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Solvation of $Mg(ClO_4)_2$ in Deuterated Acetonitrile Studied by Means of Vibrational Spectroscopy

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Vibrational characteristics of CD_3CN solution containing $Mg(ClO_4)_2$ have been studied by means of infrared and Raman spectroscopy. A large blue shift of 40 cm^{-1} and a relatively small red shift of 3 cm^{-1} of the ν_2 C≡N stretch are observed as a result of interactions of CD_3CN with Mg^{2+} and ClO_4^- ions, respectively. The Mg^{2+} ion is preferentially solvated by residual water over acetonitrile. The primary coordination number of Mg^{2+} in acetonitrile is determined as 6 from the Raman intensities of the C≡N stretch for free CD_3CN and those coordinated to Mg^{2+}. Evidently, formation of contact ion pairs of Mg^{2+} and ClO_4^- is more probable at a high concentration of $Mg(ClO_4)_2$. The IR extinction constants of the ν_2 and ν_4 stretching bands increase dramatically upon coordination. The vibrational characteristics of free CD_3CN remain the same in the solution, indicating that the electrophilicity of Mg^{2+} affects only the CD_3CN molecules directly coordinated to Mg^{2+}. DFT calculations have been performed at the BLYP/6-31+G(2d,p) level to examine the structure and vibrational characteristics of CD_3CN coordinated to Mg^{2+}. The calculated results are in good agreement with the observed vibrational characteristics.

I. Introduction

Acetonitrile has played an important role in the development of vibrational as well as rotational spectroscopy and is still an interesting compound.[1−3] While the structural and spectroscopic properties of weakly bound molecular complexes have continuously been an area of intense research, complexes of acetonitrile have been the subject of various studies.[4−7] The unusually large blue shift of the ν_2 band (the C≡N stretch), along with the frequency shifts of other vibrational bands observed in aquous solution containing inorganic salts, has been a specific focus of spectroscopic as well as theoretical studies.[5,6,8−12] Complexation of acetonitrile with other Lewis acids also leads to similar blue shifts of the ν_2 band,[13−16] and the characteristic blue shifts are generally attributed to the electrophilic coordination of Lewis acids to the lone pair electrons of nitrogen in acetonitrile.

The vibrational spectroscopy of nonaqueous electrolyte solutions is a subject that has received considerable attention. Recently studies of acetonitrile solutions of alkali metal perchlorates, especially $LiClO_4$ and $NaClO_4$, have been performed. Fawcett et al. used attenuated total reflection FT-IR spectroscopy for the improved quality of the IR spectra and analyzed the effects of the electrolytes on the vibrations of the hydrogen stretches and deformations along with the C≡N and C−C stretches.[17] More recently, Fawcett and Liu also studied the possibility of ion pairing for $Mg(ClO_4)_2$ dissolved in acetonitrile.[4] On the basis of the coordination number of 3.3 estimated for CD_3CN in their study, they argued that the primary solvation number of Mg^{2+} in acetonitrile is actually four, and therefore, 70% of the Mg^{2+} ions form contact ion pair with ClO_4^- ions.[4]

To understand the details of interaction between metal cation and acetonitrile, solvation of metal salts in binary mixtures has also been studied. Evans and Lo carried out Raman and infrared studies of aquous zinc chloride solutions containing acetonitrile and showed that the complexed nitrile retains its original C_{3v} symmetry, the point of attachment to Zn^{2+} being through the nitrogen lone-pair electrons.[18] Oliver and Janz proceeded Raman studies of silver nitrate in water−acetonitrile mixtures.[19] They investigated the most intense vibrational modes of the solute and solvent and determined the coordination number around the Ag^+ ion as 4. Wójcik et al. studied mixtures of water and acetonitrile with trivalent cations by means of infrared spectroscopy.[5] The C≡N stretching vibrations were used as probes of the structural environment to determine the composition of the solvation spheres around the metal ions. Solvation of lithium ion in binary mixtures of acetonitrile and dimethyl formamide was studied by Sajeevkumar and Singh.[20] The large frequency shifts of the C≡N stretch and NCO deformation were monitored and used to investigate the composition in the solvation shell.

Recently Pugh et al. performed an ab initio study for cluster formation of potassium ion with H_2O, methanol, and acetonitrile at the RHF/DZP level.[21] The binding energies and structures of clusters with various coordination numbers in the gas phase were calculated and compared in the three solvents. While up to coordination number 3 acetonitrile forms more stable cluster due to the large negative charge on nitrogen atom than water does, for higher coordination numbers the reverse is true. They also reported that the tetrahedral structure is more stable than the square planar structure.

We have carried out a vibrational study of CD_3CN solution containing magnesium perchlorate by means of infrared and Raman spectroscopy. Large changes of vibrational characteristics as a result of solvation were observed, and the coordination number of Mg^{2+} in CD_3CN was determined as a function of concentration from the Raman intensities of the C≡N stretch for free CD_3CN and those coordinated to Mg^{2+} in the solution. DFT calculations were also carried out and the results compared with the observed values.

II. Experimental and Computational Details

CD_3CN was used for this study, which allows us to avoid the interference originating from the strong Fermi resonance

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between the ν_2 band and the $\nu_3 + \nu_4$ combination band about 40 cm^{-1} toward higher frequency observed for CH_3CN.[4] CD_3CN (Aldrich, 99.6%) was purchased as an ampule from Aldrich and used without further treatment. Magnesium perchlorate was also used as purchased from Aldrich. The concentration (molality) of $Mg(ClO_4)_2$ in CD_3CN ranges from 0 to 2.0 *m*, close to the saturation point. The solutions and chemicals used in this study were prepared and stored under an argon atmosphere free of moisture. Spectra were collected using an FT-IR (Bio-Rad FTS 175C) with a resolution of 2.0 cm^{-1} and a Raman module incorporated into the FT-IR spectrometer with a resolution of 1.0−4.0 cm^{-1}, which is accompanied with a YAG laser and a Ge detector as the light source and detector, respectively. The spectrometer along with the sample chamber was purged with air free of moisture and CO_2. Yet, the bench was not completely free of CO_2 or water vapor. The IR sample cell was equipped with a pair of KBr windows and a spacer, but CaF_2 windows were used instead for water-containing solutions. The Raman cell was a bulb-type one with a reflective coating on one side for higher signal intensity provided by Bio-Rad. For determination of the center frequency, width, and intensity of each band, the line profile was fitted to a combination of Lorentzian and Gaussian line shapes, whose ratio of composition was adjusted for a best fit. In the process of deconvolution of the congested ν_2 band region, the center frequency of the monomer ν_2 band at about 2263 cm^{-1} was, if needed, constrained in order to break the strong correlation among the line shape parameters resulting from serious overlapping of the absorption bands. All the experiments were performed at the room temperature.

