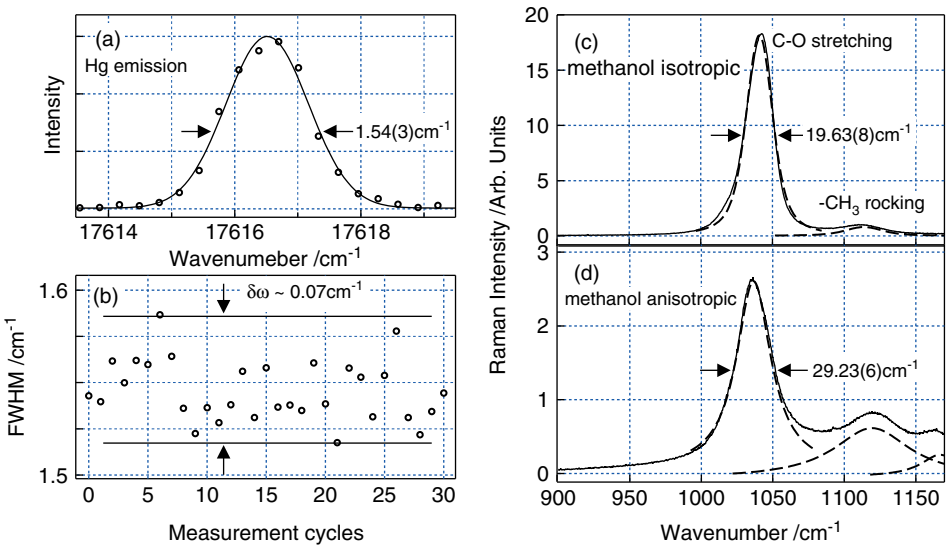

Figure 1. (a) The emission spectrum of a mercury lamp to determine the spectral resolution. (b) Collection of mercury spectral line widths from 30 measurements to determine the instrumental stability and the ability to measure the maximum relaxation time. (c) The isotropic and (d) anisotropic components of Raman spectrum for pure liquid methanol in the C–O stretching and $-CH_3$ rocking vibration region. The widths were determined from spectral fittings with a Lorentzian profile and were averaged for several independent measurements.

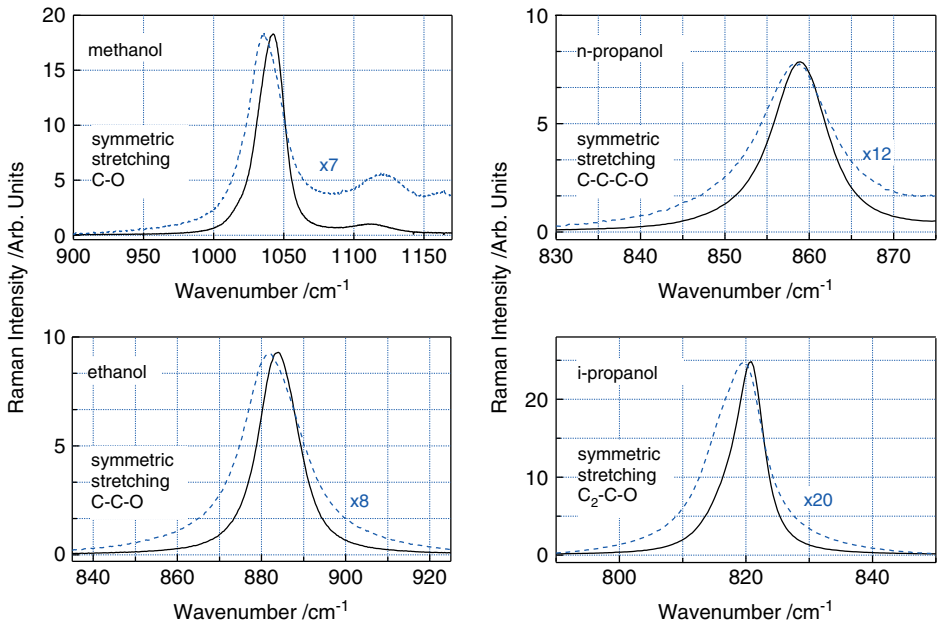

Figure 2. The isotropic (solid lines) and anisotropic (dashed lines) Raman spectral components of liquid methanol, ethanol, *n*-propanol and *i*-propanol in their skeletal vibration regions. The intensities of the anisotropic components were multiplied by the factors in each figure to compare with the isotropic components.

pure and aqueous liquids in great detail. Furthermore, the strong intermolecular-interaction-induced slightly asymmetric profiles and shift of peak positions between the isotropic and anisotropic spectral components of the C–O stretching spectra can be seen from Figs 1(c) and (d), which is generally referred to as the non-coincidence effect (NCE).[37,38]

Pure alcohols

To investigate the translational relaxation dynamics for the four kinds of liquid alcohols, i.e. MeOH, EtOH, *i*-PrOH, and *n*-PrOH, we choose their skeletal vibrational modes as the fingerprints, since they refer mainly to the center-of-mass translational motion and also since they are the strongest Raman spectral bands in the studied region. Figure 2 presents the isotropic and anisotropic Raman spectra of the four liquid alcohols in their skeletal vibrational regions. Spectral assignments are taken from the literature for MeOH,[39] EtOH,[40] *i*-PrOH,[41] and *n*-PrOH.[42] Theoretical calculations indicate that these bands are isolated and not overlapped with other bands, which allows us to obtain reliable spectral line widths. These skeletal vibrational bands were chosen not only because their contours are relatively free from other overlapping bands, but also because their corresponding displacement

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motions are relatively free from contributions involving the motions of O–H bonds and vibration–rotation couplings[39–43]: such motions particularly reflect the effects of the HB between the molecules and may have some influence on the relaxation time, and therefore would make the analysis much more complicated.

It can be seen from Fig. 2 that the spectral line widths of anisotropic bands are obviously broader than those of the isotropic bands. The large differences between the line widths of isotropic and anisotropic components enable us to fit the slightly asymmetric spectral bands with symmetric Lorentzian profiles, resulting in negligible effect on the relaxation times derived from Eqn (1). The obtained results for all the four alcohols are summarized at the last row in Table 1. For comparison, the rotational and translational relaxation times reported in the literature from MD simulations,[15,16] NMR,[11,44] DS,[17–21,32,45] OKE,[13,14] and other Raman measurements[10,18] are also listed in the table. It can be seen from these previous studies that the translational relaxation time is generally much shorter than the rotational ones. This implies that the broadening of Raman spectral profile is mainly caused by the translational motion. As mentioned in the introduction, ultrafast OKE experiments[13,14,18,22–26] can simultaneously measure the rotational and translational relaxation times from the time-dependent OKE signals. By comparing our measured data of liquid methanol with those from OKE experiments, it can be concluded that our measured relaxation times correspond to the translational motions in the liquid.

Previous studies[11,15,16] on the rotational dynamics showed that different relaxation times were obtained in view of different molecular groups. For example, from NMR experiments[11] the rotational relaxation times of liquid CH_3OD were determined to be 0.45 ps along the C–D vector, 0.9 ps along the H–H vector, and 3.7 ps along the O–D vector, while for liquid CH_3OH the times calculated from MD simulations were 1.6 ps[16] and 8.9 ps[15] along the dipole and O–H direction, respectively. For the translational motion, our measurements also indicate that different translational relaxation times were obtained from the different vibrational modes in the Raman spectra. In our experiments of liquid methanol, the relaxation times are measured to be 0.553 ps for the C–O stretching mode (~1042 cm^{-1}), 0.117 ps for the $-CH_3$ rocking mode (~1111 cm^{-1}), and 0.206 ps for the $-CD_3$ umbrella mode (~1129 cm^{-1}). For liquid ethanol, the relaxation times are 0.786 ps for the C–C–O skeleton mode (~884 cm^{-1}) and 1.015 ps for the skeleton coupled $-CH_3$ rocking mode (~1098 cm^{-1}). The differences in view of the different vibrational modes are most probably due to the anisotropic microenvironments of molecules in the liquids. More importantly, our Raman spectra have given small errors of the relaxation times for the four alcohols, which would allow us to study the translational dynamics of more complicated systems.

