INTRODUCTION

During the past several years, various researchers have been working on vibrational (IR and Raman) spectroscopy to study the molecular dynamics of liquids [1-21]. Vibrational Raman spectroscopy is one of the most informative experimental methods for investigating the liquid state of substance, which affords information that is often inaccessible by other experimental techniques. Raman technique is preferred to study biological molecules than any other techniques [22-26] such as dielectric spectroscopy, ultrasonic spectroscopy, nuclear magnetic resonance (NMR), electron spin resonance (ESR), X-ray diffraction (XRD) etc., since it is considered as nondestructive technique.

The vibrations of molecules are sensitive probe of local structure and dynamics in molecular liquids and provide microscopic information about a state of matter. The basic idea of research in molecular liquids is the careful analysis of the Raman bandshape. Vibrational Raman band of molecules are characterized by positions of band maxima, bandshape and intensity. These parameters of a Raman band depend on the molecular environment. Hence, variation of these parameters provides a wealth of information about the structure of liquids, presence of long living intermolecular complexes, associations and molecular dynamics. The isolated active oscillator of some normal mode of reference system (solute) is perturbed on introducing a solvent to it. This leads to the Raman spectral change which reflects the molecular interaction taking place in the complex molecular environment [27-29]. The solvent contribution to vibrational frequencies and line widths are due to the intermolecular interaction involving attractive and repulsive forces [30]. The Raman line width, full width at half maximum (FWHM) provides dynamical information about the vibrational relaxation and reorientational motion in the molecular liquids, whereas the peak position provides information of the static interactions mostly related to the force constant, electronic structure, bonding etc.
The vibrational and reorientational relaxations can be understood from the analysis of the experimentally recorded polarized and depolarized Raman band profiles. The vibrational relaxation is most frequently analyzed by the isotropic band profile while the reorientational relaxation is analyzed by the anisotropic band profile of a Raman band [31-32]. The isotropic and anisotropic band profiles of Raman spectra were determined by using the following relations [8]

\[
I_{iso}(v) = I_{VV}(v) - 4/3I_{VH}(v) \tag{1.1}
\]

\[
I_{aniso}(v) = I_{VH}(v) \tag{1.2}
\]

where, \(I_{VV}(v)\) and \(I_{VH}(v)\) are Raman intensities of the polarized and depolarized Raman components measured experimentally and \(v\) is the wavenumber in cm\(^{-1}\).

There are several mechanisms [31, 33] of vibrational relaxation such as the phase relaxation, the resonant energy transfer (RET), the energy relaxation etc. In liquid system, the energy relaxation spends longer time in comparison with phase relaxation. The vibrational phase relaxation process is responsible for the broadening of the isotropic Raman band.

An important factor contributing to the vibrational band profile in liquid mixture system is the fluctuation of concentration. Bondarev and Mardaeva [2] were the first to point out the influence of concentration fluctuation in liquid binary mixtures on the bandwidth of Raman spectra and developed a model known as concentration fluctuation model. They investigated that bandwidth increases upon dilution and gets maximum at about half the concentration of the binary mixture along with the linear shift of peak frequency. Further, the concentration fluctuation model improved by Knapp and Fischer [12], accounts simultaneously the static and dynamical aspect of concentration fluctuation at the reference molecule. This model also provides specific predictions upon the concentration dependence of the peak frequency shift and asymmetry of the spectral line profile in terms of the interaction with nearest neighbours and their diffusion dynamics. The model was tested with experimental results for various binary liquid mixtures [15-16]. Kim et al. [15] studied the isotropic Raman bandwidth of \(v_1\) and \(v_2\) modes of acetonitrile and deuterated acetonitrile in carbon tetrachloride solvent and investigated that bandwidth strongly depend on concentration of the binary
mixtures. Singh et al. [16] studied vibrational relaxation of $\text{C} \equiv \text{N}$ stretching of acetonitrile in binary liquid mixture with hydrogen donor solvents. The concentration dependence of wavenumber shifts and linewidth changes were examined and well explained using concentration fluctuation model.

Various theoretical models had been developed for vibrational relaxation such as isolated binary collision (IBC) model [31], hydrodynamic model [33], resonant energy transfer model [34] etc.

IBC model based on semi-classical collision theory, illustrate the dephasing phenomena of vibrational excited molecule in a liquid system. In this model Fischer and Laubereau [31] explored quantitatively the dephasing process and its interrelation to the energy relaxation. According to this model, fluctuations occur in the normal mode frequencies and such fluctuations produce dephasing without involving transitions between vibrational states. Energy dissipation and pure dephasing are assumed to be independent processes. The model is subsequently modified by Oxtoby et al. [35] with the introduction of anharmonicity and by Tanabe et al. [36] for use in binary mixtures.

