ABSTRACT
Vibrational Band Shape Analysis in Complex Molecular Systems

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There has been considerable interest in studying the molecular dynamics in liquids and disordered condensed phases. This study is of great importance for a large number of chemical, biological and physical phenomena. Liquids are strongly interacting disordered systems and are the least understood state of matter. The importance of liquid phases in chemical reactions and biology makes liquid science an important and rapidly developing field of research. The dynamics of molecules in disordered condensed phases are complicated by the presence of strong, fluctuating intermolecular interactions and the lack of long-range symmetry. Many attempts have been made in the past to analyze the
Raman band shape in liquids and to investigate which dynamic processes and interactions may contribute to the shape. The knowledge of the structure and dynamics in liquids/solutions is expected to contribute significantly to the understanding of the condensed phases and the reactions that occur in solution. The two interacting situations, in pure solute and when dissolved in solvents, differ markedly. The solvent electric field influences the band shape of a reference mode significantly. Moreover, a considerable amount of information about vibrational relaxation and non-coincidence effect can be obtained by analyzing the experimentally measured shapes of the isotropic and anisotropic components of the Raman band of molecular liquids. In our present work, we use Laser Raman technique to explore liquid structure and dynamics at the molecular level. In this study, the theoretical models are tested and the information on the nature of the solute-solvent interactions in liquid phase has been obtained. The carbonyl containing aliphatic and aromatic molecules have been chosen for laser Raman studies in order to get information about the molecular dynamics and interaction processes.

Chapter 1 contains a brief introduction to the thesis emphasizing the application of Laser Raman scattering technique in the study of vibrational relaxation and dephasing processes in liquids. The importance of analyzing the experimentally measured band shapes of isotropic and anisotropic components
of the Raman band of molecular liquids has been discussed here. The band
shape of the reference mode is influenced by the concentration fluctuations of
the environment in liquid mixtures. In order to examine the various interactions
involved in the solute-solvent interactions we have studied the Raman band
shapes of molecules containing C=O bond namely o-Chlorobenzaldehyde
(OCBD) and Methyl Isobutyl Ketone (MIBK) in various polar and nonpolar
solvents such as benzene, carbon tetrachloride, methylbenzene, chlorobenzene,
acetonitrile and chloroform. The choice of these solvents was such that the
solvent molecules are of varying size and shape, and different multipolar
moments and dielectric constants. The benzene and substituted benzene
molecules have significant effects in solute-solvent interactions from the point
of view of quadrupole moment and plate like structure. The CH₃CN and CCl₄
molecules have dipole moment and octupole moment respectively. They are
also having different shapes. The CHCl₃ has a symmetric top structure and
provides the possibility of hydrogen bonding through C-H bond as hydrogen is
acidic here. These molecules because of their different size, shape and electrical
properties are important in the study of the intermolecular forces in solute-
solvent systems. The non-coincidence effect (NCE) and the effect of van der
Waals' volume of the sphere of influence on the Raman bandwidth were
studied for OCBD in order to explain the intermolecular interactions involved.
Vibrational dephasing of the C=O stretching mode of OCBD is very sensitive to the details of the interaction potentials and it can be used to probe the influence of the solvent. The study of isotropic bandwidth of the Raman band provides a direct probe of vibrational relaxation (mainly vibrational dephasing).

Chapter 2 gives a general theoretical background including the different types of mechanism involved in vibrational relaxation, intermolecular interaction in liquids and parameters affecting the band shape of the Raman active vibration of totally symmetric type. The various types of models are also discussed which provide a good semi-quantitative description of dephasing, resonant energy transfer responsible for non-coincidence effect and vibrational relaxation phenomenon. The van der Waals' type of interactions and their role in the band shape broadening have been discussed, taking into account the van der Waals' volume of the interacting fragments of the molecules. The various types of potentials and the intermolecular potential parameters have been discussed in this chapter. The dielectric properties have also been discussed in detail.

Chapter 3 deals with the experimental work related to the recording of Laser Raman spectra of the liquid and solution. The methods adopted for the measurement of the isotropic and anisotropic Raman bandwidth are also
explained in detail. A brief description of the technique for recording Raman spectra at room temperature using Spex Ramalog 1403 double monochromator, a cooled RCA C31034 photomultiplier tube, photon counting arrangement and Ar-ion laser source is given. The brief account of HP-4263B multi-frequency LCR-meter for measuring capacitance is also given in this chapter.

Chapter 4 is devoted to the solvent dependent study of the non-coincidence effect (NCE) and anisotropic component of the Raman band. Raman Spectra of C=O stretching mode of OCBD were measured using CCl₄, CH₃CN, CH₂C₆H₅ and C₆H₅Cl solvents at different solvent concentrations ranging from 10% to 90%. The peak frequencies of isotropic and anisotropic components were found out. The anisotropy shift (δv = νaniso - νiso) was measured for different solvent concentrations ranging from 10% to 90% solvent concentrations using the above four solvents. It has been found that the anisotropy shift decreases as the solvent concentration is increased because the solvent molecules decrease the interaction between the pair of identical molecules. For the molecules having aromatic rings, the coupling mechanism for the NCE may also be associated with quadrupolar resonant coupling besides transition dipole-transition dipole interactions. The Onsager- Fröhlich dielectric model, which treats the dielectric as a continuum has been tested by studying the behaviour of the NCE at various solvent concentrations.
The parameter $F = \delta v (2\varepsilon + n^2)^2 e^{-1}$ was plotted as a function of the solute volume fraction $\phi$. The data points fit well in exponential curve rather than a straight line for all the solvents except CH$_3$CN. In case of OCBD- CH$_3$CN system, the data points are lying in a straight line, which indicates that the dielectric continuum theory probably holds better in this system. The high dielectric constant of CH$_3$CN solvent may be responsible for such behaviour. The exponential nature of the curves for the three solvents (CCl$_4$, CH$_3$C$_6$H$_5$ and C$_6$H$_5$Cl) show that the Onsager-Fröhlich dielectric continuum model does not hold good in these systems. Therefore, in these solvents, the discreteness of the medium exists. Further, the screening effect may not be as effective as envisaged by the Onsager-Fröhlich model in such systems. The role of the repulsive forces in most of the interacting situations is clearly indicated by the exponential fitting of the data points.

In order to get more information about the intermolecular interactions in liquid mixtures, the anisotropic Raman components of OCBD in different solvents were studied and the bandwidths were measured. The plot of $\Gamma_{\text{aniso}}$ as a function of solvent concentration shows that the data points are scattered and cannot be fitted into a single curve. For CCl$_4$ solvent, the data points show a decrease in the bandwidth while going from lower to higher solvent concentration, whereas for CH$_3$CN and C$_6$H$_5$Cl solvents, the data points show
an initial increase and then a decrease in the bandwidth as the concentration increases. In case of CH$_3$C$_6$H$_5$ solvent, the data points show somewhat different pattern as compared to others. However, the bandwidth is found to decrease at high solvent concentration for all the solvents. The bandwidths of isotropic Raman component ($\Gamma_{iso}$) were also found out in order to see the changing pattern according to different solvent concentrations and plotted with respect to the solvent concentration. Interestingly, the isotropic bandwidths are also found to decrease at higher solvent concentration. The dramatic change in shape on going from lower to higher solvent concentration region reflects the changes in liquid dynamics brought about by solvent collisions. This complicated nature has been explained in terms of van der Waals' volume of the sphere of influence in a solute dissolved in solvents. The calculation of van der Waals' volume assumes knowledge of bond distance, intermolecular van der Waals' radii and shapes of atoms in various molecular configurations. The main interaction is considered to be between the dipole moment of C=O and the dipole, quadrupole and octupole moments of the solvents.

The van der Waals' volume of the interacting system was calculated by using the equation

$$ V_w = \Phi V_w(\text{solute}) + (1 - \Phi) V_w(\text{solvent}) $$

where $\Phi$ is the concentration of the solute.
The values of \( \frac{\Gamma_{\text{aniso}}}{V_w} \) have been calculated for each solvent and plotted as a function of solvent concentration. This graph is an exponential curve for all the solvents, which indicates that the repulsive potential of the type \( e^{-aR} \) is playing a significant role.

**Chapter 5** deals with the studies on vibrational dephasing in molecular liquids. The vibrational phase relaxation is important for the band shape of complex molecular systems, and is responsible for the line broadening of the isotropic Raman spectral component. However, the vibrational phase relaxation process for complex molecular systems cannot be explained simply on a macroscopic perception of the interacting systems. There may be a marked difference between the interacting situations in the pure solute and when dissolved in solvents especially at high dilution. A detailed study at the microscopic level is therefore required in order to explain the interacting situations, especially the solvent effects on vibrational relaxation rates.

The Raman spectra of OCBD dissolved in various polar and non-polar solvents (\( \text{CH}_3\text{C}_6\text{H}_5, \text{C}_6\text{H}_6, \text{C}_6\text{H}_5\text{Cl}, \text{CCl}_4 \) and \( \text{CHCl}_3 \)) were recorded and the isotropic components obtained. The band shapes of the isotropic Raman component for OCBD in different solvents were checked for Lorentzian shape by curve fitting and found to be near Lorentzian in nature at high dilutions.
(\sim 90\%)}. For Lorentzian line shape the vibrational relaxation rate \( (\tau_v^{-1}) \) is related to the isotropic bandwidth by the expression,

\[
\tau_v^{-1} = \pi c \Gamma_{iso}
\]

where \( \Gamma_{iso} \) is the Full Width at Half Maximum (FWHM) of the isotropic component of the Raman band, \( \tau_v \) is vibrational relaxation time and \( c \) is the velocity of light.

The bandwidths (FWHM) of the isotropic component of \( \text{C}=\text{O} \) stretching mode of OCBD were measured at 90\% solvent concentration. The data were used to calculate the vibrational relaxation rate \( (\tau_v^{-1}) \). The various models which have been proposed for the dephasing process take into account of the dynamic viscosity \( (\eta) \) which is a macroscopic property. The parameter \( f (\rho, \eta, n) \) was calculated for OCBD and correlated with the experimental values of the vibrational relaxation rate. The correlation is roughly linear for all the solvents, with the exception of chloroform. The point for \( \text{CHCl}_3 \) is too far away from the correlation line. This indicates that the bandwidth cannot be fully explained by the molecular properties contained in this parameter.

It is probable that the discreteness of the medium due to solvent may be playing a role therefore the microscopic model was used in order to explain the environmental effects around the molecule. In this model, since the solute-solvent systems may not always be homogeneous and some heterogeneity may
exist due to associative nature of the molecules, the concept of microviscosity was taken into account.

The microviscosity ($\eta_m$) is calculated using the relation

$$\eta_m = \eta [0.16+0.4(a/b)] \quad \text{or} \quad \eta_m = \eta \gamma$$

where $\gamma = [0.16+0.4(a/b)]$ is the microfriction factor. $a$ and $b$ are the radius of solute and solvent molecules respectively.

The modified parameter has the form

$$f_m = \rho \eta_m \left[ \frac{n^2 - 1}{2n^2 + 1} \right]^{-1}$$

where $\rho$ is the density and $n$ is the refractive index of the solvent molecule.

The variation of the vibrational relaxation rate ($\tau_v^{-1}$) as a function of $f_m$ has been plotted, which is clearly a linear plot indicating a better fitting of data points. This shows the discreteness of the medium, which has significant influence on the bandwidth in such complex molecular systems. The correlation coefficient ($r$) for the $\tau_v^{-1}$ vs. $f$ ($\rho, \eta, n$) and $\tau_v^{-1}$ vs. $f_m$ plots have been calculated and their values are found to be 0.824 and 0.993 respectively. It may therefore be concluded that $f_m$ is a better parameter than $f$ for explaining the vibrational relaxation rates of OCBD molecule. Thus, the microviscosity rather than dynamic viscosity is playing a major role in determining the Raman band shape in this solute-solvent system.
Chapter 6 deals with the study of Raman anisotropic bandwidth of C=O stretching vibration of Methyl Isobutyl Ketone (MIBK) in several solvents like benzene, carbon tetrachloride, methylbenzene, chlorobenzene, acetonitrile and chloroform in order to see the effect of solvents of different nature. The anisotropic Raman bandwidth gives information about the angular dependent intermolecular forces. The dielectric measurements (capacitance) in liquid mixtures were also carried out to correlate the anisotropic Raman bandwidth with changing environment. The bandwidths of the anisotropic component of Raman band ($\Gamma_{\text{aniso}}$) of MIBK were measured at different solvent concentrations ranging from 10% to 90% using polar and non-polar solvents ($C_6H_6$, $CCl_4$, $CH_3C_6H_5$, $C_6H_5Cl$, $CH_3CN$ and $CHCl_3$) of varying dielectric constant. Examination of spectral properties reveals that the anisotropic Raman bandwidth strongly depends on solvent concentration and is sensitive to environmental changes. In low solvent concentration region, the plot of $\Gamma_{\text{aniso}}$ as a function of solvent concentration shows marked curvatures for all solvents except for $CH_3CN$. However, the data points in higher solvent concentration region appear to be linear for most of the solvents. In case of $C_6H_5Cl$ solvent, the data points cannot be fitted in one curve. However, they may be fitted in two curvatures in the two ranges; lower and higher solvent concentration. In the intermediate region, there is no uniformity or continuous pattern of the
plot. For CH₃CN solvent, the data points may be fitted in two straight lines rather than one implying a discontinuity in the uniform linear pattern in the intermediate region. This is a complicated nature, which is due to the fluctuation of the chemical composition in a given site of the liquid and to the structure breaking effects.

In order to interpret the complicated behaviour we have taken into account the van der Waals' volume \( V_w \) of the sphere of influence in solute dissolved in all solvents. The van der Waals' volume of the interacting system was calculated by using the equation

\[
V_w = \Phi V_w(\text{solute}) + (1-\Phi) V_w(\text{solvent})
\]

where \( \Phi \) is the concentration of the solute.

A quantity \( \Gamma_{\text{aniso}}/V_w \) was defined and plotted as a function of solvent concentration. The exponential nature of the graph \( \Gamma_{\text{aniso}}/V_w \) vs. solvent concentration) clearly indicates that the repulsive potential of the type \( e^{-aR} \) is playing an important role in such complex interacting systems \( R \) being the distance of closest approach and \( a \) is a constant). The pair interaction between the solute molecules leads to the local ordering in liquids under consideration. However due to the increasing concentration of the solvent the weakening of the pair correlation may occur. The hydrodynamic forces are dominant over the electrical forces in maintaining the smooth flow of the liquid. In order to study the effect of screening on the bandwidth \( \Gamma_{\text{aniso}} \), the capacitances of the
liquid mixture at different solvent concentrations varying from 10% to 90% were measured for all the solvents. The plot of capacitance vs. solvent concentrations for each solvent shows that there is no uniformity or continuity in the graph around 50% of solvent concentration. This is of somewhat similar nature as seen for the variation of bandwidth $\Gamma_{\text{aniso}}$ with solvent concentration, which supports the findings that the repulsive type of intermolecular forces are responsible in the line broadening mechanism.

Chapter 7 deals with the conclusion drawn from the present work. From the present work the following conclusions can be drawn.

1. The non-coincidence effect was studied taking into account the screening factor in order to interpret the various interaction involved in solute-solvent interactions. The continuum model of Onsager-Fröhlich is not found to be valid for most of the systems. The discreteness of the medium accounts for the complex situation in the molecular system studied by us.

2. The van der Waals' volume of the interacting systems has been found to play a very important role in the study of solute-solvent interactions. The molecular fragments are also playing significant role.
3. The complex processes involved in the interacting systems may not be understood by dynamic viscosity; therefore, there is a definite need to consider the microenvironment incorporating microviscosity.

The interesting feature of the present results is the dependence of vibrational relaxation rate on the dispersion and hydrodynamic forces. The role of microenvironment through microviscosity has been established in the interacting systems. The results also indicate that repulsive potential of the type $e^{-\alpha R}$ plays an important role in the interactions as well as in the vanishing of the anisotropy shift (non-coincidence effect) in complex molecules.