

# Variation in IR and Raman Spectra of CD<sub>3</sub>CN upon Solvation of InCl<sub>3</sub> in CD<sub>3</sub>CN: Distinctive Blue Shifts, Coordination Number, Donor-Acceptor Interaction, and Solvated Species

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Notable blue shifts of the  $\nu_2$  C $\equiv$ N stretching,  $\nu_4$  C-C stretching and  $\nu_8$  CCN deformation bands of CD<sub>3</sub>CN are observed upon solvation of InCl<sub>3</sub>, resulting from the donor-acceptor interaction. The Raman spectrum in the  $\nu_2$  region shows further details; at least two new bands emerge on the blue side of the  $\nu_2$  band of free CD<sub>3</sub>CN, whose relative intensities vary with concentration, suggesting that there exist at least two different cationic species in the solution. The strong hydrogen bonds formed between the methyl group and InCl<sub>4</sub><sup>−</sup> result in a large band appearing on the red side of the  $\nu_1$  CD<sub>3</sub> symmetric stretching band. The solvation number of InCl<sub>3</sub>, determined from the Raman intensities of the C $\equiv$ N stretching bands for free and coordinated CD<sub>3</sub>CN, increases from ~1.5 to ~1.8 with decreasing concentration.

**Key Words:** Acetonitrile-d, InCl<sub>3</sub>, Coordination, Frequency shift, Solvation number

## Introduction

The C $\equiv$ N and C-C stretching bands of acetonitrile show unusually large blue shifts upon solvation of a Lewis acid,<sup>1-7</sup> resulting from electrophilic coordination to the lone electron pair of the nitrogen end. The distinctive blue shifts, in contrast to the general trend of bond weakening in donor-acceptor complexation,<sup>8</sup> arise from alleviation of the antibonding characters of the C $\equiv$ N and C-C bonds, which supplied from the lone electron-pair of the N atom. Especially the C $\equiv$ N stretching band with its largest variation in vibrational characteristics has been used most often as a probe to determine the compositions of the solvation spheres,<sup>1,2</sup> electrophilicities of Lewis acids,<sup>9,10</sup> solvation numbers,<sup>11-16</sup> and acceptor or donor strengths of organic solvents.<sup>3,17</sup>

While various studies have been done for the donor-acceptor interactions of acetonitrile and Lewis acids, solvation of metal halides in acetonitrile have been relatively less studied, partially due to the low solubilities or the tendency to form insoluble adducts.<sup>18-21</sup> Moreover, the solutes often form more than one species in solution or solid adducts.<sup>16</sup> Solvation of Group 13 metal halides are particularly interesting. The GaCl<sub>3</sub> normally generates at least two different solid adducts with pyridine,<sup>19</sup> and AlCl<sub>3</sub> forms four different cationic complexes with acetonitrile.<sup>16,22</sup> Acetonitrile solution containing Group 13 metal halide is primarily ionic.<sup>20,23</sup> The tetra halide anions (MCl<sub>4</sub><sup>−</sup>) are also identified from the solution<sup>16,20,22,24</sup> and molten salt.<sup>25</sup>

This work is part of a continuing effort to understand the nature of solute species in acetonitrile and the variation of vibrational characteristics of acetonitrile caused by coordination of solvated species. Recently large blue shifts of the  $\nu_2$  C $\equiv$ N stretching,  $\nu_4$  C-C stretching, and  $\nu_8$  CCN deformation bands were observed upon solvation of AlCl<sub>3</sub> and GaCl<sub>3</sub>, along with the evidences for formation of several acetonitrile

complexes with the solute.<sup>16,22</sup> It is, therefore, intriguing whether or not InCl<sub>3</sub> shows similar shifts of vibrational characteristics and a continuing variation with going down the family column. In this paper, we report a vibrational study of anhydrous CD<sub>3</sub>CN solution of InCl<sub>3</sub>.

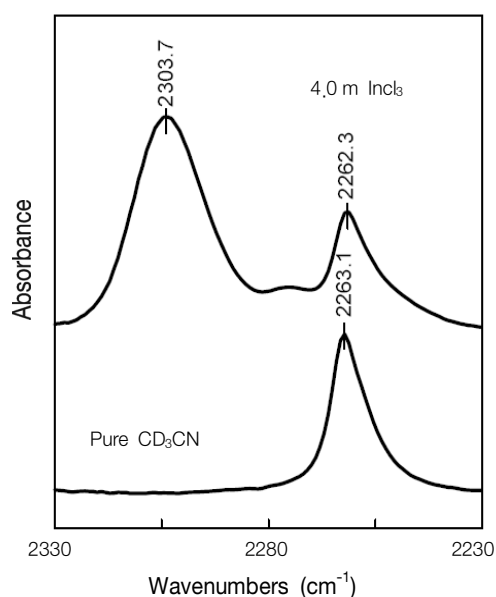
## Experimental Details

CD<sub>3</sub>CN is used for this study, which allows avoiding the interference from the strong Fermi resonance between the  $\nu_2$  and the  $\nu_3 + \nu_4$  combination modes of CH<sub>3</sub>CN.<sup>12</sup> CD<sub>3</sub>CN (99.95%) was purchased in ampule from Aldrich and used without further purification. Anhydrous InCl<sub>3</sub>, packaged under argon in ampule, was also used as purchased from Aldrich. The concentration (molality) of InCl<sub>3</sub> in CD<sub>3</sub>CN in this study ranges from 0 to 4.0 m, close to the saturation point. The solutions were prepared and stored under argon atmosphere free of moisture.

