CHAPTER 1
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INTRODUCTION

There has been a considerable interest in studying the molecular dynamics of liquids\textsuperscript{1-5}, which is of great importance for a large number of chemical, biological and physical phenomena. 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. In liquids, the densely packed molecules exhibit strong mutual interactions in rapidly changing configurations due to random thermal motion of the molecules. Many attempts have been made in the past to analyze the Raman band shape in liquids to investigate which dynamic processes and interactions contribute in determining the shape of the band\textsuperscript{1-2}. The relaxation, scattering and absorption spectroscopy provide useful information about the molecular motion in liquids. During the past several years, vibrational relaxation and molecular reorientational processes in liquids have been studied by analyzing \textsuperscript{6-25} the band shape of the isotropic (I_{iso}) and anisotropic (I_{aniso}) components of the Raman band of the molecule. The full width at half maximum (FWHM) has been used for
the analysis of band shape. The sensitivity of Raman bandwidth (FWHM) on the environment has been demonstrated by the solvent dependent studies, which have been useful in obtaining the information on the dynamics of liquids.

A variety of theoretical models has been proposed to describe the influence of a solvent on vibrational frequencies and bandwidths. These theoretical models may often be applied to data obtained by different techniques such as Nuclear magnetic resonance (NMR), Electron Spin resonance (ESR) and vibrational spectroscopy (IR and Raman). Each model has adjustable parameters that can be used to fit the data. In these cases, the electromagnetic field causes a change of state in a reference system of nuclear spin or electronic spin states or the vibrational modes (vibrational energy levels) of molecules. The reference system (molecule) immersed in a liquid will have many degrees of freedom of the bath (rotational and translational). Thus, the states of the reference system will have a finite lifetime and energy width. This amounts to a decay of the time correlation function corresponding to the reference transition.

The band shape may provide valuable information about the interaction of the reference molecule with its environments and about the dynamics of the bath. The Laser Raman scattering experiments have been used to study the vibrational and rotational frequencies of molecules, which provides detailed information about the dynamic processes involved in
liquids. In case one wants to examine the reorientation and vibrational relaxation processes separately using vibrational (IR and Raman) spectroscopy, one has to study the well-isolated vibrational modes, which might provide good and clean spectra. From the experimentally observed $I_{VV}$ and $I_{VH}$ Raman band components (where $I_{VV}$ and $I_{VH}$ have their usual meanings), one can obtain the isotropic component $I_{iso}(\nu)$ and the anisotropic component $I_{aniso}(\nu)$ of the Raman spectrum. The isotropic and anisotropic components are given by:

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

$$I_{aniso}(\nu) = I_{VH}(\nu)$$

where $\nu$ denotes the frequency in cm$^{-1}$.

The peak frequencies of isotropic and anisotropic Raman bands of many molecules do not coincide in liquid state due to the orientationally dependent intermolecular forces. The difference in peak position may sometimes be even more than 10 cm$^{-1}$. This is due to non-coincidence effect (NCE). The NCE is mostly associated with symmetric Raman active vibrational modes of polar molecules and is very pronounced for the modes, which are strongly infrared active. The solvent dependent studies have shown that the magnitude of the splitting decreases with increasing concentration of the solvent and tends to vanish in the limit of infinite...
dilution. The effect has been observed in the CO stretches in carbonyls\textsuperscript{12,15,17,24,25}, CH stretches in chloroform\textsuperscript{28} and CN in acetonitrile\textsuperscript{29}. The NCE has been mainly attributed to the resonant transfer of vibrational excitation in the presence of local order due to strong interactions between permanent dipole moments. The most common source of resonant transfer relevant to the effect is due to transition dipole-transition dipole (TD-TD) coupling. This NCE has been interpreted as being due to the coupling between vibrations of neighbouring molecules, with strongly polar bonds by intermolecular dipole interactions in the liquid phase\textsuperscript{6,11,12,30}.

The vibrational Relaxation process consists of vibrational population relaxation and vibrational phase relaxation. The population (energy) relaxation involves vibrational inelastic processes and corresponds to what is called $T_1$ relaxation spin system, while phase relaxation (dephasing) involves only quasi-elastic interaction of the molecules with their surroundings leading to perturbation of the phase of the vibrational wave functions without changing their quantum states. It can be stated that in most cases vibrational lineshapes are mainly determined by dephasing, which corresponds to $T_2$ relaxation spin system in NMR. The study of vibrational phase relaxation has been an important endeavour of a chemical physicist in the attempt to understand and quantify the interaction of a chemical bond with the surrounding solvent molecule\textsuperscript{1}. 
In liquids, the energy relaxation has longer lifetime in comparison with phase relaxation (dephasing). The vibrational phase relaxation process is responsible for the line broadening of the isotropic Raman band.

