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Improper Hydrogen-Bonding CH·Y Interactions in Binary Methanol Systems As Studied by FTIR and Raman Spectroscopy

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Fourier Transform infrared spectroscopy and Raman spectroscopy have been used to investigate hydrogen bonding of methanol in different solvents with an aim to explore potential experimental evidence for improper hydrogen bonding involving the methyl group of methanol as suggested by various computational studies. Pure methanol and solutions of methanol in water, acetonitrile, carbon tetrachloride, deuterium oxide, and deuterated acetonitrile have been studied over a range of concentrations. Wavenumber shifts of the CH stretching vibrations were examined to determine if the CH from methanol participates in hydrogen bonding. New concepts of the vibrational wavenumber and integrated intensity at infinite dilution are proposed and given the respective symbols $\tilde{\nu}^{\circ}_{CH}$ and $C^{*\circ}_{j,CH}$. Using the results obtained for methanol in carbon tetrachloride as a reference, shifts in $\tilde{\nu}^{\circ}_{CH}$ of methanol to higher wavenumbers (blue shifts) were observed in each of the other solvents studied, with the shifts being greatest for the methanol−water interactions. The shifts in vibrational wavenumber suggest possible improper hydrogen bonding, although at this stage a definitive conclusion is not possible. The $C^{*\circ}_{j,CH}$ results show that there is no distinguishable change in the methanol CH stretch integrated intensity in carbon tetrachloride and acetonitrile, while there is a significant decrease in the methanol CH stretch integrated intensity in the water solutions.

Introduction

Methanol has been widely characterized on the basis of its infrared properties, including refractive indices, absolute integrated intensities, and dipole moment derivatives.[1−4] Similar studies have also been completed on deuterated forms of methanol: methanol-*d*,[5,6] methan-d_3-ol,[6,7] and methanol-d_4.[3,6,7] Raman spectroscopy has been shown to be a useful tool for studying the characteristics of methanol in that temperature and pressure effects on the line shapes have been examined.[3,8,9] Intermolecular interactions involving methanol have been widely studied in various organic and aqueous solvents, where the proper hydrogen bond is the main stabilizing attraction and shifts in the OH and CO stretching vibrations in both the infrared and Raman spectra have been described. Strong hydrogen bonding has been observed for the OH group in methanol in aqueous solutions[10−17] and solutions of methanol in acetonitrile,[17,18] carbon tetrachloride,[17,19−21] and hydroxy esters.[22] Kabisch and Gruenloh compared the CO and OH wavenumbers of methanol in organic media with the respective wavenumbers of methanol in aqueous solutions.[23] An important feature observed in these solutions is methanol's ability to form aggregates,[15,18,21,24−26] attributed to the strong OH···O interactions between the neighboring hydroxyl groups of the individual methanol molecules.

A new type of hydrogen-bond interaction, XH···Y, where hydrogen is bonded to less electronegative atoms (X = C, Si, P) has been brought forward in the last 10 years, initially labeled "anti-hydrogen" bonds,[27] but more recently known as improper, blue-shifting hydrogen bonds.[28,29] Generally, the formation of such a complex results in a C−H bond contraction and a blue shift of its stretching frequency. Since these results are opposite (with respect to the change in the bond length and the frequency shift) to what is seen for normal hydrogen bonding, there has been much debate as to whether the blue-shifting H-bonds are distinct from normal H-bonds.[30−35] There have been several very extensive reviews of these interactions in recent years,[28,29,31,34,36] and the reader is referred to those for a more complete description of the literature.

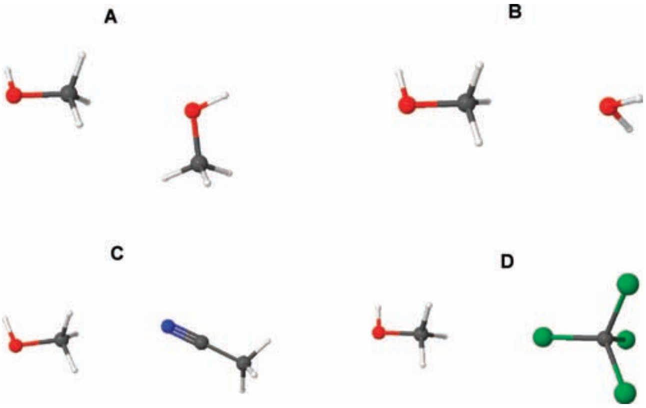

Figure 1. Models of possible improper hydrogen bonding of methanol with (a) methanol, (b) water, (c) acetonitrile, and (d) carbon tetrachloride. The figure is not an actual representation of the bonds being formed (i.e., geometries are not intended to be representative of the actual complexes) but rather a schematic of the interactions investigated.

