Hydrogen Bonding in $CHCl_3$/DMSO-d_6 and $CDCl_3$/DMSO-h_6 Mixtures

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Raman and IR spectra of solutions of $CHCl_3$/DMSO-d_6 and $CDCl_3$/DMSO-h_6 (DMSO = dimethyl sulfoxide) solutions are presented and analyzed in terms of hydrogen-bonding interactions. In the region of the C−H stretch of $CHCl_3$ or the C−D stretch of $CDCl_3$, addition of DMSO causes a new band to appear which is broadened and red-shifted with respect to the free C−H or C−D stretch. We postulate that this new band derives from chloroform hydrogen-bonded to DMSO and compare the relative intensities of the bands due to complexed and free chloroform to the ratio of the concentrations of the two species, calculated according to published equilibrium constants. It is concluded that complexation leads to considerable enhancement of the inherent Raman and infrared intensities of the C−H and C−D stretch. The vibrational spectra reveal evidence that both 1:1 and 2:1 (2 chloroform to 1 DMSO) complexes form and that the intensity enhancement of the C−H or C−D stretch is larger for the first than the second hydrogen bond. The general features of the hydrogen-bonded C−H and C−D stretch are compared to those of other hydrogen-bonded systems, and possible explanations for the intensity enhancement are considered.

1. Introduction

Exploring the interactions between molecules in the condensed phase continues to be a challenging problem. Vibrational spectroscopy has proven to be a powerful tool for unraveling the mysteries of molecular liquids. It has been shown experimentally and theoretically that solute−solvent interactions can have a measurable effect on the frequencies and intensities of infrared and Raman bands.[1−7] These effects can be attributed to specific intermolecular interactions or bulk dielectric effects.

In this work, we present vibrational spectra of $CHCl_3$/DMSO-d_6 and $CDCl_3$/DMSO-h_6 solutions which provide evidence for the formation of hydrogen-bonded complexes between chloroform and DMSO. The hydrogen-bonding interaction, while of great biological significance and part of the practicing chemist's stock in trade, is not always a well-defined concept. In the solid phase, unusually short distances between atoms A and B from X-ray crystallography are often inferred as evidence of A−H···B hydrogen bonding. In the case of solution phase interactions, it is necessary to draw upon thermodynamic and spectroscopic evidence of hydrogen bonding. The red-shifting and broadening of A−H stretching vibrations is a commonly observed consequence of hydrogen bonding.[8,9] Recent work has also identified signatures of hydrogen bonding in other types of vibrational modes.[10−12] In this work, we compare spectroscopic data as a function of concentration and temperature to previously reported thermodynamic data for the same system. We discuss the apparent intensity enhancement of the C−H stretch or C−D stretch of chloroform upon interaction with DMSO.

Chloroform is an interesting molecule in that the C−H bond is not usually polar enough to serve as a proton donor in a hydrogen bond; however, three electronegative chlorine atoms act in concert to withdraw electrons and polarize the C−H bond. Chloroform does not appear to hydrogen bond with itself, as the molar entropy of vaporization is in accordance with Trouton's rule. However, it is believed that chloroform can serve as a proton donor, as in the textbook example of the nonideal solution between chloroform and acetone, where heteromolecular attractive interactions are attributed to hydrogen bonding. Previous studies of chloroform−DMSO mixtures have indicated that both 1:1 and 2:1 complexes (2 chloroforms to 1 DMSO) are formed.[13−15] Equilibrium constants at 296 K based on NMR data have been reported to be 2.6 and 1.6 for the 1:1 and 2:1 complexes, respectively, in units of mole fraction.[13] Another study based on thermodynamic data[14] reported equilibrium constants of 1.2 and 4.5, respectively. Excess surface tension measurements over a range of concentrations were found to be negative, indicating attractive intermolecular interactions.[16] The excess thermodynamic functions Gibbs free energy (G^E), entropy (TS^E), and enthalpy (H^E) were found to have minima of about −1 kJ/mol, −2 kJ/mol, and −3 kJ/mol, respectively, at a DMSO mole fraction of about 0.4, at 298 K.[17] Enthalpies of formation obtained for the 1:1 (ΔH_1) and 2:1 (ΔH_2) complexes were reported to be −11 and −16 kJ/mol, respectively.[14] Other studies of chloroform−DMSO mixtures have included measurements of vapor pressures[17] and excess volumes of mixing.[14]

Thus, there is a great deal of evidence for attractive interactions between chloroform and DMSO, and it is reasonable to attribute them to hydrogen bonding. This type of interaction is expected to play an important role in governing the structure and dynamics in the condensed phase and to have distinct consequences on the vibrational spectra. The 1:1 complex likely involves the hydrogen of chloroform coordinated to one of the lone pairs of the oxygen atom on DMSO or possibly to the lone pair on the sulfur. The 2:1 complex may involve both lone pairs on the oxygen or possibly one oxygen lone pair and the lone pair on the sulfur, or even both. It is expected that the C−H (C−D) stretching vibration of chloroform will be rather sensitive to hydrogen-bonding interactions with DMSO. This totally symmetric mode has strong Raman and IR intensity, so vibrational spectroscopic studies were undertaken in order to investigate the nature of the intermolecular interaction. Normal-coordinate analysis, Raman and infrared spectra for DMSO-h_6 and -d_6 have been published.[19,20] Assignments for $CHCl_3$ and $CDCl_3$ vibrational bands and literature references may be found in the book by Herzberg.[21]

In neat $CHCl_3$ the C−H stretch occurs at 3018 cm^{-1} in the Raman and at 3019 cm^{-1} in the infrared. The C−D stretch of pure $CDCl_3$ occurs at 2256 cm^{-1} in the Raman and 2253 cm^{-1}

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in the infrared. In solution with DMSO-d_6, the C−H stretch of $CHCl_3$ is free from overlap with any DMSO-d_6 bands.[19,20] However, in solution with DMSO-h_6 there is much overlap with the 2995 cm^{-1} Raman band of DMSO-h_6, which is described mainly as an antisymmetric CH_3 stretch.[20] Likewise, the C−D stretch of $CDCl_3$ is free from overlap with any DMSO-h_6 bands but overlaps the 2249 cm^{-1} band (Raman) of DMSO-d_6 which is described as a CD_3 stretch.[20] Therefore, in order to study the C−H (C−D) stretch as cleanly as possible, the infrared and Raman spectra of solutions of $CHCl_3$ in DMSO-h_6 and $CDCl_3$ in DMSO-d_6 were investigated. When discussing features common to both of these solutions, the terms "chloroform" and "DMSO" will be used to denote either the deuterated and protonated species. We will also use the term "hydrogen bond" for both the A−H···B and A−D···B type complexes. The symbols X_h and X_d will be used to denote the mole fractions of DMSO-h_6 and DMSO-d_6, respectively.