Different theoretical models on phase relaxation have been developed such as the hydrodynamic model\textsuperscript{31-34}, the isolated binary collision (IBC) model\textsuperscript{35-39}, the cell model\textsuperscript{40,41} and the model based on resonant energy transfer\textsuperscript{42-47}.

A hydrodynamic model\textsuperscript{31,36} can provide a good qualitative and semi-quantitative description of dephasing in molecular liquids. It seems likely that pure dephasing has more contribution. Moreover, the relaxation time of the random force is responsible for the viscosity dependence of the diffusion coefficient.

In the Isolated binary collision (IBC) model, the transition rate is assumed as the product of the collision rate in the liquid and the transition probability per collision in the gas phase. The probability per collision may be obtained either from scattering calculations or by independent experiments on low-density gases. Various models\textsuperscript{35,36} have been proposed for the collision rate in liquid phase. Fischer and Laubereau\textsuperscript{35} introduced a gas like IBC model for pure dephasing in the liquid phase and applied it to a series of simple liquids. Litovitz\textsuperscript{40} approximated the time between collisions to an Enskog time for the rate of binary collision of hard spheres using cell model. Again, Bratos and co-workers\textsuperscript{42-43} used a stochastic model to study
the contribution of pure dephasing while the theoretical and experimental work of Döge et al\textsuperscript{44} involved studies of the resonant transfer effect as well. Several authors \textsuperscript{31,44,48-50} had shown that pure dephasing and resonant transfer are not truly separable and that the cross correlation between them can contribute significantly to the line shape.

One of the most important mechanisms that may contribute significantly to dephasing processes in liquids is the coupling between the similar modes of identical molecules (resonant energy transfer process). The interaction responsible for this coupling usually depends strongly on the relative orientation of the molecules. In some theoretical models, long-range (attractive) forces are involved. The collisional events are those, which have too short time of action to influence considerably the dephasing time. Consider the case of molecular harmonic oscillator that couples to the heat bath through translational diffusion where the effects of coupling of rotations to vibrations or translations are neglected. When dipole-dipole interactions and dispersion forces are included, there are three contributions to line broadening\textsuperscript{46}. The first ‘Self term’, the second ‘exchange term’ and the third is ‘cross self exchange term’, respectively. The exchange term is due to the transfer of vibrational quantum states between two identical molecules through corresponding normal modes. This mechanism is normally referred as resonant energy transfer. It is possible to single out this particular kind of dephasing by performing dilution measurements.
Another important coupling mechanism is transition dipole-transition dipole (TD-TD) type\textsuperscript{15}, which is possible when strongly infrared active transitions are present. The resonant transfer mechanism is identified by dilution experiments with solvents, which reduces the coupling. Such experiments may exhibit band narrowing when dilution studies are carried out \textsuperscript{46}.

Vibrational Raman band shapes observed in the spontaneous Raman scattering process are broadened by homogeneous and inhomogeneous line broadening mechanisms. The homogeneous broadening yields information about the rapidly varying dynamic modulation processes responsible for vibrational dephasing. On the other hand, the inhomogeneous line broadening gives information about slowly varying modulation processes, which lead to a distribution of vibrational frequencies. The basis of the detailed study of vibrational dephasing is band shape and solvent induced frequency shift, which are due to the competition between slowly varying attractive forces and rapid collisional forces in a weak coupling regime. Although the vibrational resonance coupling due to TD-TD interaction may be important in some modes of polar molecules, it has been pointed out by Wang and Mchale\textsuperscript{7} that the vibrational resonance coupling may also originate from quadrupole-quadrupole interaction or any other type of intermolecular interactions.
The Hamiltonian which determines the time evolution of the dynamic variables, is written as

\[ H = H_{\text{osc}} + H_B + H_{\text{coup}} \]

where \( H_{\text{osc}} \) is the sum of harmonic oscillator Hamiltonian, \( H_B \) is the bath Hamiltonian and \( H_{\text{coup}} \) is the part of the Hamiltonian, which couples the internal vibrational coordinates of the bath molecules.

There are different mechanisms that can contribute to the coupling potential: dispersion interaction, dipole and multipole interactions and repulsive forces etc. Hence, in order to understand the nature of the intermolecular interactions and molecular dynamics, there is a need of detailed studies on vibrational relaxation, reorientational motion, frequency shifts, bandwidths and band shapes in various liquids. Several models have been proposed to describe the influence of a solvent on vibrational frequencies and bandwidths. These models characterize the solute-solvent interactions ranging from empirical or macroscopic quantities such as solvent donor and acceptor numbers or the dielectric constant and index of refraction to models based on microscopic statistical mechanical theories, which incorporate solvent-solute interactions at the molecular level.

Schweizer and Chandler developed those models based on microscopic systems. These particular treatments are based on a partitioning of intermolecular forces into repulsive and attractive components. It is consistent with the van der Waals'/Weeks-Chandler-Andersen (WCA)
picture of fluids, where the short-range repulsive forces determine the fluid structure and the longer-range attractive forces can be treated by perturbation theories. This approach allows one to relate the solvent contributions to the vibrational frequencies and bandwidths to intermolecular interactions involving repulsive and attractive forces.

