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Structure and dynamics of nonaqueous mixtures of dipolar liquids. I. Infrared and far-infrared spectroscopy

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Mixtures of acetone/methanol, acetonitrile/methanol, and acetone/acetonitrile over their whole composition range were studied with infrared and far-infrared (THz) spectroscopy. Experimental spectra of all mixtures were obtained below 120 cm^{-1}, and spectra of methanolic mixtures were also measured from 400 to 1000 cm^{-1}. The mixtures display ideal absorption spectra below 120 cm^{-1}, contrasting with significant nonidealities in the absorption of aqueous mixtures in the same frequency range. Dramatic changes as a function of composition were found in methanolic mixtures at higher frequencies. The high frequency librational band of methanol, centered at 670 cm^{-1}, shifts to substantially lower frequencies upon dilution, indicating marked changes in the librational motion of the hydroxyl hydrogen of methanol. This band is a sensitive probe of the hydrogen bonding environment experienced by methanol molecules.
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I. INTRODUCTION

Despite a fair amount of investigation, the properties of dipolar liquid mixtures are still not well understood. Nonpolar liquids have relatively weak and isotropic interactions, but mixtures of dipolar liquids are more complex because dipolar molecules interact via strong dipole–dipole and dipole-induced dipole forces. Consequently, the magnitude and the direction of the dipole play an important role in the interactions in dipolar liquids. Owing to the specificity of the mixture properties to the constituent species, it is difficult to generalize about the behavior of dipolar mixtures. The presence of hydrogen bonding further complicates interactions in the liquid by making extensive, long-lived association of molecules possible. Under these circumstances, the position and orientation of a hydrogen bond donor relative to a hydrogen bond accepting molecule is a critical consideration in the pair interaction energy.

Dipolar liquid mixtures pose interesting chemical questions about how mixing affects the structure and the dynamics of a liquid, and how these change as a function of composition. Furthermore, the practical importance of these mixtures makes a more comprehensive understanding of their properties desirable. In this and the subsequent paper we shall focus on nonaqueous mixtures, which have received less attention than aqueous mixtures. The mixtures we consider are acetone/methanol, acetonitrile/methanol, and acetone/acetonitrile. These three systems allow us to compare the mixtures of a nonassociating and an associating liquid (methanol), as well as a mixture of two nonassociating dipolar liquids. In addition, the methanolic mixtures provide an interesting comparison with aqueous mixtures, since water is also an associating liquid.

Our concern in this paper is primarily with the dynamic behavior of mixtures, particularly the intermolecular motions in the liquid. In this regard, low frequency infrared (IR) and far-infrared (far-IR) spectra are especially important because they elucidate the rotational, translational, and intermolecular vibrational motion of molecules in the liquid. However, interpreting the low frequency spectra of liquids is not straightforward, because the measured spectra are the convolution of absorptions arising from different types of motion and from different species. A combination of both experimental spectroscopy and molecular dynamics (MD) simulations is the best strategy for coming to a detailed molecular understanding of the liquid dynamics. Although MD simulations readily yield dynamic information on the system being studied, we emphasize that the experimental spectra are indispensable for evaluating the accuracy of the simulations, and hence the reliability of the attendant results. MD simulations of the spectra of the mixtures will be addressed in the following paper.[1]

There is a remarkable absence of experimental spectra below 800 cm^{-1} for dipolar liquid mixtures. The lack of spectra arises in part because dipolar liquids absorb strongly at far-IR frequencies, i.e., below about 400 cm^{-1}. Furthermore, there are few intense broadband sources of radiation in the far-IR. According to Beer's Law, the intensity, I, of light transmitted through the sample varies as

$$I(\omega)=I_0(\omega)\exp(-\alpha d), \tag{1}$$

where I_0 is the incident intensity, α is the Naperian power absorption coefficient, and d is the pathlength. Consequently, it is difficult to measure accurate spectra of highly absorbing samples using transmission spectrometers. Despite these obstacles, the far-IR spectra of some important neat liquids have been determined, most notably water,[2,3] methanol,[3–5] acetonitrile,[6] and acetone.[6]