2. Experimental Section

Raman spectra were obtained using a conventional 90° scattering arrangement with incident radiation polarized perpendicular to the scattering plane. The scattered light was focused onto the entrance slit of a Spex 1401 double monochromator. A photomultiplier tube after the exit slit measured the signal which was then sent to a computer coupled to the monochromator. A polarization filter followed by polarization scrambler was placed between the sample and the entrance slit to obtain polarized and depolarized Raman spectra. Excitation was provided by the 514 nm line of a Coherent Innova 400 Ar^+ laser. The temperature of the sample was held constant by flowing temperature-controlled water through a brass jacket which surrounded the sample cell. Spectral slits were kept between 220 and 250 μm (2.7−3.1 cm^{-1}). Laser power was 200−300 mW. Scanning rates varied between 0.2 and 1 cm^{-1}/s. The signal was usually integrated every 0.5 cm^{-1} and for longer scans every 1 cm^{-1}. IR spectra were obtained with a Bomem MB-100 FTIR instrument using KBr plates. The path length was held to less than 0.5 mm, and all IR spectra were taken at room temperature. The spectral resolution was 2 cm^{-1} for all scans.

$CDCl_3$ was purchased from Cambridge Isotope Labs and was of 99.9% purity or better. DMSO-h_6 and $CHCl_3$ were purchased from Fisher and were ACS grade or better. The DMSO-d_6 was purchased from Sigma. The ethanol stabilizer present in the chloroform was removed by shaking with $CaCl_2$ and then filtering through Celite. Further purification included distillation over molecular sieves and storage under dry N_2 in dark bottles. DMSO-h_6, DMSO-d_6, and $CDCl_3$ were used without further purification but were stored over molecular sieves under dry N_2 and shielded from light. Other solvents used in this study were purchased from Sigma or Aldrich and were of HPLC grade or better and used without further purification.

3. Raman and IR Spectra

The Raman and IR spectra of neat $CHCl_3$ and $CDCl_3$ in the C−H and C−D stretching region are shown in Figures 1a and 2a, respectively. The fwhm of the Raman bands are 10 and 7 cm^{-1} for the C−H and C−D stretch, respectively. For the IR bands the fwhm is about 13 cm^{-1} for the C−H stretch and 9 cm^{-1} for the C−D stretch. The asymmetry of the band shapes probably arises from overlap with combination or overtone bands. In the Raman and IR spectra of $CHCl_3$ weak bands appearing at 2970 and 3070 cm^{-1} are clearly evident. These bands were also observed by other researchers who tentatively

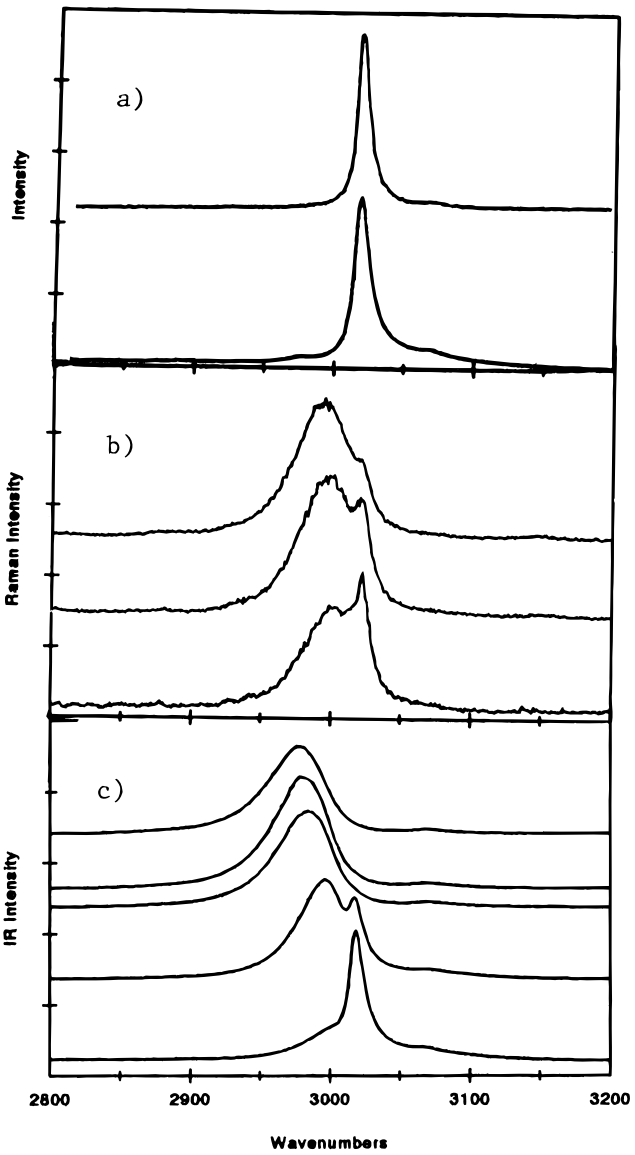

Figure 1. (a) Raman (top) and IR (bottom) spectra of $CHCl_3$ in the C−H stretching region. (b) Raman spectra of $CHCl_3$/DMSO-d_6 mixtures. Mole fraction of DMSO-d_6 from top to bottom: 0.53, 0.43, and 0.33. (c) IR spectra of $CHCl_3$/DMSO-d_6 mixtures. Mole fraction of DMSO-d_6 from top to bottom: 0.63, 0.53, 0.43, 0.11, and 0.022.

assigned them to various combination bands.[22] Weaker bands were also observed around 2900 cm^{-1}. In neat $CDCl_3$ no bands aside from the C−D stretch are evident in either the IR or Raman spectra, but the asymmetry of the bands suggests that there may be possible overlap with weak combination or overtone bands which complicate the spectra.