In order to specify the intermolecular interactions that affect the translational motion of molecules in liquids, we have also measured the temperature dependences of translational relaxation times ranging from 20 to 60 °C at intervals 10 °C, which should in principle follow the Arrhenius law[22,46]:

$$\frac{\partial \ln \tau}{\partial 1/T} = -\frac{E_a}{k_B} \tag{3}$$

where k_B is the Boltzmann constant and E_a is the activation energy of the motion. Our measurements indeed follow this law, as shown explicitly in Fig. 3. The translational activation energy for the C–O stretching motion is determined to be about 0.66 kcal/mol. This energy is lower than the energy needed to disrupt or break the HB in liquid methanol, i.e. 1.7 kcal/mol, which was obtained based on the van't Hoff equation from our previous study on the temperature-dependent Raman spectra in the O–H stretching region.[36] Therefore, it seems that the translational motion is controlled not only by the HB interaction but also by the hydrophobic–hydrophobic interaction, the latter decreasing the connecting force of a molecule with its nearby molecules and thus reducing the activation energy to some extent. It is also interesting to notice that the activation energy associated with the $-CH_3$ rocking motion is only 0.13 kcal/mol, which highlights again the hydrophobic interaction of the methyl group in methanol liquid. Since this activation energy is much smaller than that associated with C–O stretching motion, the $-CH_3$ rocking motion should be much faster than the C–O stretching motion, which has been confirmed by our results in Table 1.

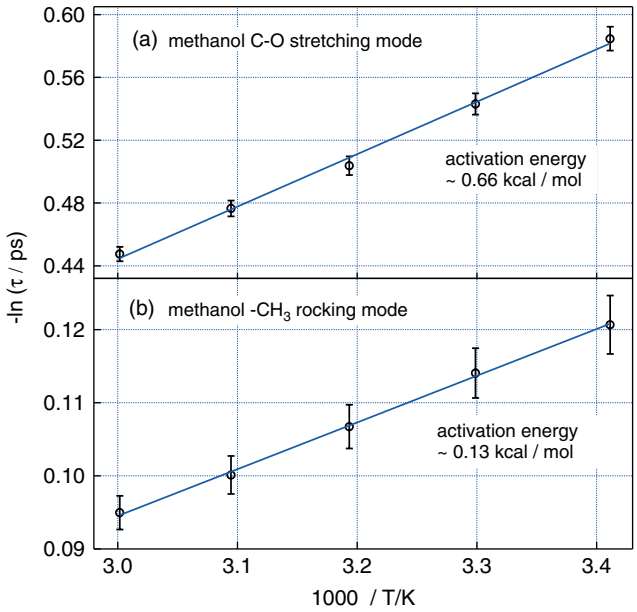

Figure 3. Temperature-dependent translational relaxation times of liquid methanol obtained from different vibrational modes. (a) C–O stretching mode with translational activation energy of 0.66 kcal/mol; (b) $-CH_3$ rocking mode with activation energy of 0.13 kcal/mol.

The dynamic studies of methanol liquid show that the translational motion is controlled by the combined effects of HB and hydrophobic interactions. A weaker interaction exerting on a molecule would result in a faster translational motion. Such studies have been extended to other alcohols to investigate the possible effects that affect the translational motions, such as the molecular size and the number of hydrophobic methyl groups. To find out the general rule between different alcohols, the relaxation times obtained from the skeletal modes are selected for comparison. It can be seen from Table 1 that the translational relaxation time increases in the order 0.553, 0.786, 1.32, and 1.63 ps for the skeletal motions of MeOH, EtOH, *i*-PrOH, and *n*-PrOH, respectively. Among these alcohol molecules, MeOH, EtOH, and *n*-PrOH are of chain structures, and all have a hydrogen-bond-forming –OH group and a hydrophobic $-CH_3$ group. Therefore, the strengths from HB and hydrophobic interactions on these three molecules should be almost the same. The increase of relaxation times following the order MeOH < EtOH < *n*-PrOH clearly indicates that a longer molecular length causes slower translational relaxation, i.e. the volume effect has a noticeable influence on the translational