While many of the previous studies of methanol have looked at some facet of hydrogen bonding, none of them have examined the CH stretching wavenumber for evidence of an improper hydrogen bonding system in liquid methanol. This work considers the possibility for improper hydrogen bonding of the CH group of methanol to regions of high electron density on neighboring molecules. The suggested interactions for the solvents studied here (pure methanol, water, acetonitrile, and carbon tetrachloride) are shown in Figure 1. Using a combination

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of Fourier Transform infrared (FTIR) spectroscopy and Raman spectroscopy, the goal of this work is to further investigate hydrogen bonding of methanol in different solvents with peak intensities and wavenumber shifting of the CH stretch being the main foci of attention.

Infrared transmission spectra are not possible in this work, as the material of the cells available in this laboratory were soluble in methanol; therefore the attenuated total reflection (ATR) technique was used. In ATR the analogue[37] to absorbance is called pATR

$$\mathrm{pATR} = -\log_{10} \frac{I_\mathrm{R}}{I_0} \tag{1}$$

where I_R is the intensity of the light reflected from the rod with the sample present, and I_0 is the intensity of the light reflected out of the rod without sample present. This method allows analysis to be completed on the spectra in an analogous fashion to transmission spectra.

The intensity of the CH stretch region is examined by way of the imaginary molar polarizability. As discussed in previous literature,[38,39] the mean polarizability of a molecule in a liquid is defined in the general form

$$\hat{\alpha}(\tilde{\nu}) = \alpha'(\tilde{\nu}) + i\alpha''(\tilde{\nu}) \tag{2}$$

and can be expressed as molar polarizability, $\hat{\alpha}_\mathrm{m}(\tilde{\nu})$, when multiplied by Avogadro's number.[38] The imaginary molar polarizability, $\alpha''_\mathrm{m}(\tilde{\nu})$, is used to describe intensities in the infrared by calculating the area under the $\tilde{\nu}\alpha''_\mathrm{m}(\tilde{\nu})$ spectrum. The polarizability, like other complex absorption quantities, gives a measure of the absorption of the electromagnetic radiation by the sample being examined. The magnitude of the transition moment for a transition may be found by determining the intensity of a band using these quantities. The main advantage of using the imaginary molar polarizability is that it provides information on the molecule independently of the effect of the surrounding medium's refractive index. In other words, it is corrected for the fact that the solvents have different refractive indices.

Experimental

Methanol, acetonitrile, and carbon tetrachloride were purchased from Fisher Chemicals. Deuterium oxide was purchased from J. T. Baker and CDN Isotopes, while acetonitrile-d_3 was purchased from CDN Isotopes. Water used in this study was distilled before use. Solutions were prepared and kept in sealed vials before use, as well as between measurements. This was especially important for the deuterated solvents to ensure limited exchange with water present in air.

Solutions of methanol in each of water, deuterium oxide, acetonitrile, acetonitrile-d_3, and carbon tetrachloride were prepared by mass. In this work, a full range of concentrations were examined for each of the solvents. Up to 10 concentrations ($x_\mathrm{MeOH} = 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$) of each solution were studied in addition to pure methanol ($x_\mathrm{MeOH} = 1.0$).

The IR spectra were recorded using either a Thermo-Nicolet 6700 or Nicolet Impact 410 FTIR spectrometer. The spectrometers both have an Ever-Glo mid-IR source, Ge-on-KBr beam splitter, and a DTGS detector. The ATR spectra were collected using a Spectra-Tech model 0005-004 cylindrical CIRCLE[40,41] cell containing a ZnSe rod. The spectra were recorded at 2 cm^{-1} resolution with 32 interferograms being averaged before Fourier Transform. A background spectrum was recorded under the same conditions before each sample measurement using the CIRLCE cell containing the rod without any solution. Six pATR spectra were collected for each of the solutions prepared.

Calibration spectra were taken with the cell filled with benzene, which was purchased from B&D Chemicals and stored over a molecular sieve. Measurements were recorded at 2 cm^{-1} resolution and 32 scans were averaged before Fourier transform. These spectra are necessary to determine the number of reflections within the cell. The effective number of reflections of the ZnSe rod within the cell was determined through calibration using the program CIRCLCAL.[37,42,43]