In both the IR and Raman spectra of $CHCl_3$/DMSO-d_6 mixtures, a new and much broader band appears at a lower frequency relative to the C−H stretch in neat solvent, as shown in Figure 1b,c. This phenomenon is also seen in the Raman and IR spectra of $CDCl_3$/DMSO-h_6 mixtures in which a broad new band appears at a lower frequency relative to the C−D stretch, as shown in Figure 2b,c. This is interesting since as stated before there are no bands present in the C−H stretching region for either the IR or Raman spectra of neat DMSO-d_6. Similarly, there are no bands evident in the IR or Raman spectra of neat DMSO-h_6 in the region of the C−D stretch for $CDCl_3$. The spectra in each of the series shown in Figures 1b,c and 2b,c span a range of DMSO mole fractions and have all been scaled to the same maximum intensity. In both mixtures the low-frequency band (I_-) appears to gain intensity from the high-

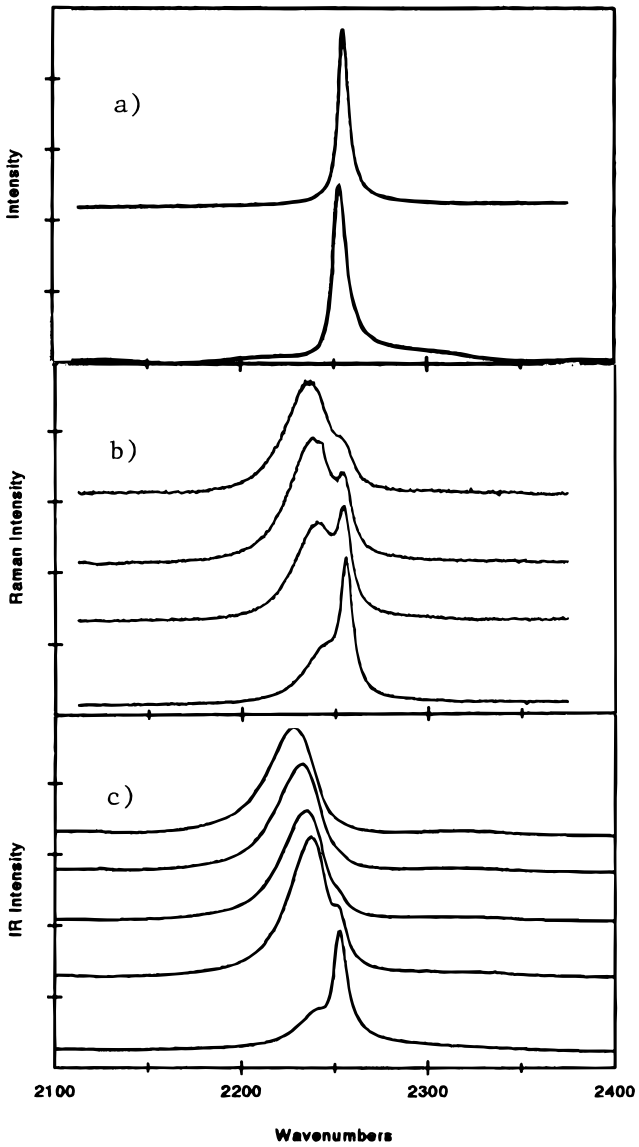

Figure 2. (a) Raman (top) and IR (bottom) spectra of $CDCl_3$ in the C−D stretching region. (b) Raman spectra of $CDCl_3$/DMSO-h_6 mixtures. Mole fraction of DMSO-h_6 from top to bottom: 0.53, 0.43, 0.33, and 0.18. (c) IR spectra of $CDCl_3$/DMSO-h_6 mixtures. Mole fraction of DMSO-h_6 from top to bottom: 0.53, 0.33, 0.12, and 0.024.

TABLE 1: Data for Raman Spectra of $CHCl_3$/DMSO-d_6 Mixtures

X_d	ν_- (cm^{-1})	ν_+ (cm^{-1})	I_-/I_+	$\Delta\nu_-$ (cm^{-1})	$\Delta\nu_+$ (cm^{-1})
0.33	3000 ± 1	3022 ± 1	5	53	10
0.43	2997 ± 1	3022 ± 1	10	56	12
0.53	2993 ± 1	3022 ± 2	50	55	11

TABLE 2: Data for Raman Spectra of $CDCl_3$/DMSO-h_6 Mixtures

X_h	ν_- (cm^{-1})	ν_+ (cm^{-1})	I_-/I_+	$\Delta\nu_-$ (cm^{-1})	$\Delta\nu_+$ (cm^{-1})
0.18	2243 ± 2	2256 ± 1	1	27	8.5
0.33	2241 ± 1	2255 ± 1	10	34	8.4
0.43	2238 ± 1	2255 ± 1	20	33	8.2
0.53	2235 ± 1	2256 ± 1	30	32	8.4

frequency band (I_+), but both bands eventually disappear as the DMSO mole fraction tends to one.

The data from this series of Raman and IR spectra are summarized in Tables 1−4. These tables include the peak positions (ν_+ and ν_-) for the high- and low-frequency bands, respectively. Also included is the ratio of peak areas (I_-/I_+) and the full width at half-maximum intensity (fwhm) $\Delta\nu_+$ and

TABLE 3: Data from IR Spectra of $CHCl_3$/DMSO-d_6 Mixtures

X_d	ν_- (cm^{-1})	ν_+ (cm^{-1})	I_-/I_+	$\Delta\nu_-$ (cm^{-1})	$\Delta\nu_+$ (cm^{-1})
0.022	3005 ± 3	3018 ± 1	1	45	13
0.11	2997 ± 1	3018 ± 1	10	44	12
0.43	2984 ± 1	NA	NA	47	NA
0.53	2979 ± 1	NA	NA	44	NA
0.63	2977 ± 1	NA	NA	49	NA

TABLE 4: Data from IR Spectra of $CDCl_3$/DMSO-d_6 Mixtures

X_h	ν_- (cm^{-1})	ν_+ (cm^{-1})	I_-/I_+	$\Delta\nu_-$ (cm^{-1})	$\Delta\nu_+$ (cm^{-1})
0.024	2243 ± 2	2253 ± 1	3	30	10
0.12	2238 ± 1	2252 ± 1	30	28	9
0.23	2235 ± 1	2252 ± 2	NA	28	NA
0.33	2232 ± 1	NA	NA	28	NA
0.53	2228 ± 1	NA	NA	30	NA

$\Delta\nu_-$ for both bands. The ratio of peak areas was calculated by fitting the spectra to two bands which were each 50% Lorentzian and 50% Gaussian in character. This introduces some error in the case of the IR spectra because the I_+ band, which appears to be the C−H (C−D) stretch of non-hydrogen-bonded chloroform, is inherently asymmetric. Furthermore, the overlapping combination bands which are especially evident in the IR spectra of $CHCl_3$/DMSO-d_6 mixtures at low concentration of DMSO-d_6 would also be expected to complicate the fitting. Thus, for the fitting of the IR spectra of $CHCl_3$/DMSO-d_6 mixtures, three bands were used to obtain the fit, where the third band was fit to the 3070 cm^{-1} combination band clearly evident in the IR spectra of neat $CHCl_3$ and the low DMSO-d_6 concentration mixtures. Though the fitting procedure is subject to errors in the assumed form of the underlying bands, it enables us to capture the trend in the relative areas of I_- and I_+ with concentration. No attempt was made to fit the IR spectra at high DMSO mole fractions where only one peak was observed, since fitting such a band to two peaks would be somewhat arbitrary. Therefore, some of the data in Tables 3 and 4 are not available. Examples of some fits to the Raman spectra of $CHCl_3$/DMSO-d_6 and $CDCl_3$/DMSO-h_6 mixtures are given in Figure 3a,b.