DFT calculations were carried out with the Gaussian 98[22] package at the BLYP/6-31+G(2d,p) level. The molecular geometries of CD_3CN and $Mg[CD_3CN]_6^{2+}$ were fully optimized without any geometrical constraints, and at the converged geometry, the vibrational frequencies were calculated. For estimation of the binding energy of the complex, the zero-point energy correction was included.

III. Results and Discussion

Figure 1 shows the ν_2 C≡N stretch regions in the infrared spectra for pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m*. There is a strong band at 2263 cm^{-1} in Figure 1a that is asymmetric with a shoulder on the low-frequency side. Studies indicate that the band actually consists of the ν_2 band of the monomer at 2263 cm^{-1} and that of the dimer at 2258 cm^{-1}.[23] In Figure 1b, one can find a new band at 2303 cm^{-1} in the IR spectrum of the $Mg(ClO_4)_2$ solution. The band is attributed to the ν_2 C≡N stretching band of the complex formed from CD_3CN and Mg^{2+}.[4] It is well-known from the spectroscopy of acetonitrile in electrolyte solution that interaction of the nonbonding electrons on the nitrogen end with cations results in blue shifts of both the C≡N (ν_2) and C−C (ν_4) stretching frequencies.[24−27] On the basis of molecular orbital calculations, the molecular orbital involved in charge donation to the electrophilic species at the nitrogen end of the molecule has substantial nitrogen lone-pair character as well as C≡N and C−C antibonding contributions.[16] Therefore, as charge is removed from this orbital by coordination to a Lewis acid, the net bond order along the CCN axis increases, and as a result, blue shifts are observed in the vibrational spectrum for the ν_2 and ν_4 bands.

The line profile of the ν_2 band region (2220−2340 cm^{-1}) of the CD_3CN solution containing $Mg(ClO_4)_2$ was fitted to four absorption bands as shown in Figure 1b. Attempts to fit the line profile with a fewer number of absorption bands were never successful. It is notable that there is a broad and strong band at 2260 cm^{-1} in the solution spectrum, which is compared to the much weaker one at 2258 cm^{-1} due to the ν_2 C≡N stretch of the CD_3CN dimer in the pure liquid (Figure 1a). The intensity of the band at 2260 cm^{-1} increases with the concentration of $Mg(ClO_4)_2$, in contrast to that of the monomer ν_2 band at 2263 cm^{-1}. The concentration of the acetonitrile dimer should be lower in the solution, since the chances that the free solvent molecules encounter each other decrease. The ν_5 CD_3 stretching band, which is believed to be overlapped by other strong bands in the region, is normally too weak to be considered.[23−28]

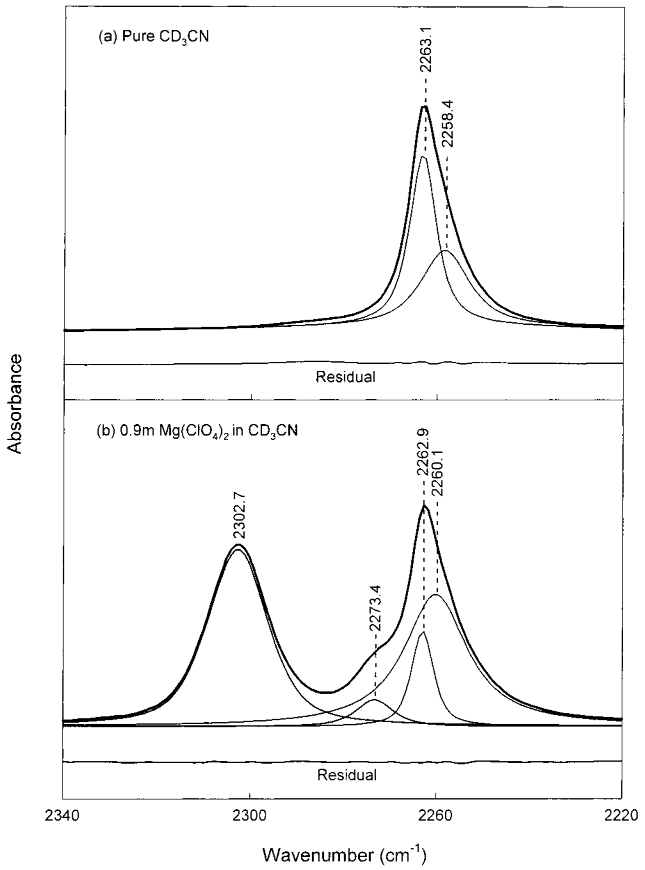

Figure 1. The IR spectra and the fitted bands in the ν_2 region for pure CD_3CN (a) and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m* (b). (a) The absorption bands at 2263.1 and 2258.4 cm^{-1} are due to the ν_2 C≡N stretches of the CD_3CN monomer and dimer, respectively. (b) The absorption features at 2302.7 and 2260.1 cm^{-1} are attributed to the C≡N stretches of CD_3CN coordinated to Mg^{2+} and ClO_4^-, respectively, and the shoulder at 2273.4 cm^{-1} is attributed to the C≡N stretch of CD_3CN in interaction with the water residue in the primary solvation shell of Mg^{2+}.

Apparently, the largest contribution to the band at 2260 cm^{-1} of the solution can only be attributed to the ν_2 C≡N stretching band of the hydrogen-bonded CD_3CN with ClO_4^-.[4] Fawcett et al. found that the ν_2 band is red-shifted up to 6.5 cm^{-1} in strongly basic solvents.[23] Lewis base interacts with the methyl group of acetonitrile, repelling the charge density associated with the σ bonds in the methyl group. This increases the electron density in the bonds along the CCN axis, weakening the bonds, since the associated HOMO carries an antibonding character.[16,29] As a result, the frequencies of the C≡N and C−C stretches decrease. When dissolved, the electron-rich oxygen atoms of the ClO_4^- ion should interact with the CD_3 groups, forming hydrogen bonds such as other Lewis bases, which leads to a red shift of the ν_2 C≡N stretching band.

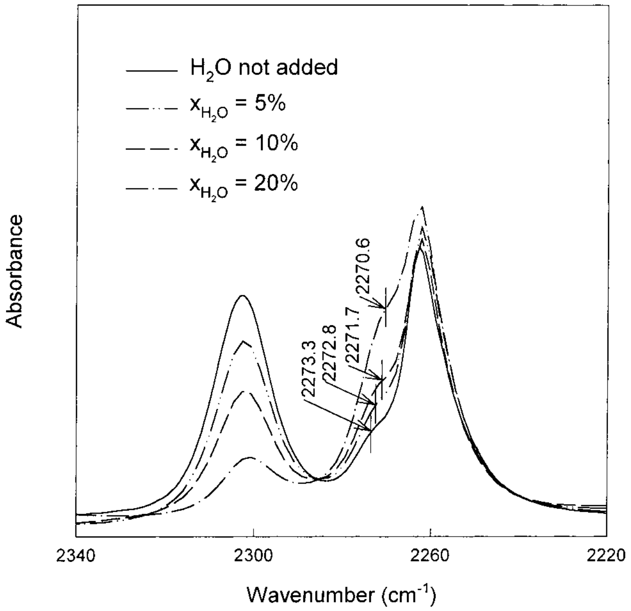

Figure 2. The IR spectra in the ν_2 region for CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m* and the same solution with additional water. The mole fractions of water in the binary mixtures of CD_3CN and water are 5, 10, and 20%. The given frequencies are the fitting results.

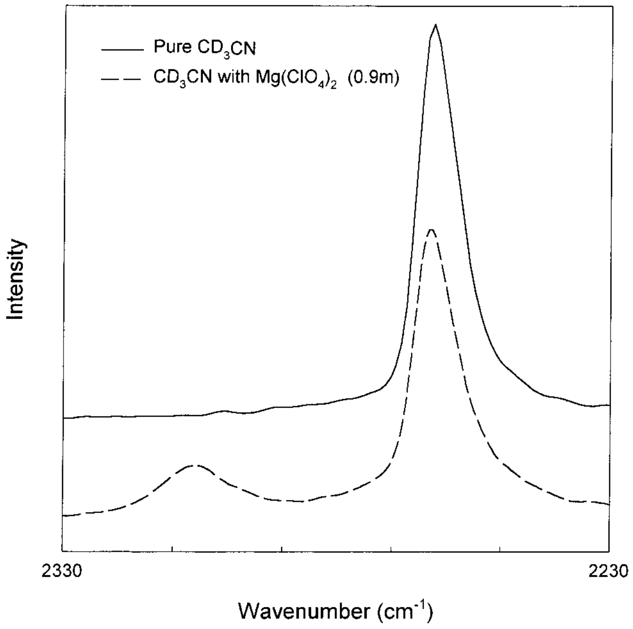

Figure 3. The Raman spectra in the ν_2 region for pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m*. The Raman intensity of the ν_2 band of CD_3CN coordinated to Mg^{2+} at 2302.7 cm^{-1} relative to that of free CD_3CN at 2263.1 cm^{-1} is much lower than the IR intensity shown in Figure 1b.

It is notable in Figure 1 that the center frequency of the monomer ν_2 band of CD_3CN in the solution (2263 cm^{-1}) is essentially the same as that in the pure liquid. The present result is consistent with the previous results for acetonitrile solutions containing other salts: the center frequency of the monomer ν_2 band does not vary with the concentration of salt.[5,17,19] The large variations in the vibrational characteristics, particularly the frequency of the ν_2 band of acetonitrile, due to interaction with electrophilic or nucleophilic species are well-known.[4−16] The ν_2 band is often used as a probe for measurement of the electrophilicity of a Lewis acid in solution. If CD_3CN that is not in the primary solvation shell interacts inductively with solvated Mg^{2+}, a frequency shift is expected to be observable from the ν_2 band. This suggests that only the directly coordinated CD_3CN molecules are affected by the electrophilicity of Mg^{2+}, leading to a blue shift of 40 cm^{-1}, while the electronic structure of other CD_3CN molecules in the solution remains virtually unaffected.

It is also notable in Figure 1b that there is a shoulder emerging at 2273 cm^{-1} that becomes more apparent with greater $Mg(ClO_4)_2$ concentration. In search for the origin of the shoulder, a small amount of water was added to the solution. Shown in Figure 2 are the spectra in the ν_2 band region of CD_3CN in the $Mg(ClO_4)_2$ solution at a concentration of 0.9 *m* and the same solution with added water. The mole fractions of water in the binary mixtures of CD_3CN and water are 5, 10, and 20%. When the mole fraction of water is 20%, there are about 5.7 and 22.7 mol of water and CD_3CN for 1 mol of Mg^{2+} in the solution, respectively. By an addition of water, the band at 2303 cm^{-1} quickly weakens and almost disappears at the 20% mole fraction of water, indicating that any residual water in the solution is preferentially coordinated to Mg^{2+} as ligands over CD_3CN. Moreover, the present result shows that most of CD_3CN coordinated to Mg^{2+} is displaced when water is added as much as six times in mole ratio to the number of moles of Mg^{2+} in the solution. Dislodging of acetonitrile from the primary solvation shell by an addition of water was also observed in studies of aquous solutions of acetonitrile containing trivalent cations by Wójcik et al.[5] In their study, new absorption bands were observed on the higher frequency side of the ν_2 band resulting from solvation of trivalent cations in a binary mixture of acetonitrile-water. The intensities of the new bands decreased with addition of water. Determination of the molecular compositions in the solvation shells of a cation as a function of concentration was attempted from the variations in the intensities of the absorption bands.