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Table 1. Relaxation times (in picoseconds) of alcohol molecules in pure liquids at 25 °C determined with different methods

Motion	Method	Methanol	Ethanol	*i*-propanol	*n*-propanol
Rotation	MD[a]	1.6(dipole)[16] 8.9 (OH)[15]	3.5(dipole)[16]		5.3(dipole)[16]
	NMR[b]	0.45(CD)[11] 0.9(HH)[11] 3.7(OD)[11]	2.5(CD)[11] 2.2(HH)[11] 8.0(OD)[11]	22[44]	
	DS[c]	2.4[17,21] 17[17,21] 19[20]	3[17,21] 40[20] 53[21] 54[17] 60[21]	4.8[17] 91[20] 120[17]	5.03[17] 110[17]
	OKE	1.96[13] 5.03[14] 15.36[13]			
	Raman[d,e]	2.5[18]	1.5[10] (CH_3 rock) 1.55[10] (CCO str.)		
Translation	DS[c]	1.12[17] 0.16[19] 0.89[18]	1.81[17] 0.22[19]	1.96[17] 2.12[32]	2.4[17] 0.2[19]
	OKE	0.18[13] 0.83[14]			
	Raman[e]	0.55[18]			
	Our Raman[d]	**0.553(5)** (CO str.) **0.117(6)** (CH_3 rock) **0.206(5)** (CD_3 umbrella)	**0.786(6)** (CCO str.) **1.015(8)** (CCO str. + CH_3 rock)	**1.32(2)** (C_2CO skeleton)	**1.63(9)** (CCCO skeleton)

[a] *Dipole* and *OH* denote, respectively, the dipole vector and the OH group.
[b] *CD, HH*, and *OD* represent respectively the motions along vectors of C–D (deuterated alkyl group), H–H (alkyl group), and O–D (deuterated hydroxyl group).
[c] The rotational relaxation times from DS are calibrated by a factor of 1/3 to be consistent with OKE measurements.[18,26]
[d] The labels represent the vibrational modes employed in Raman spectroscopy.
[e] Relaxation times in liquid methanol were obtained from low wavenumber Raman spectra.

motion. Furthermore, for the two conformers $(CH_3)_2$–CH–OH (*i*-PrOH) and CH_3–CH_2–CH_2–OH (*n*-PrOH), the strengths of HB interactions should be close to each other, but the hydrophobic interactions should increase with the number of hydrophobic groups. Therefore, it can be concluded that the faster translational motion of *i*-PrOH relative to its conformer *n*-PrOH is simply due to the increase of hydrophobic interactions among molecules.

Aqueous alcohols

As translational relaxation times in alcohol liquids are governed by the HB interaction and the hydrophobic interaction among molecules, it can be expected that by varying the alcohol concentrations in alcohol–water mixtures, the relative importance of these two kinds may be varied, and then this variation may be studied by measuring the translational relaxation times at different alcohol concentrations. The Raman spectra of four kinds of aqueous alcohols, MeOH, EtOH, *i*-PrOH, and *n*-PrOH, have been measured in the molar fraction range of $\chi = 0.01$–1 at an interval of 0.05 in the same spectral regions as in Figs 1 and 2. The derived translational relaxation times of the skeleton vibrational motions of the four alcohol molecules are plotted in Fig. 4 as a function of alcohol concentration, from which the influence of water molecules can be clearly seen.

One can immediately see from Fig. 4 that, when water molecules are added to alcohol liquids, the translational motion of alcohol molecules is slowed down. In terms of alcohol concentration, one can identify three distinct regions with very different slopes. From $\chi = 1$ to $\chi = 0.25$–0.45, the relaxation time τ increases gradually as the alcohol concentration decreases. A much faster increase of the τ is noticed in the region from $\chi = 0.25$–0.45 to $\chi = 0.05$–0.15. Most strikingly, there is a turning point for all the aqueous alcohols at low concentrations, from which τ value starts to decrease and the translational motion speeds up. Previously, the concentration-dependent translational motions in some aqueous alcohols had been studied by NMR measurements[11,47] and MD simulations.[16,31,33,48] These studies had presented the changes of macroscopic diffusion coefficient with alcohol concentrations, which decreases from pure alcohol to about $\chi = 0.2$–0.4 and then increases.[47] It is interesting to see that the macroscopic diffusion motion behaves in a consistent way with the measured translational relaxation times. However, since the relaxation time

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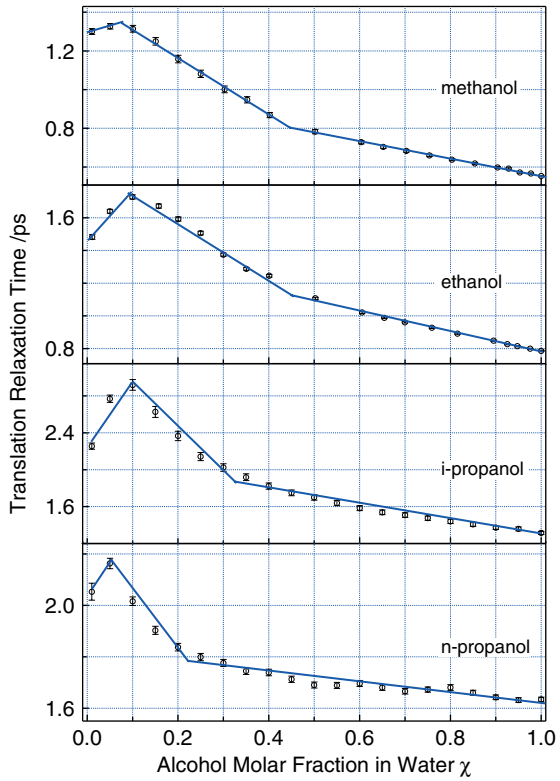

Figure 4. Concentration-dependent translational relaxation times obtained from the skeletal motion of alcohol molecules in aqueous solutions. Symbols with error bars are experimental data; the solid lines are just used to guide the eyes.

describes the microscopic dynamics of molecules in liquids, Fig. 4 displays a more complicated concentration-dependent behavior and should contain detailed dynamic information for alcohol molecules in water.

The translational motion of alcohol molecules in aqueous solution shows much more complicated patterns than in pure liquids. For pure alcohol liquids, we have demonstrated that the translational motions are influenced mainly by the HB and hydrophobic interactions. The stronger the intermolecular interaction, the slower the translational motion. We could think of four possible mechanisms that control the translational motion of alcohol molecules in aqueous solutions. The first one is the free volume mechanism, which was employed by Schindler[10] to interpret the concentration-dependent rotational motion of EtOH in aqueous solutions. Since the volume of a water molecule is smaller than that of an alcohol molecule, the aggregation of water molecules around the alcohol molecules would force the alcohol molecule to move inside a smaller free volume. This would slow down the translational motion. The second mechanism is related to the HB. It is well known that water molecules can form more HB than alcohol molecules and can hold alcohol molecules much tighter than alcohol molecules themselves. The involvement of stronger HB can thus slow down the translational motion of alcohol molecules. With these two mechanisms, one can easily explain the increase of translational relaxation time in water solution in the concentration region from $\chi = 1$ to $\chi = 0.25-0.45$. It is also known from our recent Raman spectroscopic study that the dominant structures in pure liquid methanol are the small clusters with 3–5 methanol molecules in both chain and ring conformations.[36] At certain concentrations, alcohol molecules can form complexes with water molecules which would have a considerably long lifetime. This can certainly slow down the motion of alcohol molecules drastically, which can be referred to as a 'long-lived complexes mechanism'. In fact, a long-lived ring structure with 6 and/or 8 MeOH molecules and other water molecules had been suggested to be the reason for the excess entropy in aqueous MeOH,[49] but a trimer ring complex with one EtOH molecule and two water molecules had also been proposed to explain the excess enthalpy of aqueous EtOH.[50] This mechanism might be responsible for the faster increase of the relaxation time in Fig. 4 in the concentration region of $\chi = 0.25-0.45$ to $\chi = 0.05-0.15$. One may also consider the possibility of a fourth mechanism which involves the breaking up of microsegregation.[51] The existing alcohol networks can be effectively broken up when the water concentration reaches certain levels. Further increase of water molecules will accelerate the segregation of alcohol complexes and sharply increase the contact possibility between water and alcohol molecules, resulting in a faster increase of the translational relaxation time. The microsegregation mechanism had been observed and employed to elucidate the excess entropy of aqueous MeOH,[51] and had also been used to explain the rotational dynamics of alcohol in an aqueous solution.[12,21,32] However, none of these four mechanisms can explain the behavior at very low concentrations, where the translational motion of alcohol molecule speeds up rather than slows down. One possible mechanism for this behavior could be the formation of iceberg-like water.[52] In this case, due to the hydrophobic effect, water molecules around the $-CH_3$ group of an alcohol molecule can form strong HB networks by themselves that behave like an iceberg. This in turn leaves more free volume around the alcohol molecule, which consequently can cause the alcohol molecule to move more freely and more quickly.

Following the iceberg mechanism, the decrease of translational relaxation time in the low-concentration region should be more apparent if in view of the $-CH_3$ group. To confirm this, we have measured the concentration-dependent relaxation times of the $-CH_3$ rocking motion of MeOH as well as the skeleton coupled $-CH_3$ rocking motion of EtOH, as shown in Fig. 5. As can been seen, for both cases the translational motions indeed become apparently fast in the low-concentration region. These concentration-dependent relaxation behaviors are completely different from those from the skeleton translational motions shown in Fig. 4. The reason might be that the skeleton translational motion is more affected by the HB intermolecular interactions. We also noticed that the concentration-dependent translational relaxation time is very similar to the behavior of the partial molar volume of aqueous alcohols,[53] which may have some internal relations with our observations.

Conclusions

We have shown in this study that, with high-resolution and precision Raman spectroscopy, one can characterize the translational motions of alcohol molecules in pure liquid and in water solutions. It is found that the short-chain alcohol molecules have typically translational relaxation time of around picoseconds. Our temperature-dependent measurements show that both the HB interaction and the hydrophobic interaction control the translational motion. The hydrophobic interaction reduces the relaxation time more apparently for the $-CH_3$ group than the skeleton motion. By

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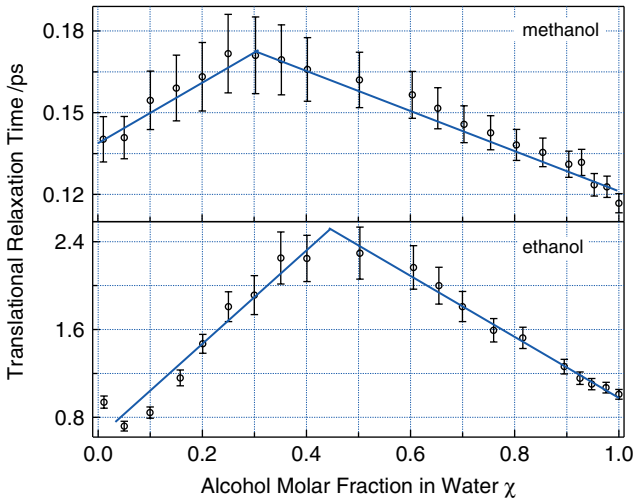

Figure 5. Concentration-dependent translational relaxation times obtained from the $-CH_3$ rocking motion of methanol and the skeleton coupled $-CH_3$ rocking motion of ethanol. Symbols with error bars are experimental data; the solid lines are just used to guide the eyes.

adding water in alcohol liquids, the translational motions are all slowed down. However, depending on the alcohol concentration, the translational relaxation time shows different concentration-dependent behaviors. Different mechanisms have been proposed to interpret these interesting observations, which can help us to gain deeper insight into the HB networks of alcohol with water molecules. Our study strongly illustrates that Raman spectroscopy is a suitable method to study fast translational motion of molecules in HB systems.

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