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## Vibrational Spectroscopy of C≡N Stretch in Mixtures of Deuterated Acetonitrile and Methanol

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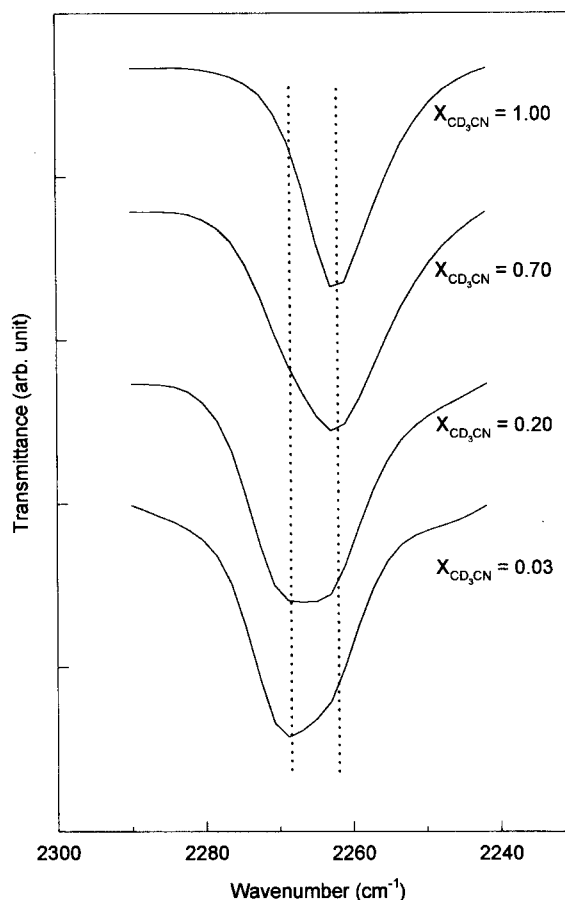
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The general spectral characteristics of hydrogen-bonded molecules have been studied since 1930's.<sup>1</sup> Yet, hydrogen bonding still remains as an intriguing subject, particularly in vibrational spectroscopy, related to aggregation,<sup>2</sup> molecular structure,<sup>3</sup> bond energy,<sup>4</sup> etc. While the effects on the frequency and the intensity of hydrogen stretch have been systematically studied,<sup>5</sup> the effects on the electron-donor are relatively less understood. Recently unusual hypsochromic shifts of C≡N stretch of acetonitrile in aqueous solution have been observed as results of hydration and co-solvation of metallic cations.<sup>6,7</sup> The large shifts (up to 50 cm<sup>-1</sup>) are attributed to electrophilic coordination of cations to the lone pair electrons of nitrogen of acetonitrile,<sup>7</sup> and the hydrogen bond formed between the nitrile group and water molecule results in a hypsochromic shift of about 4 cm<sup>-1</sup>.<sup>6</sup> In this communication, we report the hypsochromic shift of the  $\nu_2$  band of acetonitrile in methanol and ab initio results elucidating the causes of the shift.

The  $\nu_2$  band of acetonitrile, better known as C≡N stretch, is located at 2254 cm<sup>-1</sup>, and another band shifted by about 40 cm<sup>-1</sup> toward higher frequency is a combination band  $\nu_3 + \nu_4$  (CH<sub>3</sub> bending and C—C stretching modes) with enhanced intensity due to Fermi resonance.<sup>7</sup> To avoid possible interference in observation of hypsochromic shift of the  $\nu_2$  band, deuterated acetonitrile was used instead for this study. Deuterated acetonitrile (99.6%, spectroscopic grade) was purchased in ampule from Merck and used without any additional treatment. Methanol was distilled over CaH<sub>2</sub> to remove moisture. Mixtures of CD<sub>3</sub>CN and CH<sub>3</sub>OH were prepared with mole fractions of CD<sub>3</sub>CN ranging from 0.01 to 1. The sample was sandwiched with CaF<sub>2</sub> or ZnSe windows, and in order to obtain suitable absorption intensity of the  $\nu_2$  band, the sample thickness was adjusted using spacers or a variable pathlength liquid cell depending on the needed thickness. The spectra were recorded on a Biorad FTS-175C FT-IR spectrometer, which was continuously circulated with filtered air free of moisture and CO<sub>2</sub>.

The  $\nu_2$  band of CD<sub>3</sub>CN is situated at 2262 cm<sup>-1</sup> (Figure 1) and shows a slightly asymmetric lineshape due to overlap with two hotbands ( $\nu_2 + \nu_8 - \nu_8$  and  $\nu_2 + 2\nu_8 - 2\nu_8$ ) where  $\nu_8$  denotes the C—C≡N bending mode. Evidently

moderate intensity borrowing occurs between the hotbands and a C—D stretching band located at 2250 cm<sup>-1</sup>.<sup>6</sup> Figure 1 shows the spectral change in the region of the  $\nu_2$  band with mole fraction of CD<sub>3</sub>CN. While a new band emerges at about 2269 cm<sup>-1</sup> as the mole fraction lowers, the intensity of the  $\nu_2$  band at 2262 cm<sup>-1</sup> decreases. The newly observed band has been assigned to the  $\nu_2$  band of hydrogen-bonded



**Figure 1.** Variation of the  $\nu_2$  band of CD<sub>3</sub>CN as a function of mole fraction. All the spectra are taken at 4 cm<sup>-1</sup> resolution and at room temperature.

**Table 1.** Molecular characteristics for the  $\nu_2$  mode of  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CN-CH}_3\text{OH}$ 

	$r$ (C $\equiv$ N) (Å) <sup>a</sup>	$\kappa$ (C $\equiv$ N) <sup>b</sup>	$\nu$ (cm <sup>-1</sup> ) (cal.) <sup>c</sup>	$\nu$ (cm <sup>-1</sup> ) (exp.) <sup>d</sup>
$\text{CD}_3\text{CN}$	1.1291	21.084	2307	2262
$\text{CD}_3\text{CN-CH}$	1.1283	21.189	2313	2269

<sup>a</sup> CN bond length. <sup>b</sup> C $\equiv$ N stretch force constant in mdyne/Å. <sup>c</sup> Scale factor (0.89) is used. <sup>d</sup> Frequency of the  $\nu_2$  band measured in this study.

$\text{CD}_3\text{CN}$ . This hypsochromic shift of the  $\nu_2$  band is rather surprising since weakening of the CN bond, thus, a shift of the band to the lower frequency, is normally expected due to the electrostatic interaction between the hydroxy hydrogen and the nitrogen atoms. Yet, the observed hypsochromic shift is consistent with recently reported results from acetonitrile in water.<sup>6,7</sup>

In an effort to explain the unusual hypsochromic shift of the  $\nu_2$  band, *ab initio* calculations have been performed. All the calculations were proceeded at HF/6-311+G(d,p) level using the GAMESS packages,<sup>8</sup> and in geometry optimizations, all the parameters were fully relaxed. Listed in Table 1 are the molecular characteristics of  $\text{CD}_3\text{CN}$  and hydrogen-bonded complex of  $\text{CD}_3\text{CN}$  and  $\text{CH}_3\text{OH}$ . The calculated  $\nu_2$  frequency of  $\text{CD}_3\text{CN-CH}_3\text{OH}$  complex is 6 cm<sup>-1</sup> higher (after applying a scale factor of 0.89) than that of  $\text{CD}_3\text{CN}$ , which is compared to the measured difference, 7 cm<sup>-1</sup>. Analysis of electron density indicates that the

hypsochromic shift is caused by migration of the lone electron pair localized on the nitrogen atom toward the hydroxy hydrogen atom of  $\text{CH}_3\text{OH}$  in complexation. Illustrated in Figure 2 is the density diagrams of the lone electron pair of  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CN-CH}_3\text{OH}$  complex, which show the antibonding characteristics of the electron pair and the migration of electron density due to complexation. The less congested contours around the nitrogen atom in  $\text{CD}_3\text{CN-CH}_3\text{OH}$  indicate the reduction of electron density, leading to strengthening of the CN bond. Our internal mode analyses<sup>9</sup> show that the stretching force constant of the CN bond increases by  $1.05 \times 10^{-4}$  dyne/Å as a result of complexation, while the length of the CN bond decreases by 0.0008 Å. Since the C $\equiv$ N stretch consists more than 90% of the  $\nu_2$  mode, the higher force constant is most likely responsible for the higher frequency.

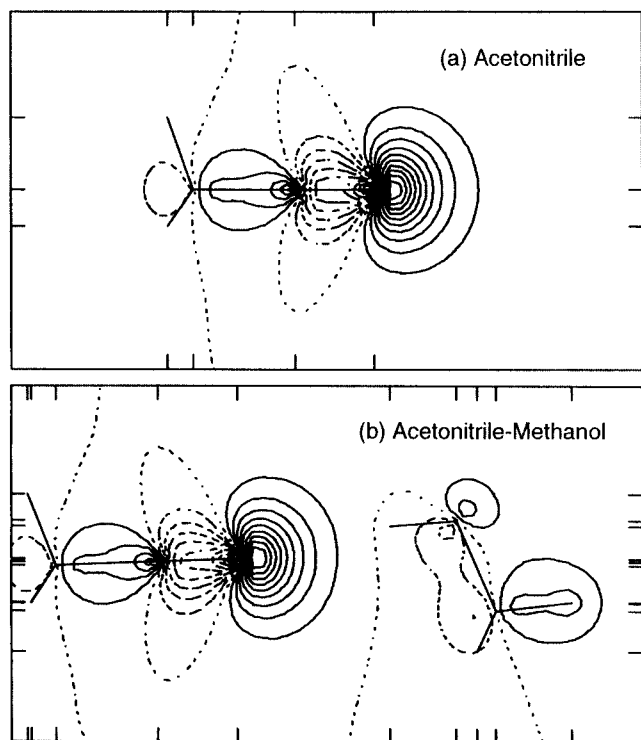
The current result also indicates that the association of  $\text{CH}_3\text{OH}$  molecules is favored over that between  $\text{CD}_3\text{CN}$  and  $\text{CH}_3\text{OH}$  molecules. At  $\text{CD}_3\text{CN}$  mole fraction of 0.5, the band at 2262 cm<sup>-1</sup> is much stronger than that at 2268 cm<sup>-1</sup>, and even at very low mole fraction (down to 0.01), the band at 2262 cm<sup>-1</sup> shows substantial intensity. This suggests that even at very low concentration, a certain portion of  $\text{CD}_3\text{CN}$  molecules stay isolated in  $\text{CH}_3\text{OH}$ . Hydrogen bonding between  $\text{CD}_3\text{CN}$  and  $\text{CH}_3\text{OH}$  molecules, which requires the effective bonding network of oxygen and hydrogen of  $\text{CH}_3\text{OH}$  to be torn down, should be energetically unfavorable over the hydrogen bonding between  $\text{CH}_3\text{OH}$  molecules.

In conclusion, we have observed the hypsochromic shift of the  $\nu_2$  band of  $\text{CD}_3\text{CN}$  as a result of hydrogen bonding with  $\text{CH}_3\text{OH}$ , and the shift has been explained by the reduction of the antibonding characteristic of the lone electron pair on the nitrogen atom. The persisting  $\nu_2$  band at 2262 cm<sup>-1</sup> even at very low  $\text{CD}_3\text{CN}$  concentration suggests that the hydrogen bond between methanol molecules is much stronger than that between acetonitrile and methanol.

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**Figure 2.** Density diagrams for the lone electron pair of the nitrogen in (a) acetonitrile and (b) acetonitrile-methanol complex. Tick marks show the locations of the atoms, and the solid and broken lines represent the signs of the molecular orbitals. Note that there is one more contour line around the nitrogen of acetonitrile, indicating higher electron density.