Schiebe and Döge have given a simple theoretical approach to the behaviour of various band shape parameters in terms of dipole-dipole interaction in the frequency domain. The structure effect seems to play an important role in influencing the band shape of polar Raman bands in liquids with dipole-dipole interaction energies of the order of thermal energy $k_B T$. The asymmetry of the $I_{VV}$ component of the band was explained based on the change in the orientation probability distribution into the direction of energetically favourable orientation. However, the theoretical approach is too simple to allow more than a qualitative interpretation of the experimental data. When the dipole sizes are comparable with those of solvent molecules, the fundamental problem lies in the determination of an effective electric permittivity of the medium. The two interacting situations in pure solute and when dissolved in solvents, differ markedly at high dilution. 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 can be obtained by analyzing the experimentally measured band shapes of the isotropic and anisotropic...
components of the Raman band of molecular liquids. The band shape of the reference mode is influenced by the concentration fluctuations of the environment in liquid mixtures. The microscopic environment affects the behaviour of a reference molecule in a very significant manner. It is therefore necessary to study the vibrational relaxation and NCE in the complex molecular systems from microscopic point of view. Moreover, the solvent effects on the NCE (anisotropy shift) and variation of bandwidth in dipolar liquids may offer new information about strong inter and intra-molecular interactions. Therefore in the present work, we have studied the Raman band shapes of the C=O stretching vibration of o-chlorobenzaldehyde (OCBD) and Methyl isobutyl ketone (MIBK) molecules in different polar and non-polar solvents. The C=O stretching mode of the carbonyl containing molecules have been chosen for the present study because of the following particular characteristics.

(1) It lies at high frequencies, so the condition $\hbar \omega >> k_B T$ is always true.

(2) Usually it is little mixed and/or coupled with other vibrations, which means that its normal coordinate may be considered as a pure one.

(3) It is well isolated from other modes of vibration in the molecules under present study.

It is, therefore, particularly suitable for probing the molecular environment and is expected to give detailed information regarding the complex
molecular systems. Moreover, these molecules have applications in chemical and biological fields. The experimental results have been explained using the concept of microenvironment, the role of hydrodynamic forces, the effective van der Waals' volume and the effect of reaction field (solvent reaction field) on the solute. These molecules with strong interactions have not been investigated fully from the vibrational relaxation and microscopic point of view. A rigorous description of the solution should take into account both the separation between molecules and their orientation with respect to each other. In this work the potential function, which incorporates the repulsive and dispersion forces found in regular fluids and the contributions of multipolar moments, specifically dipole and/or quadrupole moments have been investigated. In polar liquids, the existence of local orientational order assists the intermolecular coupling between identical vibrations in nearby molecules and induces the transfer of vibrational energy between them. The phenomenology associated with this process appears in the Raman bands of these vibrations through the non-coincidence of their isotropic and anisotropic profiles mentioned earlier. In fact, the non-coincidence of the peak frequencies of the isotropic and the anisotropic components in Raman spectra has always been considered an efficacious probe of the structure and dynamics of polar liquids. We have focussed on the NCE by taking into account the screening factor related to the permanent and transition dipoles. The study of the anisotropic
components of the Raman bands were undertaken by taking into account the van der Waals' volume of the interacting system in order to interpret the various interactions involved in solute-solvent interaction. The NCE for OCBD was studied in CCl₄, CH₃CN, CH₃C₆H₅ and C₆H₅Cl solvents. The anisotropic bandwidth and the effect of van der Waals' volume of solute-solvent systems were also studied for OCBD in different solvents in order to understand about the intermolecular interactions in liquid mixtures.

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 dephasing processes have been studied using relaxation time obtained from the FWHM of the isotropic component of Raman band of C=O stretching mode of o-chlorobenzaldehyde (OCBD) using various polar and non-polar solvents.

The anisotropic component of the Raman band gives information about the angular dependent intermolecular forces. These forces could be attractive as well as repulsive and may arise due to multipolar interaction or dispersion forces. The anisotropic bandwidth of C=O stretching mode of Methyl Isobutyl Ketone (MIBK) has also been studied in benzene, carbon tetrachloride, methylbenzene, chlorobenzene, acetonitrile and chloroform solvents by taking into account the van der Waals' volume of the sphere of influence in solute dissolved in the solvents.
The choice of these solvents was such that the solvent molecules are of different size and shape, 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 CH$_3$CN and CCl$_4$ molecules have dipole moment and octupole moment, respectively and different in shapes having cylindrical and spherical shapes. The CHCl$_3$ has a symmetric top structure and provides the possibility of hydrogen bonding through C-H bond as H is an acidic hydrogen / proton. These molecules, because of different size shape and electrical properties may be of considerable help in the study of the intermolecular forces.
REFERENCES:


