



## Effect of Hydrogen Bond on the $\nu(\text{C}\equiv\text{N})$ Stretching Mode of Acetonitrile in the Binary Mixture (Acetonitrile + Water): A Combined Raman Spectroscopy and Theoretical Study

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Hydrogen bond in the binary mixture system of acetonitrile and water has been studied by using experimental Raman spectroscopy and quantum chemical theoretical calculations. Experimentally, the  $\nu(\text{C}\equiv\text{N})$  as a marker bond for the degree of hydrogen bond in this binary mixture (acetonitrile + water) has been monitored by Raman spectroscopy. Theoretically, the optimized structures, vibrational frequencies and stabilization energies of the neat acetonitrile and the hydrogen-bonded  $\text{CH}_3\text{CN}\cdots\text{HOH}$  complexes are calculated at the B3LYP/6-311 + G(d,p), MP2/6-311+G(d,p) and CCSD/6-311+G(d,p) levels of theory, respectively. The results show that the wavenumber position of the  $\text{C}\equiv\text{N}$  stretching mode is shifted to higher wavenumber due to the hydrogen bond and the change in the line width (full width half maximum, FWHM) have been explained for neat as well as binary mixtures with different concentrations, in terms of the concentration fluctuation and the microviscosity.

**Key Words:** Raman spectra, Hydrogen bond, Line width.

### INTRODUCTION

The solvation phenomena have received considerable attention during the last decade from both the theoretical and experimental points of view due to the important role of solvation effects in the fields of chemistry, physics and biology. The acetonitrile-water system as a typical model for understanding binary mixtures leading to powerful solvation effect has been reported<sup>1-3</sup>. In addition, hydrogen bond plays an essential role not only in defining structural and functional of biologically important molecules, but also in molecular recognition processes and interactions. So, the significant effect of hydrogen bond on the nature of interaction in the acetonitrile-water system should be considered<sup>4-11</sup>.

For the hydrogen-bonded complexes whose formation and cleavage occurs rapidly, vibrational spectroscopy such as IR and Raman are ideally suited to detect hydrogen bond because they have provided a wealth of information on the structure and dynamics of such species and define a starting point for a detailed understanding of various macroscopic phenomena<sup>12-14</sup>. Whereas the wavenumber position of a vibrational band related

to the corresponding internuclear force constants is dependent on electronic structure and bonding and the line width contains information about molecular dynamics. As compared to IR spectroscopy, Raman spectroscopy can reveal additional information from a line width analysis<sup>4</sup>. Therefore, Raman spectroscopy increases our understanding of solute-solvent interactions.

Raman spectroscopic data can be supported by the theoretical calculations to interpret the corresponding experimentally observed spectral features and the information of the explicit molecular structures in the liquid phase<sup>4,15</sup>. In this respect, using Raman spectroscopy in conjunction with the modern quantum chemical approaches can strongly contribute to our understanding of the hydrogen bond. The structure, stability and strength of hydrogen bond in the hydrogen-bonded complexes can be explored by *ab initio* calculations. Recently, *ab initio* calculations at different levels of theoretical such as the hybrid density functional theory (DFT), the second-order Moller-Plesset perturbation theory (MP2) and the coupled-cluster theory (CCSD) with applications in combination with experiment have become very popular owing to their excellent

performance on the aspect of electronic structure calculations. In this study, the combination of high level quantum chemical calculations with Raman spectroscopic data has performed to investigate the effect of hydrogen bond on the  $\nu(\text{C}\equiv\text{N})$  stretching mode of acetonitrile in the binary mixture (acetonitrile + water). The concentration dependence of wave number shifts and line width change is examined in the system for the  $\text{C}\equiv\text{N}$  stretching mode of acetonitrile and line width change are explained on the basis of a model proposed recently by Ojha *et al.*<sup>16</sup>.

## EXPERIMENTAL

The sample of acetonitrile is obtained from Aldrich Co. and is used without further purification. For preparing the binary mixture, triple distilled water is used as solvent. The binary mixture of acetonitrile in water is prepared for various mole fractions of the solute.

**Spectroscopic methods:** The micro Raman spectrometer (Renishaw *in via* Raman microscope) is equipped with a 514.5nm  $\text{Ar}^+$  ion excitation laser (Spectra Physics 163-M42). 20 $\times$  objective (LEICA DMLM 0.12NA) is used for both laser illumination and Raman backscattering detection. The excitation power of 5.1 mW and exposure time (CCD integration times) of 10 s are used to collect all Raman spectra. All the experiments are performed at room temperature.

Raman spectra are recorded in the region, 2300-2200  $\text{cm}^{-1}$  for the neat as well as for ten different mole fractions,  $C = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$  and 1.0 of the reference system, acetonitrile in the binary mixture ( $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ ). These spectra are presented in Fig. 1.

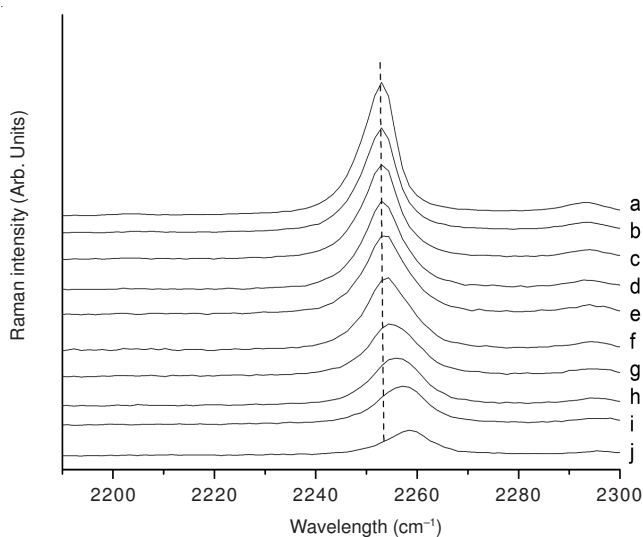


Fig. 1. Raman spectra in the region 2300-2200  $\text{cm}^{-1}$  for neat acetonitrile and its binary mixture at ten mole fractions of acetonitrile. ( $j = 0.1, i = 0.2, h = 0.3, g = 0.4, f = 0.5, e = 0.6, d = 0.7, c = 0.8, b = 0.9$  and  $a = 1.0$ .)

**Computational methods:** The optimized geometries and frequencies of the monomers and the complexes were performed using three alternative methods: (1) the density functional theory (DFT) B3LYP in conjunction with the 6-311 + G(d,p) basis set, (2) the second-order Moller-Plesset perturbation theory MP2 and (3) the quantum-chemical coupled-cluster

theory with single and double excitations coupled-cluster theory all using the same basis set. All calculations are carried out using Gaussian 03 program package<sup>17</sup>. We have calculated the stabilization energy to estimate the stability of the hydrogen-bonded systems between the various complexes at all above levels of theory. The super molecule approach determines the stabilization energies (SE) as a difference between the energy of the cluster and the energies of the isolated molecules/clusters.

$$\text{SE} = E_{\text{cluster}} - (E_{\text{Am}} + E_{\text{Wn}})$$

where  $E_{\text{cluster}}$  is the total energy of a cluster and  $E_{\text{Am}}$  and  $E_{\text{Wn}}$  are the total energies of acetonitrile and water molecules/clusters calculated.

## RESULTS AND DISCUSSION

**Optimized geometries of the neat acetonitrile, water and binary mixtures:** The basic aim of the quantum-chemical calculations is to establish the most stable structures of the hydrogen-bonded complexes between  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  and understand their observed spectral features. The optimized geometries obtained from the B3LYP/6-311+G(d,p) calculations and selected the most stable structures for  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$  and the other complexes are presented in Fig. 2. We denote the structures of various Acetonitrile  $\text{W}_x$  clusters with stoichiometric ratios 1: x ranging from 1:1 to 1:3.

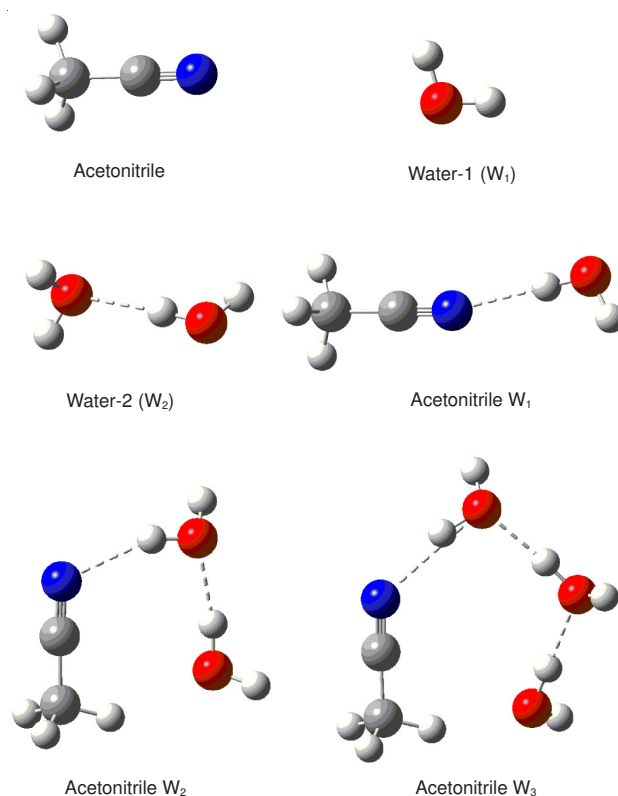


Fig. 2. Optimized molecular structure of acetonitrile, water and the hydrogen-bonded complexes (acetonitrile+water) at the B3LYP/6-311+G(d,p) level of theory

The total energies for the monomers (*i.e.*  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ ) and the hydrogen-bonded complexes (quoted in Hartree) at the different methods (B3LYP, MP2 and CCSD) are all shown in Table-1. It can be seen that the energies of the hydrogen-

bonded complexes are less than the sum of the energies of their corresponding individual monomer, which is clearly to indicate the formation of the stable complexes.

TABLE-1  
TOTAL ENERGIES FOR THE MONOMERS, *i.e.* CH<sub>3</sub>CN AND H<sub>2</sub>O, AND THE HYDROGEN-BONDED COMPLEXES (QUOTED IN HARTREE) ARE OBTAINED AT THE B3LYP/6-311 + G(d,p), MP2/6-311+G(d,p) AND CCSD/6-311+G(d,p) LEVELS OF THEORY

Methods	B3LYP	MP2	CCSD
(a)	-132.7961571	-132.4109416	-132.4284953
(b)	-76.4584627	-76.2747200	-76.281071
(c)	-152.9262248	-152.5590690	-152.5712534
(d)	-209.2622944	-208.6937083	-208.7171394
(e)	-285.7361447	-284.9856442	-285.0141052
(f)	-362.2117225	-361.2770461	-361.3109567

The stabilization energies have been calculated to analysis the strength of hydrogen bond at the different levels of theory [B3LYP/6-311 + G(d,p), MP2/6-311+G(d,p) and CCSD/6-311 + G(d,p)]. The results from the calculations are listed in Table-2. As can be seen from the data of ISEI, the calculated values of the stabilization energy with B3LYP, MP2 and coupled-cluster theory are very near and the discrepancies are found to be within 5.9 kJ/mol. The calculated values of the stabilization energy for the hydrogen-bonded complex between acetonitrile and two H<sub>2</sub>O molecules (aectonitrileW<sub>2</sub>) are approximately twice as much in comparison with the values for the hydrogen-bonded complex aectonitrileW<sub>1</sub>. Similarly, the values of the stabilization energy for the hydrogen-bonded complex aectonitrileW<sub>3</sub> (acetonitrile with there H<sub>2</sub>O molecules) are approximately twice as much in comparison with the values for aectonitrileW<sub>2</sub>.

TABLE-2  
STABILIZATION ENERGIES (ISEI) IN kJ/mol FOR THE HYDROGEN-BONDED COMPLEXES ARE OBTAINED AT THE B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) AND CCSD/6-311+G(d,p) LEVELS OF THEORY

Methods	B3LYP	MP2	CCSD
ISEId	20.1	21.4	20.1
ISEIe	36.0	41.0	37.7
ISEIf	80.8	85.0	79.1

TABLE-4  
CALCULATED STRUCTURAL PARAMETERS OF NEAT ACETONITRILE AND AECTONITRILEW<sub>1</sub> (d) AT THE B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) AND CCSD/6-311 + G(d,p) LEVELS OF THEORY. BOND LENGTHS ARE IN ANGSTROMS AND ANGLES ARE IN DEGREES

	Acetonitrile			(d)		
	B3LYP	MP2	CCSD	B3LYP	MP2	CCSD
C <sub>1</sub> -H <sub>2</sub>	1.0917	1.0915	1.0930	1.0917	1.0915	1.0929
C <sub>1</sub> -H <sub>3</sub>	1.0917	1.0915	1.0930	1.0917	1.0915	1.0929
C <sub>1</sub> -H <sub>4</sub>	1.0917	1.0915	1.0930	1.0917	1.0912	1.0929
C <sub>1</sub> -C <sub>5</sub>	1.4570	1.4627	1.4703	1.4550	1.4618	1.4698
C <sub>5</sub> -N <sub>6</sub>	1.1526	1.1738	1.1598	1.1513	1.1722	1.1586
H <sub>3</sub> -C <sub>1</sub> -H <sub>2</sub>	108.79	109.07	109.17	108.86	109.12	109.30
H <sub>4</sub> -C <sub>1</sub> -H <sub>2</sub>	108.79	109.07	109.17	108.89	109.21	109.32
C <sub>5</sub> -C <sub>1</sub> -H <sub>2</sub>	110.15	109.87	109.77	110.12	109.81	109.68
N <sub>6</sub> -H <sub>2</sub> -C <sub>1</sub>	50.91	51.28	51.31	50.87	51.26	51.32
H <sub>4</sub> -C <sub>1</sub> -H <sub>2</sub> -H <sub>3</sub>	118.37	119.02	119.28	118.55	119.29	119.59
C <sub>5</sub> -C <sub>1</sub> -H <sub>2</sub> -H <sub>3</sub>	-120.82	-120.49	-120.36	-120.68	-120.28	-120.16
N <sub>6</sub> -H <sub>2</sub> -C <sub>1</sub> -C <sub>5</sub>	0.00	0.00	0.00	-0.03	-0.03	-0.04

The corresponding distances of N...HO bond and C≡N bond for CH<sub>3</sub>CN and the hydrogen-bonded complexes between CH<sub>3</sub>CN and H<sub>2</sub>O obtained at the different levels of theory (B3LYP, MP2, CCSD) are summarized in Table-3. For the complex acetonitrileW<sub>1</sub> the calculated values of the N...HO bond are in the range from 0.2079 to 0.2145 nm. The values of the N...HO bond are in the range from 0.2046 to 0.2104 nm for the complex acetonitrileW<sub>2</sub>, while from 0.1926 to 0.1993 nm for the complex acetonitrileW<sub>3</sub>. The values of the N-H-O angles for the complexes acetonitrileW<sub>1</sub>, acetonitrileW<sub>2</sub> and acetonitrileW<sub>3</sub> are from 177.9 to 180.0, from 152.2 to 154.6 and from 161.5 to 163.2 degree, respectively. The C≡N bonds are changed slightly in the complexes acetonitrileW<sub>1</sub>, acetonitrileW<sub>2</sub> and acetonitrileW<sub>3</sub> with the formation of the hydrogen bonds. In addition, the remaining geometrical parameters of the monomer (acetonitrile) in the complexes acetonitrileW<sub>1</sub>, acetonitrileW<sub>2</sub> and acetonitrileW<sub>3</sub> are either unchanged or changed with small values upon formation of the hydrogen bonds. So the structural parameters for the neat acetonitrile and the hydrogen-bonded complexes between acetonitrile and H<sub>2</sub>O (acetonitrileW<sub>1-3</sub>) obtained at the different levels of theory are listed in Tables 4 and 5. These changes have very intriguing influence on the spectral features in solution.

TABLE-3  
CALCULATED BOND DISTANCES OF HYDROGEN BONDS AND ν(C≡N) BONDS DISTANCES FOR NEAT ACETONITRILE AND VARIOUS HYDROGEN-BONDED COMPLEXES AT THE B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) AND CCSD/6-311 + G(d,p) LEVELS OF THEORY

Complex	d(N...H)(nm)			d(C≡N)(nm)		
	B3LYP	MP2	CCSD	B3LYP	MP2	CCSD
Acetonitrile	-	-	-	0.1153	0.1173	0.1160
AectonitrileW <sub>1</sub>	0.2078	0.2103	0.2145	0.1151	0.1172	0.1159
AectonitrileW <sub>2</sub>	0.2046	0.2046	0.2104	0.1153	0.1174	0.1160
AectonitrileW <sub>3</sub>	0.1926	0.1943	0.1993	0.1153	0.1172	0.1159

**Concentration dependence of wave number shifts for ν(C≡N) stretching mode:** The variation of peak positions with concentration for one major Raman mode, namely ν(C≡N) stretching, appear in the region 2300-2200 cm<sup>-1</sup> (as shown in Fig. 1)<sup>18</sup>. In this study, the Raman peak position of ν(C≡N)

TABLE-5  
CALCULATED STRUCTURAL PARAMETERS OF AECTONITRILE $\text{W}_2$  (e) AND AECTONITRILE $\text{W}_3$  (f) AT THE  
B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) AND CCSD/6-311+G(d,p) LEVELS OF THEORY. BOND  
LENGTHS ARE IN ANGSTROMS AND ANGLES ARE IN DEGREES

	(e)			(f)		
	B3LYP	MP2	CCSD	B3LYP	MP2	CCSD
C <sub>1</sub> -H <sub>2</sub>	1.0917	1.0915	1.0931	1.0920	1.0917	1.0932
C <sub>1</sub> -H <sub>3</sub>	1.0917	1.0915	1.0930	1.0919	1.0916	1.0932
C <sub>1</sub> -H <sub>4</sub>	1.0940	1.0920	1.0927	1.0957	1.0929	1.0931
C <sub>1</sub> -C <sub>5</sub>	1.4532	1.4603	1.4689	1.4523	1.4600	1.4686
C <sub>5</sub> -N <sub>6</sub>	1.1532	1.1735	1.1598	1.1525	1.1724	1.1590
H <sub>3</sub> -C <sub>1</sub> -H <sub>2</sub>	109.10	109.30	109.40	109.04	109.28	109.36
H <sub>4</sub> -C <sub>1</sub> -H <sub>2</sub>	109.80	110.09	110.15	109.80	110.20	110.26
C <sub>5</sub> -C <sub>1</sub> -H <sub>2</sub>	110.21	109.79	109.63	110.04	109.63	109.47
N <sub>6</sub> -H <sub>2</sub> -C <sub>1</sub>	50.44	51.10	51.20	50.61	51.28	51.37
H <sub>4</sub> -C <sub>1</sub> -H <sub>2</sub> -H <sub>3</sub>	120.34	121.10	121.27	120.34	121.17	121.35
C <sub>5</sub> -C <sub>1</sub> -H <sub>2</sub> -H <sub>3</sub>	-121.14	-120.50	-120.26	-120.80	-120.23	-119.98
N <sub>6</sub> -H <sub>2</sub> -C <sub>1</sub> -C <sub>5</sub>	1.02	0.69	0.62	0.72	0.39	0.33

stretching mode serves as a probe for monitoring the degree of hydrogen-bonding between acetonitrile and water. The degree of hydrogen-bonding in this binary system varies with mixture composition. In water as solvent, there is a possibility for intermolecular hydrogen bond between the  $\text{C}\equiv\text{N}$  stretching band of the acetonitrile and the hydroxyl proton of the water molecule. When water is added into the solute, it will form  $\text{OH}\dots\text{N}\equiv\text{C}$  type hydrogen bond. When more water is added, more number of solute molecules will be hydrogen-bonded. As a consequence, the peak position of the  $\text{C}\equiv\text{N}$  stretching wave number is shifted to higher wave number for decreasing concentration of acetonitrile. These results are supported by our calculation. As shown in Fig. 2, when there are more water molecules, the (N...H) bond distances of hydrogen bonds are closer (0.2079 to 0.1926 nm). In addition, for the analysis of the strength of hydrogen bond, |SEIs| are considered (Table-2). In the series of the hydrogen-bond complexes, the |SEI| of acetonitrile $\text{W}_3$  is the largest and the (N...H) bond distance of hydrogen bond of acetonitrile $\text{W}_3$  is the closest, which indicates the hydrogen-bonded complex (acetonitrile $\text{W}_3$ ) of the strongest hydrogen bond. Judging from the overall results, the values of |SEIs| are increasing with the increase of the numbers of water molecular at all of the above methods. Furthermore, it is clearly seen that the  $\text{C}\equiv\text{N}$  bond lengths shorten with increasing concentration of water (see Table-1). Hence, it can be concluded that the  $\text{C}\equiv\text{N}$  band, after hydrogen bond formation with water, withdraws some charge density from the band and thereby increases the force constant of the  $\text{C}\equiv\text{N}$  stretch which, in turn, increases  $\nu(\text{C}\equiv\text{N})$  stretching wave number.

**Variation of the line width of the  $\nu(\text{C}\equiv\text{N})$  stretching mode of acetonitrile with concentration:** The variation of the line width of the  $\nu(\text{C}\equiv\text{N})$  stretching mode of acetonitrile with concentration shows an increase upon dilution and the results are presented in Fig. 3 and Table-6. The  $\text{C}\equiv\text{N}$  bond of acetonitrile involves hydrogen bonding with the solvent molecule between the H atom of the water and the N atom of acetonitrile. The motion of the reference molecule, acetonitrile, is constrained owing to this hydrogen-bond formation with the solvent molecule. This would give rise to the phenomenon of motional narrowing as discussed by Oxtoby<sup>19</sup>, according to which the dipolar interaction and resonant energy transfer are mainly responsible for motional narrowing. An empirical model has been recently proposed by Ojha *et al.*<sup>4</sup>. According

to the model, the charges in the linewidth is not only due to the concentration fluctuation as in the model given by Bondarev and Mardaeva<sup>20</sup>, but also due to the change of the microviscosity at different relative concentrations of the solute and the solvent as well as the effect of concentration fluctuation as the microlevel. The viscosities of the different mixtures can be calculated using the relation:

$$\eta_{\text{mix}} = \eta_{\text{solute}}C + \eta_{\text{solvent}}(1-C) \quad (1)$$

where C is the mole fraction of the solute and  $\eta_{\text{solute}}$  and  $\eta_{\text{solvent}}$  are the bulk viscosities of the solute and the solvent, respectively. The variation of the linewidth with the concentration is given by the relation:

$$\Gamma(C) = \Gamma_C + \Gamma_i(\eta_C) \quad (2)$$

where  $\Gamma_C$  is the contribution due to the concentration fluctuation and  $\Gamma_i$  is the intrinsic linewidth, given by:

$$\Gamma_i(\eta_C) = \Gamma_i \exp \left[ -a \left( 1 - \frac{\mu_2 \eta_C}{\mu_2 \eta_{\text{solute}}} \right) \right] \quad (3)$$

$$\Gamma_C = 2\sqrt{2 \ln 2} \Delta\Omega \sqrt{\frac{C(1-C)}{n}} \quad (4)$$

$$\eta_m = \mu\eta = \eta \left[ 0.16 + 0.4 \left( \frac{r_1}{r_2} \right) \right] \quad (5)$$

where  $\mu$  is the microfriction parameter,  $\eta$  is the dynamic viscosity and  $r_1$  and  $r_2$  are the radii of the solute and the solvent molecules, respectively. We have calculated the microfriction parameter for the neat liquid as well as the mixtures, which are represented by  $\mu_1$  and  $\mu_2$ , respectively;  $\Delta\Omega$  is the amplitude of the wave number shift between the neat liquid and infinite dilution, n is the number of the neighboring molecules influencing the reference mode. In the case of hydrogen-bonded system, the value of the van der Waals radius of the terminal atom through which the hydrogen bonding takes places was taken as the solute radius  $r_1$  and similarly the value of the van der Waals radius of the terminal atom of the solvent involved in the hydrogen bonding was taken as the solvent radius  $r_2$  for calculating microviscosity  $\eta_{\text{mix}}$  using the eqn. (5). The parameter 'a' in eqn. (3) is an adjustable parameter which is basically vibrational mode dependent and also it depends upon the polarizability of the vibrational mode under investigation

and thereby also on its contribution to the line width. If  $a = 1$  is substituted in eqn. (3), it still fits the qualitative trend, but by adjusting this parameter one can get a quantitative agreement with the experimental data.

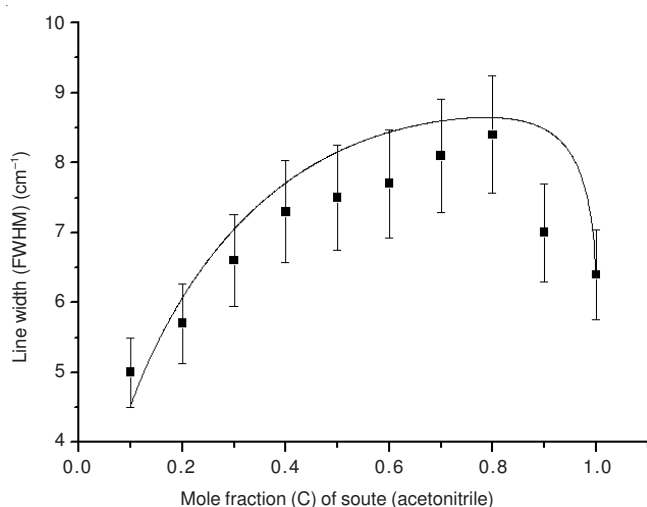


Fig. 3. Experimental data points for the Raman line width varying with concentration of the solute (Acetonitrile) at mole fraction  $C$  for the  $\nu(\text{C}\equiv\text{N})$  stretching mode in the binary mixture and the solid line represents the fit obtained using eqn. 2

Mole fraction(C) of acetonitrile	Peak position (cm <sup>-1</sup> )	Line width (FWHM)
1.0	2252.8	6.4
0.9	2253.1	7.0
0.8	2253.3	8.4
0.7	2253.6	8.1
0.6	2254.0	7.7
0.5	2254.2	7.5
0.4	2254.7	7.3
0.3	2256.6	6.6
0.2	2257.3	5.7
0.1	2258.9	5.0

In this case, the H atom of the solute molecule forms a hydrogen bond with the N atom of the solvent molecule and the values of  $r_1$  and  $r_2$  are taken to be 0.12 and 0.15 nm, respectively. The value of  $\Delta\Omega = 6.1 \text{ cm}^{-1}$  and  $\Gamma_i = 6 \text{ cm}^{-1}$  in this case. Further, the viscosities of water and acetonitrile are 1.002 and 0.38 mPa.s, respectively. Furthermore, if  $\eta_{\text{solute}} > \eta_{\text{solvent}}$ , eqn. (3) would lead to line narrowing and for  $\eta_{\text{solute}} < \eta_{\text{solvent}}$ , it would lead to line broadening with the decreasing mole fraction,  $C$ . It is also obvious from eqn. (3) that in the case where  $\eta_{\text{solute}} = \eta_{\text{solvent}}$ ,  $\Gamma_i(\eta_C)$  becomes independent of the change in concentration. In this study,  $\eta_{\text{solute}} > \eta_{\text{solvent}}$ , it give rise to linenarrowing with the decreasing mole fraction. Therefore, in the present study, the variations in linewidths with concentration in the case are mainly governed by the change in viscosity of the mixture and the concentration fluctuation.

## Conclusion

In this study, Raman spectra of acetonitrile have been taken for neat and binary in different concentrations. The peak position and Raman line width of the  $\nu(\text{C}\equiv\text{N})$  mode of acetonitrile have been analyzed in full range of concentration. From this study, it has been concluded that the wave number position of the  $\text{C}\equiv\text{N}$  stretching mode is shifted to higher wavenumber due to the hydrogen bond and the changes in the line width have been explained for neat as well as binary mixtures, in terms of the concentration fluctuation and the microviscosity. Furthermore, the combination of Raman spectroscopy and quantum chemical theoretical calculations study would be a quite suitable method for studying the structures and the properties of the hydrogen-bonded systems.

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