The hydrodynamic model provides a good qualitative vibrational relaxation in terms of dephasing phenomena in molecular liquids. This hydrodynamic model [37] notifies that the dephasing rate for polyatomic systems depends on viscosity and temperature which results line broadening of Raman band. Furthermore, Kim et al. [38] developed a theory which incorporates both the collisional and collective effects of molecular interactions in the dephasing dynamics for fast modulation processes by considering atoms in the vibrating molecule as a solute particle dissolved in a solvent composed of structure less spherical particle. They well explained the isotropic Raman spectra quantitatively incorporating the collisional and collective effects in fluctuating environment for fast modulation. Then, Purkayastha and Kumar [39] developed a model which provides a better picture of phase relaxation as a function of parameters related to the hydrodynamic and dispersion forces in liquid state. The model so far has been tested successfully for various molecules such as aldehyde, nitriles, amides etc. [39, 40].

RET has a major contribution to the dephasing process in which the coupling takes place between the similar modes of identical molecules. The interaction
responsible for this coupling depends on the relative orientation of the molecules. TD-TD coupling between the identical molecules is the most favourable one. 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 molecules result in the gradual fall of the contribution through RET mechanism. This leads to the band narrowing upon the dilution of the reference molecule [41-42].

Bratos and Tarjus [43] proposed a theory describing Raman band profiles of binary liquid mixtures of van der Waals liquids. It was shown that the Raman bandwidth varies with concentration according to whether vibrational modulation is slow or fast. Extensively different effects were predicted for chemical and isotopic solutions. The difference is due to the fluctuation of the chemical composition in a given site of the liquid and to the structure–breaking effects which are present in the chemical solution. Recently, Ojha et al. [44] formulated an empirical model to study the vibrational band profile taking microviscosity as the prime factor. Their model well supports the experimental results in various molecules.

Various researchers [45-57] studied about the solvent dependent Raman bandshape to gain more insight about the solute-solvent interaction and molecular dynamics. Singh et al. [45] studied the shift and linewidth changes of three vibrational modes of C₆H₅Cl in methanol. The study reveals that the phenomenon of motional narrowing and diffusion play significant roles in dephasing. Navarro et al. [46] carried out vibrational relaxation study of C=O stretching mode of ethyl trichloroacetate in different solvent systems. They observed that the vibrational processes in the relaxation of this mode seem to be dominant on long time scale (from ca. 0.4ps), the vibrational line width increases according to different solvents studied of the order C₆H₁₄<CS₂<CCl₄<CHCl₃. Musso et al. [47] focused on the concentration dependent study of specific band profile parameters such as bandwidth and asymmetry of the isotropic and anisotropic Raman components of C=O stretching vibration of acetone in CCl₄ solvent. They compared their findings with the results obtained by using Monte Carlo simulations. As per Datta and Kumar [48] the microenvironment (microviscosity,
density, refractive index, and molecular radius) plays an important role in the vibrational relaxation of C=O stretching of methyl acetate in various polar and non-polar solvents. Fathima et al. [49] studied different stretching vibrations of salicylaldehyde in different polar and non-polar solvents. The spectral changes observed on changing solvent concentration have been well explained using the concentration fluctuation model and solute-solvent interaction.

A few works have been done on reorientational relaxation of liquid molecules using polarized Raman spectroscopy. Alms et al. [51] measured the reorientational relaxation times of CHCl₃ in mixture solution of CCl₄ and isopentane. As per Tanabe et al. [4] the intermolecular associations between solute and solvent greatly affects the reorientational relaxation time of chloroform in binary liquid mixture. Reorientational relaxation of C=O mode of ethyl trichloroacetate has been studied in different solvent systems such as C₆H₁₄, CS₂, CCl₄ and CHCl₃ [46]. The reorientational relaxation was found to be dominant at short time, below ca. 0.4ps. T. G. Devi [50] carried out vibrational and molecular reorientational relaxation study on some carbonyl-containing liquid molecules using acetonitrile solvent. She reveals that repulsive types of intermolecular forces play an important role in the complex binary mixture systems. According to her the change in reorientational relaxation time with the change in solute concentration may be due to the screening effect of high dielectric constants of the solvents.

An important phenomenon considered as resourceful probe of the structure and dynamics of polar liquids in Raman spectroscopy is non-coincidence effect (NCE). It has been observed in many molecules that the peak frequencies of Raman bands corresponding to the isotropic and anisotropic components of a reference mode do not coincide in liquid state [58-63]. The difference in peak frequencies of these two components of Raman band is defined as NCE. It arises due to the manifestation of vibrational energy transfer induced by TD-TD interaction and is usually occurred in the presence of a short-range or long-range orientational order of molecular dipoles [61-63]. The magnitude and sign of NCE provides the detail information of the orientational structure of the molecular liquids. The NCE has been studied extensively in different
molecules [58-83] such as ketones [58-61, 66-68], alcohols [69-71], aldehydes [72] and amides [73-74] etc.