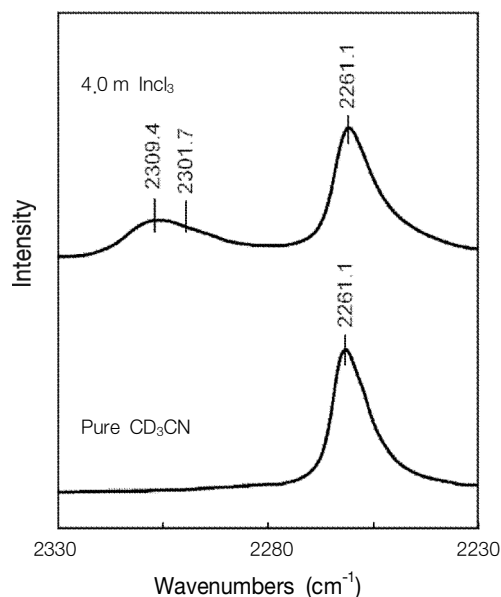
Spectra were recorded using an FT-IR spectrometer (Nicolet Magna 560) at a resolution of 1.0 cm<sup>−1</sup> and a Raman module incorporated into another FT-IR spectrometer (Bio-Rad FTS 175C) at a resolution of 4.0 cm<sup>−1</sup>, which was accompanied with a YAG laser, a Ge detector, and a dielectric Rayleigh filter. The FT-IR spectrometer along with the sample chamber was purged with air free of moisture and CO<sub>2</sub>. However, the bench was not completely free of CO<sub>2</sub> or water vapor. Bulb-type Raman cell (Bio-Rad 925-0101) with reflective coating on one side was used for higher signal intensity.

## Results and Discussion

Figure 1 shows the infrared spectra in the  $\nu_2$  C $\equiv$ N stretching region for pure CD<sub>3</sub>CN and CD<sub>3</sub>CN solution of InCl<sub>3</sub> at a concentration of 4.0 m. The strong absorption peaked at 2263



**Figure 1.** Infrared spectra in the  $\nu_2$  region for pure  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CN}$  solution of  $\text{InCl}_3$  at a concentration of 3.8 m. The  $\nu_2$   $\text{C}\equiv\text{N}$  stretching absorption of pure  $\text{CD}_3\text{CN}$  at  $2263\text{ cm}^{-1}$  is largely asymmetric because of the shoulder at  $2258\text{ cm}^{-1}$ . Another strong absorption at  $2304\text{ cm}^{-1}$  arises from the  $\text{C}\equiv\text{N}$  stretching mode of  $\text{CD}_3\text{CN}$  coordinated to the solute.



**Figure 2.** Raman spectra in the  $\nu_2$  region for pure  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CN}$  solution of  $\text{InCl}_3$  at a concentration of 4.0 m. In contrast to the single strong band in the IR spectrum, at least two bands emerge on the blue side of the  $\nu_2$  band of free  $\text{CD}_3\text{CN}$ . The new bands in the Raman spectrum, arising from the  $\text{C}\equiv\text{N}$  stretching mode of  $\text{CD}_3\text{CN}$  coordinated to the solute, are much weaker than the single strong one in the infrared spectrum shown in Figure 1.

$\text{cm}^{-1}$  in the pure  $\text{CD}_3\text{CN}$  spectrum is asymmetric with a shoulder on the low frequency side. The band consists of the  $\nu_2$  band of free and associated  $\text{CD}_3\text{CN}$  at  $2263$  and  $2258\text{ cm}^{-1}$ .<sup>17</sup> In the solution spectrum, a very strong and broad band emerges at  $2304\text{ cm}^{-1}$  on the blue side of the original  $\nu_2$  band. The new band is believed to arise from the  $\text{C}\equiv\text{N}$  stretching mode of  $\text{CD}_3\text{CN}$  coordinated to the solute on the basis of the substantial blue shift and previous solvation studies, and the gain in absorption intensity originates from the increase in molar absorption constant by the electrophilic coordination.<sup>16</sup>

Previous investigations of acetonitrile in electrolyte solutions reveal that the considerable blue shifts of the  $\nu_2$   $\text{C}\equiv\text{N}$  and  $\nu_4$   $\text{C}-\text{C}$  stretching frequencies are caused by the interaction of the lone electron pair on the nitrogen end with an electron acceptor.<sup>25-28</sup> The molecular orbital involved in charge donation to the electrophilic species at the nitrogen end has substantial  $\text{C}\equiv\text{N}$  and  $\text{C}-\text{C}$  antibonding contributions.<sup>9</sup>

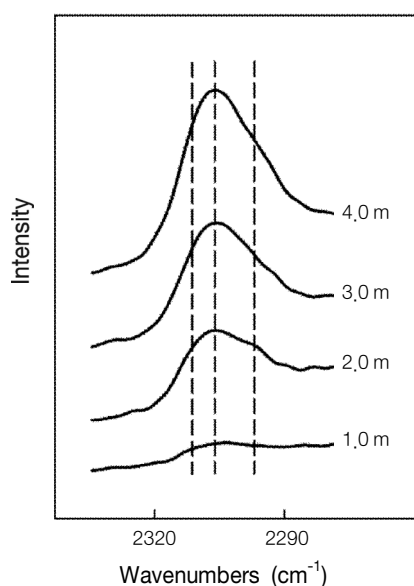
Therefore, as charge is removed from the orbital by coordination to a Lewis acid, the net bond order along the  $\text{CCN}$  axis increases, leading to the blue shifts.