The higher frequency spectra of hydrogen bonding liquids can also be difficult to determine, owing to the intense absorption of the hydroxyl H librational band, which peaks at a frequency of about 650 cm^{-1}. In water and methanol, for instance, the absorption coefficient at the center of the librational band corresponds to about 3500 per cm and 1000 per cm, respectively. The measurement of such high absorption coefficients requires very short pathlengths for transmission spectrometers. Attenuated total reflection (ATR) spectroscopy overcomes the obstacle of high sample absorption and has been used to determine the spectra of neat water and neat methanol over this whole region.[2,4] However, we have not found any reports applying this technique to measure the librational band of mixtures.

There are few, if any, experimental results on the structure or dynamic properties of the mixtures examined in this paper. Eaton *et al.* have observed in the mid-infrared that the intramolecular CO stretch of acetone and the CN stretch of acetonitrile split into two peaks in methanolic solution.[7–9] They attribute this to two types of acetone or acetonitrile molecules in the mixture: those with zero hydrogen bonds, and those accepting one hydrogen bond. In methanol-rich solution, 90% of acetone and 50% of acetonitrile molecules accepted one hydrogen bond. In contrast to dilution in methanol, the CO stretch of acetone is not much affected by dilution in acetonitrile.

Our purpose in this and in the following paper is to investigate the structure and dynamics of mixtures of acetone/methanol, acetonitrile/methanol, and acetone/acetonitrile over their entire range of compositions. In this paper, we report the IR and far-IR spectra of the mixtures. Initial interpretations of the spectra are presented, which are expanded upon in the subsequent paper with the inclusion of MD simulation results.

II. EXPERIMENT

Infrared and far-infrared spectra were recorded at room temperature (18–21 °C). Methanol, acetonitrile, and acetone of greater than 99.5% purity were obtained from Baker and were used as received. Mixtures were made as described previously.[10] The compositions studied were 0.00, 0.10, 0.25, 0.50, 0.75, 0.90, and 1.00 by volume fraction, and the uncertainty in the volume fractions of the mixtures was less than 0.2%. We have previously discussed the use of volume fraction in preference to mole fraction when interpreting spectra.[10] In this paper, we denote the volume fraction of component i with the symbol, V_i. The component i may be written as AT for acetone, AN for acetonitrile, or ME for methanol.

Spectra of the liquids in the IR region were measured by transmission through a variable pathlength cell mounted in a standard FTIR spectrometer (Midac M1200). The cell was designed such that a sealed 5 μm thick polyethylene bag containing the sample was sandwiched between two 2.5 mm thick AgCl windows. The windows were attached to blocks mounted on a translation stage, which could be adjusted to a precision of better than 0.5 μm using a differential micrometer. Spectra were measured over a range of pathlengths and the absorption coefficient was calculated using Beer's Law, Eq. (1). In this manner, the absorption coefficients of the liquids were determined for frequencies above 400 cm^{-1}. An absorption band of the polyethylene bag gave rise to an artifact in the spectra between 715 and 735 cm^{-1}, which sometimes necessitated eliminating data between these frequencies. Although reflection techniques (such as ATR) are preferable to transmission techniques for highly absorbing samples, we note that our results for neat methanol are in quantitative agreement with those of Bertie.[4]

Spectra in the far-IR were measured using femtosecond terahertz (fs-THz) pulse spectroscopy. Intense subpicosecond far-IR pulses, with frequency components from 0.1 to about 4 THz (3 to 133 cm^{-1}), are propagated through samples of variable thickness. The arrival time of a visible gating pulse at a suitable detector is varied, relative to that of the THz pulse, to map out the amplitude of the pulse in the time-domain. Fourier transformation of the time-domain spectrum gives the frequency-domain power spectrum and phase delay. The spectrometer and the data acquisition procedure have been detailed in earlier work, and we have demonstrated that this technique is well suited to measuring far-IR spectra of strongly absorbing liquids.[3,10] Our spectrometer has useable spectral coverage of roughly 5–120 cm^{-1} for strongly absorbing liquids. This technique has the advantage of measuring both the absorption coefficient and the index of refraction, thereby allowing the complex-valued dielectric constant to be determined. The complex-valued dielectric constant is useful in determining the Debye relaxation times,[10,11] as well as in other theoretical treatments of solvent relaxation.[12]

