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Study of Concentration Dependence of Frequency Shift and Linewidth of C=O Stretching mode of Ethyl Acetate in Methanol



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Abstract

The isotropic component of the Raman bands corresponding to the C=O stretching mode of ethyl acetate ($C_4H_8O_2$) in mixture with methanol (CH_3OH) in different concentrations were recorded in the 1600-1800 cm^{-1} region. The Raman spectrum of neat ethyl acetate appears asymmetric. The asymmetry in the spectral features was assumed to be due to the interaction among various solute molecules. The present work describes the variations of linewidth and frequency shift as a function of solvent concentration. The band at 1749 cm^{-1} shows increase in peak frequency and linewidth. The band at 1739.50 cm^{-1} also shows linear increase in the peak frequency. The linewidth shows a maximum at a mole fractions of $C=0.7$ and it starts decreasing gradually with increasing solvent concentration. The variation of the peak frequency and linewidth of C=O stretching mode shows a trend as expected on the basis of concentration fluctuation model. The peak position at 1733 cm^{-1} shows a decrease in the linewidth with concentration. This has been explained in terms of formation of hydrogen bonded complexes, motional narrowing and diffusion mechanisms.

Keywords: Ethyl Acetate, C=O Stretching Mode, Hydrogen Bonding, Peak Frequency and Linewidth Variation, Diffusion and Motional Narrowing.

Introduction

Interactions involving hydrogen bonding is the most investigated subject. Hydrogen bonding has been known to play very important role in understanding the behavior of molecular and biological systems^{6-14, 36-41}. Hydrogen bonded systems has been studied by several techniques such as NMR, Raman and IR, dielectric measurements etc, however, vibrational spectroscopic techniques such as Raman and IR are most suited to understand the inter-molecular and intra-molecular interactions including the hydrogen bonding. Moreover these techniques also cover structural and dynamic aspects of the molecular systems very precisely⁶⁻⁸. Besides various experimental techniques, DFT calculations have proved to be a powerful tool for analyzing the intermolecular interactions in various hydrogen-bonded systems. It has become popular for its better performance and reasonably good efficiency^{1,12,13,14,36,37,38,39}. In liquid mixtures, the study of vibrational and rotational motions using Raman spectroscopy provides a better understanding of the structures and dynamic processes taking place in it. The intermolecular effects taking place during the solute solvent interactions are capable of providing details regarding the dependence of the bandwidth and frequency of the Raman bands on the environment. The broadening of the Raman band shape of a molecule draws major contributions from isotropic and anisotropic Raman components. The isotropic part of the Raman components is mostly influenced by the homogenous broadening and is directly related to vibrational dephasing whereas the broadening of the anisotropic Raman components comes from the reorientational motions.^{15-21, 34}

Extensive studies on the hydrogen bonded systems using Raman Spectroscopic techniques were carried out earlier. Attempts to explain the experimental results of the concentration dependence of the wave number and line width changes for different kind of binary systems were made using various theoretical models^{14-26, 31-37}. Bondarev and Mardaeva¹⁷ first suggested the influence of concentration fluctuation on wave number and

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line width of vibrational band in binary mixtures. Extension of the model was carried out by Knapp and Fischer²⁵ for the non-linear concentration dependence of the isotropic line width. On the other hand, Bratos²⁶ and coworkers could only explain the shape of vibrational isotropic Raman band profiles for isotopic mixtures which was similar to the results of Fujiyama et al.^{20, 27}. However, no proper explanation was provided for the binary mixtures. Th. Gomti⁴² studied the vibrational and reorientational processes in C=O stretching mode of ethyl acetate + acetonitrile mixture in correspondence with correlation times. Her study showed the role of repulsive type of intermolecular forces in the complex systems. Similarly, solvent dependent studies on C=O stretching mode of ethyl acetate in chloroform and chlorobenzene solvents was analyzed in details by Th. Gomti and Ganesh Upadhaya⁴³. They studied the variation of vibrational and reorientational processes corresponding to correlation times. Their study showed that reorientational correlation times follows with the liquid viscosity in this kind of molecules. It also reflects about the nature of solvent molecules hindering to the orientation motion of solute in liquid solution. Our study highlights on the systematic investigation of solute-solvent interactions with Ethyl acetate as the solute in a polar protic solvent such as methanol. It provides information about spectroscopic analysis of Ethyl acetate with hydrogen donor solvents. The spectroscopic analysis of hydrogen bond formation in aqueous solution was first carried out in the year 1941 for formamide²⁸. Ojha et al²⁴ investigated detailed spectroscopic analysis on the hydrogen bonding between formamide-methanol system using Polarization-resolved Raman spectroscopy and DFT calculation technique. They reinvestigated the variation of line width of $\nu(\text{C}=\text{O})$ stretching mode and NH_2 bending mode as a function of mole fractions using an empirical formula^{19, 29}. The hydrogen-bonded complexes were formed which gave peculiar linewidth pattern. It was explained in terms of motional narrowing and diffusion phenomena. In the recent study by Singh et al³¹, the experimental results and theoretical calculations indicate the co-existence of two conformers with hydrogen bonded complex with methanol in the binary mixture, $[(\text{C}_2\text{H}_5)_2\text{C}=\text{O} + \text{CH}_3\text{OH}]$ at intermediate concentrations. They concluded that a significant amount of narrowing in the Raman band was due to caging effect of the reference molecule by the solvent molecules at high dilution. The temperature dependent Raman spectroscopic analysis on the hydrogen bonded network in the crystal structure of creatine in a wide temperature range and correlation to DFT calculations was done by Gangopadhyay et al.³⁶ They reported that the hydrogen bond interactions changes with temperature and different hydrogen bonded aggregates may exist at different temperatures. Their precise analysis gave information about thermal motion and intermolecular interactions with respect to temperature in the crystal lattice. In some recent studies, strong hydrogen bonding has been observed in aqueous solutions such as pyridine-water, pyrimidine-water and many other systems.^{38, 39} In

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pyridines/pyrimidine + water mixtures, at higher water concentration the original reference peak of solute completely vanishes due to strong intermolecular hydrogen bonding interactions. Various researchers^{40, 41} recently made advancement in the solvation dynamics and strong influence of weak hydrogen bonding in the hydrogen bonded system.

In the present paper, we have analyzed the frequency shifts and linewidth variation of C=O stretching band of ethyl acetate as a function of concentration in a hydrogen donor solvent (methanol). In order to correlate the experimental Raman spectra, we have optimized the structures of ethyl acetate at B3LYP/6-311++G (d, p) method level of theory using DFT and calculated their Raman spectra. The experimental results are in good agreement with the theoretical results. The comparison of experimental Raman spectra and DFT calculation provide good information about structural changes and hydrogen bond formation. The experimental results were interpreted in terms of hydrogen bonding between ethyl acetate in methanol and the influence of intermolecular hydrogen bonding on the spectral features were investigated.

Experimental

Raman spectrum of C=O stretching mode of ethyl acetate at different methanol concentrations were recorded using Horriba LabRam HR Evolution. Second harmonic at 532nm of Nd: YAG laser was used as exciting line. It is fitted with band pass filters. The output power was 100mw at 1MHz bandwidth. Labspec 6 software was used with motorized optics for recording the spectrum. The external black platform was supplied with necessary coupling to spectrograph. The commercially available sample of ethyl acetate and methanol obtained from and used without further purification.

The isotropic and anisotropic part of the Raman scattered intensity were obtained by using the relationship,

$$I_{\text{iso}}(\nu) = I_{\text{vv}}(\nu) - 4/3 I_{\text{vh}}(\nu) \quad (1)$$

$$I_{\text{aniso}}(\nu) = I_{\text{vh}}(\nu) \quad (2)$$

Where $I_{\text{vh}}(\nu)$ is the intensity of the Raman band with polarization perpendicular to the laser beam, and $I_{\text{vv}}(\nu)$ is the intensity of the Raman band with polarization parallel to the laser beam measured experimentally in any Arbitrary Unit (A. U) and ν is the wavenumber measured in cm^{-1} .

Computational Methodology:

The geometries of isolated monomers ethyl acetate (EA) and methanol CH_3OH (ML) and their hydrogen-bonded complexes were fully optimized using the DFT based B3LYP/6-311++G (d, p) method¹. B3LYP functional is found to be very reliable for hydrogen bonding studies and has been used quite frequently in various recent studies². Harmonic frequency calculations were carried out at the same level to characterize the stationary points. The hydrogen bonding interaction energies of the complexes were calculated by using the usual definition where the energies of the isolated molecules E_A and E_B are subtracted from the total energy E_{AB} of the complex

$$E_{\text{HB}} = E_{\text{AB}} - E_A - E_B \quad (3)$$

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The calculated values include the zero-point energy (ZPE) corrections and the basis set superposition errors (BSSE) computed by the counterpoise method³. The natural bond orbital (NBO) population scheme⁴ was used in order to discuss important parameters such as charges on individual atom, charge transfer and hyper conjugation energies. The Gaussian 09 package⁵ was used for all of the calculations analyzed in the present work.