On the other hand, the intensity of the shoulder at 2273 cm^{-1} increases and the frequency shifts slightly to the red with addition of water. Lindgren et al. studied CD_3CN−water mixtures and reported that the ν_2 band of CD_3CN coordinated to water is located at about 2267 cm^{-1} (blue shifted 4 cm^{-1} from the ν_2 band of pure CD_3CN).[30] The water molecules coordinated to Mg^{2+} should be more electrophilic, and the interaction energy of CD_3CN with the water molecule directly coordinated to Mg^{2+} is expected to be much higher than that with free water, leading to a larger blue shift of the ν_2 band. This leads us to attribute the shoulder at 2273 cm^{-1} in Figure 1b to the ν_2 C≡N stretch of the CD_3CN molecules complexed with residual water in the solution, which is first coordinated to Mg^{2+}. Unlike acetonitrile, water, mainly due to its smaller size and polar structure, allows the electrophilicity of Mg^{2+} to be conveyed through the water molecules in the primary solvation shell. As the water content increases, more water molecules are coordinated to Mg^{2+}, and the average electrophilicity that the water molecules carry in the solution should decrease. This leads to a smaller blue shift of the ν_2 band of CD_3CN complexed with water at a higher water content, while the intensity increases as shown in Figure 2. A similar result was reported recently by Wójcik et al. in their work on the solvation of Cr^{3+} in acetonitrile−water mixtures.[31] The emerged bands at about 2281 and 2270 cm^{-1} were attributed to the C≡N stretches of acetonitrile coordinated to water in the solvation shell of Cr^{3+}.

Shown in Figure 3 are the Raman spectra in the ν_2 band region of pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m*. It is noticeable that the

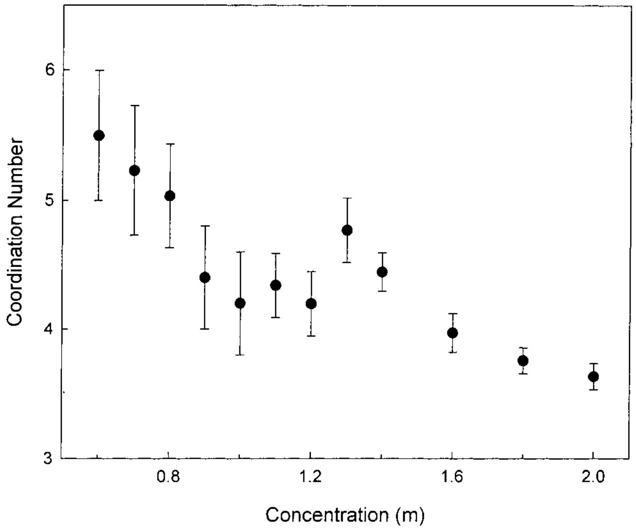

Figure 4. The primary solvation number of CD_3CN around Mg^{2+} as a function of concentration. The concentration is in molality. The uncertainty in determination of the primary solvation number increases at low concentration due to the low intensity of the band at 2302.7 cm^{-1}.

Raman intensity of the ν_2 band of CD_3CN coordinated around the Mg^{2+} ion (2303 cm^{-1}) relative to that of free CD_3CN (not coordinated to Mg^{2+}) in the solution is much lower than the IR intensity of the band shown in Figure 1b. The IR intensity often shows a large variation resulting from various intermolecular interactions. On the other hand, Raman intensity measurements have been used to determine the primary solvation numbers 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 intensities of the band shifted by solvation and the band of free acetonitrile, respectively; c_{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.[32] Previous studies showed that the molar Raman intensity for the ν_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.[19]

Figure 4 shows the primary solvation number of CD_3CN for Mg^{2+} as a function of concentration determined from the integrated intensities of the ν_2 bands at 2303 cm^{-1} (CD_3CN directly coordinated to Mg^{2+}) and 2263 cm^{-1} (free CD_3CN) in the Raman spectrum. The solvation number varies between 3.6 and 5.5, depending on the concentration. At a low concentration, Mg^{2+} ions are probably coordinated only with CD_3CN molecules, leading to a large solvation number, whereas at a high concentration close to the saturation point, the Mg^{2+} ion has more chances to form a contact ion pair with one or more ClO_4^- ions, leading to a smaller solvation number for CD_3CN. The present result indicates that the primary coordination number of Mg^{2+} in acetonitrile is probably 6; at low concentration, most of the six coordination sites are filled with CD_3CN, whereas at high concentration, one or more of the sites are more likely filled with the counterions.

Recently Fawcett and Liu suggested, from the variation in the IR intensity of the monomer ν_2 band of CD_3CN as a function of concentration, that the solvation number of Mg^{2+} in acetonitrile is 3.3.[4] They also argued that 70% of the Mg^{2+} ions form contact ion pairs, assuming that the primary solvation number is 4. However, the effects of concentration on the solvation number were not examined, and when the solvation number itself is a function of concentration, the solvation number cannot be determined correctly from the variation in the IR intensity of the ν_2 C≡N stretch against concentration. It should be remembered that Mg^{2+} is generally regarded as having a primary solvation shell containing six molecules in a variety of nonaqueous solvents, including methanol, ethanol, dimethyl formamide, and dimethyl sulfoxide.[4] The solvation number is determined by NMR spectroscopy for alcohols and by IR transmission spectroscopy for other solvents. At this point, it appears more reasonable that the primary solvation number of Mg^{2+} in acetonitrile is indeed six.

Shown in Figure 5 a,b are the ν_4 C−C stretch and the ν_8 CCN deformation regions in the Raman spectra of pure CD_3CN and CD_3CN in the $Mg(ClO_4)_2$ solution at a concentration of 0.9 *m*. Due to the strengthening of the bonds in the CCN axis by nucleophilic coordination to Mg^{2+}, the frequency shifts

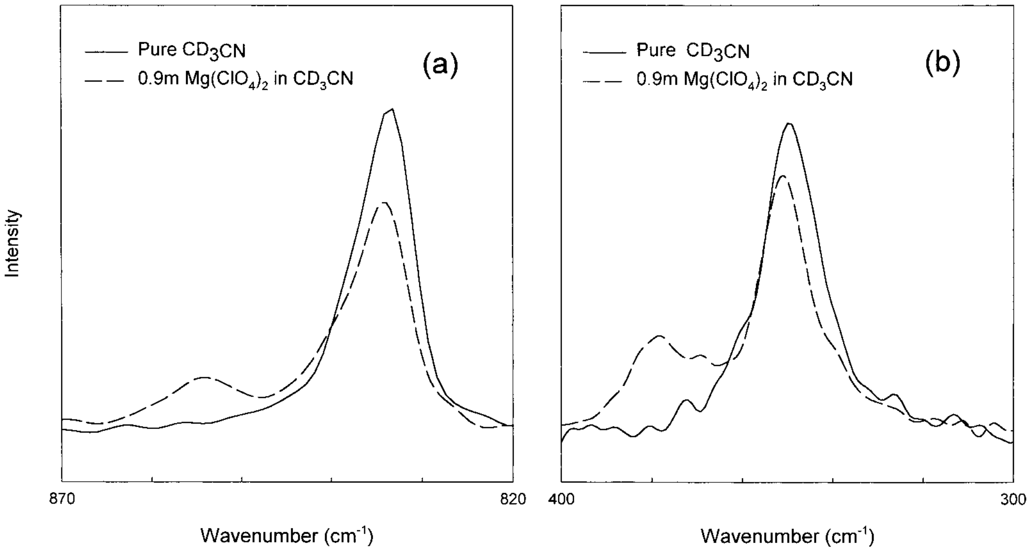

Figure 5. The Raman spectra in the ν_4 (a) and ν_8 (b) regions of pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m*. (a) The bands at 832 and 852 cm^{-1} are due to the ν_4 C−C stretches of the free and CD_3CN coordinated to Mg^{2+}, respectively. (b) The bands at 349 and 378 cm^{-1} are due to the ν_8 CCN deformations of free CD_3CN and CD_3CN coordinated to Mg^{2+}, respectively.

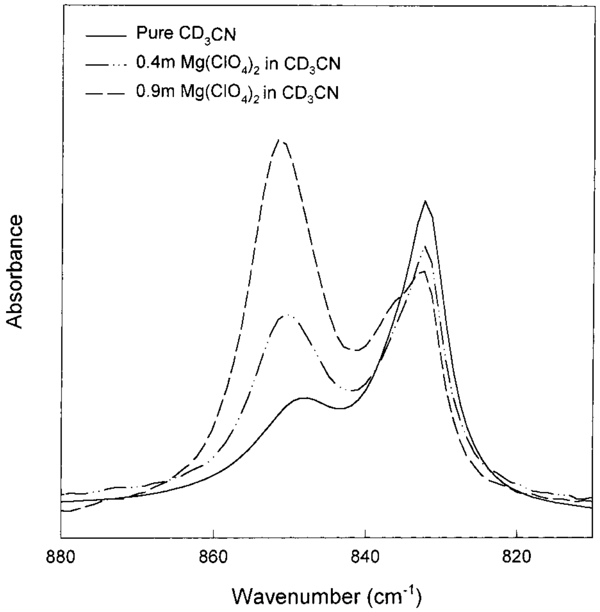

Figure 6. The IR spectra in the ν_4 region of pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$. Under the line profile, there are four absorption bands overlapped: the ν_4 bands of free CD_3CN and CD_3CN interacting with the water residue in the primary solvation shell of Mg^{2+} at 832 and 837 cm^{-1}, respectively;[4] the ν_7 band at 849 cm^{-1}; and the ν_4 band of CD_3CN coordinated to Mg^{2+} at 852 cm^{-1}. The IR intensity ratio of the ν_4 band of CD_3CN coordinated to Mg^{2+} at 852 cm^{-1} relative to that of free CD_3CN at 832 cm^{-1} is much larger than the Raman intensity ration in Figure 5a.

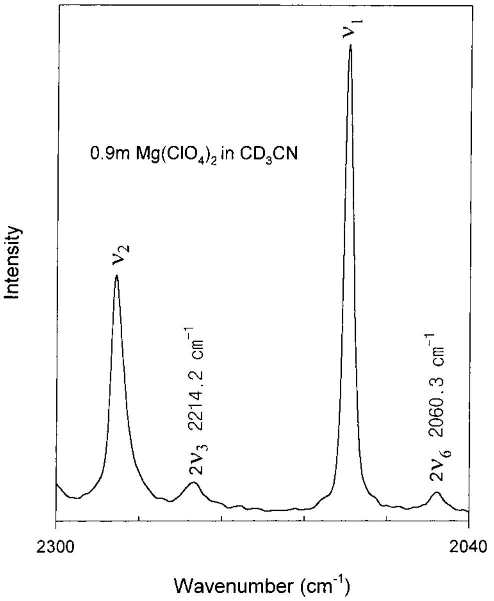

Figure 7. The Raman spectrum in the region of 2300−2040 cm^{-1} of pure CD_3CN and CD_3CN solution containing $Mg(ClO_4)_2$ at a concentration of 0.9 *m*. The absorption bands at 2214.2 and 2060.3 cm^{-1} are due to the overtones of the ν_3 CD_3 symmetric deformation and the ν_6 CD_3 antisymmetric deformation, respectively. The intensities of the bands are quite large considering that they are overtones.

are both in the blue direction. Shown in Figure 6 are the IR spectra in the ν_4 region of pure CD_3CN and CD_3CN solutions containing $Mg(ClO_4)_2$ at 0.4 and 0.9 *m*. Under the line profile shown in Figure 6, there are four absorption bands overlapped: the ν_4 C−C stretching band of free CD_3CN and CD_3CN complexed with residual water first coordinated to Mg^{2+} at 832 and 837 cm^{-1}, respectively;[4] the ν_7 CD_3 rocking band at 849 cm^{-1}; and the ν_4 band of CD_3CN coordinated to Mg^{2+} at 852 cm^{-1}. As observed from the ν_2 band, the vibrational characteristics of the ν_4 and ν_8 bands of free CD_3CN in the solution remain the same, indicating that the CD_3CN molecules only in the primary solvation shell are affected by coordination. Three overtone bands, the $2\nu_3$, $2\nu_6$, and $2\nu_8$ bands, are observed at 2214, 2061, and 688 cm^{-1} in the Raman spectrum, respectively (Figure 7). Particularly the $2\nu_2$ and $2\nu_6$ bands are quite strong, even stronger than the fundamental bands in the Raman spectrum. This indicates that the $2\nu_3$ and $2\nu_6$ bands are in Fermi resonance with the ν_2 and ν_1 bands, respectively, as Evans and Bernstein suggested.[33]

As shown in Figures 1 and 3, the ν_2 intensity of the coordinated CD_3CN at 2303 cm^{-1} relative to those of other bands in the IR spectrum is apparently much stronger than in the Raman spectrum. On the basis of the ratio in integrated intensities between the band at 2303 cm^{-1} (coordinated to Mg^{2+}) and the bands at 2260, 2263, and 2273 cm^{-1} (not coordinated Mg^{2+}) in the IR spectrum with that in Raman spectra, the increase in the IR extinction constant of the ν_2 C≡N stretch by coordination to Mg^{2+} is about 4.4-fold. The absorption band at 852 cm^{-1}, which is due to the ν_4 C−C stretch of CD_3CN coordinated to Mg^{2+}, also shows a dramatic increase in IR intensity, as shown in Figure 6. From the intensity ratio between the ν_4 band at 852 cm^{-1} (coordinated to Mg^{2+}) and the ν_4 bands at 832 and 837 cm^{-1} (not coordinated Mg^{2+}) in the IR spectrum and that in the Raman spectrum, the increase in the IR extinction constant of the ν_4 band by coordination to Mg^{2+} is estimated to be about 4-fold. The large increases in the IR intensities of the C≡N and C−C stretches are originated from the charge redistribution along the CCN axis, which is in turn generated by the interaction of the electron-rich nitrogen end of CD_3CN with Mg^{2+}.

The free perchlorate anion with T_d symmetry has four vibrational modes: A_1 symmetric stretch (933 cm^{-1}), E symmetric deformation (459 cm^{-1}), F_2 asymmetric stretch (1000−1160 cm^{-1}), and F_2 asymmetric deformation (625 cm^{-1}).[4] Among them only the latter two are IR active, whereas all of them are Raman active. The F_2 asymmetric stretch band, which is very strong, is originally located at 1119 cm^{-1}. When the anion is bound through one of the oxygen atoms, its symmetry is reduced to C_{3v}, and therefore, the F_2 band is split into two bands (A_1 and E). Various interactions with solvent molecules through hydrogen bonding with the methyl groups further split the band, and as a result, the F_2 asymmetric stretching band is very broad, due to overlapping of the bands (Figure 8).

The frequencies of CD_3CN and frequency shifts upon solvation of $Mg(ClO_4)_2$ observed in this study are summarized in Table 1. While the ν_2 C≡N stretch, ν_4 C−C stretch, and ν_8 CCN deformation show large variations in the frequencies and intensities, the vibrational characteristics of other vibrational modes including the CD_3 stretches remain virtually the same, indicating that the interaction between acetonitrile and Mg^{2+} does not occur through the methyl group of acetonitrile. This more evidences that the point of attachment to the cation is through the nitrogen lone-pair electrons. As mentioned above, the frequencies of free CD_3CN in the solution do not show substantial shifts from those of pure CD_3CN. This indicates that while the chemical bonds in the CCN axis of the CD_3CN molecules directly coordinated to Mg^{2+} are greatly affected by the electrophilicity of the cation, the induction effects to the remaining CD_3CN molecules through the primary shell of coordination is very small. The present result suggests that there is probably only a single solvation shell of CD_3CN around the

TABLE 1: Observed Frequencies of Free and Coordinated CD_3CN^a

mode		description	pure CD_3CN	$Mg(ClO_4)_2$ solution			coordinated to water
				free^b	coordinated^c	$\Delta\nu^d$	
A_1	ν_1	CD_3 sym str	2116.6	2115.2	2115.2	−1.4	
	ν_2	C≡N str	2263.1	2263.0	2302.7	39.7	2273.3
	ν_3^e	CD_3 sym def	1101.9				
	ν_4	CC str	832.0	832.2	852.1	19.9	837.1
E	ν_5^f	CD_3 antisym str					
	ν_6^e	CD_3 antisym def	1038.1				
	ν_7	CD_3 rock	848.7	849.4	849.4	0.7	
	ν_8^g	CCN def	349.3	350.9	378.2	27.3	
overtones	$2\nu_3^g$	CD_3 sym def	2213.6	2214.2	2214.2	0.6	
	$2\nu_6^g$	CD_3 antisym def	2060.6	2060.3	2060.3	−0.3	
	$2\nu_8$	CCN def	688.3	688.5	734.4	45.9	

[a] All frequencies are in cm^{-1}. [b] Free CD_3CN in CD_3CN solution containing $Mg(ClO_4)_2$. [c] Coordinated to Mg^{2+} in CD_3CN solution containing $Mg(ClO_4)_2$. [d] Frequency difference between the vibrational bands of pure CD_3CN and CD_3CN coordinated to Mg^{2+}. [e] Overlapped by the F_2 asymmetric stretching band of ClO_4^- in the solution. [f] Overlapped by the ν_2 band of CD_3CN. [g] Frequency determined from the Raman spectrum.

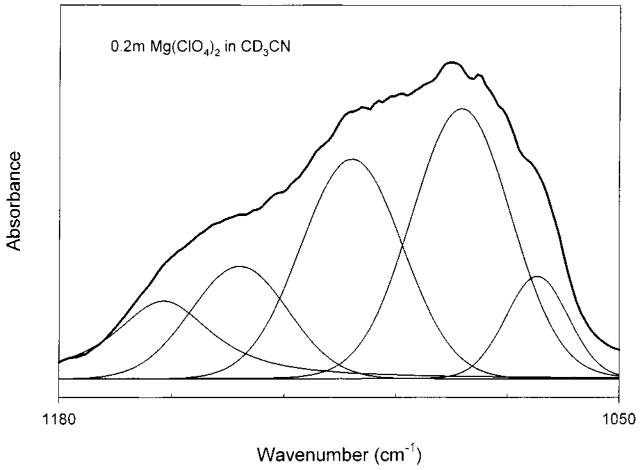

Figure 8. The F_2 asymmetric stretch region of ClO_4^- in CD_3CN at 0.2 m $Mg(ClO_4)_2$. Due to symmetry lowering of ClO_4^- by interaction with solvent molecules, the F_2 asymmetric stretching band is split into several bands in the solution.

Mg^{2+} ion in which the electronic or vibrational characteristics of acetonitrile are noticeably affected by Mg^{2+}.

The present result is in contrast to the common idea of solvation of metal cation in polar solvents. For instance, the metal cation in inorganic solvents such as water and ammonia carries multiple sheaths of solvation. Unlike water or ammonia, acetonitrile has a considerably large molecular size, and the molecular dipole moment is primarily originated from the nitrile group. As a result, a single solvation shell of acetonitrile may be able to block effectively the induction of the cation. It is interesting that recently Wójcik et al. studied acetonitrile−water mixtures containing trivalent cations Al^{3+}, Fe^{3+}, and Cr^{3+} and assumed more than one solvation shells of acetonitrile to explain their results including new absorption features emerging on the higher frequency side of the monomer ν_2 band. However, they did not clearly explain the effects of water in the solvation shell.[5] The water molecules coordinated to a cation can in turn interact with acetonitrile, resulting in a considerable blue shift of the ν_2 and ν_4 bands. Apparently further studies are required to understand the properties and structure of the solvation shell of a cation that consists of an organic solvent.

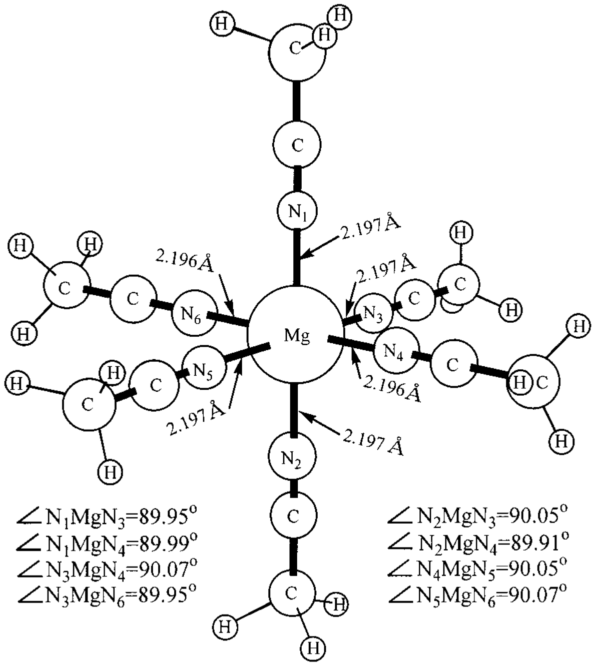

Figure 9. The optimized geometry of $Mg[CD_3CN]_6^{2+}$ at BLYP/6-31+G(2d,p). Due to the geometrical characteristics of acetonitrile (C_{3v}), the complex has C_1 symmetry.

TABLE 2: Geometrical Parameters of Free CD_3CN and CD_3CN Coordinated to Mg^{2+}

geometrical parameters	CH_3CN		$Mg[CD_3CN]_6^{2+\,a}$
	expl^b	calcd	
r(C−H), Å	1.094	1.089	1.101
r(C−C), Å	1.460	1.465	1.460
r(C≡N), Å	1.157	1.176	1.165
∠HCH, deg	109.0	109.0	109.0
∠CCH, deg		110.0	110.0
∠NCC, deg	180.0	180.0	180.0
μ,^{c} D	3.9252^d	4.34	0.0031
q^e		0.24	0.26
ΔE,^{f} kJ/mol			31.6

[a] Calculated values. [b] Reference 16. [c] Dipole moment. [d] Reference 29. [e] Mulliken charge on nitrogen. [f] Binding energy for $Mg[CD_3CN]_6^{2+}$.

DFT calculations at the BLYP/6-31+G(2d,p) level were carried out for CD_3CN coordinated to Mg^{2+}. The coordination number was assumed to be 6, the optimized geometry is shown in Figure 9, and the geometrical parameters of CD_3CN coordinated to Mg^{2+} are compared with those of free CD_3CN in Table 2. The variation of Mulliken charge on the nitrogen atom and the binding energy are also listed in Table 2. Because the structure of acetonitrile has C_{3v} symmetry, the solvated $Mg[CD_3CN]_6^{2+}$ does not have O_h symmetry, resulting in the slightly different Mg^{2+}−N distances. Nevertheless, the geometrical parameters for the six CD_3CN molecules are essentially the same. The shortening of the C≡N bond length, consequent to complex formation, is consistent with the previous results

TABLE 3: Calculated Frequencies of Free CD_3CN and CD_3CN Coordinated to Mg^{2+a}

mode	CD_3CN^b	$Mg(CD_3CN)_6^{2+\,b}$	$\Delta\nu^c$
ν_1 CD_3 sym str	2142 (2.7)	2145 (4.3)	3
ν_2 C≡N str	2257 (9.5)	2286 (120)	29
ν_3 CD_3 sym def	1092 (0.22)	1086 (0.82)	−6
ν_4 CC str	819 (0.80)	838 (4.8)	19
ν_5 CD_3 antisym str	2258 (2.0)	2267 (2.3)	9
ν_6 CD_3 antisym def	1036 (9.9)	1023 (13)	−13
ν_7 CD_3 rock	836 (0.77)	839 (7.8)	3
ν_8 CCN def	337 (1.3)	397 (65)	60

[a] All frequencies are averaged values for six CD_3CN molecules, in cm^{-1}. [b] Numbers in parentheses are the calculated IR intensities. [c] Frequency difference between the vibrational bands of pure CD_3CN and coordinated CD_3CN to Mg^{2+}.

observed in other systems.[5,8] This distinctive behavior of the C≡N bond is in contrast to the general trend of bond lengthening in donor−acceptor complexation,[34] which is generally thought to be due to alleviation of the antibonding character of the C≡N bond as a result of electron donation to the electron acceptor. A reduction in the antibonding character of the C≡N bond has also been found in analysis of the present calculation. In addition, the rearrangement in the electronic structure, particularly for the CCN moiety, as a result of solvation is further indicated by the change in the vibrational characteristics and force constants.