Refractive indices were recorded using a Bellingham and Stanley *abbe*60/ED refractometer using sodium D, cadmium, cadmium F′, mercury g, mercury h, and helium d lamps. Real refractive indices were calculated using the program ABBEUTIL version 4.00 from Bellingham and Stanley. The real refractive indices were fit to the equation

$$n(\tilde{\nu}) = n_\infty + a_2\tilde{\nu}^2 + a_4\tilde{\nu}^4 \tag{3}$$

where $\tilde{\nu}$ is the wavenumber expressed in cm^{-1}, and the coefficients n_∞, a_2, and a_4 describe how the refractive index of the liquid changes with varying wavenumber. Note that these refractive indices were only measured for six mole fractions (0, 0.2, 0.4, 0.6, 0.8, 1) for each system studied. The required parameters in eq 3 were then determined by linear interpolation for the other mole fractions. These parameters were important requirements in computing the real and imaginary refractive index spectra using the program PKREF.[37,42−44] PKREF uses the effective number of reflections within the ZnSe rod and the pATR spectrum of a solution to calculate the imaginary refractive index spectrum $k(\tilde{\nu})$ spectrum and, in turn, to convert the k spectrum to the real refractive index spectrum $n(\tilde{\nu})$ via the Kramers−Kronig transform. Using the real and imaginary refractive indices and DEQUANT,[45] the imaginary molar polarizability spectra were determined. It was assumed that the molar volumes vary linearly with mole fraction between pure solvent and pure methanol for each of the solvents.

The Raman spectra were recorded using a Nicolet NXR 9650 spectrometer with NXR FT-Raman module from Thermo Electron with an InGaAs detector and CaF$_2$ beam splitter. A 1064 nm laser was used at nominal 0.5 W power. In most cases, a NMR tube was used as a sample container, since it required a limited amount of solution; however, in some cases the spectra were recorded directly from the sample vial. A resolution of 2 cm^{-1} was used and 80−100 interferograms were averaged before Fourier transform. Spectral quality checks for sample heating and fluorescence peaks were also in place. The Raman spectra were normalized by the actual laser power and averaged for each of the solutions prepared.

Results and Discussion

A common concept applied when studying the behavior of solutions is that of an ideally dilute solution. A solution that is ideally dilute is one in which the solute molecules essentially interact only with those of the solvent, due to the extremely low concentration of solute molecules in comparison to the solvent.[46] This model was used to introduce the concept of *vibrational wavenumber and relative intensity at infinite dilution* or, in other words, the vibrational wavenumber and relative intensity in the limit as x_MeOH goes to zero. The vibrational wavenumber in solution can be modeled by

$$\tilde{\nu}_{\mathrm{CH},x} = \tilde{\nu}^\circ_\mathrm{CH} + (\tilde{\nu}_{\mathrm{CH,CH_3OH}} - \tilde{\nu}^\circ_\mathrm{CH})x_\mathrm{MeOH} \tag{4}$$

where x_MeOH is the mole fraction of methanol, $\tilde{\nu}_{\mathrm{CH,CH_3OH}}$ is the vibrational wavenumber in pure methanol, and $\tilde{\nu}^\circ_\mathrm{CH}$ is the

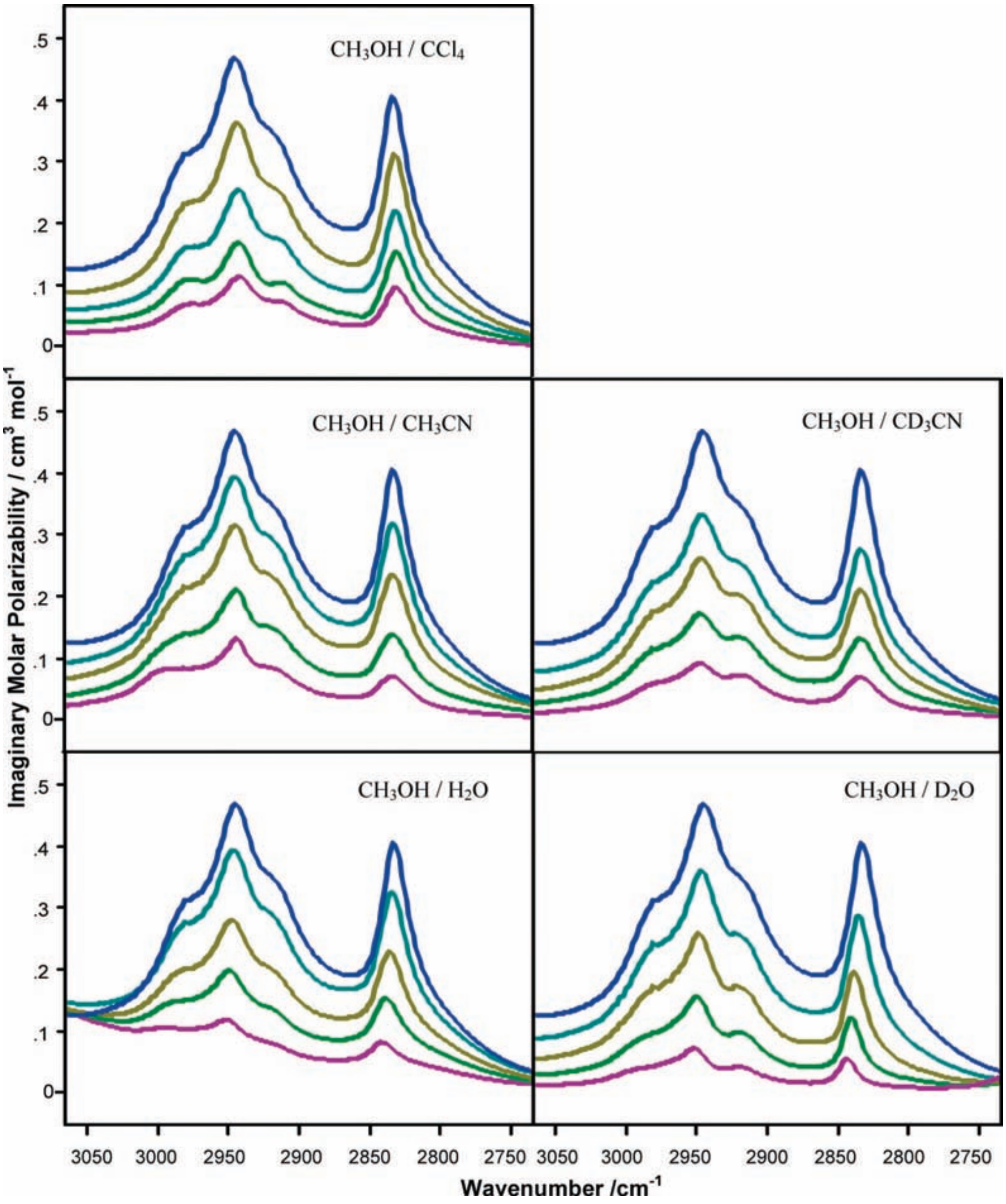

Figure 2. The imaginary molar polarizability spectra of the systems studied. In each box, from top to bottom, the spectra are for pure methanol, $x_{\mathrm{MeOH}} = 0.8$, 0.6, 0.4, 0.2.

vibrational wavenumber at infinite dilution. Note that pure methanol can be considered a "solution" of methanol in methanol, and thus, the peak positions in pure methanol can be considered the vibrational wavenumber at infinite dilution for methanol.

The peaks at approximately 2945 and 2830 cm^{-1} are assigned[47] to the asymmetric and symmetric CH stretching vibrations, respectively. The proximity of the OH and CH stretching peaks are most noticeable in the spectra of methanol in water. This overlap was not seen with any of the other spectra. The CH stretch regions of the imaginary molar polarizability spectra are shown in Figure 2 for a range of mole fractions for each solution in addition to the spectrum of pure methanol. For clarity, only four concentrations are shown. It is clear that for the CCl_4 solutions, there is very little shift in the CH stretching vibrations, while for both the normal and deuterated acetonitrile solutions there is a slight blue shift, and for both the normal and deuterated water solutions the blue shift is more pronounced. Figures 3 and 4 show plots of the peak position for both the asymmetric and symmetric CH stretch vibrations in the imaginary molar polarizability and Raman spectra, respectively. The peak positions were determined by parabolic interpolation of the three positions with the largest intensities for each of the peaks using PEAKINFO.[48] It is clear that there is an extremely good linear dependence of the peak position on the mole fraction for all the solutions.

The $\tilde{\nu}^{\circ}_{\mathrm{CH}}$ values for the asymmetric and symmetric vibrations from both the imaginary molar polarizability and Raman spectra for each solvent are tabulated in Table 1. The interactions between the CH_3 of methanol and the solvent are expected to be weakest for the carbon tetrachloride solutions. Thus, carbon tetrachloride was taken as a reference solvent and the shifts of $\tilde{\nu}^{\circ}_{\mathrm{CH}}$ from $\tilde{\nu}^{\circ}_{\mathrm{CH,CCl_4}}$ are considered as potential evidence of interactions between the CH_3 of methanol and the solvent. The shifts from the $\tilde{\nu}^{\circ}_{\mathrm{CH,CCl_4}}$ are shown for each of the solvents in Figure 5. Note that acetonitrile and methanol shifts are small and on the same order, whereas there are much larger shifts for the water solutions, and can be taken as possible evidence of improper hydrogen bonding occurring in these solutions. This is discussed in more detail below.

