LASER RAMAN SCATTERING STUDIES OF VIBRATIONAL RELAXATION AND NON-COINCIDENCE EFFECT OF THE ISOTROPIC AND ANISOTROPIC RAMAN SPECTRAL COMPONENTS OF MOLECULAR LIQUIDS

ABSTRACT

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SYNOPSIS

Laser Raman Scattering studies of vibrational relaxation and Non-coincidence effect of the isotropic and anisotropic Raman spectral components of molecular liquids.

The above mentioned thesis is based on the results of studies which involved the vibrational relaxation studies of liquid N,N-Dimethylacetamide, N,N-Dimethylformamide and Cyclohexanone. Particularly, studies in which solvents were used as an experimental variable have contributed in a major way to our understanding of vibrational relaxation mechanism in liquids. The thesis is limited to Laser Raman scattering studies of liquids with some help from IR band intensities. Raman scattering studies are restricted usually to simpler liquids but provide detailed information about specific dynamic processes in liquids. The main goal of this thesis is to show that solvent is an essential experimental variable in all studies that attempt to improve our basic understanding of the liquid state and the effect of environment on the molecular vibrations and coupled oscillators.

Chapter I presents a brief introduction to the work embodied in the thesis. It highlights the importance of laser Raman scattering studies of vibrational relaxation, the importance of analyzing the experimentally measured lineshapes of the isotropic and anisotropic components of the Raman spectrum of a molecular liquid. The careful investigation of Raman spectra shows that the peak frequencies of the isotropic and anisotropic components do not coincide and lead to the non-coincidence effect. These studies are performed for the totally symmetric modes of the molecules. The important aspects of the mechanism of vibrational relaxation have been mentioned and the role of Transition dipole-Transition dipole interactions in the dephasing process has been indicated. In case of polar Raman bands such as C=O stretching vibration it is possible to separate the vibrational relaxation from reorientational effects, hence the studies have been limited to the C=O stretching mode vibrations of the polar molecules.

Chapter II gives the general theoretical background in order to understand the different types of mechanisms involved in vibrational relaxation and parameters affecting the band shape of the Raman active vibrations of totally symmetric type. In liquids with strong intermolecular interactions, broadening parameters normally taken into account are second moment $\langle \Delta \omega^2 \rangle$ and the linewidth (FWHH). Sometimes the shift of the maximum frequency or the first moment of the band against the gas frequency is also taken into consideration. Theoretical background for all these parameters has been outlined and the relation to the intermolecular potential mainly of the dipole-dipole type has been given. The various types of potential and the intermolecular potential parameters have been discussed. The van der Waal type of interactions and their role in the bandshpe broadening and other effects has to be considered in a detailed manner which has been attempted in this Chapter.

Chapter III deals with the experimental aspects and describes the various aspects which have to be taken into consideration for accurate measurements of the lineshapes of the Raman bands. Mention has been made for the errors involved in the measurement of the depolarization ratio which has to be kept in mind in order to separate the isotropic component from the polarized (I_{VV}) component of the Raman spectrum. The spectrometer used and the importance of the slitwidth etc. on the Raman band has also been indicated.

Chapter IV gives an account of the experimental work performed by us on the N,N-Dimethyl acetamide (DMA) molecule in neat liquid and under varying environmental conditions by varying solvents. The solvents chosen were acetonitrile (CH_3CN), chloroform ($CHCl_3$), carbontetrachloride (CCl_4) and benzene (C_6H_6). These four solvents were found suitable after considerable screening taking into consideration, no overlapping bands, avoiding strong hydrogen bonding effects. Out of these four solvents two ($CHCl_3$ and CH_3CN) solvents belong to the category of polar molecules and two (CCl_4 and C_6H_6) are non-polar in nature. The dipolar effects may be studied using $CHCl_3$ and CH_3CN and these solvents are therefore quite effective in reducing the interactions between the solute molecules. Besides the dipolar interactions, the inductive and dispersion forces are also operative and play quite significant role in liquid structure. These interactions are easily studied in non-polar solvents as dipole-dipole interactions are absent here. In case of polar molecules all the three types of interactions are effective. The screening effects due to the dielectric constant of the medium may also be investigated using these four solvents as their dielectric constants are quite different from each other. The studies on dilute solutions are especially of considerable importance as it deals with the situation where the solute molecule is surrounded mainly by solvent molecules. Under these conditions the influence of the solvent molecules becomes quite important. The van der Waals attractions (dipole-dipole, dipole-induced dipole and dispersion type) have been taken into consideration to see their role in the line broadening mechanism. The variation of the linewidth of the isotropic component, Γ_{iso} (FWHH) has been studied as a function of the total interaction energy involving D-D, D-ID and dispersion forces. It is seen that Γ_{iso} varies linearly as a function of the dispersion energy parameter given as $F(n,I) = \frac{3}{2n^4} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j$ where I_i, I_j are the ionization potential of the molecules i and j, α_i, α_j are the polarizabilities and n is the refractive index of the medium. This parameter is for a pair of interacting molecules i and j.

The calculations of D-D, D-ID and dispersion energy have been carried out for the systems DMA-$CHCl_3$, DMA-CH_3CN, DMA-CCl_4 and DMA-C_6H_6 taking into consideration the dielectric constant and refractive index of the medium. These calculations clearly show that the dispersion energy is the most significant one even in case of polar solvent molecules due to the presence of high dielectric constant in the denominator of D-D and D-ID energy expressions. The solvent dependence has also shown that the transition dipole-transition dipole (TD-TD) interaction is the main coupling mechanism responsible for the noncoincidence effect in DMA molecule.

Chapter V deals with the vibrational relaxation studies on N,N-Dimethylformamide (DMF) molecule. This molecule is similar to N,N-Dimethylacetamide except that it has H atom in place of the methyl group near the C=O bond. The hydrogen bonding effect may therefore be present in linear chain. This system is quite interesting from intermolecular interaction point of view. The studies were performed in dilute solutions using the polar and nonpolar solvents which clearly show same type of behaviour of Γ_{iso} in dilute solutions. The relation between the Γ_{iso} and the dispersion energy parameter is linear here too indicating that dispersion forces override all other forces (electrical forces) so far as the line broadening is concerned. One very interesting thing which we have investigated in case of DMF molecule is the combined effect of the parameters related to the hydrodynamic force, and dispersion force on the lineshape. For the hydrodynamic force, η, the dynamic viscosity, and for the dispersion force the quantity $\frac{n^2-1}{2n^2+1}$, which comes from Lorentz's local field have been taken into consideration. The vibrational relaxation rate $(\tau_v^{-1}) = \pi c \Gamma_{iso}$, is found to be clearly related to a parameter $f(\rho, \eta, n) = \rho\eta\left(\frac{n^2-1}{2n^2+1}\right)^{-1}$ in a linear fashion, where being the density and n is the refractive index of the medium. This is an interesting empirical finding as it takes care of many aspects related to the molecular parameters. The solvents have been varied from polar to non-polar and it has been found that τ_v^{-1} is a linear function of $f(\rho, \eta, n)$ for dilute solutions. The TD-TD type of interactions are again seem to be responsible for noncoincidence effect in DMF. In addition we have studied the variation of $\delta\nu\,(2\epsilon + n^2)^2 \epsilon^{-1}$ as a function of volume fraction of solute (φ). It is seen that this variation is also linear in nature. This correlation is indicative of the screening effects due to dielectric properties of the medium.

Chapter VI has been mainly devoted to studies on Cyclohexanone molecule showing the effect of the dispersion energy parameter on linebroadening in a system where the dipole moment of the entire molecule is almost concentrated on the C=O bond only. The C=O is the only polar group in cyclohexanone molecule. The dipole, as well as the transition-dipole both will be in the same direction in this case. The system is considered to be in the chair conformation. It is quite interesting to see that the relationship which we observed in case of N,N-Dimethylacetamide and N,N-Dimethylformamide are also holding good in this molecule. The dispersion energy parameter is well correlated with the Γ_{iso} and the parameters $f(\rho, \eta, n)$ is found to be very well fitting with the τ_v^{-1} in a linear fashion. The non-coincidence effect is again very well explained in terms of TD-TD interactions.

The last Chapter VII gives the conclusions drawn from the present work.