III. RESULTS

A. Far-infrared spectra

The frequency-dependent absorption coefficients and indices of refraction of the mixtures are shown in Figs. 1–3. The spectra extend to about 130 cm^{-1} in favorable situations, and cover almost the entire absorption band of acetone (peak frequency at 60 cm^{-1}, and reach the maximum of the acetonitrile absorption (peak frequency at 90 cm^{-1}). Our results for the neat liquids show good agreement with previous work.[6] Librational motions are largely responsible for the far-IR absorption band, although translational motions also contribute to the spectra through induced dipole effects.[13] These spectra ostensibly cover a small frequency range; however, considering that over a decade is spanned between 5 cm^{-1} and 100 cm^{-1}, it is apparent that this spectral coverage probes molecular motions of substantially different energies.

For the most part, the absorption coefficients and indices of refraction of the mixtures change monotonically in going from one neat liquid to another. An isosbestic point in the absorption coefficient occurs at just above 80 cm^{-1} in acetone/methanol mixtures (Fig. 1). Isosbestic points are also apparent in the refractive indices for each of the mixtures. These occur at about 15 cm^{-1}, 45 cm^{-1}, and 90 cm^{-1} for the acetone/methanol, acetonitrile/methanol, and acetone/acetonitrile mixtures, respectively.

The composition dependence of the absorption coefficients and indices of refraction of the mixtures is shown in Figs. 4–6. The ideal values for the optical constants are given by

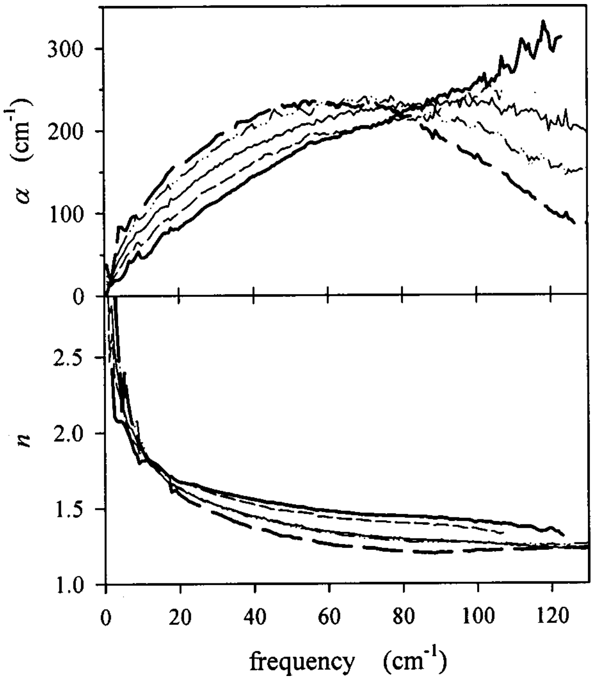

FIG. 1. The far-IR absorption coefficient and index of refraction of acetone/methanol mixtures. Neat acetone is shown as a bold dashed line and neat methanol as a bold solid line. Spectra of the mixtures are displayed as thin lines for the following compositions (by acetone volume fraction): 0.25 (short dashes), 0.50 (solid line), and 0.75 (dot-dot-dashes).

$$\alpha_{\mathrm{ideal}}(\omega)=\rho_{\mathrm{real}}/\rho_{\mathrm{ideal}}[V_1\alpha_1(\omega)+V_2\alpha_2(\omega)] \tag{2}$$

and

$$n_{\mathrm{ideal}}(\omega)=\rho_{\mathrm{real}}/\rho_{\mathrm{ideal}}[V_1 n_1(\omega)+V_2 n_2(\omega)], \tag{3}$$

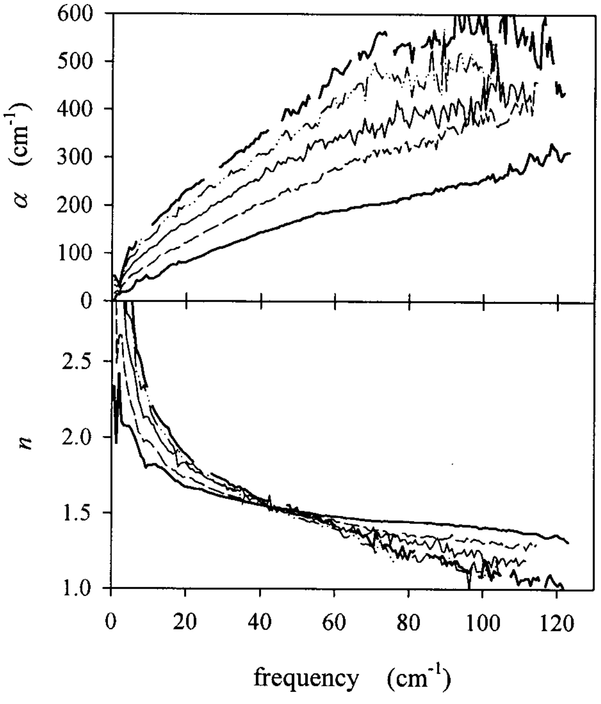

FIG. 2. As for Fig. 1, except for acetonitrile/methanol mixtures. Volume fractions are in terms of acetonitrile.

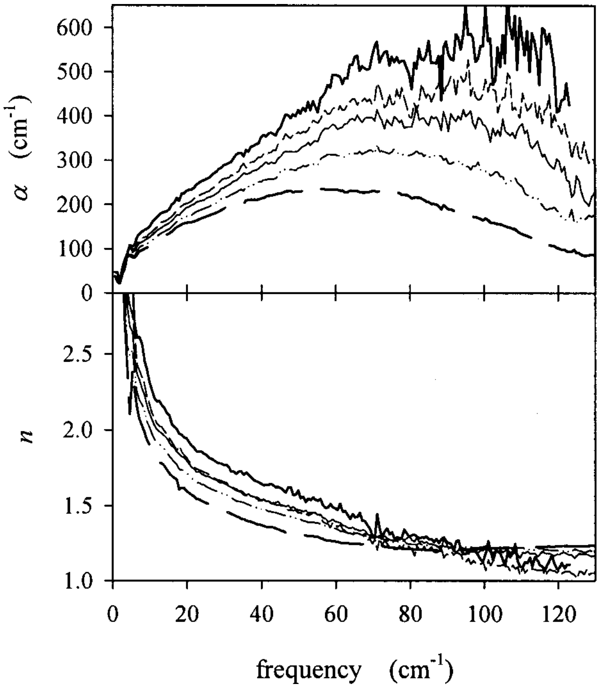

FIG. 3. As for Fig. 1, except for acetone/acetonitrile mixtures. Volume fractions are in terms of acetone.

where V_i is the *volume* fraction, and α_i and n_i are, respectively, the absorption coefficient and index of refraction of component i. The ratios of the real and ideal densities ($\rho_{\mathrm{real}}/\rho_{\mathrm{ideal}}$) are included to account for small nonidealities in the volumes of mixing.

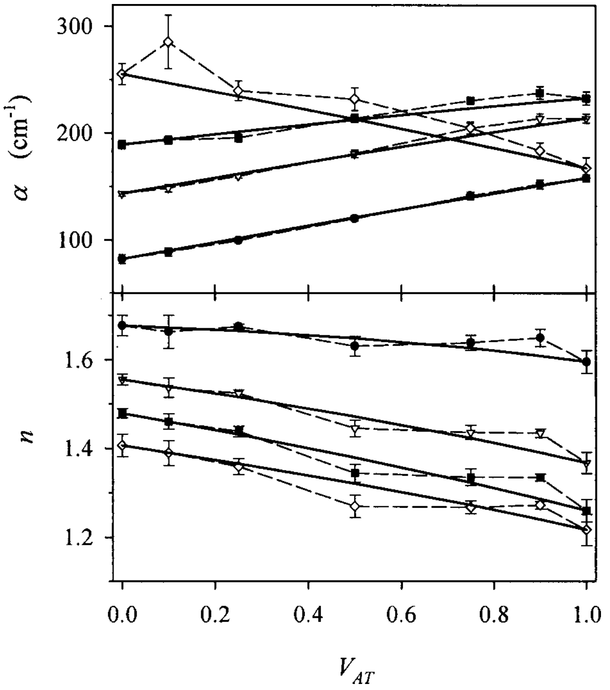

FIG. 4. The composition dependence of the absorption coefficient and index of refraction of acetone/methanol mixtures. The frequencies shown are 20 cm^{-1} (filled circles), 40 cm^{-1} (open triangles), 60 cm^{-1} (filled squares), and 100 cm^{-1} (open diamonds). Thin dashed lines connecting the points are shown as a guide to the eye. Ideal optical constants for the mixtures [cf. Eqs. (2) and (3)] are represented by bold solid lines.

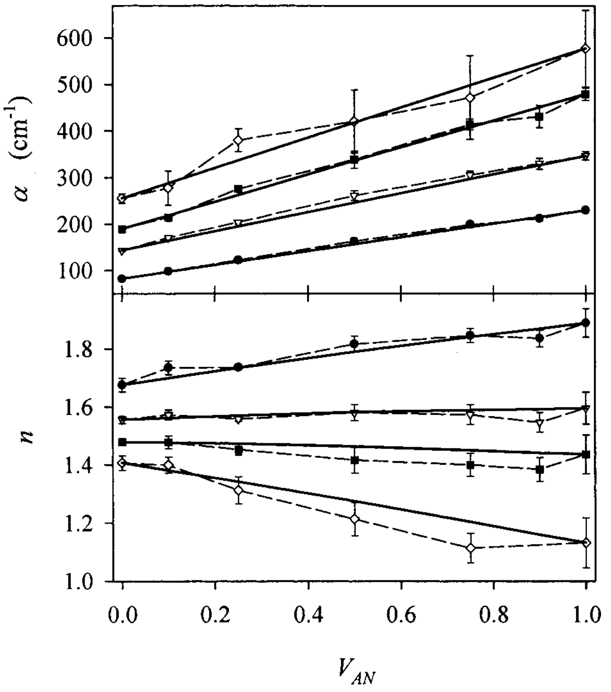

FIG. 5. As for Fig. 4, for acetonitrile/methanol mixtures.

The absorption coefficients of these mixtures show ideal behavior (bold line in figures), except at high frequencies in acetone/methanol mixtures when a slight excess absorption is visible (Fig. 4). The indices of refraction of these mixtures are also essentially ideal, within experimental uncertainty. Deviations from ideality are only consistently significant in the acetone/acetonitrile mixtures (Fig. 6), showing a negative deviation at acetonitrile-rich compositions, and a positive deviation at acetone-rich compositions. The refractive index of acetone/methanol mixtures may also be nonideal for acetone-rich compositions (Fig. 4).

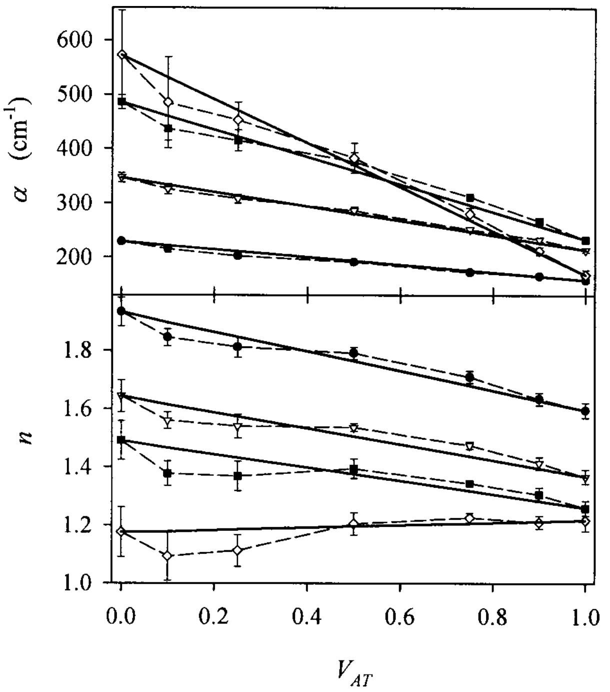

FIG. 6. As for Fig. 4, for acetone/acetonitrile mixtures.

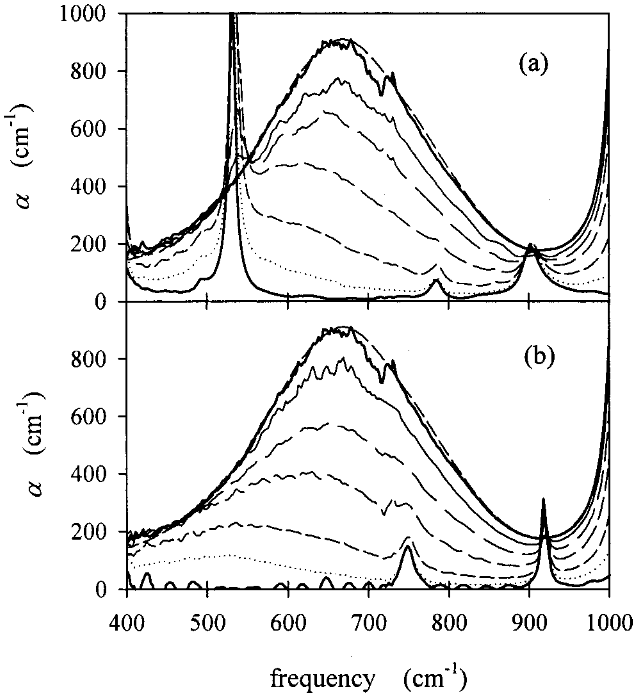

FIG. 7. The change in the high frequency intermolecular absorption spectra upon addition of (a) acetone or (b) acetonitrile to methanol. Bold solid lines represent both neat liquids; the broad, intense absorption is that of neat methanol. The compositions shown (by methanol volume fraction) are 0.10 (dotted), 0.25 (short dashes), 0.50 (intermediate dashes), 0.75 (long dashes), and 0.90 (solid line). Our spectrum of neat methanol shows excellent agreement with that of Bertie *et al.* (thin dashed line) (Ref. 4).

B. Infrared absorption

The absorption coefficients of acetone/methanol and acetonitrile/methanol mixtures between 400 and 1000 cm^{-1} are shown in Fig. 7. The feature of interest in these spectra is the broad librational band of the methanol molecule that peaks at 670 cm^{-1} in the neat liquid. This librational band has been attributed to hindered rotation of the hydroxyl H atom around the C–O axis of the methanol molecule.[14] Our spectrum of neat methanol compares well with the results of Bertie (see Fig. 7).[4] The sharp peaks at 530 and 785 cm^{-1} in acetone-rich mixtures, and at 750 cm^{-1} in acetonitrile-rich mixtures, result from intramolecular motions of these molecules. As the focus of these two papers is on *inter*molecular behavior, we will not consider these absorptions any further.

Unlike the far-IR spectra, the high frequency librational band of the methanolic mixtures does not behave ideally, as is readily apparent in the position of the peak maximum. The methanol librational band was fitted to a Gaussian function to quantify changes in the absorption. (Additional Gaussian profiles were included as necessary to account for the narrow intramolecular absorption bands of acetone and acetonitrile.) The fits of the Gaussian curve to the librational band were very good at most compositions, although in acetone-rich mixtures the absorption band of acetone at 530 cm^{-1} partially obscured the methanol libration. The results at V_{AT}

TABLE I. The parameters for the methanol high frequency libration band, obtained by fitting the spectra to a Gaussian function.