As seen in Tables 1−4, the position of the high-frequency band remains nearly constant with respect to changes in concentration for both mixtures. The low-frequency band, on the other hand, red shifts considerably and broadens with increasing DMSO concentration. The relative intensity I_-/I_+ increases with DMSO concentration. An interesting feature evident in the comparison of the Raman and IR spectra is the relative magnitude of I_-/I_+ with respect to concentration. For the IR spectra I_- appears as a distinct band at very low concentrations of DMSO, and by the time the mole fraction of DMSO reaches 0.2, the high-frequency band has nearly disappeared. In contrast, both bands are clearly present in the Raman spectra up to a mole fraction of DMSO equal to about 0.7. For comparable mixtures, it is also evident that the line width of I_- is broader in Raman than in infrared, opposite to the situation for neat chloroform where the IR band is broader than the Raman. Also, one notes that the fwhm $\Delta\nu_-$ in either Raman or IR is larger for the mixtures containing $CHCl_3$ than those with $CDCl_3$. This is the same trend as in neat chloroform, where the fwhm in either Raman or IR is greater for $CHCl_3$ than for $CDCl_3$. Finally, the relative intensity I_-/I_+ in either Raman or IR is about a factor of 2 larger for $CDCl_3$ mixtures than for $CHCl_3$ mixtures.

Polarized and depolarized Raman spectra were also obtained, and it was found that both bands are strongly polarized. For both mixtures, the depolarization for the I_+ and I_- bands were

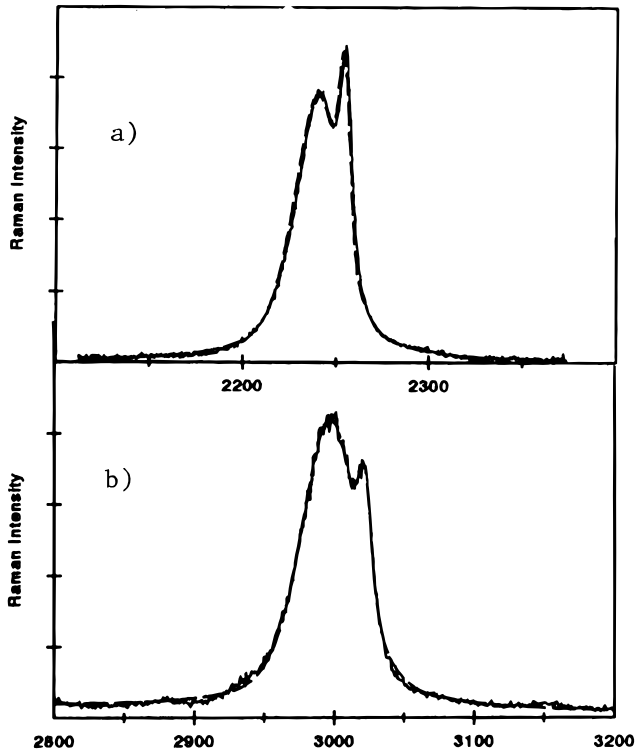

Figure 3. (a) Raman spectrum of $CDCl_3$/DMSO-h_6, $X_h = 0.33$. The solid line is the actual spectrum, and the dashed line is the fitted spectrum. (b) Raman spectrum of $CHCl_3$/DMSO-d_6, $X_d = 0.43$. The solid line is the actual spectrum, and the dashed line is the fitted spectrum.

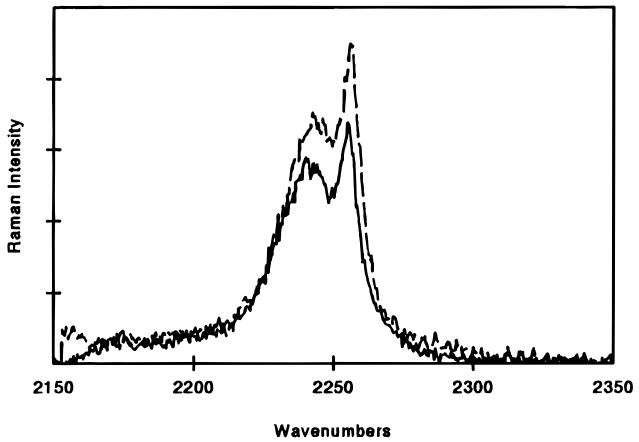

Figure 4. Raman spectrum of $CDCl_3$/DMSO-h_6, $X_h = 0.33$, at 14 °C (solid line) and 57 °C (dashed line).

determined to be about 0.2 and 0.1, respectively. The low depolarization ratios indicate that the vibrations associated with these bands are totally symmetric. The depolarization ratios of the C−D and C−H stretching bands for neat $CDCl_3$ and $CHCl_3$ were found to be 0.2 and 0.1, respectively.

The red-shifting and broadening of A−H vibrations on hydrogen bonding is a well-known effect.[8,9] Thus, we propose that the I_- band is due to the C−H or C−D stretch of hydrogen-bonded chloroform. For further insight into the effect, we examined the influence of temperature on the Raman spectra of $CDCl_3$/DMSO-h_6 mixtures in the C−D stretching region. Figure 4 shows the Raman spectra for mole fraction of DMSO-h_6 equal to 0.33 at temperatures of 14 and 57 °C. Surprisingly, the intensity ratio of the two peaks (I_-/I_+) is the same for both spectra, within experimental error. (The intensities are not normalized in Figure 4, so the apparently higher intensity at higher temperature is not meaningful.) Table 5 shows temperature data for solutions of DMSO-h_6 with X_d equal to 0.33 and 0.53. Although the temperature change results in little change in relative intensity, the peak frequency ν_- is blue-shifted by a few wavenumbers on going from 14 to 57 °C. The peak frequency ν_+ undergoes only a slight blue shift with increase in temperature. These results will be considered further below, where they are compared to the calculated change in concentration of hydrogen-bonded complexes.

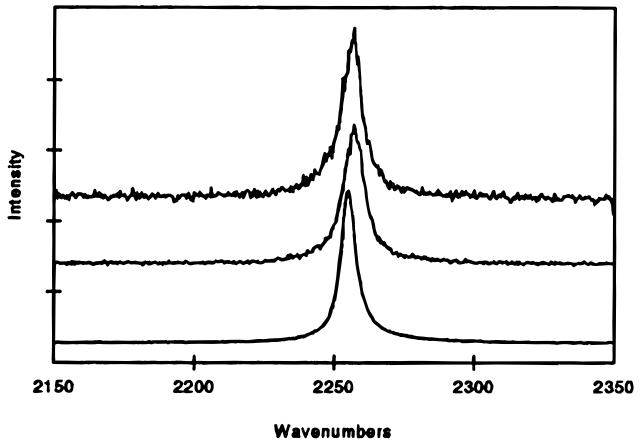

Figure 5. Raman spectra of $CDCl_3$/acetone mixtures. From top to bottom the mole fraction of $CDCl_3$ is 0.28, 0.48, and 1.0. Intensity units are arbitrary.