Optimized Geometries and Vibrational Spectra

The structures of the various possible complexes between the EA and CH₃OH molecule are illustrated in fig 1. As shown in fig 1, the hydrogen bonded complexes are formed either by O-H...O_{EA} interaction or C-H...O_{ML} interaction in all the complexes. The O-H...O=C intermolecular distances for complex-1 and complex-2 are found to be 1.923 and 1.931 Å. These complexes are further stabilized by secondary C-H...O interactions whose intermolecular distances were found to be 2.586 (complex-1) and 2.870 and 2.863 Å (complex-2) respectively. The binding energies of the hydrogen bonded complexes are found to be -18.47, -18.23 and -7.73 kJ mol⁻¹ for Complex-1, Complex-2 and Complex-3, respectively. The proton affinities of O1 and O2 of EA are also calculated and are found to be 820 and 760 kJ mol⁻¹ calculated at the B3LYP/6-311++G(d,p) level. It is clearly evident that the proton affinity of O1 is about 60 kJ mol⁻¹ higher than that of O2. The binding energies of the complexes are also in good agreement with the proton affinities of the two oxygen atoms in EA, i.e. complex-1 and complex-2 are forming a hydrogen bonded complex involving O1 are characterized with higher binding energy whereas complex-2 which involves O2 in complex formation is characterized with lower binding energy. D.K. Singh et.al³¹ in their hydrogen bonding studies reported a binding energy of 23.64 kJ mol⁻¹ (without BSSE correction) for the complex between (C₂H₅)₂C=O and one CH₃OH molecule. Our calculation for the present systems (complex-1 and complex-2) reports a binding energy of 20 kJ mol⁻¹ (without BSSE correction) which is very close to the binding energy of (C₂H₅)₂C=O...CH₃OH complex.

The most characteristic features of classical hydrogen bond are the lengthening of the donor bond with a corresponding red shift and an increase in IR intensity. These structural and spectral changes are mostly seen in complexes having polar O-H and N-H groups as the donor bond. Similar observation can be observed from the results for the O-H bond of CH₃OH

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participating in hydrogen bond formation. The NBO calculated charges on O1 and O2 of EA are found to be -0.601 e and -0.574 e which are in better agreement with the higher proton affinity of O1 than O2. On complex formation, for Complex-1 and the Complex-2, there is a charge transfer from EA to CH₃OH which attains a value of -0.016 e and -0.013 e respectively. This charge transfer is mainly happening from the lone pair of O1 to the antibonding orbital of O-H bond of CH₃OH. The hyperconjugation energy (LP(O1) → (O-H)) which amounts to 35.6 and 31.4 kJ mol⁻¹ in Complex-1 and Complex-2 is responsible for the lengthening of the OH bond and the red shift of OH) of CH₃OH on complex formation. This is due to the fact that, generally more hyperconjugation energy means more transfer of electrons to the hydrogen bond donor antibond orbital which leads to lengthening of the O-H bond.

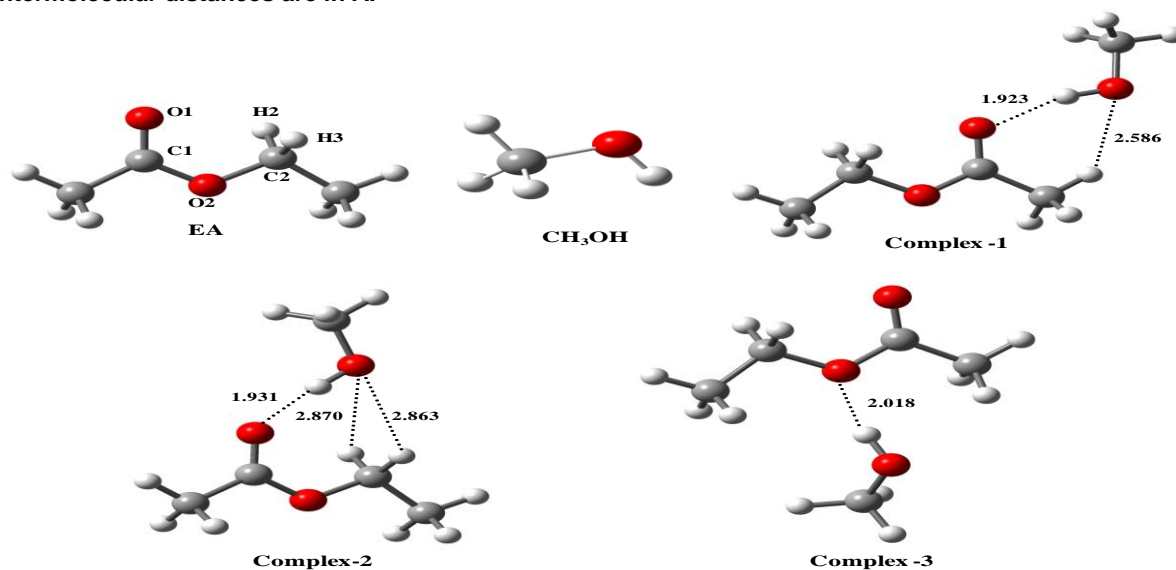
The optimized C=O bond length of EA is 1.207 Å. The C=O bond length in complexes involving carbonyl oxygen (complex-1 and complex-2) are calculated to be 1.215 and 1.214 Å which are slightly larger than in isolated EA. Changes in bond length and vibrational frequency of C-H bond of EA can also be observed which are involved in the secondary interactions with the oxygen of CH₃OH. The calculated vibrational wavenumber of ν (C=O) mode of free EA molecule is 1791 cm⁻¹. This value is scaled to match with the experimentally measured wavenumber of the ν (C=O) mode and the scaling factor comes out to be 0.967. It should be noted that only the scaled ν (C=O) vibrational modes are used for further discussions. Complex formation between EA and CH₃OH results in a red shift of 31 cm⁻¹ and 26 cm⁻¹ in ν (C=O) vibrational frequency for Complex-1 and Complex-2. On the other hand, in Complex-3 (where C=O is not involved in hydrogen bond formation), the ν (C=O) vibrational frequency shows a blue shift of 12 cm⁻¹. The red shift in the wavenumber of ν (C=O) is quite consistent with the lengthening of the C=O bond in both Complex-1 and complex-2 respectively. Our present calculation shows a strong evidence on the formation of a very stable hydrogen bonded complex involving the C=O of EA. Moreover, this red shifts in ν (C=O) are in well agreement with experimental data which shows that on increasing the solvent (CH₃OH) ratio, the possibility of hydrogen bond formation increases which consequently leads to the downshift of the peak frequency.

Table 1

Experimentally observed, calculated and scaled ν (C=O) stretching frequency (cm⁻¹) in isolated EA and in hydrogen bonded complexes with CH₃OH. The bond length, r (C=O) in isolated and complexes are in Å.

Systems	ν (C=O) _{exp}	ν (C=O) _{cal}	ν (C=O) _{scaled}	r (C=O)
EA	1739	1791 (7.37)	1732	1.207
Complex-1		1759 (10.84)	1701	1.215
Complex-2		1764 (11.42)	1706	1.214
Complex-3		1804 (8.54)	1744	1.204

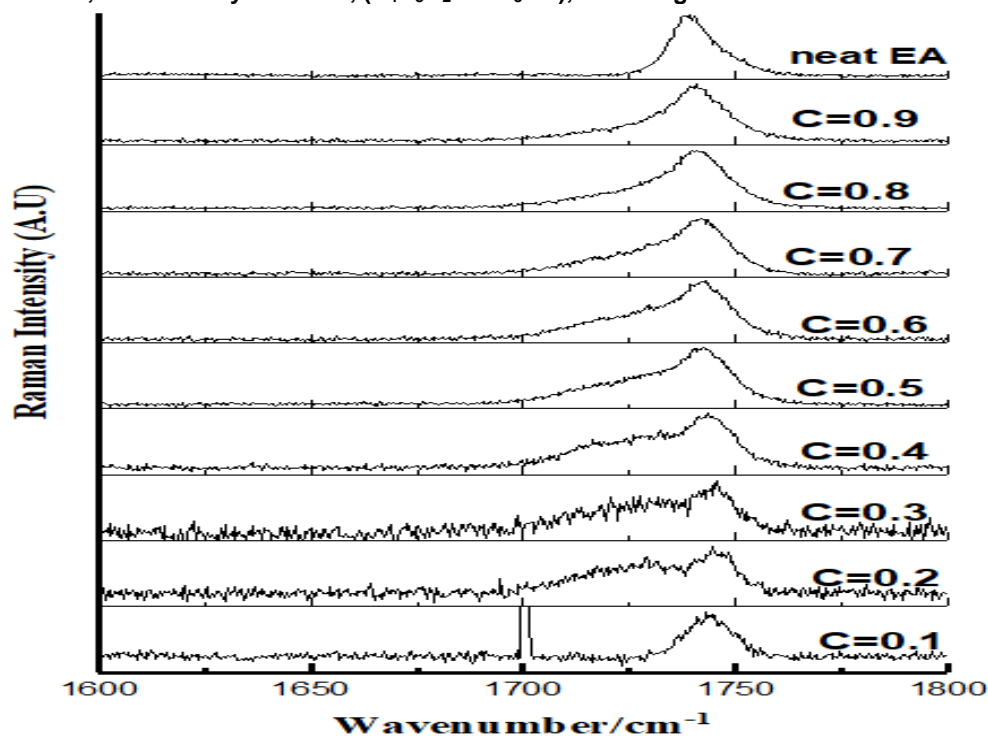
Fig. 1. The optimized geometries of EA, CH₃OH and the hydrogen bonded complexes between them. All the intermolecular distances are in Å.



Analysis of the Raman Line Shape in the C=O Stretching Region

The isotropic part of Raman spectra of neat ethyl acetate as well as nine other reference systems in the region 1600-1800 cm⁻¹ is shown in the fig 2.

Fig. 2. The isotropic parts of the Raman Spectra of C=O stretching mode for neat C₄H₈O₂, with nine other mole fractions, in the binary mixtures, (C₄H₈O₂ + CH₃OH), in the region 1600-1800 cm⁻¹.

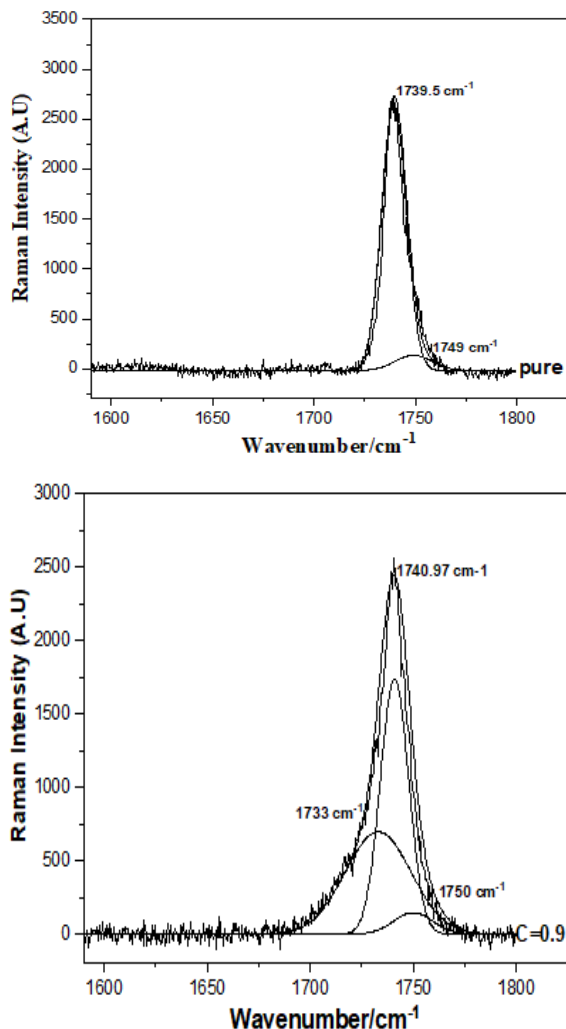


The composite peak which may be decomposed into two or more bands is fitted for two Raman peaks for neat ethyl acetate and three peaks on going from mole fractions C= 0.9 to 0.1. The Raman spectra of neat ethyl acetate and the other mole fractions C=0.9, 0.5 and 0.1 with respect to the reference system is shown in fig 3. The overall band profile of experimentally obtained spectra recorded in

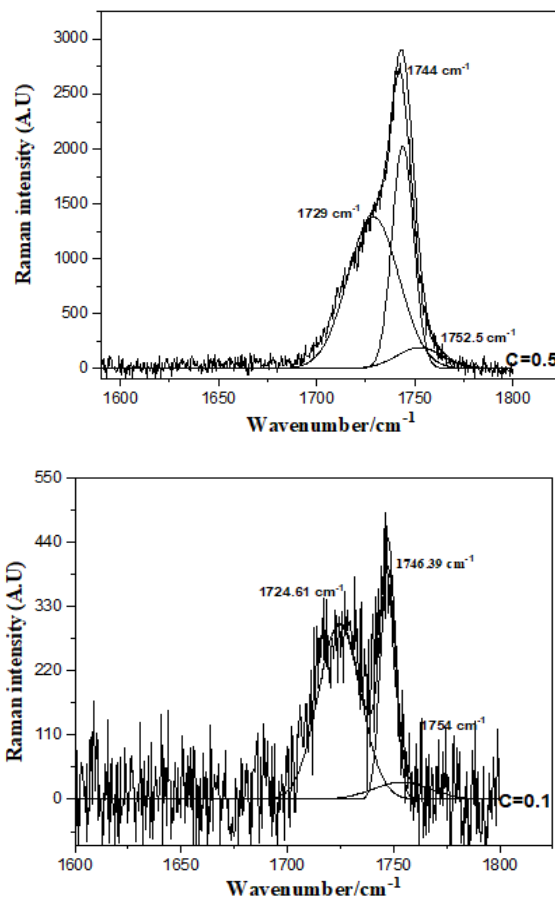
v (C=O) stretching region were analysed using origin 8.5 software. The fitting process was carried out taking into consideration the band as a mixture of Lorentzian and Gaussian, which is basically a Voigt profile. It shows the existence of chemically separated species consisting of non-hydrogen bonded and hydrogen bonded ethyl acetate respectively (fig 3).

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Fig. 3 Isotropic components of the Raman spectra in the region, 1800–1600 cm^{-1} for neat $\text{C}_4\text{H}_8\text{O}_2$ and three other mole fractions, $C = 0.9$, 0.5, and 0.1 in the binary mixture, ($\text{C}_4\text{H}_8\text{O}_2 + \text{CH}_3\text{OH}$).



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The peak corresponding to C=O stretching mode in the Raman spectra shows asymmetry on the higher wavenumber side (fig 2). The precise examination of the spectra and careful analysis of lineshape yields a new band at mole fraction $C=0.9$ (fig 2 and 3). It is also interesting to note that as the concentration of solvent increases, this additional spectral band becomes more and more distinct. This shows that the existence of the solvent causes the spectral feature of the Raman band in the C=O stretching region to vary appreciably. The variation of peak frequency and linewidth obtained from fitting procedure for neat $\text{C}_4\text{H}_8\text{O}_2$ and ($\text{C}_4\text{H}_8\text{O}_2 + \text{CH}_3\text{OH}$) binary mixtures for different mole fraction are shown in Table 2.

Table 2: Experimentally observed peak frequencies, linewidths for the $\nu(\text{C}=\text{O})$ stretching frequency (cm^{-1}) in pure EA and in hydrogen bonded complexes with CH_3OH .

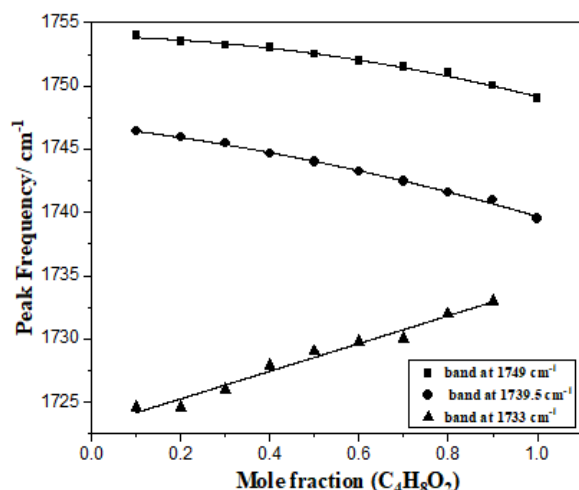
% mole fraction	First peak		Second peak		Hydrogen-bonded peak	
	Peak frequency	linewidth	Peak frequency	linewidth	Peak frequency	Linewidth
1	1739.50	14.13	1749	21.19	-	-
0.9	1740.97	16.18	1750	22.73	1733	37.67
0.8	1741.59	16.48	1751	23.55	1732	34.15
0.7	1742.46	17.66	1751.50	24.73	1730	32.96
0.6	1743.25	14.12	1752	25.90	1729.8	31.79
0.5	1744	12.95	1752.5	27.08	1729	30.61
0.4	1744.63	11.77	1753	28.26	1727.89	29.44
0.3	1745.43	10.59	1753.20	29.44	1726	27.08
0.2	1745.96	9.42	1753.5	30.61	1724.61	24.73
0.1	1746.39	8.24	1754	31.79	1724.61	23.25

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Variation of peak frequency and Linewidth the Raman bands in C=O stretching mode of C₄H₈O₂ with varying CH₃OH concentration

The isotropic part of C=O stretching mode of neat ethyl acetate shows a Raman band at 1739.50 cm⁻¹ and an additional band at 1749 cm⁻¹ on the higher wavenumber side. On addition of methanol, a new band evolves in the region 1733 cm⁻¹ on going from mole fractions C=0.9 to 0.1 as shown in the fig 2. The new peak appears as a result of hydrogen bonding between solute and solvent molecules. At very high concentrations, the involvement of hydrogen bonded species takes over the solute species which results in the change of intensity and wavenumbers. In the present case, for C₄H₈O₂ + CH₃OH system, the first two bands on the higher wavenumber side are assigned to the non-hydrogen bonded or free species and the third band on the lower wavenumber side is assigned to the presence of hydrogen bonded complexes when methanol content is increased. Asthana and co-workers^{14, 16,29,31,32} made various studies on the influence of hydrogen bonding on spectral character of the vibrational bands corresponding to the normal modes related with the hydrogen bond formation. The changes in linewidths and wavenumber shifts of the selected vibrational modes with varying concentration were explained on the basis of results obtained from ab-initio and DFT calculations... The variation of peak frequency and linewidths of the Raman bands vs. mole fractions in the present experiment are shown in the fig 4 and 5 respectively.

Fig. 4. Variation of isotropic peak frequencies of the Raman bands in the C=O stretching mode of C₄H₈O₂ in the (C₄H₈O₂ + CH₃OH) binary mixture as the function of mole fraction.



The isotropic part of the Raman spectra shown in fig 2 corresponding to C=O stretching vibration band at different concentrations was analyzed for the three peaks. The peak position of the band at 1739.34 cm⁻¹ corresponding to $\nu(\text{C}=\text{O})$ vibration shows shifts towards higher wavenumber side (blue shift) linearly with increasing dilution as shown in fig 4. The observed linear shift in the peak position with dilution is due to the increasing interaction between the solute and its environment

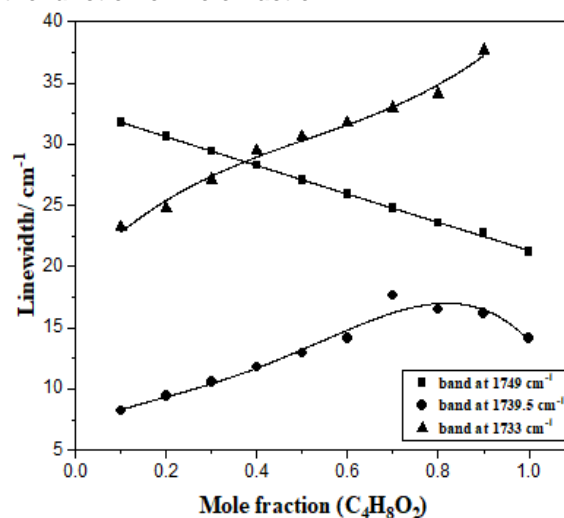
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with the increase in concentration of the solvent in the binary mixture. When the solute is introduced to polar protic solvents, the diffusion mechanism as well as motional narrowing phenomena starts operating, it can be seen from fig 5 that on increasing the concentration of the solvent, the linewidth at first increases reaches a maximum at C=0.7 and then starts decreasing. This is in agreement with concentration fluctuation model¹⁷ which says that the bandwidth increases and get maximum at about half the concentration of the binary mixture with linear shift in peak frequency upon dilution. The model puts forward a linear relationship for the concentration dependence of wavenumber for the reference mode as

$$\nu(C) = \nu_0 + C\Delta\Omega \quad (4)$$

where C is the concentration of solute molecules (in mole fraction), $\nu(C)$ the concentration dependent wavenumber position and $\Delta\Omega$ is the amplitude of the wavenumber shift between neat liquid (C = 1) and infinite dilution (C = 0). In this interacting system, the pair interaction becomes weak at sufficiently high concentration of methanol where several methanol molecules surround the solute molecules. At high dilution the solvent molecules diffuse towards the reference molecule breaking its structure, thereby weakening the dipole-dipole interaction of the solute molecules. The decrease in linewidths is due to the motional narrowing where the atoms of the reference system are restricted due to the involvement of hydrogen bonding which gives rise to motional narrowing and hence the line width starts decreasing with increasing solvent concentration.^{19,31,34,35} The weak band corresponding to 1749 cm⁻¹ on the higher side also shows increase in the wavenumbers as well as linewidth. This increase in the wavenumber and linewidth may be attributed due to mutual interactions between ethyl acetate molecules. It is found that on further increase in methanol molecules, this band becomes broader and weaker.

Fig. 5. Variation of isotropic Linewidths of the Raman bands in the C=O stretching mode of C₄H₈O₂ in the (C₄H₈O₂ + CH₃OH) binary mixture as the function of mole fraction.



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The peak position of the band at 1733 cm^{-1} corresponds to the hydrogen-bonded complex shows a red shift upon dilution, the peak position of this band also varies linearly with concentration. This is also in agreement with the concentration fluctuation model¹⁷. The linear variation of the peak position with concentration may be explained in a similar approach using the Equation 4. Deckert et al³³ suggested that the attractive interaction causes downshift in the peak position due to intermolecular hydrogen bond formation. In the present case, it is seen that on increasing solvent concentration, the motional narrowing phenomena dominates the entire system causing a drastic drop in the line width. At high methanol content, the solvent molecules dominate over solute molecules giving rise to the formation of hydrogen bond in binary mixtures. In CH_3OH solvent, which is polar protic, the protons try to make direct intermolecular hydrogen bonding with the oxygen of the carbonyl group of the solute and the interaction between solute and solvent may be of the form $\text{C=O}\cdots\text{H-O}$. As the concentration of the solvents increases, the methanol molecules diffuse in the solute system as a result of which the interaction between the carbonyl fragments of the solute becomes weak. This provides possibilities for more hydrogen bonding with the reference molecule which directly relates the carbonyl group of the solute whereby increasing the solute-solvent interactions and thus constraining the motion of the atoms of the reference molecules. This is responsible for the decreasing in the line width. Experimental result shows similar qualitative trend as in DFT calculation where the decrease in the peak frequency was due to the lengthening of C=O bond in both the complexes. Our results are in close agreement with the studies of A. K. Ojha et al²⁴ and D. K. Singh et al³¹, which predicted the change in the pattern of the line width was mainly due to diffusion mechanism and motional narrowing.

Conclusion

Polarized Raman spectroscopy and DFT calculations techniques were used to investigate intermolecular hydrogen bonding in the binary mixture. Analysis of line shape reveals several interesting features. The asymmetric nature of the Raman band for the C=O stretching mode was assigned to the $\nu(\text{C=O})$ stretching vibrations at 1749 and 1739.50 cm^{-1} . It can be seen that a new peak corresponding to the C=O stretching mode of the hydrogen bonded complex starts appearing upon dilution. The additional peak at $\sim 1733\text{ cm}^{-1}$ was assigned to the hydrogen bonded complex. With dilution the peak position corresponding to C=O stretching band at $\sim 1739.50\text{ cm}^{-1}$ shows a blue shift. The variation of the linewidth of the C=O vibration with concentration was explained qualitatively as the coexistence of two competing phenomena, namely, diffusion causing an increase in linewidth initially and motional narrowing causing a decrease in linewidth. The weak band at $\sim 1749\text{ cm}^{-1}$ shows a blue shift upon dilution and significant increase of linewidth was attributed due interaction among various ethyl acetate molecules. The peak at $\sim 1733.31\text{ cm}^{-1}$ shows a red

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shift, and a significant amount of decrease in linewidth with concentration was explained in terms of motional narrowing of the reference molecule by the solvent molecules at high dilution. The theoretical calculations of optimized structures using DFT reveals the complex formation of ethyl acetate with methanol molecule in two different configurations. Both experimental and theoretical results indicate the existence of hydrogen bonded complex.

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