The blue shift of  $41\text{ cm}^{-1}$  for the  $\nu_2$  band is smaller than those of  $65$  and  $62\text{ cm}^{-1}$  observed from the  $\text{AlCl}_3$  and  $\text{GaCl}_3$  solutions, but still substantial. Studies show that the valency of the cation in the electrolyte solution primarily determines the magnitude of the blue shift.<sup>1,2,11-16</sup> Similar magnitudes of blue shift of the  $\text{C}\equiv\text{N}$  stretching band have been observed from water-acetonitrile solutions of the perchlorates of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$  cations.<sup>1,2</sup> The blue shift by solvation of Group 13 metal chloride clearly decreases with going down the column. The lower charge density due to larger ionic size leads to a weaker Lewis acid, lowering the donor-acceptor interaction strength. The variation is particularly obvious with

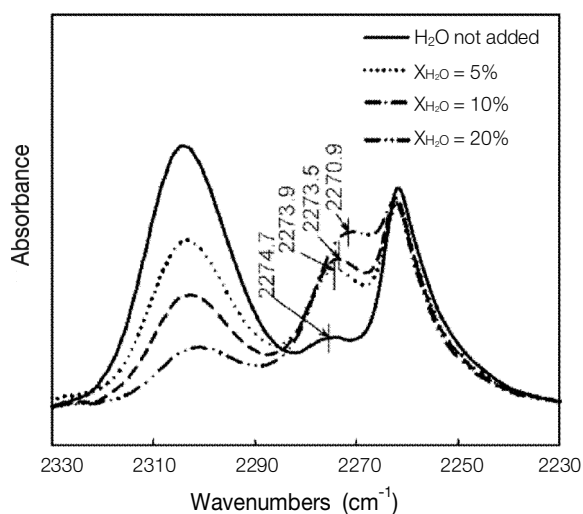
moving from the second to third row. The blue shifts are compared with the Pauling's ionic radii of  $0.50$ ,  $0.62$ , and  $0.81\text{ \AA}$  for  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$ .

Figure 2 shows the Raman spectra in the  $\nu_2$  region of pure  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CN}$  solution of  $\text{InCl}_3$  at a concentration of  $4.0\text{ m}$ . In contrast to the single strong band observed on the blue side of the  $\nu_2$  band of free  $\text{CD}_3\text{CN}$  in the IR spectrum in Figure 1, there are two bands emerging at  $2309$  and  $2302\text{ cm}^{-1}$ . They suggest that at least two cationic species are present in the solution. The total band intensities in the  $\text{C}\equiv\text{N}$  stretching region of pure  $\text{CD}_3\text{CN}$  and the  $\text{InCl}_3$  solution are, however, basically the same. It is also worth mentioning that a single band normally arises from the  $\text{C}\equiv\text{N}$  stretching mode of coordinated acetonitrile in the metal perchlorate solutions, and therefore, the IR and Raman frequencies coincide each other.<sup>13,14</sup> Multiple bands have been observed normally from binary mixtures of acetonitrile (such as water-acetonitrile system) containing metal salts.<sup>1,2</sup> In contrast, similar multiple bands (in this case, two bands) have been observed in the previous solvation studies of  $\text{AlCl}_3$  and  $\text{GaCl}_3$ .<sup>16</sup>

Being consistent with the previous solvation studies of  $\text{AlCl}_3$  and  $\text{GaCl}_3$ , the two bands at  $2309$  and  $2302\text{ cm}^{-1}$  are attributed to the  $\text{C}\equiv\text{N}$  stretching modes of  $\text{CD}_3\text{CN}$  coordinated to major cationic species in the  $\text{InCl}_3$  solution.<sup>16</sup> The presence of those Group 13 metal complexes was in fact previously suggested in NMR and X-ray studies as well.<sup>22</sup> Apparently the shoulder at  $2258\text{ cm}^{-1}$ , which arises from associated  $\text{CD}_3\text{CN}$  including the dimer and multimers, weakens, as the new bands emerge. It is expected that the concentration of associated acetonitrile is lower in solution because the chances for free acetonitrile molecules to collide



**Figure 3.** The emerging bands on the blue side of the  $\nu_2$  C $\equiv$ N stretching band of free CD<sub>3</sub>CN in the Raman spectrum with increasing InCl<sub>3</sub> concentration. The lineshape varies with concentration, suggesting that each band originates from a different species. The broken lines indicate the positions of the consisting absorptions.



**Figure 4.** IR spectra of CD<sub>3</sub>CN solution containing InCl<sub>3</sub> at a concentration of 4.0 m in the  $\nu_2$  region and its variation with additional water. The mole fractions of water in the binary mixtures of CD<sub>3</sub>CN and water are 5, 10, and 20%. Notice the variation of frequency with increasing water concentration.

each other should be lower than in pure acetonitrile, as more acetonitrile molecules being coordinated to the solute.

The new bands in the solution Raman spectrum are remarkably weaker than the single strong band in the IR spectrum. The IR intensity and bandwidth often varies dramatically resulting from various intermolecular interactions.<sup>1,2,12,14</sup> Previous studies show that the C $\equiv$ N stretching bands in the IR spectra of acetonitrile coordinated to Lewis acids are often not only very strong but broad as well.<sup>12,14</sup> Most probably the new bands observed in the Raman

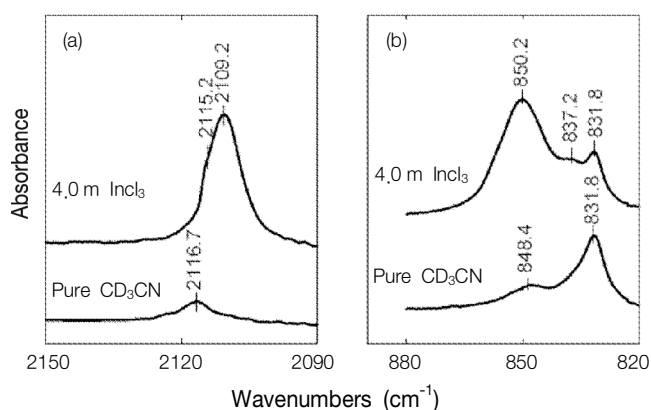
spectrum in Figure 2 are overlapped to appear as the strong, broad band in the IR spectrum shown in Figure 1.

Figure 3 shows emerging of the new bands in the Raman spectrum in the  $\nu_2$  region with increasing concentration in the range of 1.0 - 4.0 m for InCl<sub>3</sub>. Evidently the lineshape as well as the integrated intensity varies with concentration, indicating that the intensity ratio between the new bands changes. The band at 2309 cm<sup>-1</sup> becomes more dominant over the one at 2302 cm<sup>-1</sup> with increasing concentration of InCl<sub>3</sub>. This is consistent with the suggestion that each new band in the  $\nu_2$  region arises from a different species in the solution. The two new bands 7 cm<sup>-1</sup> apart each other are believed to arise from the acetonitrile complexes with cationic species in the solution with different electrophilicities. The electronic structure of CD<sub>3</sub>CN coordinated to a stronger electron acceptor should be more affected and, therefore, results in a larger blue shift.

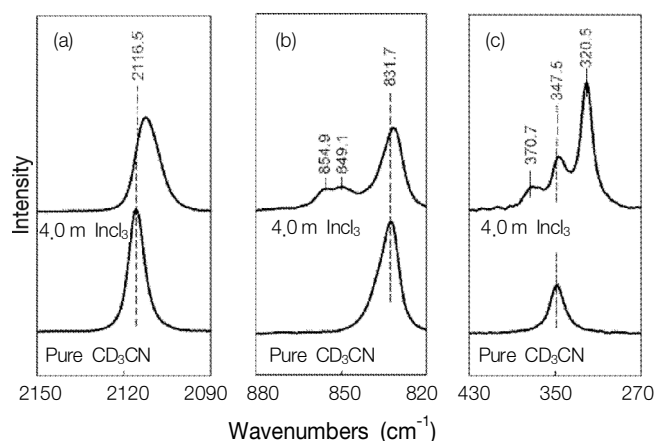
Figure 4 shows the IR spectrum in the  $\nu_2$  band region of CD<sub>3</sub>CN solution at a concentration of 3.0 m and its variation with addition of water. The mole fractions of water are 0, 5, 10, and 20%. When the mole fraction of water is 20%, there are about 1.7 and 6.9 moles of water and CD<sub>3</sub>CN for one mole of InCl<sub>3</sub> in the solution, respectively. By addition of water, the band at 2304 cm<sup>-1</sup> quickly weakens and almost disappears at the mole fraction of water of 20%, indicating that any residual water in the solution is preferentially coordinated to the cationic species as ligand over CD<sub>3</sub>CN. Moreover, the present result shows that coordinated CD<sub>3</sub>CN is mostly displaced when water is added 1.7 times in mole ratio as much as InCl<sub>3</sub> in the solution. Dislodge of acetonitrile from the primary solvation shell by an addition of water was also observed in studies of aqueous solutions of acetonitrile containing trivalent cations by Wójcik *et al.*<sup>1,2</sup>

Shown in Figure 5 are the  $\nu_1$  CD<sub>3</sub> symmetric stretching (a) and  $\nu_4$  C-C stretching (b) regions in the infrared spectra of pure CD<sub>3</sub>CN and InCl<sub>3</sub> solution of at a concentration of 4.0 m. The  $\nu_1$  region (a) shows dramatic changes upon solvation of InCl<sub>3</sub>. A strong band emerges at 2109 cm<sup>-1</sup> on the red side of the  $\nu_1$  band of free CD<sub>3</sub>CN, and in the spectrum, the  $\nu_1$  band of free CD<sub>3</sub>CN also shows a slight red shift. The magnitude of variation in the  $\nu_1$  region is quite unusual. A comparable magnitude of change in the  $\nu_1$  region has been observed only in the IR spectrum of the AlCl<sub>3</sub> and GaCl<sub>3</sub> solutions, where metal tetrachloride anion (MCl<sub>4</sub><sup>-</sup>) is the primary anion.<sup>16</sup> No other vibrational bands are expected than the  $\nu_1$  band of CD<sub>3</sub>CN in the frequency region. We assign the new bands to the CD<sub>3</sub> symmetric stretching mode of CD<sub>3</sub>CN hydrogen-bonded to InCl<sub>4</sub><sup>-</sup>.

The hydrogen stretching band in the IR spectrum often shows a large increase in its intensity and bandwidth as well as a red shift. Normally the frequency and bandwidth are linearly related to the red shift over a broad frequency range.<sup>29,30</sup> The red shift of the  $\nu_1$  band is consistent with previous spectroscopic studies of CD<sub>3</sub>CN solutions containing AlCl<sub>3</sub> and GaCl<sub>3</sub>.<sup>16</sup> The methyl group of acetonitrile is expected to form considerably strong hydrogen bonds with the chlorine atoms of InCl<sub>4</sub><sup>-</sup> in the solution, whose IR and Raman spectra are reported previously.<sup>24</sup> Figure 5(a) also shows a slight red shift



**Figure 5.** IR spectra of the  $\nu_1$  CD<sub>3</sub> symmetric (a) and C-C (b) stretching regions of neat CD<sub>3</sub>CN and CD<sub>3</sub>CN solution of InCl<sub>3</sub>. (a) A strong band at 2109 cm<sup>-1</sup> emerges on the red side of  $\nu_1$  band of free CD<sub>3</sub>CN. (b) The  $\nu_4$  region becomes much more congested upon solvation of InCl<sub>3</sub>. A strong band and a shoulder at 850 and 837 cm<sup>-1</sup> appear on the blue side of the  $\nu_4$  band of free CD<sub>3</sub>CN in the spectrum of the InCl<sub>3</sub> solution.



**Figure 6.** Raman spectra of pure CD<sub>3</sub>CN and CD<sub>3</sub>CN solution of InCl<sub>3</sub> in the  $\nu_1$  CD<sub>3</sub> symmetric stretching (a),  $\nu_4$  C-C stretching (b), and  $\nu_8$  CCN deformation (c) regions. (a) The CD<sub>3</sub> stretching band of the CD<sub>3</sub>CN solution is asymmetric due to a shoulder at 2109 cm<sup>-1</sup>, which corresponds to the much stronger infrared absorption in Figure 5(a). (b) Notice the two new bands at 855 and 849 cm<sup>-1</sup> on the blue side of the  $\nu_4$  band of free CD<sub>3</sub>CN. (c) Two new bands appear at 371 and 321 cm<sup>-1</sup> on the blue side of the  $\nu_8$  band of free CD<sub>3</sub>CN.

of the  $\nu_1$  band of free CD<sub>3</sub>CN. Acetonitrile molecules easily aggregate through hydrogen bonding, and the dimer and multimers often exist even in gas phase.<sup>31,32</sup> The slight red shift of the  $\nu_1$  band of free CD<sub>3</sub>CN suggests that free CD<sub>3</sub>CN also forms more effective hydrogen bonds with CD<sub>3</sub>CN that are already strongly hydrogen-bonded to the chlorine atoms. Figure 5(b) shows the variation in the  $\nu_4$  C-C stretching region. In the IR spectrum of pure CD<sub>3</sub>CN, the  $\nu_4$  C-C stretching and  $\nu_7$  CD<sub>3</sub> rocking bands are observed at 832 and 848 cm<sup>-1</sup>, respectively. A strong band appears at 850 cm<sup>-1</sup> and a shoulder at 837 cm<sup>-1</sup>, respectively, while the  $\nu_4$  band of free CD<sub>3</sub>CN at 832 cm<sup>-1</sup> weakens slightly. The strong band at 850 cm<sup>-1</sup> is attributed to the C-C stretching mode of CD<sub>3</sub>CN coordinated to the solute while the shoulder at 837 cm<sup>-1</sup>

originates from associated CD<sub>3</sub>CN.<sup>16</sup> The  $\nu_4$  absorption intensity in the IR spectrum, similar to the  $\nu_2$  absorption intensity, increases dramatically by the electrophilic coordination of the solute.<sup>14,16</sup>

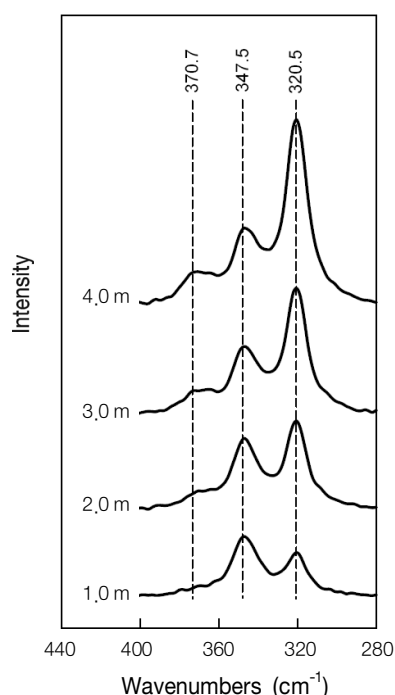
Shown in Figure 6 are the Raman spectra in the  $\nu_1$  CD<sub>3</sub> symmetric stretching (a),  $\nu_4$  C-C stretching (b), and  $\nu_8$  CCN deformation (c) regions of pure CD<sub>3</sub>CN and InCl<sub>3</sub> solution at a concentration of 4.0 m. Despite considerable variation in the spectra, the total band intensity in each region remains almost the same, parallel to the  $\nu_2$  C≡N stretching region. The  $\nu_1$  CD<sub>3</sub> stretching band in the Raman spectrum of the solution is largely asymmetric due to the band at 2109 cm<sup>-1</sup> appearing on the red side as shown in Figure 5(a). The new band, which is the CD<sub>3</sub> symmetric stretching band of CD<sub>3</sub>CN hydrogen-bonded to InCl<sub>4</sub><sup>-</sup>, is relatively weaker than the same band observed in the IR spectrum shown in Figure 4(a). The remarkable increase in intensity of the hydrogen stretching band in the IR spectrum, as a result of hydrogen bonding, apparently does not occur in the Raman spectrum.