TABLE 5: Effect of Temperature on the Raman Spectra of $CDCl_3$/DMSO-h_6 Mixtures at DMSO-h_6 Mole Fraction of 0.33 and 0.53

X_d	temp (°C)	ν_- (cm^{-1})	ν_+ (cm^{-1})	I_-/I_+	$\Delta\nu_-$ (cm^{-1})	$\Delta\nu_+$ (cm^{-1})
0.33	14	2241	2255	3	28	7.3
	57	2243	2256	3	30	7.7
0.53	14	2234	2255	30	29	7.3
	54	2237	2256	30	32	8.7

Since it has been reported that chloroform and acetone form 1:1 and possibly 2:1 hydrogen-bonded complexes,[5,23,24] we measured the Raman and IR spectra of some acetone−chloroform mixtures in order to compare to those obtained for DMSO−chloroform. Raman spectra of $CDCl_3$ dissolved in acetone with mole fraction of $CDCl_3$ equal to 0.28 and 0.48 were examined in the C−D stretching region. The spectra are shown in Figure 5. Unlike the Raman spectra of $CDCl_3$/DMSO-h_6 and $CHCl_3$/DMSO-d_6 mixtures, only one band is evident, though there is a slight increase in bandwidth compared to neat chloroform. These results are similar to those obtained by other researchers who studied $CDCl_3$/acetone mixtures with IR spectroscopy.[2,5,25] Equilibrium constants in units of mole fraction for the formation of the 1:1 complex acetone−chloroform were reported by various researchers to be between 0.35 and 1.03 at 293 K.[23] These are somewhat smaller than the reported values for DMSO−chloroform, namely 1.2 from ref 14 and 2.6 from ref 13. In addition, the excess enthalpy of mixing of acetone−chloroform is about −2 kJ/mol, compared to −3 kJ/mol for DMSO−chloroform.[14] The thermodynamic data thus suggest that hydrogen bonds in DMSO-chloroform are stronger than in acetone−chloroform. Our spectroscopic evidence also supports this conclusion, since one expects a greater red shift of the C−H (or C−D) stretch with increasing hydrogen bond strength.

4. Discussion of Spectra

It is hypothesized that the high- and low-frequency bands are due to the C−H or C−D stretch of free and hydrogen-bonded chloroform, respectively. Several features of the I_+ band

TABLE 6: Comparison of the Calculated Ratio of 1:1 to 2:1 Hydrogen-Bonded Complexes to the Intensity Ratio I_-/I_+ for $CDCl_3$/DMSO-h_6 Mixtures[a]

X_d	P	I_-/I_+ (IR)	I_-/I_+ (Raman)	$X_{1:1}/X_{2:1}$
0.024	0.038	3	NA	0.31
0.12	0.25	30	NA	0.34
0.18	0.43	NA	1	0.36
0.33	10	NA	10	0.60
0.43	1.4	NA	20	0.83
0.53	1.6	NA	33	1.1

[a] P is defined as the ratio of total number of chloroform molecules which are hydrogen bonded to the number of free chloroform molecules. Also shown is the calculated ratio of the mole fractions of the 1:1 and 2:1 complexes.

lend credence to the hypothesis that it is due to free chloroform. Perhaps the most convincing evidence is that the peak position and bandwidth remain nearly constant with respect to changes in concentration. In contrast, the lower frequency band tends to broaden and red shift as DMSO is added, suggesting it is due to the hydrogen-bonded C−H or C−D stretch. One explanation for band broadening due to hydrogen bonding is that a distribution of frequency shifts results from a range of different environments for the A−H bond;[26,27] i.e., it is inhomogeneously broadened. Alternatively, the breadth of the A−H stretching vibration could result from an underlying progression in the low-frequency stretch of the hydrogen bond.[26−28] It should be noted that since both the I_+ and I_- peaks disappear at high DMSO concentration, it is reasonable to associate both of them with chloroform.

Our assignment of the I_- band to hydrogen-bonded chloroform is consistent with thermodynamic evidence for strong attractive interactions of this type in DMSO−chloroform solutions.[13−15] Therefore, it is of interest to compare the calculated concentration ratio of complexed to free chloroform, ($P = C_{comp}/C_{free}$) using published equilibrium constants, with the observed intensity ratio I_-/I_+ from IR and Raman spectra. Table 6 compares the experimentally determined values of I_-/I_+ to the calculated ratio P. We chose the equilibrium constants $K_1 = 1.2$ and $K_2 = 4.5$ reported in ref 14 to calculate C_{comp} as the total concentration of complexed chloroform in both the 1:1 and 2:1 forms. In either Raman or IR, the intensity ratio I_-/I_+ increases with increasing concentration of DMSO for both mixtures. It has been previously observed that hydrogen bond formation leads to enhancement of the infrared intensity of A−H stretching.[9,31,33] If only one kind of complex were present (e.g., the 1:1), then the ratio I_-/I_+ would exceed the ratio $P \equiv C_{comp}/C_{free}$ by this enhancement factor, and the enhancement factor would be the same at all mole fractions. Comparing the IR data for $CDCl_3$/DMSO-h_6 mixtures having $X_h = 0.024$ and 0.12, the calculated ratios P are 0.04 and 0.25, respectively, and the corresponding values of I_-/I_+ are 2.5 and 33. In other words, as the relative amount of complexed chloroform increases by a factor of about 6, the intensity ratio increases by a factor of about 13. Inspection of the Raman data, for example the solutions having $X_d = 0.33$ and 0.43 in Table 6, shows that as the calculated concentration ratio P goes from 1.0 to 1.4, the intensity ratio I_-/I_+ increases from about 10 to about 20. In both these examples, the intensity ratio increases by a factor larger than that for the increase in the concentration ratio. This suggests that there is considerable contribution from more than one hydrogen-bonded species, presumably the 1:1 and 2:1 forms. The data indicate that intensity enhancement is observed in both the Raman and the infrared but that it is larger in the infrared.

As the DMSO mole fraction increases from 0.02 to 0.5, the calculated concentration ratio of the mole fractions of the 1:1 to 2:1 complexes, $X_{1:1}/X_{2:1}$, increases from about 0.3 to 1.0, as shown in Table 6. Thus, we may assume that as the DMSO mole fraction increases, the relative amount of the 2:1 complex decreases. The corresponding trend in I_-/I_+ can be rationalized if the inherent Raman or IR intensity of the C−H stretch in the 2:1 complex is less than that of the 1:1 complex, when compared on a "per bond" basis. In the 2:1 complex, the C−H stretch splits into symmetric and antisymmetric modes. In the absence of perturbations to the electronic structure, the total Raman or IR intensity of both of these modes should be conserved. In other words, the intensity for two C−H bond stretches is redistributed between the symmetric and antisymmetric modes. Thus, mere formation of the 2:1 complex alone cannot account for the intensity data unless the perturbation to the transition moment of the C−H bond is different for the 1:1 and 2:1 complexes. In particular, the data suggest that the transition moment increase on hydrogen bonding is greater for the first hydrogen bond than for the second. It has been previously observed that infrared intensity enhancement of the A−H stretch increases with hydrogen bond strength.[8] The thermodynamic data for DMSO−chloroform indicate that the first hydrogen bond is stronger than the second, since ΔH is −11 kJ/mol for the first and −5 kJ/mol for the second hydrogen bond.[14] Thus, the spectroscopic data are consistent with the idea of 1:1 and 2:1 complexes, where the first hydrogen bond is stronger than the second, though it remains to explain the basis for the intensity enhancement. The intensity trends are consistent with the increasing red shift of ν_- as DMSO mole fraction increases. If the average hydrogen bond strength is less in the 2:1 complex than in the 1:1, than the red shift of the C−H or C−D stretch should be greater for the 1:1 complex. As more DMSO is added to chloroform, the proportion of 2:1 complexes drops and the number of 1:1 complexes increases, leading to an apparent red shift of the I_- band, which is presumed to consist of unresolved overlapping bands of the 1:1 and 2:1 complexes.

Much experimental evidence has been previously presented for IR intensity enhancement and red-shifting of hydrogen bonded A−H stretches. Infrared intensity enhancement of the C−H (C−D) stretch of hydrogen-bonded $CHCl_3$ ($CDCl_3$) has been reported previously.[2,5,23,25] Huggins et al.[2] observed large IR intensity enhancement of the C−D stretch of $CDCl_3$ dissolved in acetone. The IR intensity of the O−H bond in ice has been found to increase by a factor of 20 on formation of strong hydrogen bonds.[33] It has been reported that the infrared intensity of the hydrogen-bonded phenol O−H stretch increases with base strength and that the increasing red shift of this band (as hydrogen bond strength increases) correlates with increasing intensity.[8] The enhancement effect has also been observed in gas phase hydrogen-bonded complexes.[29] Previous studies of intensity enhancement of hydrogen-bonded A−H stretches seem to have been limited to the infrared. In this work, we find the hydrogen bonding leads to intensity enhancement in the Raman as well, but apparently to a lesser degree.

For example, the I_- peak is more easily observed at low concentrations of DMSO in the IR spectra relative to the Raman spectra. In the IR spectra the I_- peak contains most of the intensity relative to I_+ even at mole fractions of DMSO as low as 0.1. By the time the mole fraction of DMSO is raised to about 0.2, the I_- peak dominates the IR spectra relative to the I_+ peak. At this concentration, there are four chloroform molecules for every DMSO molecule and thus a considerable amount of free chloroform. Thus, we cannot dismiss the intensity enhancement as due to errors in the published equilibrium constants. We are forced to conclude that the inherent infrared and Raman intensity of the C−H or C−D stretch is much larger in the hydrogen-bonded complex.

It is also significant that, for the same concentration of DMSO in chloroform, the intensity enhancement is generally greater for the $CDCl_3$/DMSO-h_6 complex than for $CHCl_3$/DMSO-d_6, in either the Raman or the infrared. One would *not* expect the C−D···B and C−H···B hydrogen bond strengths to be very different in this system, as there is little change in the reduced mass for the dissociation coordinate. If the hydrogen bond strength depended strongly on isotope, we would probably observe a larger red shift of the C−D or C−H stretch for the more strongly bound species, and in fact the red shifts, like the peak frequencies of the bound and free stretch, are roughly in the expected ratio ν (C−H)/ν(C−D) $\approx \sqrt{2}$. Thus, the isotope effect on the intensity probably reveals something about the nature of coupling between the hydrogen bond dissociation coordinate and that of the C−H or C−D stretch, rather than the strength of the hydrogen bond. This will be considered further below.

Although one can envision how formation of a hydrogen bond can increase both the dipole moment derivative and the polarizability derivative (with respect to the C−H or C−D stretching coordinate), the fact that enhancement of both Raman and infrared intensities is observed suggests a common explanation. Some possible explanations will be considered below.

We expected that increasing the temperature would decrease the proportion of hydrogen-bonded complexes and thus decrease the intensity of I_- relative to I_+. As seen in Table 5, the intensity ratio for mixtures of $CDCl_3$ and DMSO is constant with respect to temperature within experimental error. However, it was not possible to vary the temperature over a large range, due to the fact that neat DMSO freezes at 18 °C and $CDCl_3$ boils at 61−62 °C. A definite blue shift of the I_- band was observed as the temperature was increased. This is consistent with a weakening of the hydrogen bond with increasing temperature.

From the data of Fenby and Helper,[14] the equilibrium constants for the 1:1 and 2:1 complex were obtained for temperatures of 14 and 57 °C from the van't Hoff equation.[32] The ratio of the number of complexed $CHCl_3$ molecules to the number of free $CHCl_3$ molecules at equilibrium was then calculated for temperatures of 14 and 57 °C. For a DMSO mole fraction of 0.5, 65% of the available chloroform is calculated to be complexed at 14 °C, while 51% is complexed at 57 °C. Given the large inherent intensity of the hydrogen-bonded species, the temperature increase should have led to an observable decrease in the intensity of the I_- band relative to I_+, which we did not observe. We suggest that this indicates that the actual enthalpies of formation of the hydrogen-bonded species may be larger (more negative) than those reported in ref 14. Indeed, in that work, it was assumed that the observed enthalpy of mixing was entirely due to the hydrogen-bonded species. The nonspecific interactions between DMSO and chloroform might be expected to contribute to a positive enthalpy of mixing, since the polarities of the neat liquids are quite different. (The dielectric constant of chloroform is about 5 while that of DMSO is about 48). Thus, the assumption of ref 14 might have underestimated the formation enthalpies of the complexes, as suggested by our data.

We have also investigated the Raman spectra of DMSO/chloroform mixtures in the spectral region from about 200 to 800 cm^{-1}.[34] In mixtures of $CHCl_3$ and DMSO-h_6, the symmetric C−Cl stretch of chlorooform is coincident in frequency with the symmetric C−S−C stretch of DMSO. This leads to intensity perturbations due to vibrational resonance coupling as discussed in ref 34. The frequencies and intensities of all other DMSO and chloroform bands in the 200−800 cm^{-1} range were found to be insignificantly perturbed compared to the neat liquid spectra. This suggests that the spectral perturbations reported in this work reflect specific interactions at the site of the chloroform C−H or C−D bond.

The possibility was considered that the I_- and I_+ bands were the result of vibrational resonance coupling (VRC). Whether such coupling is intermolecular or intramolecular in nature (the latter is commonly referred to as Fermi resonance), the observed frequency splitting and intensity borrowing between the two coupled modes would depend on the existence of nearly coincident vibrational frequencies of the unperturbed modes.[34,35] The similarity of the spectra in both $CHCl_3$/DMSO-d_6 and $CDCl_3$/DMSO-h_6 mixtures eliminates VRC as a possible mechanism, since isotope shifts of vibrational frequencies would make it highly unlikely for a pair of vibrational states to be resonant in both mixtures.[35]

Finally, since both solutions in this study involve a mixture of nondeuterated and deuterated species, it is necessary to consider the possibility of hydrogen−deuterium exchange. Fortunately, this mechanism is easily ruled out because if such an exchange were taking place, characteristic bands related to the deuterated species would be evident in the spectra, and these are clearly absent. Moreover, when it is taken into account that the acid dissociation constant for a hydrogen attatched to a methyl group is $<10^{-40}$, hydrogen/deuterium exchange appears to be a very unlikely possibility.[36]

5. Discussion of Spectral Consequences of Hydrogen Bonding

We have shown that interaction with DMSO leads to significant changes in width, frequency, and intensity of the chloroform C−H or C−D stretch, due to hydrogen bonding. The concentration dependence of these spectral perturbations can be understood in terms of relative changes in the amount of 1:1 and 2:1 complexes as well as the total proportion of complexed chloroform. The red shift of an A−H bond on hydrogen bonding can be considered to result from depletion of electron density from the A−H bond. The basis for the increase in bandwidth is less certain, in particular, whether it is homogeneously or inhomogeneously broadened. Homogeneous broadening of the hydrogen-bonded A−H stretch ν_s can result from progressions in the low-frequency complex vibrations, in particular the hydrogen bond stretching frequency, ν_σ. The ν_σ mode is presumably quite low in frequency, on the order of 100 cm^{-1}, and bending vibrations of the hydrogen bond would be lower still. Arrivo and Heilwiel[37] recently reported picosecond FTIR studies of the O−H stretch in the complex between triethylsilanol and acetonitrile. They concluded that the band is *homogeneously* broadened. The general features of the vibrational spectra of DMSO−chloroform are similar to those reported for triethylsilanol/acetonitrile: a sharp band due to free O−H and a broad red-shifted band due to O−H···N. The extreme sensitivity of the A−H stretching intensity to hydrogen bond strength suggests that the coordinates for ν_s and ν_σ are strongly coupled. Thus, we will consider whether this sort of coupling can explain the observed Raman and infrared data and their dependence on isotope.

Let the normal coordinate for the high-frequency mode ν_s (the C−H or C−D stretch) be called q and that for the low-frequency hydrogen bond stretch ν_σ be called Q. It has been suggested[29,30] that the breadth of the ν_s band in the complex can be attributed to anharmonic coupling, e.g., a potential energy term Vq^2Q. Alternatively, one can consider the frequency ν_s to be a linear function of Q. The time-scale separation of the high- and low-frequency vibrations, analogous to the Born−

Oppenhiemer separation of electron and nuclear motions, leads to a picture like that employed in the analysis of vibrational progressions in electronic spectra. The potential energy as a function of Q depends on the vibrational state for the C−H or C−D stretch. If the intermolecular distance at equilibrium (the minimum in this potential) changes when the fundamental of ν_s is excited, then the fundamental transition of ν_s will be accompanied by a progression in the ν_σ vibration. If one makes a Condon-like approximation, i.e., the transition moment is assumed independent of the coordinate Q, then this mechanism would contribute the *same line width* to the Raman and the infrared spectra. In the IR, the total intensity would be proportional to the square of the dipole derivative $\mu' \equiv (d\mu/dq)_0$, while the Raman intensity would depend on the polarizability derivative $\alpha' \equiv (d\alpha/dq)_0$. Though these may be differently perturbed by hydrogen bonding, the assumptions of the mechanical coupling model lead to a conclusion which is in conflict with our observation that the Raman line widths are larger than the infrared line widths. However, if one postulates electrical anharmonicity in addition to mechanical anharmonicity, then additional line-shaping effects could result from the Q dependence of μ' and α', causing the line widths in Raman and IR to differ. The Q dependence of μ' and α' can also contribute to the intensity enhancement, which in a sense derives from intensity borrowing from the ν_σ vibration. Thus, electrical anharmonicity could be responsible for both the line shape and intensity differences in Raman and IR. It is conceivable that hydrogen bonding leads to a larger change in the magnitude of μ' than α' but that the latter is a stronger function of hydrogen bond distance. This is worthy of further study.

We have recently shown that vibrational resonance coupling can lead to particularly large intensity perturbations for low-frequency modes.[34] The effect is a strong function of the relative distance and orientation of the coupled molecules. If the red-shifted C−H or C−D stretch is a combination involving overtones of a low-frequency mode of the complex, then vibrational resonance coupling could be responsible in part for the highly nonlinear dependence of I_-/I_+ on DMSO mole fraction. We do not think this effect is the only reason for the intensity enhancement, however, as studies have shown that infrared enhancement of hydrogen-bonded A−H vibrations is possible in isolated complexes.[9,29,31] Nevertheless, it is important to keep in mind that more than one effect may complicate the analysis of vibrational intensity in solution phase hydrogen-bonded complexes.

The isotope effects on the line width and intensity are also worth considering. For the same mixture, in either IR or Raman, the line widths are larger for the complex with $CHCl_3$ than $CDCl_3$. This is in accord with the mechanical coupling model[29,30] discussed above. We observe an approximately 2-fold greater intensity enhancement of I_- compared to I_+ in the case of the complex with $CDCl_3$, in either Raman or IR. While this is further evidence of coupling between ν_s and ν_σ, it is difficult to rationalize the direction of the change, except to postulate stronger coupling in the case where the frequencies of ν_s and ν_σ are less widely separated. The mechanical coupling model leads to the prediction that the I_- band intensity decrease by $\sqrt{2}$ on replacing hydrogen by deuterium, but the intensity of the free C−H stretch (the I_+ band) decreases by the same factor on deuteration. Again, the data suggest that electrical anharmonicity plays an important role in the intensity enhancement effect; otherwise, the ratio I_-/I_+ would be insensitive to deuteration.

Finally, we would like to place this work in perspective by comparing our data to vibrational spectroscopic studies of other hydrogen-bonded complexes. Figure 6 compares the line width of the methanol O−H stretch in the neat liquid to the C−H stretch in a DMSO−chloroform mixture. Clearly, the line width in methanol greatly exceeds that of the hydrogen-bonded C−H or C−D stretch of chloroform. The hydrogen bonds in methanol are probably stronger and there is no doubt more inhomogeneous broadening due to the coexistence of various hydrogen-bonded oligomers. The acetone−chloroform system, on the other hand, appears to be less strongly interacting than the subject of this study, since hydrogen bonding leads to a small increase in line width and no observable red shift of the chloroform C−H or C−D stretch. Nevertheless, intensity enhancement of this vibration has been observed and attributed to hydrogen bonding.[2] This suggests that intensity enhancement may serve as a very sensitive indicator of these types of intermolecular interactions. We hope the results presented here will stimulate further studies of intensity effects in hydrogen-bonded systems.

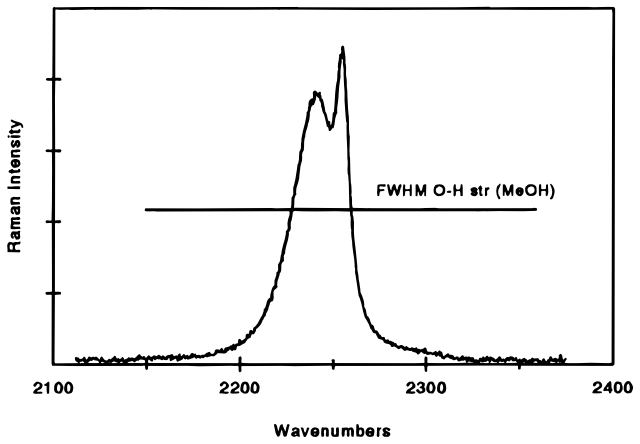

Figure 6. Raman spectrum of $CDCl_3$/DMSO-h_6, with $X_h = 0.33$. Superimposed is the fwhm of the O−H stretch of methanol.

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References and Notes

(1) Schwiezer, K. S.; Chandler, D. *J. Chem. Phys.* **1982**, *76*, 2296.
(2) Huggins, C. M.; Pimentel, G. C. *J. Chem. Phys.* **1955**, *23*, 895.
(3) Akins, D. L. *J. Phys. Chem.* **1986**, *90*, 1530.
(4) Mortenson, A.; Nielsen, O. F.; Yarwood, J.; Shelley, V. *J. Phys. Chem.* **1995**, *99*, 4435.
(5) Lord, R. C.; Nolin, B.; Stidham, H. D. *J. Am. Chem. Soc.* **1955**, *77*, 1365.
(6) McHale, J. L. *Int. J. Quantum Chem. Symp.* **1991**, *25*, 593.
(7) Veas, C. H.; McHale, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 7042.
(8) Laurence, C.; Guiheneuf, G.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1979**, *101*, 4793.
(9) Bakkas, N.; Bouteiller, A.; Loutellier, A.; Perchard, J. P.; Racine, S. *J. Chem. Phys.* **1993**, *98*, 5982.
(10) (a) Triggs, N. E.; Bonn, R. T.; Valentini, J. J. *J. Phys. Chem.* **1993**, *97*, 5535. (b) Dixon, D. A.; Dobbs, K. D.; Valentini, J. J. *J. Phys. Chem.* **1994**, *98*, 13435.
(11) Mayne, L. C.; Hudson, B. *J. Phys. Chem.* **1991**, *95*, 2962.
(12) Wang, Y.; Purello, R.; Georgiou, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1991**, *113*, 6369.
(13) McClellan, A. L.; Nicksic, S. W.; Guffy, J. C. *J. Mol. Spectrosc.* **1963**, *11*, 340.
(14) Fenby, D. V.; Helper, L. G. *J. Chem. Thermodyn.* **1974**, *6*, 185.
(15) Rintoul, L.; Shurvell, H. F. *J. Raman Spectrosc.* **1990**, *21*, 501.
(16) Agarwal, D. K.; Gopal, R.; Agarwal, S. *J. Chem. Eng. Data* **1979**, *24*, 181.
(17) Philipe, R.; Jambon, C.; Clechet, P. *J. Chem. Thermodyn.* **1973**, *5*, 431.

(18) Lau, C. F.; Wilson, P. T.; Helper, D. V. *Aust. J. Chem.* **1970**, *23*, 1143.
(19) Horrocks, W. D.; Cotton, F. A. *Spectrochim. Acta* **1961**, *17*, 134.
(20) Forel, M. T.; Tranquille, M. *Spectrochim. Acta* **1970**, *26A*, 1023.
(21) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand: New York, 1945.
(22) Hinze, J. *Energy Storage and Redistribution in Molecules*; Plenum Press: New York, 1983.
(23) Green, R. D. *Hydrogen Bonding by C-H Groups*; Halsted Press: New York, 1984.
(24) Kearns, E. R. *J. Phys. Chem.* **1961**, *65*, 314.
(25) Kagarise, R. E. *Spectrochim. Acta* **1963**, *19*, 629.
(26) Rothschild, W. G. *Dynamics of Molecular Liquids*; John Wiley & Sons: New York, 1984.
(27) Rothschild, W. G.; Moller, K. D. *Far-Infrared Spectroscopy*; Wiley-Interscience: New York, 1971.
(28) Tanbe, K. *J. Raman Spectrosc.* **1982**, *12*, 20.
(29) Maréchal, Y. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; John Wiley and Sons: Chichester, 1980; Vol. 1, pp 231−272.
(30) Bratos, S.; Lascombe, J.; Novak, K. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J. Eds.; John Wiley and Sons: Chichester, 1980; Vol. 1, pp 302−346.
(31) Lausch, C.; Lisy, J. M.; Huisken, F.; Kulcke, A. *J. Chem. Phys.* **1993**, *98*, 5982.
(32) Atkins, P. W. *Physical Chemistry*, 4th ed.; W. H. Freeman and Co.: New York, 1990.
(33) Green, J. L.; Lacey, A. R.; Sceats, M. G. *J. Phys. Chem.* **1986**, *90*, 3958.
(34) Daniel, D. C.; McHale, J. L. *J. Chem. Phys.* **1997**, *106*, 1699.
(35) Daniel, D. C. PhD Thesis, University of Idaho, 1996.
(36) March. J. *Advanced Organic Chemistry Reactions, Mechanisms and Structure*; McGraw-Hill Book Co.: New York, 1968.
(37) Arrivo, S. M.; Heilweil, E. J. *J. Phys. Chem.* **1996**, *100*, 11975.