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

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The general spectral characteristics of hydrogen-bonded molecules have been studied since 1930's.¹ Yet, hydrogen bonding still remains as an intriguing subject, particularly in vibrational spectroscopy, related to aggregation,² molecular structure,³ bond energy,⁴ etc. While the effects on the frequency and the intensity of hydrogen stretch have been systematically studied,⁵ 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.^{6,7} The large shifts (up to 50 cm⁻¹) are attributed to electrophilic coordination of cations to the lone pair electrons of nitrogen of acetonitrile,⁷ and the hydrogen bond formed between the nitrile group and water molecule results in a hypsochromic shift of about 4 cm⁻¹.⁶ In this communication, we report the hypsochromic shift of the ν_2 band of acetonitrile in methanol and ab initio results elucidating the causes of the shift.

The ν_2 band of acetonitrile, better known as C≡N stretch, is located at 2254 cm⁻¹, and another band shifted by about 40 cm⁻¹ toward higher frequency is a combination band $\nu_3 + \nu_4$ (CH₃ bending and C—C stretching modes) with enhanced intensity due to Fermi resonance.⁷ To avoid possible interference in observation of hypsochromic shift of the ν_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 CaH₂ to remove moisture. Mixtures of CD₃CN and CH₃OH were prepared with mole fractions of CD₃CN ranging from 0.01 to 1. The sample was sandwiched with CaF₂ or ZnSe windows, and in order to obtain suitable absorption intensity of the ν_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 CO₂.

The ν_2 band of CD₃CN is situated at 2262 cm⁻¹ (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 ν_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⁻¹.⁶ Figure 1 shows the spectral change in the region of the ν_2 band with mole fraction of CD₃CN. While a new band emerges at about 2269 cm⁻¹ as the mole fraction lowers, the intensity of the ν_2 band at 2262 cm⁻¹ decreases. The newly observed band has been assigned to the ν_2 band of hydrogen-bonded

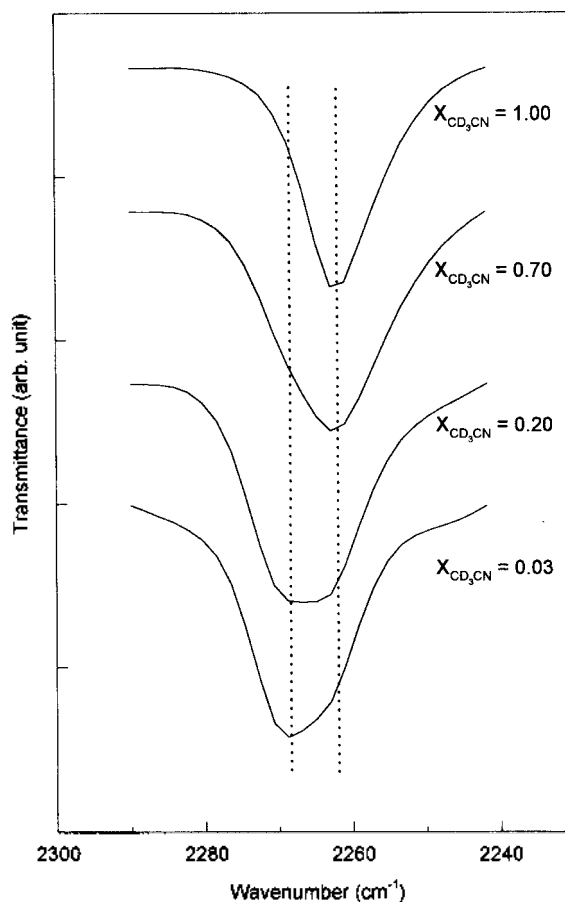


Figure 1. Variation of the ν_2 band of CD₃CN as a function of mole fraction. All the spectra are taken at 4 cm⁻¹ resolution and at room temperature.

Table 1. Molecular characteristics for the ν_2 mode of CD_3CN and $\text{CD}_3\text{CN-CH}_3\text{OH}$

	$r(\text{C}\equiv\text{N})$ (Å) ^a	$\kappa(\text{C}\equiv\text{N})$ ^b	$\nu(\text{cm}^{-1})$ (cal.) ^c	$\nu(\text{cm}^{-1})$ (exp.) ^d
CD_3CN	1.1291	21.084	2307	2262
$\text{CD}_3\text{CN-CH}$	1.1283	21.189	2313	2269

^a CN bond length. ^b $\text{C}\equiv\text{N}$ stretch force constant in $\text{mdyne}/\text{Å}$. ^c Scale factor (0.89) is used. ^d Frequency of the ν_2 band measured in this study.

CD_3CN . This hypsochromic shift of the ν_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.^{6,7}

In an effort to explain the unusual hypsochromic shift of the ν_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,⁸ and in geometry optimizations, all the parameters were fully relaxed. Listed in Table 1 are the molecular characteristics of CD_3CN and hydrogen-bonded complex of CD_3CN and CH_3OH . The calculated ν_2 frequency of $\text{CD}_3\text{CN-CH}_3\text{OH}$ complex is 6 cm^{-1} higher (after applying a scale factor of 0.89) than that of CD_3CN , which is compared to the measured difference, 7 cm^{-1} . 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 CH_3OH in complexation. Illustrated in Figure 2 is the density diagrams of the lone electron pair of CD_3CN 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 analyses⁹ show that the stretching force constant of the CN bond increases by $1.05 \times 10^{-4}\text{ dyne}/\text{Å}$ as a result of complexation, while the length of the CN bond decreases by 0.0008 Å . Since the $\text{C}\equiv\text{N}$ stretch consists more than 90% of the ν_2 mode, the higher force constant is most likely responsible for the higher frequency.

The current result also indicates that the association of CH_3OH molecules is favored over that between CD_3CN and CH_3OH molecules. At CD_3CN mole fraction of 0.5, the band at 2262 cm^{-1} is much stronger than that at 2268 cm^{-1} , and even at very low mole fraction (down to 0.01), the band at 2262 cm^{-1} shows substantial intensity. This suggests that even at very low concentration, a certain portion of CD_3CN molecules stay isolated in CH_3OH . Hydrogen bonding between CD_3CN and CH_3OH molecules, which requires the effective bonding network of oxygen and hydrogen of CH_3OH to be torn down, should be energetically unfavorable over the hydrogen bonding between CH_3OH molecules.

In conclusion, we have observed the hypsochromic shift of the ν_2 band of CD_3CN as a result of hydrogen bonding with CH_3OH , and the shift has been explained by the reduction of the antibonding characteristic of the lone electron pair on the nitrogen atom. The persisting ν_2 band at 2262 cm^{-1} even at very low CD_3CN concentration suggests that the hydrogen bond between methanol molecules is much stronger than that between acetonitrile and methanol.

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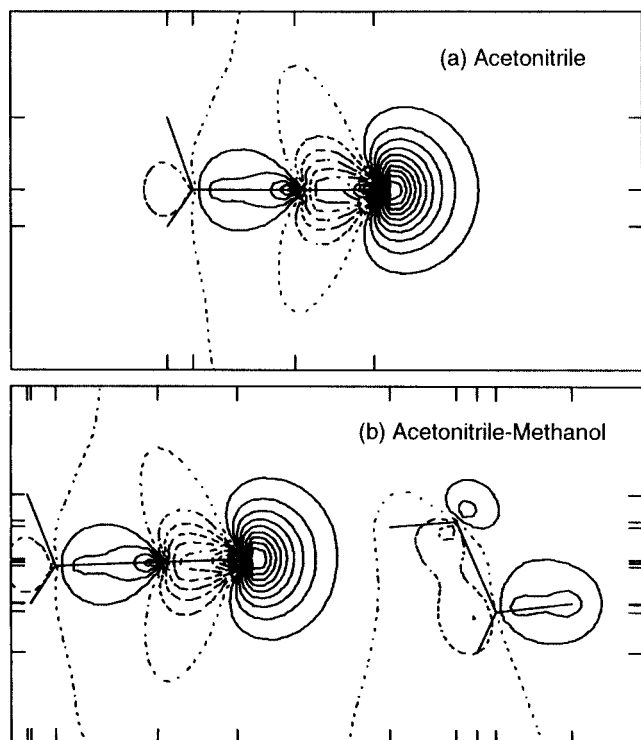


Figure 2. Density diagrams for the lone electron pair of the nitrogen in (a) acetonitrile and (b) acetonitrile-methanol complex. Tick marks show the locations of the atoms, and the solid and broken lines represent the signs of the molecular orbitals. Note that there is one more contour line around the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