Several theoretical models [59-65] had been proposed to describe the dependence of the NCE on concentration in binary liquid mixtures. Models are applied assuming the binary mixture as an ideal solution such that all the concentrations on a mole fraction scale are easily converted into volume fractions. P. Mirone et al. [60] developed a theoretical model to explain about the parameters on which the NCE depend. Further, McHale [63] simplified the model assuming that dielectric constant of the solution depends linearly on the volume fractions of the solute and solvent. Wang and McHale [62] developed a general expression for a coupling Hamiltonian to explain NCE and suggested that the basic reason for NCE is due to the fact that the resonance coupling potential is angular dependent. The angular dependent intermolecular forces modify the force constants of the harmonic oscillators, yielding an anisotropic frequency shift. In the paper [64], D.E Logan developed a molecular theory of NCE for pure dipolar liquids and their isotopic mixtures. The theory predicted to the dependence of the non-coincidence splitting on thermodynamic state variables such as mole fraction of the active species, total number density and temperature etc. This theory carried out reasonably well for pure liquids and isotopic binary mixtures. Later on, the author [65] developed similar theory for dipolar binary mixtures which was supported well with the experimental results.

With the advancement of new idea and technology, various researchers used different simulation methods such as Monte Carlo (MC), molecular dynamics (MD) simulations and quantum chemical modeling methods to support the experimental findings in studying the interaction between binary liquid mixtures [68-83]. Theoretical study has been performed by H. Torii [69] to show a relationship between the liquid structures, vibrational interactions and the wavenumber differences among the infrared, isotropic Raman and anisotropic Raman components of OH and CO stretching bands of neat methanol and a methanol-LiCl solution. The investigation of the origin of the NCE shows that the vibrational interactions within hydrogen-bonded chain explain the major part of the NCE for the OH stretching band of liquid methanol, while the negative NCE
arises in CO stretching band due to the vibrational interactions between hydrogen bonded molecules is partially canceled by the contribution of the interactions between molecules which are not directly bonded by hydrogen. Giorgini et al. [80] studied NCE of C=O stretching mode in acetone/DMSO and acetone/CCl₄ binary liquid mixtures. The experimental results were found well supported by MD simulations and by theoretical predictions. Musso et al. [82] studied the NCE of C=O stretch of acetone and O-H stretch of methanol in acetone/methanol mixtures. The experimental results were in good agreement with the results obtained from MC simulation. Ramakrishnan et al. [83] carried out NCE in substituted benzaldehyde binary mixtures and according to them hydrogen bond formation between the solute and solvent molecules plays an important role in the variation of NCE.

It was found from the detail literature review done on several research papers that Raman bandshape study on binary liquid mixtures provide detail information to the molecular structure and dynamics of molecules taken under study. In the present work, we made an attempt of Raman spectroscopic study on some medicinal and biological important compounds such as dimethyl sulfoxide (DMSO), acetone (ACT), ethyl acetate (EA) and methyl isobutyl ketone (MIBK) in various solvents to gain more insight about the solute-solvent interactions taken under study. Such study may help in designing and synthesizing new drugs or inventing new materials with desirable properties. The study may also provide a clear understanding why certain molecules prefer to associate and why others would rather leave each other. DMSO is a molecule having wide applications in industrial, biological and medicinal sciences because of its specific properties. DMSO, apart from being used as a solvent, is a plasticizer and chemical intermediate. It has a great value in pharmaceutical and medicinal sciences due to its skin penetration enhancer property. Any drugs dissolved in it can penetrate through the skin of our body. This compound has been used to treat pain relieving and anti-inflammatory respectively. Hence, the study of its interaction with other biological molecules is highly important in medicinal science. In this dissertation, the solvent dependent study of various stretching modes, namely S=O, CH and CSC were undertaken in chemical and isotopic solvents such as chloroform (CLF), deuterated
chloroform (CLFd), acetonitrile (ACN) and deuterated acetonitrile (ACNd). Different four theoretical models such as McHale’s model, Mirone’s modification of McHale’s model, Logan’s model and Onsager- Fröhlich dielectric continuum model were tested with the experimental findings. Vibrational relaxation of S=O, CH and CSC stretching modes of DMSO were studied in CLF, CLFd, ACN and ACNd solvents to gain more information about the structural dynamics and self-association of the molecules in binary liquid systems. Quantum-chemical calculations have been carried out to gain more insight into the self-association of DMSO and its interactions with the solvents. Theoretically determined results have been compared with the experimentally observed results.

Furthermore, MIBK, ACT and EA molecules are studied using chloroform and chlorobenzene solvents in binary liquid mixtures. These molecules, besides being used as solvent, are widely used as chemical intermediates in pharmaceutical science. The variation of bandwidth with the solvent concentration was discussed using different mechanisms. The vibrational and reorientational processes are studied corresponding to correlation times. Viscosity is correlated with the vibrational and reorientational relaxation times to understand its role in the binary liquid mixtures.
REFERENCES:


