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Solvent dependent analysis of isotropic Raman band shape of C=O stretching vibration

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Abstract

The isotropic Raman band shape corresponding to C=O stretching vibration of some molecules has been studied in neat liquids and as a function of solvent concentration using both polar and non-polar solvents. The Raman band shape was analyzed on the basis of correlation with the Lorentzian line shape by employing a simple method of linear curve fitting. In neat liquids and in low solvent concentration region, the band shape was found to be non-Lorentzian. With the gradual increase in solvent concentration the band shape approaches a Lorentzian function. The plot of the correlation coefficient for a Lorentzian shape shows a discontinuity in the intermediate range of solvent concentration. The influence of the structural characteristics of the solute and the solvent systems on the reference mode and various multipolar interactions together with the time varying spatial distribution of solvent molecules with respect to the reference molecule are expected to govern the microenvironmental fluctuations. This may be responsible for the discontinuity in the intermediate solvent concentration region. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Band shape analysis; Solvent effect; Intermolecular interactions

1. Introduction

The influence of intermolecular forces on molecular vibrations is of great importance in the studies of dynamic processes and vibrational relaxation in molecular liquids [1–7]. The sensitivity of certain vibrations in a molecular system towards intermolecular forces provides vibrational spectroscopy a phenomenological approach for its application as a probe in extracting information from the complexity of solute–solvent interactions. The frequency as well as the bandwidth of the vibrational bands of the solute system is influenced by the solvent induced perturbations [8–12]. The effect of average intermolecular forces with reference to the vibrational coordinates is reflected by the frequency of the corresponding vibrational mode. The dynamic fluctuations about the average force of interactions manifest the nature and shape of the relevant vibrational band. The modifications imparted in the band shape of such a characteristic band may be correlated to the microscopic origin of interaction forces [13–

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17]. At room temperature, since the typical vibrational frequencies lie much higher as compared with the thermal energy, the probability of the vibrational states being thermally populated is less. The Raman band corresponding to symmetric C=O stretching vibration of *p*-methyl acetophenone (PMA), benzaldehyde (BH), *N*,*N*-dimethyl acetamide (DMA) and cyclohexanone (CH) has been chosen to study the influence of environmental modulation on the band shape. The choice of this mode of vibration as a probe is based on the fact that it is well separated from other vibrational transitions and hence the intramolecular coupling of the C=O stretching vibration to other internal vibrations is less probable. Moreover, the non-degenerate nature of this mode minimizes the possibility of interference of population relaxation processes with those of dephasing phenomena.

2. Experimental

The samples used for spectroscopic measurements were of spectroscopic grade and were used without further purification. Raman spectra for different molecular systems were recorded in a 90° scattering geometry with a SPEX Ramalog 1403 double monochromator equipped with a photomultiplier and a photon counting arrangement. The spectrometer control and data processing were achieved with the help of a DATAMATE using DM-3000 software. Excitation wavelength of 4880 Å provided by a Spectra Physics model 165 Ar^+ laser was used for PMA, DMA and CH and that of 4416 Å provided by Liconix model 4240 He–Cd laser was used for BH for recording the Raman spectra. A slit width of 1.5 cm^{-1} was maintained while recording the Raman spectra. The isotropic band shape can be obtained from the polarized and depolarized components using the relation

$$I_{iso} = I_{VV} - \frac{4}{3} I_{VH}$$

The effect of the finite slit width on the observed band was corrected [18] by using the relation

$$\Gamma_t = \Gamma_a \left[1 - \left(\frac{S}{\Gamma_a} \right)^2 \right]$$

where Γ_t and Γ_a are the true and apparent Raman band width (FWHM), respectively, and S is the spectral slit width in cm^{-1}. Other spectral conditions were adjusted to get the best possible spectra. The accuracy of measurements is believed to be ± 0.5 cm^{-1}.

3. Results and discussion

The Raman band shapes of the C=O stretching vibration of the molecules PMA, BH, DMA and CH have been studied in neat liquids and at various solvent concentrations ranging from 10 to 90% using CH_3CN, $CHCl_3$, C_6H_6 and CCl_4 as solvents. The numerical analysis of the band shape may be carried out by fitting either a pure Gaussian or a pure Lorentzian function in the relevant band in the Raman spectra. An alternative analytical approach may also be considered by obtaining the convolution of a Gaussian or a Lorentzian band shape. However, in the present work, since the Raman band shape was to be studied as a function of the solvent properties and its concentrations, the data were analyzed by a simple linear curve fitting. By assuming that the band shape is a Lorentzian function, $\omega(t)$ was transformed to a linear equation

$$\frac{1}{I_{iso}} = K_1(\omega - \omega_0) + K_2$$

where I_{iso} represents the height of the isotropic component of the Raman band and K_1 and K_2 are the constant terms.

The correlation coefficient '*r*' was calculated for the Raman band corresponding to C=O stretching mode of vibration for each of the solute systems at various solvent concentrations as well as in neat liquids. The variation of the correlation coefficient '*r*' as a function of solvent concentration is represented in Figs. 1–4. The correlation coefficient that essentially reflects the nature of the band shape with reference to the Lorentzian character is found to exhibit interesting concentration dependent features. The variation of '*r*' in PMA and BH as a function of solvent concentration has been found to be of similar nature both in polar and non-polar solvents. The value of '*r*' for PMA and BH has been found to increase linearly till the solvent concentration attains a critical value of around 40%. With further increase in solvent concentration, the value of '*r*' exhibits a sharp fall (Figs. 1 and 2). This occurs between 40% to 50% concentration of the solvent. At a still higher

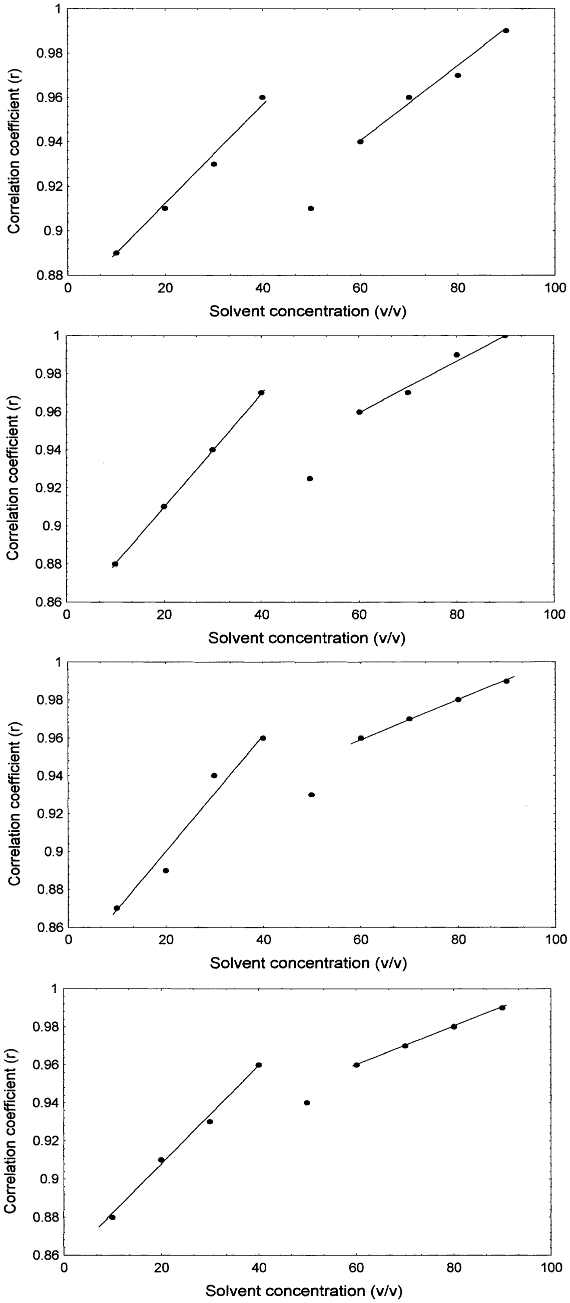

Fig. 1. Correlation coefficient '*r*' at various solvent concentration for *p*-methyl acetophenone in (a) C_6H_6, (b) $CHCl_3$, (c) CH_3CN and (d) CCl_4.

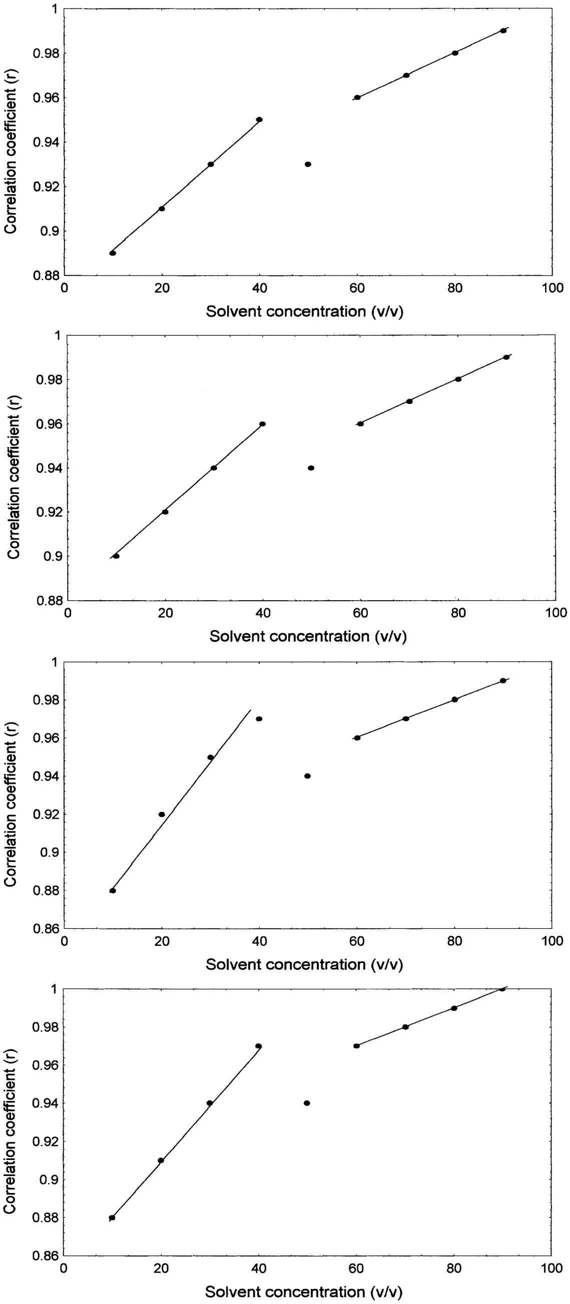

Fig. 2. Correlation coefficient '*r*' at various solvent concentration for benzaldehyde in (a) C_6H_6, (b) $CHCl_3$, (c) CH_3CN and (d) CCl_4.

solvent concentration (> 50%), ‘*r*’ again shows a linear increase, which attains a maximum at a very high dilution (around 90%).

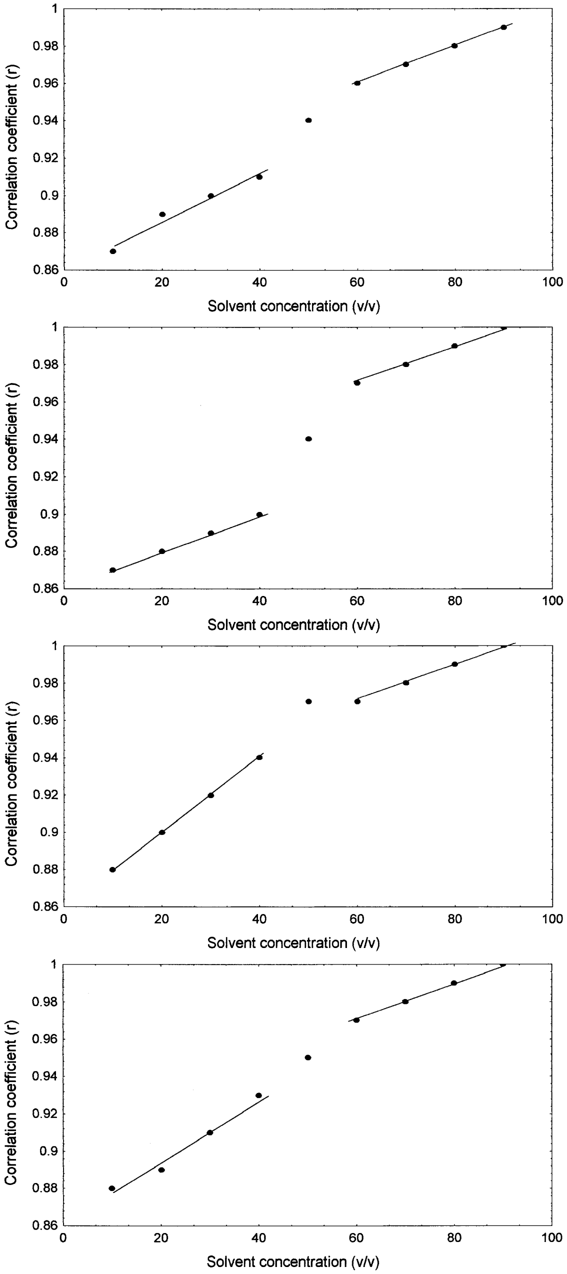

Fig. 3. Correlation coefficient ‘*r*’ at various solvent concentration for *N*,*N*-dimethylacetamide in (a) C_6H_6, (b) $CHCl_3$, (c) CH_3CN and (d) CCl_4.

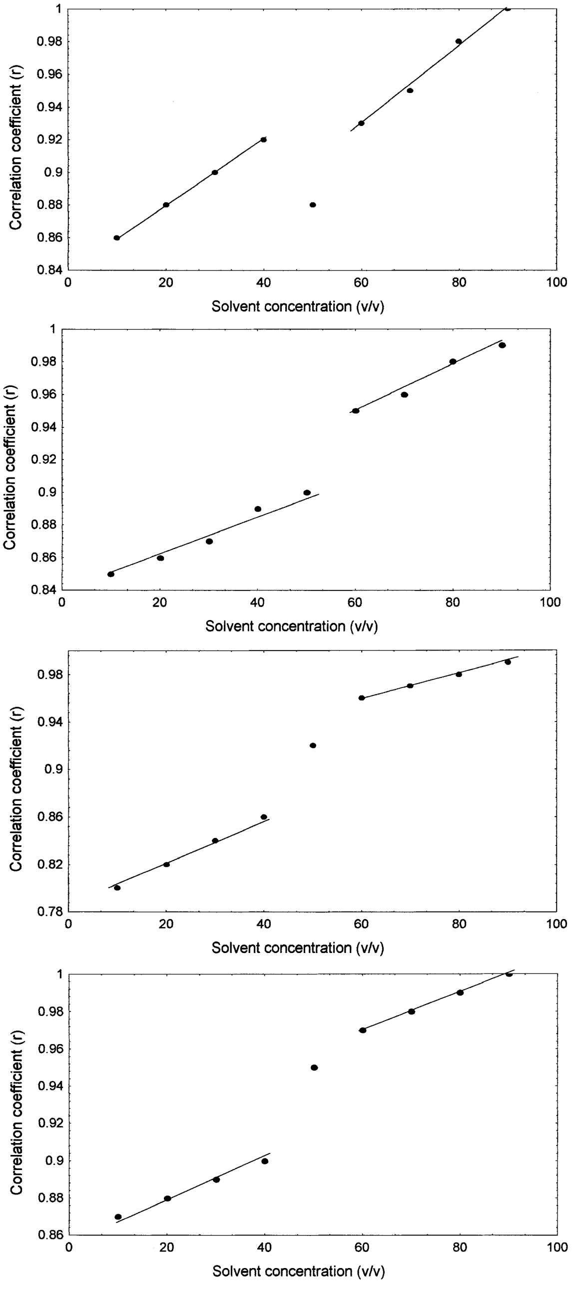

Fig. 4. Correlation coefficient ‘*r*’ at various solvent concentration for cyclohexanone in (a) C_6H_6, (b) $CHCl_3$, (c) CH_3CN and (d) CCl_4.

In case of DMA the correlation coefficient ‘*r*’ shows a linear increase at low solvent concentration between 10 and 50%. Although the variation of ‘*r*’ at higher concentration again shows a linear behavior, yet a prominent discontinuity has been found to occur around 50% concentration that separates the two concentration-dependent behavioral regions (Fig. 3). An almost similar behavior of variation of '*r*' at the two limiting regions of solvent concentrations has also been observed in case of CH (Fig. 4). The point of discontinuity has been found to be a common feature in all the four molecules irrespective of the nature of the solvent molecules.

These characteristic features indicate that the Raman band shapes of C=O stretching mode in these molecular systems are dependent strongly on solvent concentrations and are sensitive to environmental changes. The change in '*r*' from the region of lower to higher solvent concentration with the discontinuity in the intermediate region reflects that the structural characteristic of the substituents in the solute molecule is also responsible in determining the band shape. In case of molecular systems containing benzenoid ring (PMA and BH), the correlation coefficient '*r*' shows a fall at the region of discontinuity while undergoing environmental modification from lower to higher limit of solvent concentration. On the other hand, for the molecular system DMA, having lesser degree of conjugate character towards C=O, the decrease in '*r*' is not observed at the point of discontinuity; instead the correlation coefficient in this case shows a tendency towards its discontinuous enhancement from lower to higher region of solvent concentration. The nature of this transition reveals that in case of DMA the band shape has a tendency towards more Lorentzian character, whereas in PMA and BH a significant deviation from the Lorentzian character is a prominent feature in the intermediate region of solvent concentration.

From the observed data it is evident that in neat liquids and at very low solvent concentrations, the band shape of the isotropic Raman band of C=O stretching mode in these molecular systems exhibits a strong non-Lorentzian character. Such a non-Lorentzian band shape was observed by Moser et al. [19] for symmetric C–H stretching vibration in neat CH_2I_2. The non-Lorentzian character of the Raman band shape appears to derive its major contribution through the resonance energy transfer (RET) processes where the microscopic local order in liquid phase permits the coupling between the vibrational states of the solute molecule through neighboring transition dipoles [16,17]. The vibrational line broadening through RET (transition dipole–transition dipole interactions) occurs due to interaction between identical molecules and hence appears prominently in neat liquids [15]. The effects of resonant transfer are decreased as the concentration of the active molecule is gradually diminished. The observed higher degree of non-Lorentzian nature in the isotropic Raman band of C=O stretching vibration of PMA, BH, DMA and CH is a common feature in neat liquids. The gradual approach of the Raman bands towards Lorentzian shape with the increase in solvent concentration is found to be characteristic of these solute molecules irrespective of the nature of the solvent systems. The intermolecular coupling through RET is a function of inter-molecular separation and depends on the spatial distributions of the interacting dipoles through angular dependence. The angular dependence of the intermolecular potential in this situation is expected to determine the relative alignment of the pair of molecules between which RET occurs. With the increase in solvent concentration the changes incorporated in terms of spatial distribution of active molecule compounded with the diminution in the degree of microscopic local order by the solvent molecule results in the gradual fall of the contribution through RET mechanism. This, as a consequence imparts a gradual enhancement in the Lorentzian nature of the Raman band shape at low solvent concentration region ($<50\%$). As the solvent concentration is increased beyond the critical region of 50% concentration, the interactions between the solute and the solvent systems begin to dominate over the RET coupling interactions. In solution phase, both RET and solvent induced interactions are expected to contribute in determining the Raman band shape. However, the relative magnitude of the two interactions arising as a result of the competition between the rapidly decreasing RET term and the increasing number of solvent induced perturbations seem to have significant contribution in determining the Raman band shape in the intermediate solvent concentration region.

The interaction energy due to solute–solvent interactions may arise due to the contribution from one or more coupling terms, such as dipole–dipole, dipole–quadrupole, quadrupole–quadrupole etc. [20–22]. In PMA and BH the quadrupole moment associated with the benzenoid moiety takes part in quadrupole–quadrupole interaction. The magnitude of these interactions together with the time varying spatial distribution of solvent molecules with respect to the reference solute [22] molecules is expected to govern the nature and extent of environmental fluctuations. The molecular structures of the solute molecules play a key role in determining the magnitude of such interactions. The interaction energies are influenced both by the nature of the interacting multipoles as well as by the nature of the intervening media. From the concentration dependent variation of '*r*' the solute–solvent interaction energy appears to provide greater contribution in PMA and BH as compared with that in DMA and CH in both polar and non-polar solvents. It is possible that the magnitude of these interactions play a significant role in determining the microenvironmental states around the active site of the molecule thus leading to the transition of the band shape in the intermediate region of solvent concentration. The size and shape of the molecules may be crucial in determining the transition from non-Lorentzian to Lorentzian shape. The DMA and CH molecules being comparatively smaller than PMA and BH may be having more collisions with the solvent molecules due to greater velocity. Hence collision broadening may become dominant over RET thus leading to early onset of Lorentzian line shape in these molecules. The transition from the non-Lorentzian line shape to Lorentzian line shape is, therefore, determined by the relative magnitudes of RET and solute–solvent interactions.

Assuming that the perturbation provided by the interaction to the vibrational mode of the active oscillator acts independently, each perturber at an appropriate distance and orientation contributes towards coupling between the reference mode and its neighbors [1,2,15]. The frequency of the vibrational mode is thus modulated by a component that fluctuates with time such that the amplitude of the fluctuating component depends on the nature of the interactions. The transition of the environmental state from the resonance energy transfer to that of the pure dephasing mechanism presumably governs the width of the vibrational band leading to the discontinuous variation in the band shape in the intermediate solvent concentration region.

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