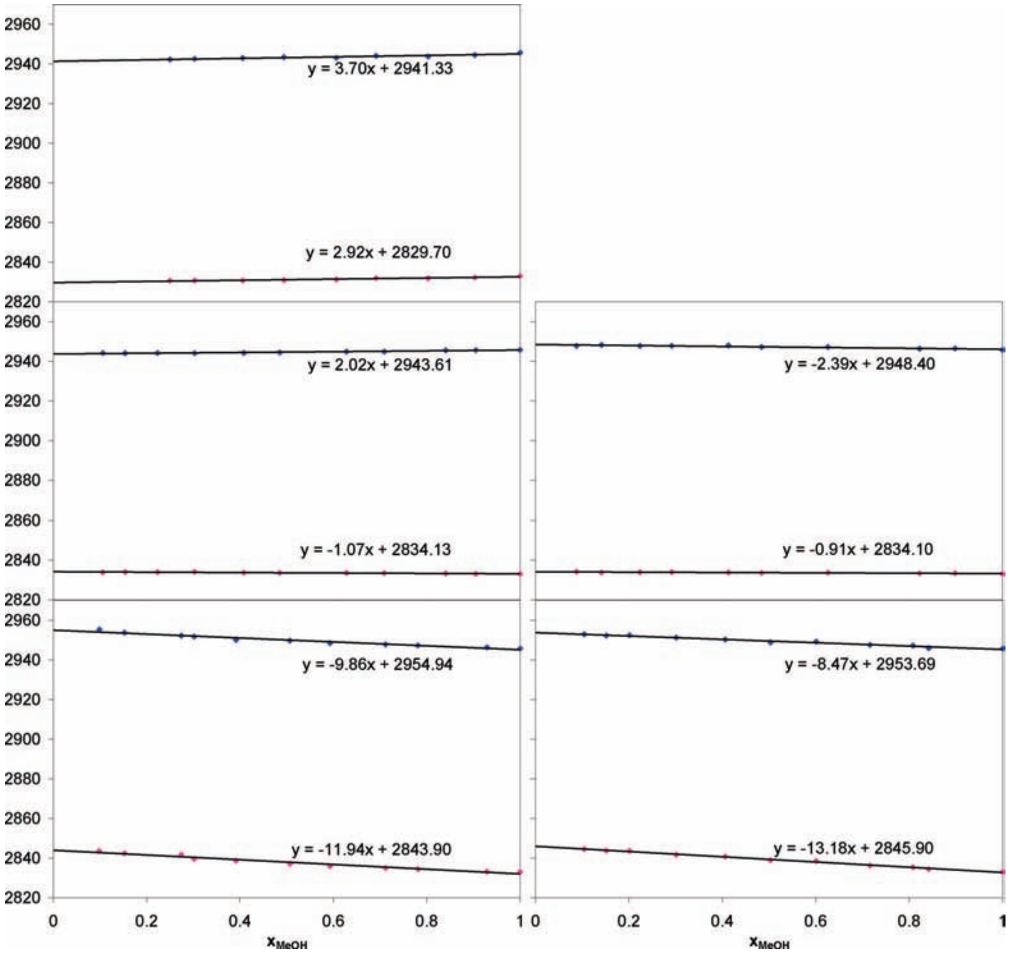

Figure 3. Peak position of CH stretching wavenumbers in the imaginary molar polarizability spectra as a function of concentration of x_{MeOH}. The top box is for CH_3OH/CCl_4, middle boxes for CH_3OH/CH_3CN (left) and CH_3OH/CD_3CN (right), and the bottom boxes for CH_3OH/H_2O (left) and CH_3OH/D_2O (right).

The same concept can be applied to the integrated intensity. The integrated intensity C_j is defined[49] as the area under the $\tilde{\nu}\alpha''_m(\tilde{\nu})$ spectrum

$$C_j = \int \tilde{\nu}\alpha''_m(\tilde{\nu})\, d\tilde{\nu} \tag{5}$$

However, the integrated intensity will naturally go to zero for both ideal and real solutions as the concentration goes to zero, and thus, it is harder to distinguish between ideal and nonideal behavior. For an ideal solution, the integrated intensity will be proportional to the mole fraction and thus the *relative* intensity will be a constant. Thus, in the following discussion, the relative intensity is defined as

$$C_j^* = C_j/x_j \tag{6}$$

and the relative intensity at infinite dilution is given the symbol $C_j^{*\circ}$. For an ideal solution, the relative intensity would be constant and thus the deviation from this constant can be taken as a measure of the nonideal nature of the solution. Ideally, the integration would be over the full range of wavenumbers, but due to the overlap of peaks, this is not possible in this case. The integrated intensities were determined as the area above a linear baseline between the integration limits of 3073 and 2735 cm^{-1}. For the CH_3CN and H_2O solutions, there are problems with overlap of adjacent bands; thus, these solutions were not used in the analysis of the relative intensities. The relative intensities for the CCl_4, CD_3CN, and D_2O solutions as a function of mole fraction are plotted in Figure 6. Typically, integrated intensities measured in this manner have an uncertainty of approximately 3−5% when measured for pure liquids. The uncertainty will increase when the bands measured are weak, due to the solutions being dilute. Thus, the uncertainties in the integrated intensities are conservatively taken to be approximately 0.07 km mol^{-1} for all the measurements. This is approximately 5% for the higher mole fractions, but it is obviously a much larger percentage for the lower mole fractions.

It is clear that for the CD_3CN solutions there is no distinguishable change in the relative intensity. For the CCl_4 solutions, there is much more scatter from the constant, and the values for the solutions around 0.5 mol fraction are consistently lower; this may be an indication of some local structure with a 1:1 mixture giving the optimal interaction. In contrast, the plot for the D_2O solutions tells a markedly different story. The relative intensity decreases significantly as the mole fraction decreases. It is clear that the integrated intensity of the CH stretch vibrations of CH_3OH decreases much more rapidly than can be contributed to the decrease in the number of molecules alone. This decrease is attributed to the intermolecular interactions between the methanol and water molecules. It is also clear that it is not simply a 1:1 complex that gives the strongest stablization due to the fact that the intensity decreases with an increase in water molecules surrounding a given methanol molecule.

The fact that the CH stretch vibrations of CH_3OH are blue-shifted in pure methanol, acetonitrile solutions, and aqueous

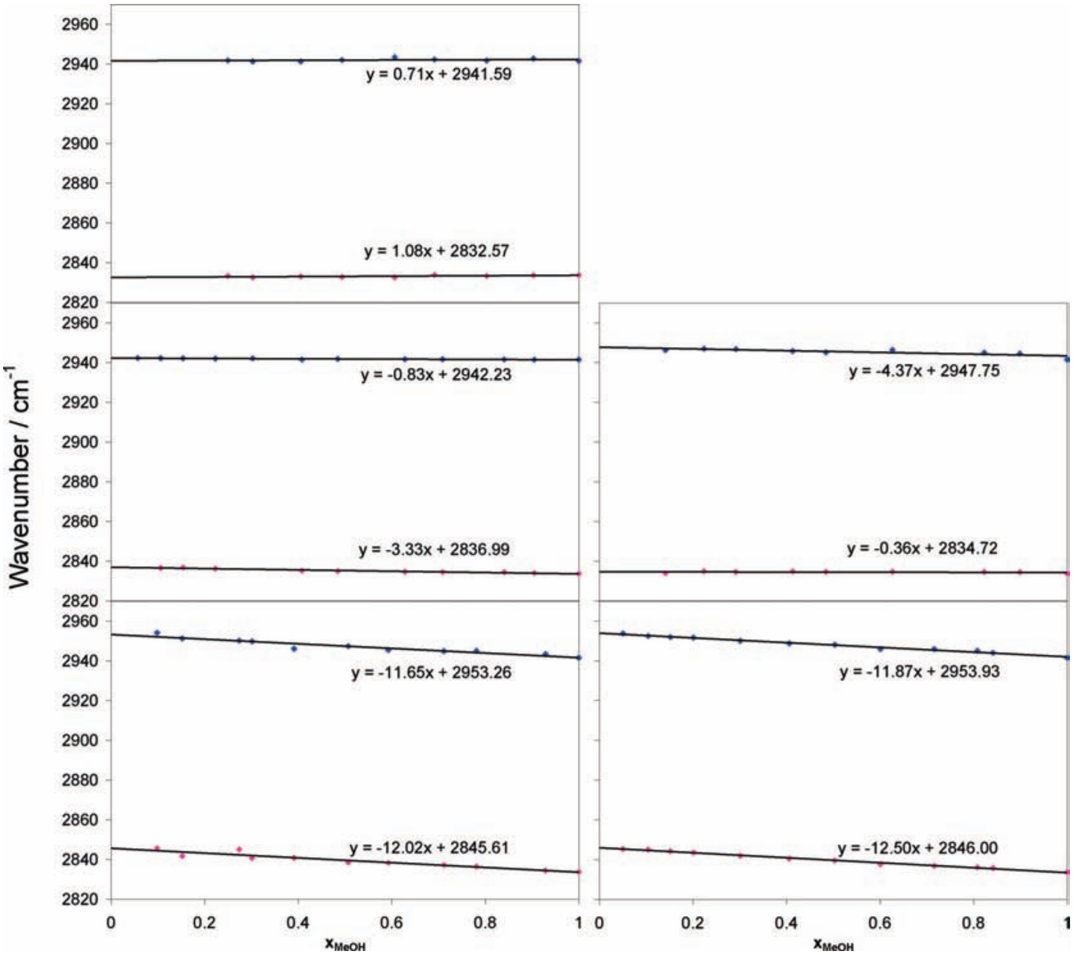

Figure 4. Peak position of CH stretching wavenumbers in the Raman spectra as a function of concentration of x_{MeOH}. The top box is for CH_3OH/CCl_4, middle boxes for CH_3OH/CH_3CN (left) and CH_3OH/CD_3CN (right), and the bottom boxes for CH_3OH/H_2O (left) and CH_3OH/D_2O (right).

TABLE 1: Vibrational Wavenumbers at Infinite Dilution for the Asymmetric and Symmetric CH Stretch Vibrations in the Imaginary Molar Polarizability and Raman Spectra for the Solvents Studied

	$\tilde{\nu}^{\circ}_{CH}$/cm^{-1}			
	asymmetric		symmetric	
solvent	α''_m	Raman	α''_m	Raman
CCl_4	2941.33	2941.59	2829.70	2832.57
CH_3CN	2943.61	2942.23	2834.13	2836.99
CD_3CN	2948.40	2947.75	2834.10	2834.72
CH_3OH	2945.44	2942.04	2832.76	2833.75
H_2O	2954.94	2953.26	2843.90	2845.61
D_2O	2953.69	2953.93	2845.90	2846.00

solutions as compared to carbon tetrachloride solutions is in agreement with the improper hydrogen bond effects discussed in the literature and may be evidence of improper hydrogen bonds between the CH_3 group and the O and N of the solvent molecules. However, there is no doubt that there is strong normal hydrogen bonding between methanol molecules and methanol with acetonitrile and water. This will cause a red shift and significant enhancement of the OH stretching fundamental. It is also possible that the normal hydrogen bonding of the OH group of methanol with solvent molecules could affect other portions of the methanol molecule and result in a blue shift of the CH_3 stretching wavenumbers. To this end, another project was initiated in this laboratory, a computational examination of normal and improper hydrogen bonding in methanol complexes. These calculations will be presented and discussed in a future paper,[50] but the preliminary results indicate that the CH stretch blue shift observed in this work cannot be attributed entirely to normal hydrogen bonding. Until that project is

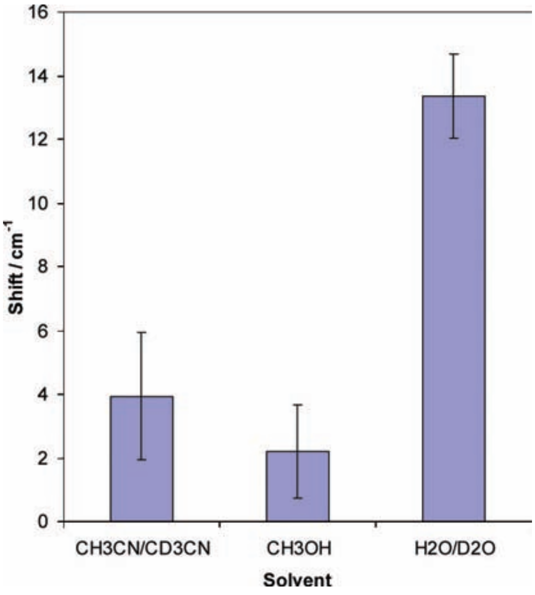

Figure 5. Average wavenumber shifts of $\tilde{\nu}^{\circ}_{CH}$ from $\tilde{\nu}^{\circ}_{CH,CCl_4}$ for the various solvents studied. The error bars represent one standard deviation.

complete, it is impossible to say conclusively whether or not the methyl group is involved in improper hydrogen bonding; however, this type of interaction may play an important role in the structure of alcohols and other similar organic compounds and should be considered when trying to model or explain the structure of dimers, liquids, etc.

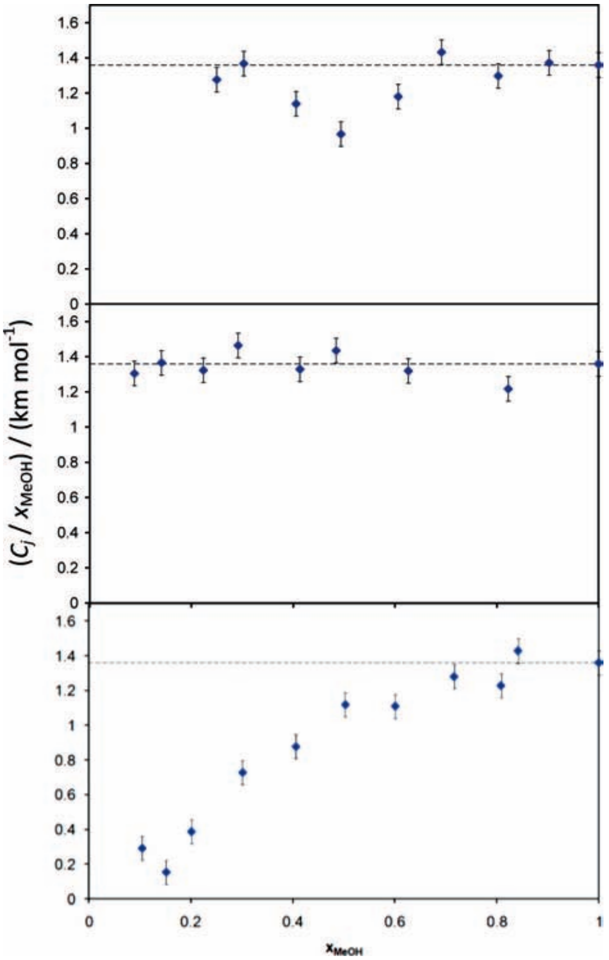

Figure 6. Variation of the relative integrated intensity as a function of mole fraction for the systems CH_3OH/CCl_4, CH_3OH/CD_3CN, and CH_3OH/D_2O. The error bars represent ±0.07 km $\mathrm{mol^{-1}}$, a conservative estimate of the uncertainty in determining the integrated intensity.

Summary

Pure methanol and solutions of methanol in water, acetonitrile, carbon tetrachloride, deuterium oxide, and deuterated acetonitrile were studied over a range of concentrations. Wavenumber shifts of the CH stretching vibrations were examined to determine if the CH from methanol participates in improper hydrogen bonding.

The peak wavenumbers and integrated intensities of the CH stretch region of the imaginary molar polarizability and Raman spectra are reported for pure methanol and solutions of methanol in each of carbon tetrachloride, acetonitrile, acetonitrile-d_3, water, and deuterium oxide. Shifts in peak position toward higher wavenumbers are observed in all solutions as the concentration of methanol in solution decreases, with the exception of methanol in carbon tetrachloride, which shows little to no change. A greater shift in peak position of both the asymmetric and symmetric CH stretch vibrational wavenumbers is observed in the methanol/water and methanol/deuterium oxide solutions when compared to methanol/acetonitrile and methanol/acetonitrile-d_3 systems.

New concepts of the vibrational wavenumber and integrated intensity at infinite dilution are proposed and given the respective symbols $\tilde{\nu}^{\circ}_{\mathrm{CH}}$ and $C^{*\circ}_{\mathrm{j,CH}}$. Using the results obtained for methanol in carbon tetrachloride as a reference, shifts in $\tilde{\nu}^{\circ}_{\mathrm{CH}}$ of methanol to higher wavenumbers (blue shifts) were observed in each of the other solvents studied, with the shifts being greatest for the methanol−water interactions. The shifts in vibrational wavenumber suggest possible improper hydrogen bonding. The $C^{*\circ}_{\mathrm{j,CH}}$ results show that there is no distinguishable change in the methanol CH stretch integrated intensity in carbon tetrachloride and acetonitrile, while there is a significant decrease in the methanol CH stretch integrated intensity in the water solutions.

Hydrogen bonding is likely to be weakest between hydrogen and chlorine compared to hydrogen bonding with oxygen or nitrogen. For this reason, the results obtained for methanol in carbon tetrachloride at infinite dilution were used as the reference for other solvents. Using this method, shifts in $\tilde{\nu}^{\circ}_{\mathrm{CH}}$ to higher wavenumbers were observed in pure methanol and solutions of methanol in water, deuterium oxide, acetonitrile, and acetonitrile-d_3, with the larger shifts occurring in the solutions of methanol in water and deuterium oxide. This not only suggests that improper hydrogen bonding is possible, but also that it would be stronger in the case of methanol in water as compared to acetonitrile. Results obtained for the vibrational wavenumber at infinite dilution were consistent for the IR and Raman spectra, as well as for the asymmetric and symmetric CH stretches. Shifts observed for the solutions of water and acetonitrile were also consistent with their respective deuterated forms.

The relative integrated intensities for the various solutions indicate that, for the carbon tetrachloride and acetonitrile solutions, there is very little change in the intensity as the concentration of methanol is varied. However, in stark contrast, the integrated intensity of the CH_3 stretching vibrations of methanol significantly decreases for low concentrations of methanol in water. This could be evidence that the improper hydrogen bonding of the CH_3 of methanol to water significantly decreases the transition moment as opposed to the drastic increase in intensity associated with normal hydrogen bonding.

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