

RAMAN SPECTRAL STUDIES ON THE STRUCTURE OF ACETONITRILE AND ITS SOLUTIONS WITH ELECTROLYTES AND NONELECTROLYTES

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ABSTRACT

Raman spectra of acetonitrile is reported in its solutions with carbon tetrachloride, water, methanol, dimethyl sulphoxide (DMSO) and some electrolytes in C≡N stretching as well as in CH₃ stretching regions. Vibrational correlation functions are computed for the CH₃ stretching mode for varying concentrations of solutions. The vibrational relaxation times evaluated are also reported for these systems. It is found that association of acetonitrile through dipolar interactions is accompanied by an increase in intensity and a decrease in the frequency of C≡N band, whereas interactions through hydrogen bonding are accompanied by a decrease in intensity and increase in frequency. In the case of hydrogen bonding through methanol and also interactions through cations, new bands on the high frequency side appear, which are assigned to the complexed C≡N stretching bands. The CH₃ vibrational relaxation times are found to decrease on dilution for aqueous solutions of acetonitrile, whereas an increase in the vibrational relaxation times is found in the solutions of acetonitrile in CCl₄. In the case of solutions of electrolytes in acetonitrile, the vibrational relaxation times decrease with increasing concentration of electrolyte. The results are explained on the basis of the effect of complexation of C≡N on the CH₃ group.

INTRODUCTION

ACETONITRILE is highly polar liquid ($\mu = 3.9$ D), and because of its physical behaviour as well as its importance as water like organic solvent, considerable interest has been shown in studies relating to its structure in liquid, solution and solid phases¹⁻⁴. Recent reviews¹⁻³ summarize the various aspects of studies on the structure of acetonitrile in condensed phases. Liquid acetonitrile contains molecules with antiparallel molecular orientations. Because of such alignment it is deduced that the charges of the dipoles are located at the ends of the molecules and not on the nitrile group. The centre of the dipole and the centre of the molecule are therefore similarly placed. Dielectric investigations of acetonitrile in gaseous⁴ and liquid state⁵ as well as infrared investigations in argon matrices⁶ and in solutions^{7,8} evinced that the antiparallel arrangement of the dipoles is more stable than the axial arrangement.

As discussed by Lippert and Michel¹ the nitrile group is influenced by four effects, two axial and two perpendicular. The methyl group is influenced by three effects, one axial, one perpendicular and one in the direction of the C-H bond. The electrons of the nitrile bond can be polarized by electric fields in axial and perpendicular directions. While axial fields increase the CN stretching band intensity, the perpendicular fields decrease it. Besides the dipole interactions, perpendicular π -complexes and axial ' σ ' complexes of Lewis acids with the free pair of electrons of the nitrile group can be predicted. Kecki and Wojtczak⁹ calculated the frequency shifts and intensities of the CN stretching bands by CNDO method. It is shown that the frequencies are influenced by the lone pair electrons, while the intensities are influenced by the polarization of the π -electrons. Because the lone pair electrons have in part an antibonding character, the normal decrease in force constant due to intermolecular interactions gets compensated

by increase in the force constant due to reduction in the antibonding character, and a slight high frequency shift in C≡N stretching band is observed on molecular interaction through lone pair electrons.

The vibrational relaxation in solutions of acetonitrile in CD₃CN, CCl₄, CH₃OH, CD₃NO₂, C₆D₆ by considering CH₃ symmetric stretching band was studied earlier¹⁰⁻¹⁵. As an extension to the studies on the effect of molecular interactions on vibrational relaxation and other spectral parameters, Raman spectra were recorded for solutions of acetonitrile in carbon tetrachloride, water, methanol and dimethyl sulphoxide as well as for its solutions with NaClO₄, LiClO₄, and LiBr. The vibrational relaxation times for the CH₃ symmetric stretching band of acetonitrile in all these systems are computed. The results are discussed in the light of the molecular interactions of acetonitrile with other solvent molecules as well as with the electrolytes.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Analar acetonitrile (MERCK) was distilled and kept on 4A Linde sieves. Sodium perchlorate (FLUKA), Lithium perchlorate (BDH) and Lithium bromide (FLUKA) were used without further purification. They were stored in desiccator over calcium chloride. Analar methanol (MERCK) was distilled and kept on 4A Linde sieves. Triple distilled water was used for preparation of solutions.

Raman spectral measurements were made at room temperature, on a Cary 82 Laser Raman Spectrometer equipped with Spectra Physics argon ion laser (model 165), with the sample contained in a glass cell. All the spectra were recorded employing 514.5 nm exciting line, with a power output varying in the range 200-400 mW. A 90° scattering geometry was employed. Slit widths of 1.0-2 cm⁻¹ were used for different concentrations, with 1-5 sec constant. Spectra were recorded with 0.10 cm⁻¹/sec monochromator speed. Both parallel and

perpendicularly polarized spectra were recorded at the same instrumental settings. The spectra were reproducible to within ± 1 cm⁻¹.

All the Raman spectra were digitized manually and the digitized Raman data in parallel and perpendicular polarization modes were employed to compute the isotropic Raman spectra.

$$I_{\text{iso}} = I_{\text{VV}} - (4/3) I_{\text{VH}} \quad (1)$$

The spectrum is normalized according to the following equation

$$\hat{I}_{\text{iso}}(\omega) = I_{\text{iso}}(\omega) / \int_{\text{band}} I_{\text{iso}}(\omega) \cdot d\omega \quad (2)$$

On Fourier transformation the \hat{I}_{iso} spectra lead to pure vibrational correlation function.

$$\begin{aligned} \phi_V(t) &= \langle Q_i(0) \cdot Q_i(t) \rangle \\ &= \int_{\text{band}} \hat{I}_{\text{iso}}(\omega) \cdot \exp(i\omega t) \cdot d\omega \quad (3) \end{aligned}$$

A computer program in Basic language was used for Fourier transformation of the \hat{I}_{iso} spectra. The relaxation times are calculated by several methods as follows:

(i) The correlation function on integration in the specific time limit, t_L yields the relaxation time using the equation

$$\tau_v = \int_0^{t_L} \phi_V(t) dt, \quad (4)$$

where t_L depends on the resolution, $\Delta\omega_r$,

$$t_L = (2\pi C \Delta\omega_r)^{-1} \quad (5)$$

(ii) If the correlation function $\phi_v(t)$ is written as $\phi_v(t) = \exp(-t/\tau_v)$, the integrated value τ_v in (4) is equivalent to the decay time τ_v^c measured directly from the $\phi_v(t)$ vs t curve. Thus τ_v^c can be obtained as the time required for $\phi_v(t)$ to fall from 1 to $1/e$ value.

(iii) The relaxation times can also be calculated from the band halfwidth parameter.

$$\tau_v^h = (\pi C \Delta\bar{\nu}_{1/2})^{-1} \quad (6)$$

$\Delta\bar{\nu}_{1/2}$ is the apparent full width at half maximum (FWHM).

RESULTS AND DISCUSSION

The methyl stretching bands of pure acetonitrile in the parallel (I_{VV}) and perpendicular (I_{VH}) polarization modes are shown in figure 1. Since it is found that the depolarization ratio of the band is <0.01 , as an approximation I_{VV} is directly taken as a measure of the I_{iso} spectrum. Fourier transforms of parallel polarized bands for the symmetric methyl stretching mode of acetonitrile for various systems considered were computed and the vibrational relaxation times τ_v , τ_v^e , τ_v^h are evaluated using (1) to (6).

ACETONITRILE-CARBON TETRACHLORIDE SYSTEM

In figure 2 are given plots of vibrational correlation functions for a series of solutions of

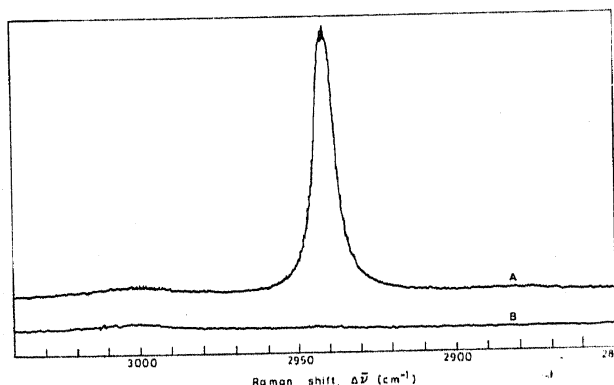


Figure 1. C-H stretching bands in Raman spectra of pure acetonitrile in (A) I_{VV} mode, (B) I_{VH} mode.

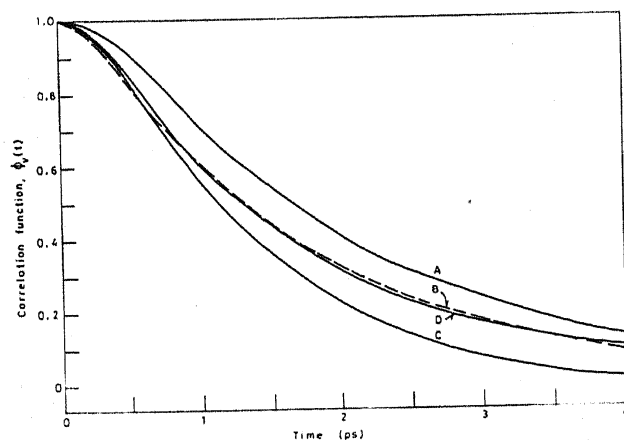


Figure 2. Vibrational correlation functions for CH_3 stretching mode of CH_3CN in CCl_4 , mole fraction of CH_3CN , A - 0.18; B - 0.64; C - 0.94; D - 1.0.

acetonitrile in carbon tetrachloride. In table 1 are given the band positions, the FWHM and the vibrational relaxation times τ_v^h , τ_v^e , τ_v for solutions of acetonitrile in carbon tetrachloride at various concentrations ranging from 1 to 0.17 mole fractions.

The half bandwidths (table 1) are slightly higher than those reported¹⁰ as the present data have not been corrected for the finite slit width (the half bandwidth reported¹⁰ for pure CH_3CN is 6.5 cm^{-1}). Though, to a small extent, the half bandwidth is found to decrease on dilution. The τ_v^e values are on the higher side, whereas τ_v and τ_v^h values are in general comparable. The τ_v values are more reliable as they are evaluated by integrating the correlation function plots directly, whereas the τ_v^h values are computed on the basis of the assumption that the isotropic Raman spectra have Gaussian band shape. The vibrational correlation times increase with dilution showing that the normal mode under consideration associated with CH_3 stretch relaxes faster in concentrated solutions.

It is reported earlier¹³ that while going from liquid acetonitrile to dilute solution of acetonitrile in CD_3CN the half bandwidth of the isotropic Raman band decreases by 0.5 cm^{-1} only and that the τ_v value does not change significantly. On the basis of the above observations, as suggested earlier¹⁰, the vibrational energy transfer caused by the transition dipole-transition dipole interactions are of minor importance. Because, in the concentrated solutions of acetonitrile in carbon tetrachloride the band broadens and the vibrational relaxation time decreases, it appears that the principal relaxation mechanism leading to broadening of the band is controlled very largely by short range 'repulsive' interactions, resulting from solute-solute and solute-solvent hard collisions¹⁰. The effect may also be due to involvement of CH_3 groups in dipolar interactions for self association of CH_3CN as the positive end of the dipole is assumed to be located on the CH_3 group.

Table 1 Spectral parameters and vibrational relaxation times for CH_3 symmetric stretching mode in solutions of CH_3CN in CCl_4

| Mole fraction of CH_3CN | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | FWHM (cm^{-1}) | τ_v^h (psec) | τ_v^e (psec) | τ_v (psec) |
|---|---|---------------------------|-------------------|-------------------|-----------------|
| 1.0 | 2941.5 | 7.5 | 1.42 | 1.61 | 1.42 |
| 0.94 | 2941.5 | 8.5 | 1.26 | 1.63 | 1.46 |
| 0.81 | 2941.5 | 7.7 | 1.38 | 1.68 | 1.52 |
| 0.64 | 2941.0 | 6.9 | 1.54 | 1.80 | 2.56 |
| 0.44 | 2940.0 | 6.7 | 1.59 | 1.92 | 1.68 |
| 0.17 | 2940.0 | 6.5 | 1.64 | 2.03 | 1.76 |
| 0.01* | — | 4.4 | — | — | 2.72 |

* values from ref. 10

In figure 3 are shown the $\text{C}\equiv\text{N}$ stretching bands of solutions of CH_3CN in CCl_4 at various concentrations. The band shows a gradual shift to the high frequency side on dilution and in general the band gets narrower (table 2). A small component in the form of a weak shoulder accompanies the $\text{C}\equiv\text{N}$ band at $\sim 2247 \text{ cm}^{-1}$. The second derivative spectrum of the Raman spectrum clearly shows the two components in the $\text{C}\equiv\text{N}$ band contour (figure 4). This has been assigned² to a hot band of the

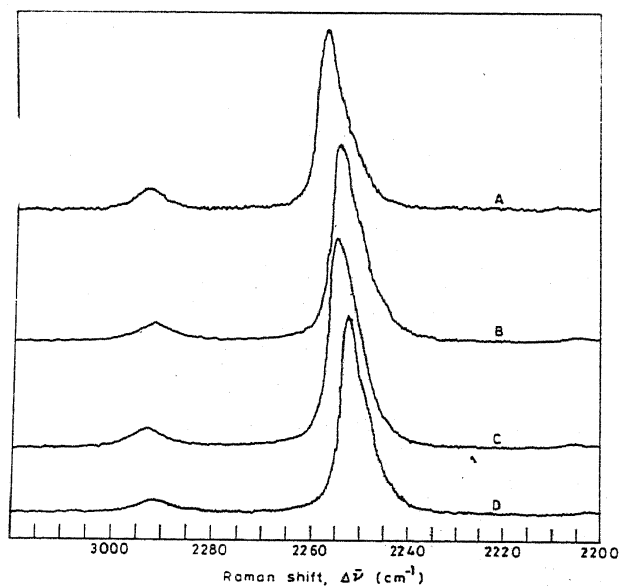


Figure 3. $\text{C}\equiv\text{N}$ stretching bands in Raman spectra of CH_3CN in CCl_4 (I_{VV} mode), mole fraction of CH_3CN , A—0.17; B—0.65; C—0.94; D—1.0.

Table 2 Spectral parameters of $\text{C}\equiv\text{N}$ stretching band for solutions of CH_3CN in CCl_4

| Conc. of CH_3CN (mf) | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | FWHM (cm^{-1}) | Integrated intensity |
|--------------------------------------|---|---------------------------|----------------------|
| 1.0 | 2252.0 | 7.5 | 13.4 |
| 0.94 | 2254.0 | 7.5 | 8.6 |
| 0.64 | 2253.0 | 7.1 | 9.3 |
| 0.17 | 2255.5 | 7.0 | 6.9 |

type $(\nu_2 + \nu_8) - \nu_8$. The relative intensity of the $\text{C}\equiv\text{N}$ band with respect to the high frequency combination band at $\sim 2290 \text{ cm}^{-1}$ is found to decrease with dilution. The intensity is ~ 13 units for pure acetonitrile and ~ 7 units for 0.17 mf acetonitrile in CCl_4 .

ACETONITRILE—WATER, METHANOL AND DIMETHYL SULPHOXIDE SYSTEMS

In figure 5 are shown the plots of vibrational correlation functions for aqueous solutions of acetonitrile at various concentrations. In table 3 are given the band positions, the FWHM and the vibrational relaxation times τ_v^h , τ_v^e , τ_v for aqueous solutions of acetonitrile at various concentrations ranging from 1 to 0.13 mole fraction. The half bandwidth increases on dilution (the width is $\sim 7.5 \text{ cm}^{-1}$ in pure

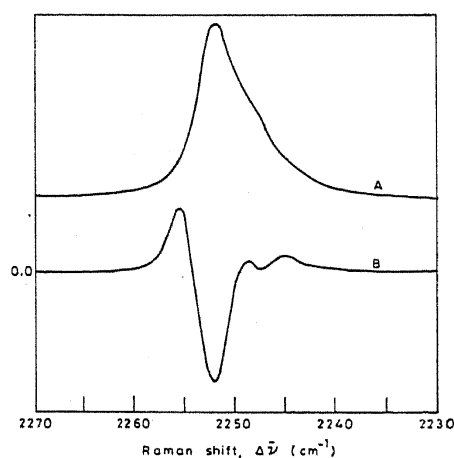


Figure 4. $\text{C}\equiv\text{N}$ stretching band of pure acetonitrile (A) and its second derivative (B).

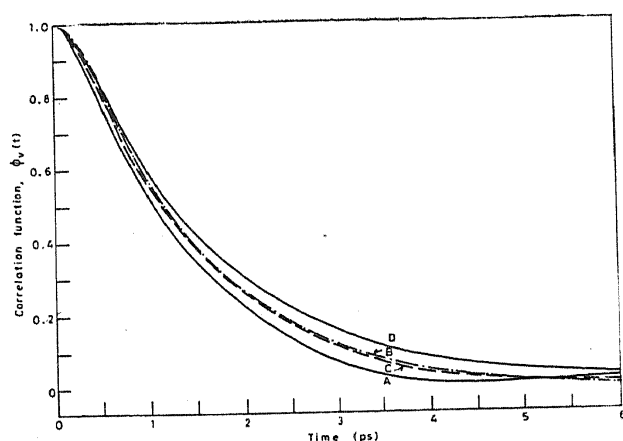


Figure 5. Vibrational correlation functions for CH_3 stretching mode of CH_3CN in aqueous solutions of CH_3CN , mole fraction of CH_3CN : A-0.13; B-0.45; C-0.76; D-0.87.

acetonitrile and $\sim 10.4 \text{ cm}^{-1}$ in solution of 0.13 mole fraction of acetonitrile in water) and the band shifts to higher frequency. The vibrational correlation times decrease on dilution indicating that the methyl stretching mode relaxes faster in dilute solutions. Perhaps the formation of hydrogen bonded complex with water through the lone pair of electrons on nitrogen atom of the $\text{C}\equiv\text{N}$ group gets reflected in CH_3 stretching mode which causes the broadening of the band and a decrease in the vibrational relaxation time in its dilute aqueous solutions. These observations are similar to the studies reported¹¹ on solutions of acetonitrile in methanol.

In figure 6 are shown the $\text{C}\equiv\text{N}$ stretching bands of aqueous solutions of acetonitrile at

Table 3 Spectral parameters and vibrational relaxation times for CH_3 symmetric stretching mode of CH_3CN in aqueous solutions of CH_3CN

| Mole fraction of CH_3CN | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | FWHM (cm^{-1}) | τ_v^h (psec) | τ_v^e (psec) | τ_v (psec) |
|---|---|---------------------------|-------------------|-------------------|-----------------|
| 1.0 | 2941.5 | 7.5 | 1.42 | 1.61 | 1.42 |
| 0.87 | 2942.5 | 7.9 | 1.35 | 1.69 | 1.38 |
| 0.76 | 2942.5 | 7.9 | 1.35 | 1.66 | 1.34 |
| 0.45 | 2942.5 | 8.9 | 1.20 | 1.49 | 1.23 |
| 0.26 | 2943.5 | 9.5 | 1.12 | 1.36 | 1.15 |
| 0.13 | 2944.5 | 10.4 | 1.02 | 1.23 | 1.06 |

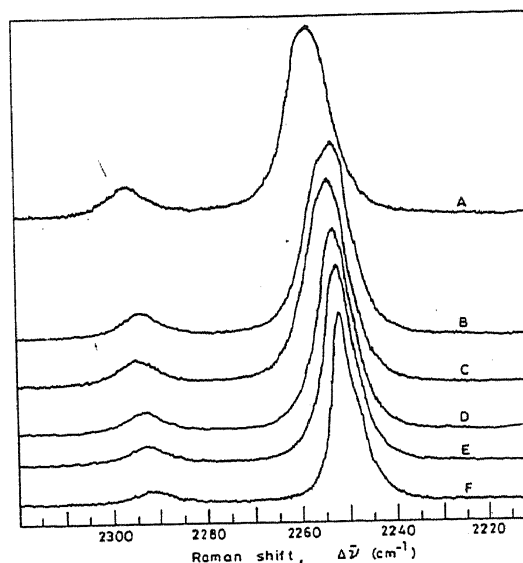


Figure 6. $\text{C}\equiv\text{N}$ stretching bands in Raman spectra of aqueous solutions of CH_3CN (I_{VV} mode), mole fraction of CH_3CN : A-0.18; B-0.26; C-0.45; D-0.76; E-0.87; F-1.0.

various concentrations. The bands show a gradual shift to the high frequency side on dilution. In general the band gets broadened (the half band width changes by about 3 cm^{-1} in the concentration range studied) indicating the formation of hydrogen bonded complex with water on dilution. The various band parameters are given in table 4. The relative intensity of the $\text{C}\equiv\text{N}$ band with respect to the high frequency combination band at $\sim 2290 \text{ cm}^{-1}$ is found to decrease on dilution as in the case of solutions of acetonitrile in CCl_4 . The intensity is ~ 13 units for pure acetonitrile and ~ 7 units for 0.02 mf aqueous solution of

Table 4 Spectral parameters of $\text{C}\equiv\text{N}$ stretching band for aqueous solutions of CH_3CN

| Conc. of CH_3CN (mf) | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | FWHM (cm^{-1}) | Integrated intensity |
|--------------------------------------|---|---------------------------|----------------------|
| 1.0 | 2252.0 | 7.5 | 13.40 |
| 0.87 | 2252.5 | 7.5 | 10.60 |
| 0.75 | 2253.5 | 8.2 | 13.99 |
| 0.58 | 2254.0 | 10.5 | 9.98 |
| 0.44 | 2254.0 | 10.8 | 9.60 |
| 0.25 | 2258.0 | 11.0 | 8.07 |
| 0.13 | 2258.5 | 10.5 | 8.10 |
| 0.02 | 2261.0 | 9.0 | 6.55 |

acetonitrile. It may be inferred that the dissociation of structured acetonitrile on dilution in water is accompanied by a decrease in intensity of the $C\equiv N$ band, an increase in its frequency and decrease in the vibrational relaxation time of CH_3 stretching mode.

To distinguish between the effects of dipolar interactions and hydrogen bonding on $C\equiv N$ stretching band, Raman spectra of acetonitrile in methanol and dimethyl sulphoxide (DMSO) at various concentrations were also recorded. Raman spectra of acetonitrile in methanol at various concentrations are shown in figure 7. The bands show a gradual shift to the high frequency side on dilution in methanol (table 5) and an increase in the band width, indicating the formation of hydrogen bonded complex with methanol on dilution. Appearance of new band at $\sim 2262\text{ cm}^{-1}$ can also be noticed for most dilute solutions. No such high frequency band is observed for aqueous solutions, this perhaps shows that the hydrogen bond formation of $C\equiv N$ with methanol is stronger than that with water. In Raman spectra of acetonitrile in DMSO, the $C\equiv N$ stretching band shows a gradual shift to the low frequency side on

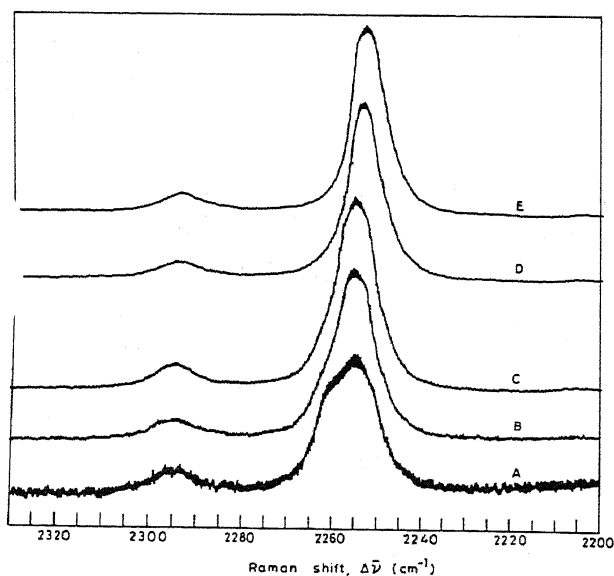


Figure 7. $C\equiv N$ stretching bands in Raman spectra of CH_3CN in CH_3OH (I_{VV} mode), mole fraction CH_3CN : A—0.08; B—0.25; C—0.44; D—0.64; E—0.87.

Table 5 Spectral parameters of $C\equiv N$ stretching band for solutions of CH_3CN in CH_3OH and DMSO

| System | Conc. of CH_3CN (mf) | $\bar{\nu}_{max}$ (cm^{-1}) | FWHM (cm^{-1}) | Integrated intensity |
|------------------------|------------------------|---------------------------------|--------------------|----------------------|
| CH_3CN + CH_3OH | 1.0 | 2252.0 | 7.5 | 13.4 |
| | 0.87 | 2252.5 | 8.6 | 11.3 |
| | 0.64 | 2253.0 | 8.6 | 11.3 |
| | 0.44 | 2255.0 | 10.5 | 9.6 |
| | 0.25 | 2255.0 | 11.5 | 11.0 |
| | 0.08 | 2255.0 2261.0 | 15.0 | 8.3 |
| CH_3CN + DMSO | 1.0 | 2252.0 | 7.5 | 13.4 |
| | 0.77 | 2252.0 | 9.0 | — |
| | 0.58 | 2251.0 | 7.5 | — |
| | 0.37 | 2250.0 | 7.2 | — |
| | 0.07 | 2249.5 | 7.5 | — |

dilution (table 5). In general the bandwidth remains constant. The relative intensity of the $C\equiv N$ band with respect to the high frequency combination band at $\sim 2290\text{ cm}^{-1}$ could not be measured because of high noise level.

ACETONITRILE-ELECTROLYTE SYSTEMS

In figure 8 are shown the plots of vibrational correlation functions for CH_3 stretching mode for solutions of $LiClO_4$ in acetonitrile* and in table 6 are given the band positions, FWHM and the vibrational relaxation times τ_v^h , τ_v^c , τ_v for solutions of $LiClO_4$, $NaClO_4$ and $LiBr$ in acetonitrile at various concentrations. The half bandwidth shows an increase on increasing the concentration of electrolytes and relaxation times show a decrease. It is known that electrolytes in organic solvents form ion pairs, solvent separated ion-pairs and cation solvates. One can, therefore, expect changes in the structure of liquid acetonitrile, which may reflect on the relaxation times of CH_3 stretching mode particularly if solvent separated ion-pairs are formed through the CH_3 and nitrogen ends of the dipole.

* Plots of correlation functions and Raman spectra in $C\equiv N$ stretching region for other systems are not included for the sake of brevity.

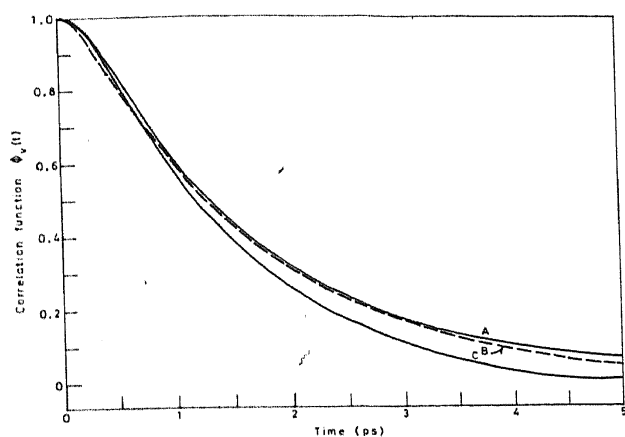


Figure 8. Vibrational correlation functions for solutions of lithium perchlorate in CH_3CN ; concentration of salt: A—0.0 M; B—0.5 M; C—1.0 M.

In figure 9 are shown the $\text{C}\equiv\text{N}$ stretching bands of solutions of sodium perchlorate in acetonitrile* at various concentrations. New bands appear at $\sim 2265\text{ cm}^{-1}$ in solutions of NaClO_4 and at $\sim 2270\text{ cm}^{-1}$ in solutions of LiClO_4 and LiBr . The intensity of these bands increases with respect to the main band centered at $\sim 2252\text{ cm}^{-1}$ on increasing the concentration of the electrolytes (table 7). In some earlier studies^{9,16,17} it was shown that pronounced changes occur in the acetonitrile spectrum when the $(\text{MCH}_3\text{CN})^{n+}$ solvates are formed. Chang and Irish¹⁸ and Janz and Muller¹⁹ studied the effect of AgNO_3 on acetonitrile and assigned the band at

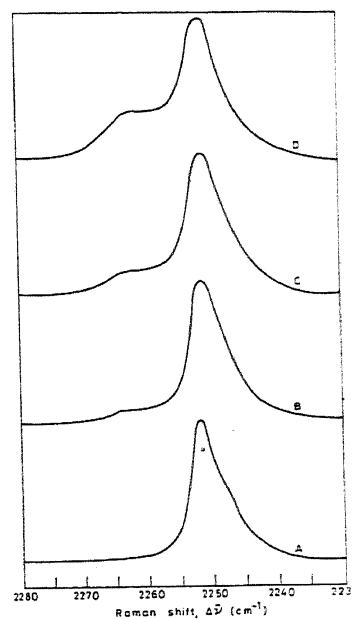


Figure 9. $\text{C}\equiv\text{N}$ stretching bands in Raman spectra of solutions of NaClO_4 in CH_3CN , concentration of NaClO_4 : A—0.0 M; B—0.5 M; C—1.0 M; D—2.0 M.

$\sim 2270\text{ cm}^{-1}$ to $\text{Ag}(\text{CH}_3\text{CN})^+$ solvate and Sze¹⁶ showed that $\text{Zn}(\text{NO}_3)_2$ also forms solvate, which gives rise to a band at $\sim 2290\text{ cm}^{-1}$. On the basis of the above studies and the position of the $\text{C}\equiv\text{N}$ band for $\text{M}(\text{CH}_3\text{CN})^+$ solvates it may be concluded that Li^+ has stronger interactions with acetonitrile than Na^+ . In addition to the effects of electrolytes on $\text{C}\equiv\text{N}$ band, it is also observed that a

Table 6 Spectral parameters and vibrational relaxation times for CH_3 symmetric stretching mode in solutions of electrolytes in CH_3CN

| System | Conc. of salt (M) | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | FWHM (cm^{-1}) | τ_v^h (psec) | τ_v^c (psec) | τ_v (psec) |
|------------------|-------------------|---|---------------------------|-------------------|-------------------|-----------------|
| NaClO_4 | 0.0 | 2941.5 | 7.5 | 1.42 | 1.61 | 1.42 |
| | 0.5 | 2940.5 | 7.5 | 1.42 | 1.58 | 1.41 |
| | 1.0 | 2941.0 | 9.0 | 1.18 | 1.50 | 1.17 |
| | 2.0 | 2941.0 | 9.2 | 1.14 | 1.51 | 1.15 |
| LiClO_4 | 0.0 | 2941.5 | 7.5 | 1.42 | 1.61 | 1.42 |
| | 0.5 | 2940.5 | 7.5 | 1.42 | 1.71 | 1.52 |
| | 1.0 | 2941.5 | 9.5 | 1.12 | 1.58 | 1.21 |
| LiBr | 0.0 | 2941.5 | 7.5 | 1.42 | 1.61 | 1.42 |
| | 0.5 | 2940.5 | 7.5 | 1.42 | 1.46 | 1.45 |
| | 1.0 | 2941.0 | 9.5 | 1.12 | 1.05 | 1.09 |

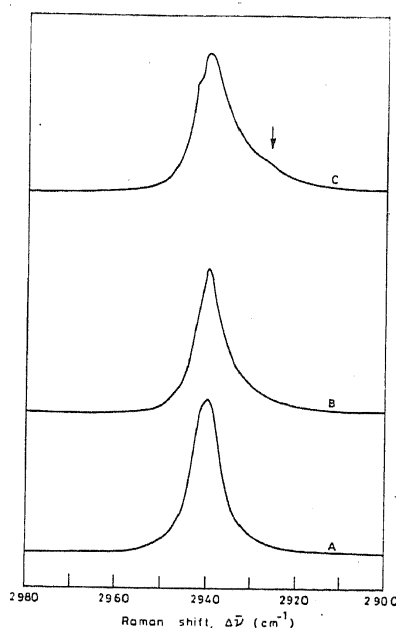


Figure 10. C-H stretching bands in Raman spectra of solutions of Lithium bromide in CH_3CN , concentration of salt; A - 0.0 M; B - 0.5 M; C - 1.0 M.

low frequency component of CH_3 symmetric stretching band starts rising (figure 10) with increasing concentration of LiBr , the band gets asymmetric on the low frequency side thus indicating hydrogen bonding interaction of Br^- with methyl group. Such a clear indication on anion bonding is not shown by perchlorates.

The observation of hydrogen-bonded CH_3 symmetric stretching band may further support the idea that positive charge of the dipole is located on the CH_3 group of the molecule and not on the carbon atom, of the nitrile bond. Perchlorate ions however may not show strong bonding with CH_3 group because of their bulkiness. The effect of addition of LiBr to CH_3CN on $\text{C}\equiv\text{N}$ as well as CH_3 stretching bands simultaneously, indicates the formation of solvent separated ion-pairs or complexes of CH_3CN with anion and cation separately.

CONCLUSIONS

From the above studies on solutions of acetonitrile in a series of non-electrolytes and electrolytes, the following important conclusions can be made.

Vibrational relaxation time of the CH_3 stretching mode increases on dilution of acetonitrile in CCl_4 , whereas a decrease in vibrational relaxation time is observed when solutions of acetonitrile with water and electrolytes, are considered. This shows that the vibrational relaxation time of the stretching mode of methyl group decreases when acetonitrile molecules get involved in dipolar, hydrogen bonding or ion-molecular interactions. The

Table 7 Spectral parameters of $\text{C}\equiv\text{N}$ stretching band for solutions of electrolytes in CH_3CN

| System | Conc. of salt (M) | $\bar{\nu}_{\text{max}}$ (cm^{-1}) | | FWHM (cm^{-1}) for free $\text{C}\equiv\text{N}$ band | Relative intensity I_f/I_c |
|------------------|-------------------|---|--|--|------------------------------|
| | | Free CH_3CN (ν_f) | Complexed CH_3CN (ν_c) | | |
| NaClO_4 | 0.0 | 2252.0 | - | 7.5 | - |
| | 0.5 | 2252.0 | 2264.0 | 7.0 | 8.83 |
| | 1.0 | 2251.5 | 2263.5 | 7.5 | 5.15 |
| | 2.0 | 2251.5 | 2262.5 | 8.5 | 2.84 |
| LiClO_4 | 0.0 | 2252.0 | - | 7.5 | - |
| | 0.5 | 2252.0 | 2272.5 | 7.0 | 16.9 |
| | 1.0 | 2252.0 | 2273.5 | 7.7 | 9.13 |
| LiBr | 0.0 | 2252.0 | - | 7.5 | - |
| | 0.5 | 2251.5 | 2272.0 | 7.5 | 14.13 |
| | 1.0 | 2251.5 | 2272.5 | 7.2 | 9.23 |

half bandwidth as well as vibrational frequency of the CH_3 band also increase on association. It is observed that when concentration of LiBr is increased the CH_3 stretching band shows the formation of a low frequency component, thus indicating that the CH_3 group gets involved in anion-molecular interactions. These observations support that the positive end of the dipole is situated on the methyl group which renders the methyl group more acidic, enabling it to involve in hydrogen bonding and also in dipolar interactions. Earlier investigations¹¹ on vibrational relaxation studies of CH_3CN in CD_3OD also indicate a decrease in vibrational relaxation times of CH_3 stretching band with increasing concentration of CD_3OD . It was pointed out in these studies that the effect of CD_3OD on the vibrational relaxation times of the CH_3 stretching mode was not clear. In the light of the above suggestions, the possibility of hydrogen bonding of CH_3 group of acetonitrile with the oxygen lone pair of CD_3OD may not be ruled out and this may affect the vibrational relaxation time of CH_3 stretching mode.

For processes involving intermolecular interactions leading to a distribution of vibrational frequencies, the following expression proposed by Kubo²¹ can be given for vibrational relaxation function.

$$\phi_v(t) = \exp[-M_2(\tau_c^2(\exp(-t/\tau_c) - 1 + \tau_c t))], \quad (7)$$

where M_2 , the second spectral moment of the band contour is given by

$$M_2(\text{vib}) = \int_{-\infty}^{+\infty} I_{\text{iso}}(\omega) (\omega - \omega_0)^2 d\omega / \int_{-\infty}^{+\infty} I_{\text{iso}}(\omega) d\omega, \quad (8)$$

and the correlation time τ_c determines the correlation decay of the stochastic perturbation Hamiltonian $H_1(t) = \hbar_1(t)$, assumed in the simple form

$$\begin{aligned} \chi_t &= \langle \omega_1(t) \omega_1(0) \rangle \langle \omega_1(0) \rangle^{-2} \\ &= \exp(-t/\tau_c). \end{aligned} \quad (9)$$

Depending on the speed with which χ_t decays on account of the fluctuating intermolecular potentials of the lattice, the processes which modulate $\omega_1(t)$ are called 'fast' or 'slow' having

$$M_2^{1/2} \tau_c \gtrless 1 \quad (10)$$

respectively.

For systems with fast modulation the correlation time τ_c can be obtained from experimental τ_v and M_2 values by the relationship

$$\tau_c = (M_2 \tau_v)^{-1}. \quad (11)$$

Using the experimental values of τ_v and M_2 for the systems considered the approximate τ_c values are calculated using the relationship (11) and the exact values are obtained by iterative procedure using the experimental values of $\phi_v(t)$ and M_2 in (7). It is found that in all the systems considered irrespective of the concentration used the values of $M_2^{1/2} \tau_c$ are always < 1 , indicating that in all the cases the effect of perturbation decreases rapidly and the original phase is remembered for a longer time which is a characteristic of fast modulation²².

Further parallel to some of the earlier observations^{10,20}, association of acetonitrile through dipolar interactions is accompanied by an increase in intensity and decrease in frequency of $\text{C}\equiv\text{N}$ band, whereas interaction through hydrogen bonding is accompanied by a decrease in intensity and an increase in frequency. Strong hydrogen bonding interaction as well as cation molecular interaction give rise to the appearance of new bands in high frequency region due to the formation of $\text{C}\equiv\text{N}$ complexed species.

The studies in general show that liquid acetonitrile is associated through dipolar interactions in the antiparallel fashion with the positive end of the dipole on the CH_3 group and negative end of the dipole on the N atom. On dilution with CCl_4 the structure breaking takes place. Dipolar, hydrogen bonding and ion-dipole interactions present in dilute solutions of acetonitrile in polar and hydrogen bonding solvents as well as in solutions of

electrolytes are responsible for the observed effects on various spectral parameters.

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