Acetone/Methanol				Acetonitrile/Methanol			
V_{AT}	Position (cm^{-1})	Amplitude (cm^{-1})	Width (cm^{-1})	V_{AN}	Position (cm^{-1})	Amplitude (cm^{-1})	Width (cm^{-1})
0.00	669	867	114	0.00	669	867	114
0.10	660	707	118	0.10	661	751	117
0.25	647	625	121	0.25	648	561	126
0.50	616	475	124	0.50	612	396	134
0.75	575	298	113	0.75	552	218	140
0.90	540	178	80	0.90	509	111	116

$=0.75$ and 0.90 are therefore less reliable than other values. The results of the fits are listed in Table I and are shown in Fig. 8.

Deviations from ideal behavior of the methanol libration are reflected in the position and width of the absorption band. In particular, the frequency of the peak maximum has a strong red shift in both mixtures. This red shift occurs upon addition of acetone or acetonitrile to methanol, and changes increasingly rapidly as the methanol is diluted further. The peak position decreases in frequency by about 130 cm^{-1} in acetone/methanol mixtures, and by 160 cm^{-1} in acetonitrile/methanol mixtures, in going from neat methanol to $V_{AN}=0.90$. The presence of acetone or acetonitrile also affects the width of the librational band. The width of the absorption initially increases on dilution of methanol, but narrows sharply when the methanol comprises only a small fraction of the mixture, especially in the acetone/methanol mixtures.

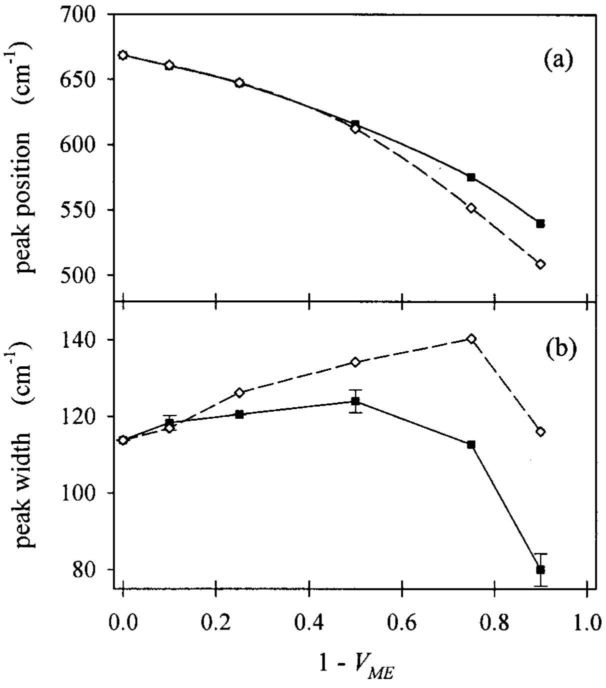

FIG. 8. Variation of the peak position (a) and width (b) of the high frequency methanol libration band as a function of the acetone or acetonitrile volume fraction $(1-V_{ME})$. Filled squares with solid lines indicate acetone/methanol mixtures, and open diamonds with dashed lines show acetonitrile/methanol mixtures. Uncertainties in the fits of the experimental data to a Gaussian curve are shown for the acetone/methanol mixtures.