Since the oscillators of the six CD_3CN molecules are coupled in the complex, each fundamental mode leads to six vibrational modes. However, the differences in frequency, particularly for the IR active modes, are quite small (less than 2 cm^{-1}). Listed in Table 3 are the calculated frequencies and IR intensities of the fundamental vibrations for the $Mg[CD_3CN]_6^{2+}$ complex. The frequency shifts and large increases in the IR intensity by solvation of $Mg(ClO_4)_2$, particularly for the ν_2 and ν_4 bands, are well-reproduced by calculation. The large frequency shift and intensity change of the ν_8 band are partly due to mixing of the CCN deformations and the Mg^{2+}−N stretches. Calculations show that the force constant of the C≡N stretch increases about 3% upon solvation, which is also consistent with those determined for acetonitrile complexes with other Lewis acids, including metal cations and haloboranes.[13−16]

IV. Conclusions

Infrared studies were carried out for CD_3CN solutions containing $Mg(ClO_4)_2$. A large blue shift (40 cm^{-1}) of the ν_2 C≡N stretch results from solvation of Mg^{2+} and a small red shift (3 cm^{-1}) from solvation of ClO_4^- ion. Mg^{2+} is preferentially solvated by water over acetonitrile, and the shoulder found at 2273 cm^{-1} is attributed to the ν_2 band of CD_3CN complexed with the water molecules (included in the solution as an impurity) contained in the primary solvation shell. By measuring the Raman intensities of the ν_2 bands of CD_3CN coordinated to Mg^{2+} and free CD_3CN, the primary coordination number of the cation in acetonitrile is determined as 6. The solvation number of CD_3CN approaches 6 at a low concentration of $Mg(ClO_4)_2$, whereas the number becomes about 4 at a high concentration, indicating that the chances for the Mg^{2+} ion to form contact ion pairs with one or more ClO_4^- ions increase with increasing concentration. The IR extinction constants of the ν_2 C≡N stretch and the ν_4 C−C stretch increase 4.4- and about 4-fold upon coordination, respectively. The solvation effects for the vibrational characteristics of other vibrational bands are also observed and summarized. The vibrational characteristics of free CD_3CN in the solution remain essentially the same as those of pure CD_3CN, indicating that the induction effect through the primary solvation shell of acetonitrile is virtually negligible.

The structure and vibrational characteristics of CD_3CN coordinated to Mg^{2+} were also examined by means of DFT methods at the BLYP/6-31+G(2d,p) level, assuming the primary solvation number 6. The C≡N bond shortens and the force constant increases upon solvation, consistent with the previous results observed in studies of interaction of acetonitrile with other Lewis acids. The variation in the vibrational characteristics, particularly the increases in intensity and the blue shifts of the C≡N and C−C stretches, are well-reproduced. The variation of the structure and vibrational characteristics originated from the rearrangement in the electronic structure, including alleviation of the antibonding character along the CCN moiety as a result of solvation.

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References and Notes

(1) Sandholm, S. T.; Bjarnov, E.; Schwendeman, R. H. *J. Mol. Spectrosc*. **1982**, *95*, 276.

(2) Kukolich, S. G. *J. Chem. Phys*. **1982**, *76*, 997.

(3) Sassi, P.; Paliani, G.; Cataliotti, R. S. *J. Chem. Phys*. **1998**, *108*, 10197.

(4) Fawcett, W. R.; Liu, G. *J. Phys. Chem*. **1992**, *96*, 4231.

(5) Jamrós, D.; Wójcik, M.; Lindgren, J.; Stangret, J. *J. Phys. Chem. B* **1997**, *101*, 6758.

(6) Miyaji, K.; Morinaga, K. *Bull. Chem. Soc. Jpn*. **1986**, *59*, 1695.

(7) Cabaleiro-Lago, E. M.; Ríos, M. A. *J. Phys. Chem*. **1997**, *101*, 8327.

(8) Nyquist, R. A. *Appl. Spectrosc*. **1990**, *44*, 1405.

(9) Dimitrova, Y. *J. Mol. Struct*. **1995**, *343*, 25.

(10) Saito, T.; Yamakawa, M.; Taksuka, M. *J. Mol. Spectrosc*. **1981**, *90*, 359.

(11) Bertie, J. E.; Lan, Z. *J. Phys. Chem. B* **1997**, *101*, 4111.

(12) Hoskins, A. R.; Edwards, H. G. M.; Johnson, A. F. *J. Mol. Struct*. **1991**, *263*, 1.

(13) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem*. **1969**, *8*, 2183.

(14) Swanson, B.; Shriver, D. F. *Inorg. Chem*. **1970**, *9*, 1406.

(15) Shriver, D. F.; Swanson, B. *Inorg. Chem*. **1971**, *10*, 1354.

(16) Vijay A.; Sathyanarayana, D. N. *J. Phys. Chem*. **1996**, *100*, 75.

(17) Fawcett, W. R.; Liu, G.; Faguy, P. W.; Foss, C. A., Jr.; Motheo, A. J. *J. Chem. Soc., Faraday Trans*. **1993**, *89*, 811.

(18) Evans, J. C.; Lo, G. Y.-S. *Spectrochim. Acta* **1965**, *21*, 1033.

(19) Oliver, B. G.; Janz, G. J. *J. Phys. Chem*. **1970**, *74*, 3819.

(20) Sajeevkumar, V. S.; Singh, S. *J. Mol. Struct*. **1996**, *382*, 101.

(21) Islam, M. S.; Rethrick, R. A.; Pugh, D. *J. Phys. Chem. A* **1998**, *102*, 2201.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Fawcett, W. R.; Liu, G.; Kessler, T. E. *J. Phys. Chem*. **1993**, *97*, 9293.

(24) Jurgens, R.; Almlöf, J. *Chem. Phys. Lett*. **1991**, *176*, 263.

(25) Ablaeva, M. A.; Zsidomirov, G. M.; Pelmenshchikov, A. G.; Burgina, E. B.; Baltakhinov, V. P. *React. Kinet. Catal. Lett*. **1992**, *48*, 569.

(26) Miller, J. M.; Onyszchuk, M. *Can. J. Chem*. **1966**, *44*, 899.

(27) Pews, R. G.; Tsuno, Y.; Taft, R. W. *J. Am. Chem. Soc*. **1967**, *89*, 2391.

(28) Freedman, T. B.; Nixon, E. R. *Spectrochim. Acta* **1972**, *28A*, 1375.

(29) Cho, H.-G.; Cheong, B.-S. *J. Mol. Struct. (THEOCHEM)* **2000**, *496*, 185.

(30) Jamroz, D.; Stangret, J.; Lindgren, J. *J. Am. Chem. Soc*. **1993**, *115*, 6165.

(31) Jamroz, D.; Wójcik, M.; Lindgren, J. *Spectrochim. Acta* **2000**, *A 56*, 1939.

(32) Balasubrahmanyam, K.; Janz, G. J. *J. Am. Chem. Soc*. **1970**, *92*, 4189.

(33) Evans, J. C.; Bernstein, H. J. *Can. J. Chem*. **1955**, *33*, 1746.

(34) Gutmann, V.; Resch, G.; Linert, W. *Coord. Chem. Rev*. **1982**, *43*, 133.