Figure 6(b) and (c) also show that the new bands arising from CD<sub>3</sub>CN complexed to the solute are all on the blue sides of the  $\nu_4$  and  $\nu_8$  bands of free CD<sub>3</sub>CN, due to the strengthened bonds in the CCN axis by the electrophilic coordination. The  $\nu_4$  C-C stretching band, shown in Figure 6(b), is weaker than the  $\nu_2$  C≡N stretching band. Two new bands at 855 and 849 cm<sup>-1</sup>, parallel to the  $\nu_2$  region, emerge in the  $\nu_4$  region, indicating that at least two acetonitrile complexes exist in the solution. In comparison with the strong new band emerging at 850 cm<sup>-1</sup> in the IR spectrum, the new bands observed in the Raman spectrum are again much weaker. The shoulder at ~863 cm<sup>-1</sup> in the IR spectrum and the  $\nu_7$  CD<sub>3</sub> rocking band, which is expected at 849 cm<sup>-1</sup>, are too weak to be resolved in the Raman spectrum.

In the  $\nu_8$  CCN bending region shown in Figure 6(c), which is often not observed in the ordinary IR spectrum because of its low frequency, two new bands appear, one on the blue and the other on the red side, in contrast to the new bands observed on blue sides of the  $\nu_2$  and  $\nu_4$  regions. The band on the blue side at 371 cm<sup>-1</sup> is designated to the CCN deformation mode of coordinated CD<sub>3</sub>CN.<sup>33</sup> Consequently, the vibrational modes primarily affected by the strengthened bonds in the CCN axis by the electrophilic coordination, the  $\nu_2$  C≡N stretching,  $\nu_4$  C-C stretching, and  $\nu_8$  CCN deformation modes, lead to the similar sets of new bands with noticeable blue shifts.

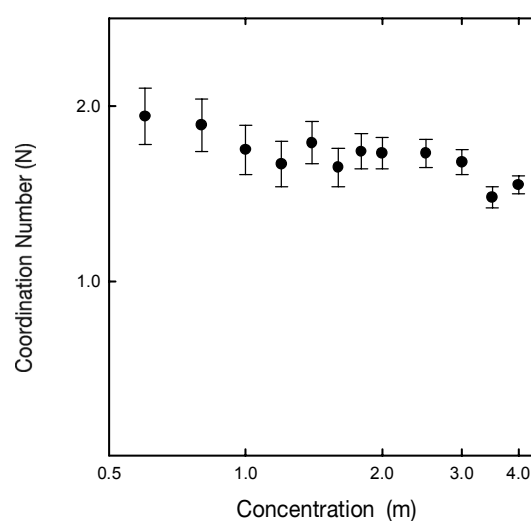
Figure 6(c) also shows another immersing band at 321 cm<sup>-1</sup> in on the red side of the  $\nu_8$  band with increasing concentration. Figure 7 shows variation of the  $\nu_8$  region, revealing that the band at 321 cm<sup>-1</sup> proportionally increases with InCl<sub>3</sub> concentration, and it eventually becomes much stronger than the free CD<sub>3</sub>CN band at 348 cm<sup>-1</sup> unlike other much weaker Raman bands arising from coordinated CD<sub>3</sub>CN. Recent studies show that the strong band at 321 cm<sup>-1</sup> from the InCl<sub>3</sub> solution originates from the A<sub>1</sub> symmetric stretching mode of InCl<sub>4</sub><sup>-</sup>.<sup>24</sup> Existence of InCl<sub>4</sub><sup>-</sup> ion strongly suggests that disproportion reaction of InCl<sub>3</sub> occurs in the solution, producing the tetra chloride anion.

The frequencies and frequency shifts observed in this study are summarized in Table 1. Noticeable blue shifts are observed



**Figure 7.** Variation of Raman spectrum in the  $\nu_8$  CCN bending region. Notice that the two bands at 371 and 321  $\text{cm}^{-1}$  increase with  $\text{InCl}_3$  concentration. Particularly the one at 321  $\text{cm}^{-1}$  eventually becomes much stronger than the  $\nu_8$  band of free  $\text{CD}_3\text{CN}$ .

only from the  $\nu_2$  C $\equiv$ N stretching,  $\nu_4$  C-C stretching, and  $\nu_8$  CCN deformation bands upon solvation of  $\text{InCl}_3$  in  $\text{CD}_3\text{CN}$ . This strongly suggests that only the chemical bonds in the CCN axis strengthen by the electrophilic coordination of the solute to the nitrogen end, whereas the effects to the remaining bonds in acetonitrile appear very small. In addition to that, the



**Figure 8.** Estimated solvation number of  $\text{InCl}_3$  in acetonitrile as a function of concentration. The solvation number is determined from the ratio between the integrated Raman intensities of the C $\equiv$ N stretching bands of free  $\text{CD}_3\text{CN}$  and those coordinated to the solute. The uncertainty in determination of the solvation number increases at low concentration due to the low intensities of the bands arising from the coordinated  $\text{CD}_3\text{CN}$ .

vibrational characteristics of free  $\text{CD}_3\text{CN}$  in the solutions remain essentially the same, indicating that while the acetonitrile molecules directly coordinated to the cationic species are affected, and the effects are hardly conveyed to free acetonitrile.<sup>1-7,13-16</sup>

The solvation number of an electrophilic solute has been determined from the intensity ratio of the bands arising from free solvent and those coordinated to the solute. Particularly the  $\nu_2$  C $\equiv$ N stretching band of acetonitrile has been used most

**Table 1.** Observed frequencies of  $\text{CD}_3\text{CN}$  free and coordinated to  $\text{InCl}_3$

Pure $\text{CD}_3\text{CN}^a$		$\text{InCl}_3$ solution <sup>a</sup>			Description
Free $\text{CD}_3\text{CN}$	Associated $\text{CD}_3\text{CN}$	Free $\text{CD}_3\text{CN}^b$	Coordinated $\text{CD}_3\text{CN}^b$	$\text{InCl}_4^-$	
2116.7		2115.2 (-1.5)	2109.2 (-7.4) <sup>c</sup>		$\nu_1$ $\text{CD}_3$ sym. str.
2263.1	2258	2262.3 (-0.8)	2301.7 (38.6) <sup>d,e</sup> 2309.4 (46.3) <sup>d,e</sup>		$\nu_2$ C $\equiv$ N str.
1101.9		1101.1 (-0.8)			$\nu_3$ $\text{CD}_3$ sym. deform
831.8	837	831.8 (-0.0)	849.1 (17.3) <sup>d,e</sup> 854.9 (23.1) <sup>d,e</sup>		$\nu_4$ C-C str.
1038.1		1035.2 (-2.9)			$\nu_5$ $\text{CD}_3$ antisym. str. <sup>f</sup>
848.4		848.0 (-0.4)			$\nu_6$ $\text{CD}_3$ antisym. deform
347.5 <sup>e</sup>		346.9 (-0.6) <sup>e</sup>	370.7 (23.2) <sup>d,e</sup>		$\nu_7$ $\text{CD}_3$ rock $\nu_8$ CCN deform <sup>e</sup>
				321	$A_1$ sym. str.
				89	$E$ sym. deform
				337	$F_2$ antisym. str.
				112	$F_2$ antisym. deform

<sup>a</sup>All frequencies are in  $\text{cm}^{-1}$ . Frequencies are determined after deconvoluting the consisting components. <sup>b</sup>Numbers in parentheses are the frequency shifts relative to the frequencies of free  $\text{CD}_3\text{CN}$  in the pure  $\text{CD}_3\text{CN}$ . <sup>c</sup> $\text{CD}_3\text{CN}$  hydrogen-bonded to the chlorine atoms of  $\text{InCl}_4^-$  in the solution. <sup>d</sup> $\text{CD}_3\text{CN}$  complexed to the cationic species. <sup>e</sup>Determined from the Raman spectrum. Other frequencies are determined from the IR spectrum. Other frequencies are determined from the IR spectrum. <sup>f</sup>Frequencies not determined because of severe overlap by the  $\nu_2$  band of  $\text{CD}_3\text{CN}$ .

often as a probe in both IR and Raman studies for determination of solvation numbers. The band not only is very strong and located in a relatively clean area but shows large variations upon solvation in the vibrational characteristics as well. Because the molar IR absorption constant, as noted above, often shows dramatic variations upon complexation, it is essential in determination of the concentration of a species from the IR intensity for the sample thickness to be controlled accurately.<sup>11,12</sup> On the other hand, the Raman intensity is known to be in general much less sensitive to various intermolecular interactions in solution.<sup>13</sup>

Previous studies show that the molar Raman intensity for the  $\nu_2$  C≡N stretching band is numerically the same for the solvated acetonitrile and bulk, and as a result, there is a direct proportionality between the intensity and the species concentration.<sup>13</sup> Therefore, the primary solvation numbers have often been determined for solutions of salts in acetonitrile using the relation

$$\frac{I_b}{I_b + I_f} = N \frac{c_{\text{salt}}}{c_{\text{acetonitrile}}}$$

where  $I_b$  and  $I_f$  are the Raman intensities of the band shifted by solvation and the band of free acetonitrile, respectively,  $c_{\text{salt}}$  and  $c_{\text{acetonitrile}}$  are the concentrations of the salt and acetonitrile, respectively, and  $N$  is the average number of solvent molecules coordinated to the solute in the primary layer.<sup>35</sup>

Figure 8 shows the primary solvation number of  $\text{InCl}_3$  in  $\text{CD}_3\text{CN}$  as a function of concentration, determined from the integrated Raman intensities of the C≡N stretching bands of free  $\text{CD}_3\text{CN}$  and those coordinated to the solute. The solvation number varies between  $\sim 1.5$  and  $\sim 1.8$  for  $\text{InCl}_3$  depending on concentration. It is notable that the solvation numbers of  $\text{AlCl}_3$  (1.5–1.8) and  $\text{GaCl}_3$  (1.3–1.7) in acetonitrile vary in similar ranges.<sup>16</sup> The present result is, on the other hand, compared with the much larger solvation numbers of metal cations, generated from perchlorates, e.g. six for  $\text{Mg}^{2+}$  and four for  $\text{Ag}^+$ ,  $\text{Li}^+$ , and  $\text{Na}^+$ .<sup>11,13,14</sup> The metal cation is exposed isotropically to all the directions in solution for solvation, leading to a higher solvation number.

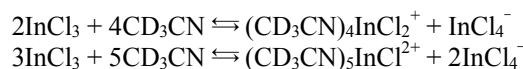
The increase in solvation number with decreasing concentration is in fact common. At a high concentration particularly close to the saturation point, much less free solvent molecules are available for a solute species than in a dilute solution. Only about 5.6  $\text{CD}_3\text{CN}$  molecules are present for each solute molecule at a solute concentration of 4.0 m. Previous studies on acetonitrile solutions of metal perchlorates also show that the solvation number increases with decreasing concentration, whereas the chances to form counter-ion pairs rise.<sup>14,15</sup>

There is thus far not enough information about the types of species present in the  $\text{InCl}_3$  solution. In the solid state, the complex is formulated as  $[(\text{MeCN})_2\text{InCl}_2^+ \cdot \text{InCl}_4^-]$  in both the cation and anion being four-coordinate.<sup>21</sup> If there, like in the solid state, exist only  $(\text{MeCN})_2\text{InCl}_2^+$  and  $\text{InCl}_4^-$  in the solution, the solvation number of  $\text{InCl}_3$  would be one. On the other hand, the presence of six-coordinate species (such as  $(\text{MeCN})_4\text{InCl}_2^+$ ,  $(\text{MeCN})_5\text{InCl}^{2+}$ , or  $(\text{MeCN})_6\text{Ga}^{3+}$ ) or five-coordinate species (e.g.,  $(\text{MeCN})_3\text{InCl}_2^+$ ,  $(\text{MeCN})_4\text{InCl}^{2+}$ , or

$(\text{MeCN})_5\text{Ga}^{3+}$ ) or four-coordinate species of the type  $(\text{MeCN})_2\text{InCl}_2^+ \cdot \text{Cl}^-$  would increase the solvation number above one.

As described above, the new bands observed on the blue sides of the  $\nu_2$  and  $\nu_4$  bands of free  $\text{CD}_3\text{CN}$  in the Raman spectra in Figures 2 and 5 indicate that there are at least two different cationic species. While the ambiguity over the types of solvated species and the solvation number of  $\text{InCl}_3$  in acetonitrile is still far from settled, the present results suggest that there exist significant concentrations of six-coordinate or five-coordinate species in the  $\text{InCl}_3$  solution. Moreover, the composition of the complexes most likely changes with the concentration of the solute. The substantial blue shifts indicate that the solvent is coordinated to strong electron acceptors.<sup>1,2,11–16</sup>

As shown in Figure 3, the relative intensity of the band at  $2309\text{ cm}^{-1}$  in the  $\nu_2$  region apparently increases with increasing concentration, while that of the one at  $2302\text{ cm}^{-1}$  decreases. Similar variations in the relative intensities are also observed in the  $\nu_4$  region. The complex that gives a lower solvation number is expected to be more favorable at higher concentration of  $\text{InCl}_3$ , and the electronic structure of acetonitrile is probably more affected by an electron acceptor with a higher positive charge. Therefore, the band at  $2302\text{ cm}^{-1}$  most probably arises from the C≡N stretching mode of  $(\text{CD}_3\text{CN})_4\text{InCl}_2^+$  and/or  $(\text{CD}_3\text{CN})_5\text{InCl}^{2+}$ . These species would give solvation numbers of 2.00 and 1.67, respectively, based upon the following reactions.



Among the plausible solvated complexes, only the two species would give the solvation number higher than 1.60.

On the other hand, the band with smaller blue shift at  $2309\text{ cm}^{-1}$  then probably arises from one or more the C≡N stretching modes of  $(\text{CD}_3\text{CN})_5\text{In}^{3+}$ ,  $(\text{CD}_3\text{CN})_4\text{InCl}^{2+}$ , and  $(\text{CD}_3\text{CN})_6\text{In}^{3+}$ , which would give a solvation number of 1.25, 1.33, and 1.5, respectively. At high concentration of  $\text{InCl}_3$ , the band at  $2309\text{ cm}^{-1}$  becomes prominent as shown in Figure 3 and the solvation number falls to about 1.5. Accordingly, among the two bands on the blue side of the  $\nu_4$  band of free  $\text{CD}_3\text{CN}$ , the one at  $849\text{ cm}^{-1}$  can also be designated to the C–C stretching modes of  $(\text{CD}_3\text{CN})_4\text{InCl}_2^+$  and/or  $(\text{CD}_3\text{CN})_5\text{InCl}^{2+}$ .

## Conclusions

Vibrational studies have been carried out for  $\text{CD}_3\text{CN}$  solution of  $\text{InCl}_3$ . The  $\nu_2$  C≡N stretching band of  $\text{CD}_3\text{CN}$  coordinated to the Lewis acid emerges with a blue shift of  $41\text{ cm}^{-1}$  and a large increase in intensity in the IR spectrum. In contrast, the Raman spectrum shows further details in the  $\nu_2$  region while the total intensity remains virtually the same; two new bands arise on the blue side of the  $\nu_2$  band of free  $\text{CD}_3\text{CN}$ , and the intensity ratio between the new bands vary with concentration. Parallel to the  $\nu_2$  region, similar new bands are observed in the  $\nu_4$  C–C stretching and  $\nu_8$  CCN deformation regions. The blue shifts of the  $\nu_2$ ,  $\nu_4$ , and  $\nu_8$  bands

upon solvation indicate that the bonds in the CCN molecular axis are strengthened by coordination of cationic species in the solution. The solvation number of InCl<sub>3</sub> in acetonitrile, determined from the integrated Raman intensities of the C≡N stretching bands of free CD<sub>3</sub>CN and those coordinated to the Lewis acid, ranges from ~1.8 at low concentration to ~1.5 near the saturation point. The present results suggest that at low concentration (CD<sub>3</sub>CN)<sub>4</sub>InCl<sub>2</sub><sup>+</sup> and/or (CD<sub>3</sub>CN)<sub>5</sub>InCl<sup>2+</sup> is the major species while one or more of (CD<sub>3</sub>CN)<sub>5</sub>In<sup>3+</sup>, (CD<sub>3</sub>CN)<sub>4</sub>InCl<sup>2+</sup>, and (CD<sub>3</sub>CN)<sub>6</sub>In<sup>3+</sup> become primary solvation products.

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