IV. DISCUSSION AND SUMMARY

Infrared absorption arises from dipole fluctuations,[15] which in liquids are primarily caused by translational and librational motions. Librations are usually spectroscopically visible because they typically involve reorientation of the dipole. Translational motions alter the induced dipoles among molecules and thereby contribute to the infrared spectra. For highly polar liquids, such as those considered here, librational motions are the largest contributor to the far-IR spectrum.[5,6] This is apparent from dilution studies of acetone and acetonitrile in cyclohexane, which show that the total absorption of dilute solutions (adjusted for volume fraction) is almost the same as that of the neat liquids.[5]

The experimental far-IR spectra of acetone/methanol, acetonitrile/methanol, and acetone/acetonitrile mixtures have an apparently ideal dependence on composition. The ideal absorption is exemplified by the isosbestic point found in acetone/methanol mixtures. However, ideal *spectra* are not unambiguous evidence for ideal *dynamic* behavior, because the underlying motions may affect the spectra in opposite ways upon mixing, thereby canceling out each other's effect. Nonetheless, for the mixtures studied here, it still seems reasonable to assert that any changes in the rotational and translational motions of each species are small.

The spectra of the nonaqueous mixtures contrast markedly to our results for aqueous mixtures, in which the absorption coefficients show large negative deviations from ideality.[10,11] The dissimilarity in the absorption between aqueous and acetone/acetonitrile mixtures is perhaps not surprising, as neither acetone nor acetonitrile is an associating liquid like water. On the other hand, methanol *is* an associating liquid, and similarities in the behavior of the absorption of the methanolic and aqueous mixtures might be expected. That this is not so suggests that the molecular motions in this frequency range are affected much less in methanolic mixtures than in aqueous mixtures.

The reason for the dissimilar far-IR behavior of aqueous and methanolic mixtures probably resides in differences in the reorientational and librational motions. In water, the primary absorption at far-IR frequencies arises from Debye relaxation—that is, rotational diffusional relaxation. Since all three principal moments of inertia of water are small and intermolecular interactions are large, librational motions are found at higher frequencies and contribute little to the spectrum below 150 cm^{-1}. The lower-than-ideal absorption in aqueous mixtures is due to a slowing of the Debye relaxation, as indicated by increases in the Debye time constants.[10,11] In methanol, on the contrary, librational motions are responsible for most of the absorption in the far-IR, as will be seen in the following paper.[1]

Obvious nonidealities occur in the experimental absorption of methanolic mixtures at higher frequencies. The absorption centered at 670 cm^{-1} in neat methanol is caused by librational motions of the methanol molecule around its C–O axis. The high frequency of the absorption is a result of the hydrogen bonding environment and the small moment of inertia about this axis. Because the most prominent feature of this libration is rotation of the hydrogen atom, this absorption band is a sensitive probe of the hydrogen bonding environment.

Addition of either acetone or acetonitrile to methanol results in a large red shift of the high frequency librational band. We believe that this is the first experimental study of this absorption band of these mixtures. The dependence of the peak position on concentration is similar in both acetone and acetonitrile mixtures. The magnitude of the shift (130–160 cm^{-1}) relative to the peak position in neat methanol (670 cm^{-1}) is indicative of a marked weakening of hydrogen bonding in the liquid. The results of Eaton and co-workers clearly demonstrate that there is a significant amount of hydrogen bonding between methanol and acetone or acetonitrile.[7–9] However, it would be premature to ascribe the observed red shift to hydrogen bonding between methanol and its co-solvent, because it might also be explained by changes in the degree of association of methanol molecules.

The shape of the absorption band is essentially Gaussian at all compositions. The peak width changes with addition of co-solvent, at first increasing slightly, and thereafter dropping steeply. These changes indicate a more heterogeneous environment of the methanol molecules as solvent is added. However, the decrease when methanol is rather dilute suggests that the opposite effect occurs: namely, that the environment of the methanol molecules tends to become more homogeneous. Changes in the hydrogen bonding environment take place in a gradual manner as methanol is replaced by co-solvent.

The above experimental observations will be interpreted more fully in the following paper,[1] in which microscopic details of the structure and the dynamics of the mixtures are investigated using MD simulations. An advantage of computational studies is that the system can be dissected such that information about only certain species, or certain types of motion is considered. The IR spectrum provides a test of the interaction potentials that is different from typical bulk properties, such as viscosity, transport coefficients, heat capacities, etc., that are used when developing the potentials. If the intermolecular potentials adequately describe the interactions, the results of the simulations can be analyzed with confidence.

ACKNOWLEDGMENT

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