RELAXATION STUDIES AND INTERMOLECULAR INTERACTIONS IN SOME COMPLEX MOLECULES

By

ARPITA DAS

Department of Physics

A thesis submitted in partial
fulfilment of the requirement of the degree of

DOCTOR OF PHILOSOPHY

in

PHYSICS

of

North Eastern Hill University
Shillong
INDIA

The North-Eastern Hill University

October 1999

DECLARATION

*I **ARPITA DAS** hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other university/institute.*

This is being submitted to the North-Eastern Hill University for the degree of Doctor of Philosophy in School of Physical Sciences.

Arpita Das.
(ARPITA DAS)

(Dr.C. S. Shastry) 6/10/99
Professor and Head,
Department of Physics

K Kumar 6/10/99
(Dr. Kamal Kumar)
Professor
Department of Physics

ACKNOWLEDGEMENT

It gives me immense pleasure and satisfaction in bringing forth my research work under the supervision of Dr. Kamal Kumar, Professor, Department of Physics, NEHU. I take the opportunity to express my deep sense of gratitude to him for his guidance and constant encouragement throughout the entire course of my research work.

I also take the opportunity to thank Prof. C. S. Shastry, Head, Department of Physics, NEHU, Prof. A. L. Verma and other faculty members for their encouragement during the course of my work.

I am privileged to thank Mr. A. K. Rathore for helping me in doing experiments. My sincere thanks go to all of my friends for their helpful cooperation in my research work. My thanks also go to Dr. Anusree Ghosh and Dr. Radhendu Das for their wishes of success in this regard.

I owe my regards to my parents for their blessings and moral support throughout my life. My best regards also goes to other family members who stood by me for completing this work .

Arpita Das 6.10.99

(ARPITA DAS)

CONTENTS

Chapter 1

INTRODUCTION

Considerable interest has been shown for the study of molecular dynamics in liquids, liquid crystals, polymers (in bulk and solution) and biopolymers all of which exhibit relaxation phenomena at different frequencies.The relaxation, scattering and absorption spectroscopy provide useful information about the molecular motion in liquids. The molecular motion may be illustrated by the study of vibrational relaxation, orientational relaxation, dielectric relaxation, quasielastic scattering and others. The study of vibrational relaxation in condensed phase has been considered a way of investigating dynamic processes[1–12].

The vibrations of a molecule are sensitive probes of local structure and dynamics in molecular liquids and therefore provide microscopic

information about a state of matter which is relatively poorly understood. The basic idea of research in molecular liquids consists in a careful analysis of the bandshape of the isotropic (I_{iso}) and anisotropic (I_{aniso}) components of the Raman band of the molecule[1–5,13–15]. The sensitivity of Raman peak position and band width (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.

Theoretical models for bandshape may often be applied to data obtained by different techniques such as **NMR, ESR** and **vibrational spectroscopy.** Each model has adjustable parameters and could 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[9].

The bandshape may give valuable information about the interactions of the reference molecule with its environment. In addition, it may provide information about the dynamics of the bath.

The vibrational and rotational frequencies of molecules can be studied by **Raman spectroscopy** as well as by **IR spectroscopy.** It is, however, **the laser Raman scattering experiment** which provides a detailed information about a specific dynamic process in the liquid. In order to understand the vibrational relaxation, one has to study the well isolated vibrational modes. The vibrational relaxation can be understood from the analysis of **Raman band profiles** of **polarized** and **depolarized** configurations, by calculating the intensity of the isotropic component[12]. Only vibrational processes contribute to I_{iso} whereas both vibrational and reorientational processes contribute to I_{aniso}.

For any given system the isotropic Raman band is broadened and the broadening may be influenced by several mechanisms[9]. The two dominant ones are **energy relaxation** and **phase relaxation.** The energy relaxation involves vibrationally inelastic processes and corresponds to what is called T_1 relaxation for spin system, while phase

relaxation involves only quasielastic interactions of the molecules with their surroundings leading to perturbation of the phase of the vibrational wavefunctions without changing their quantum states. Vibrational phase and energy relaxation times can be as short as a few pico seconds and may thus be comparable to the bath relaxation times. This has important consequences for the dynamics of the coupled system. However, phase relaxation (dephasing) in liquids normally occurs much faster than energy relaxation.

Experimental measurements of vibrational phase and energy relaxation may be carried out in either the time or frequency domain. Population (energy) relaxation measurements in the time domain involve pulsed excitation (by stimulated Raman scattering or IR absorption) followed by detection of level populations after a time delay t. In this way relaxation times have been measured ranging from seconds to picoseconds. Picosecond spectroscopy may be used to measure phase relaxation. Frequency domain studies of vibrational energy relaxation involves either ultrasonic absorption or Brillouin line width measurements. Frequency domain measurements of phase relaxation are quite extensive.

Different theoretical models[13–25] on vibrational dephasing have been developed, examples of which are **isolated binary collision (IBC) model**[13,14] **, the hydrodynamic model**[15–17]**, the cell model** and the model based on **resonant energy transfer**[18–25]. In the IBC model the transition rate is assumed to be the product of the collision rate in the liquid and the transition probability per collision in the gas phase. Litovitz[26] approximated the time between collisions to be an Enskog time for the rate of binary collision of hard spheres using cell model. Oxtoby[14,15] has shown that the relaxation time of the random force is responsible for the viscosity dependence of the diffusion coefficient. Fluctuations with wavelengths longer than a molecular diameter decay hydrodynamically with rates characterized by the liquid viscosity but for shorter wavelengths the simple nature is lost.

One of the most important mechanism that may contribute significantly to dephasing processes in liquids is the coupling between the similar modes of identical molecules that results in resonant energy transfer[5]. In some theoretical models long range forces are involved, the collisional events that are considered are those which have too short a time of action to influence cosiderably the dephasing time.

The molecular harmonic oscillator couples to the heat bath through translational diffusion; 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 the line broadening[24]: the first is indicated as 'self term' ; the second is named the 'exchange term' and a 'cross self exchange term' is also present. 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 to as resonant energy transfer. It is possible to single out this particular kind of dephasing by performing dilution measurements.

An important coupling mechanism is **transition dipole - transition dipole (TD-TD)** type[5] which is possible when strong IR 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[24].

The basis of the detailed study of vibrational dephasing is band-shape and solvent induced frequency shift as a result of a competetion

between slowly varying attractive forces and rapid collisional forces in a weak coupling regime. It has been observed in cases of many molecules that the peak frequencies of the Raman bands corresponding to the isotropic and anisotropic components do not coincide in liquid state[23–35]. The difference in peak positions may sometimes be about 15 cm^{-1} or even more. This non-coincidence in Raman spectrum has been observed for many IR active modes. 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 is widely observed for example in the CO stretches in carbonyls[29–31], SO stretches in sulphones[1], CN in nitriles[21], CH stretch of chloroform[35] and several others. The non-coincidence effect has been 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.

The non-coincidence effect can arise simply from an angular dependent interaction potential which preferentially weights the relative

alignment of a pair of molecules between which resonant excitonic transfer can occur. This concept does not contradict the dynamic nature of the liquid phase, since it is only necessary that the lifetime of the quasicrystalline regions (local ordering) be long compared to the vibrational period.

Although the vibrational resonance coupling due to the TD-TD interaction may be important in some polar modes, it has been pointed out earlier by Wang and McHale[4] that the vibrational resonance coupling Hamiltonian may 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

$$H = H_{osc} + H_B + H'$$

Where H_{osc} is the sum of harmonic oscillator Hamiltonian, H_B is the bath Hamiltonian and H' is the part of the Hamiltonian which couples the internal vibrational coordinates of the bath molecules.

In order to understand the nature of the intermolecular interactions and molecular dynamics, there is a definite need for additional systematic studies on vibrational relaxation, reorientational motion,

frequency shifts and band shapes in various liquids. The information content of the solvent effects on frequency shifts and shapes of various vibrational bands has not yet been fully explored. In particular the anisotropy shift and variation of band width in dipolar liquids may offer new information about strong inter- and intra-molecular interactions. The study of the influence of the solvents on the band shape parameters is of permanent importance not only in connection with molecular structure and liquid dynamics, but also with solution kinetics. For analyzing the anisotropy shift and dephasing results we have chosen C=O symmetric stretching mode. Its normal mode presents particular characteristics that make its study of great importance:

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

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

(iii) It is a well separated mode in all the molecules under study. Therefore it is particularly suitable for probing the molecular environment.

A simple theoretical approach[24,25] to the behaviour of various bandshape parameters in terms of dipole-dipole interactions has been worked out in the frequency domain. The structural effect seems to play an important role in influencing the bandshape of polar Raman bands in liquids with dipole-dipole interaction energies of the order of kT. The asymmetry of the I_{VV} component of the band was explained on the basis of the change in the orientation probability distribution into the direction of energeticallly favourable orientations. However, the theoretical approach is too simple to allow more than a qualitative interpretation of the experimental data. Moreover, 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 explanation for vibrational relaxation and non-coincidence for complex molecular systems, sometimes cannot be given on the basis of a macroscopic perception of the solute-solvent system. The two interacting situations, in the pure solute and when dissolved in a solvent differ markedly especially at high dilution. The solvent electric field influences the bandshape of a reference mode significantly. In the present work we have studied the

Raman bandshape of several molecules and tried to explain the experimental results by taking into consideration the concept of microenvironment, the role of various multipolar interactions and the concept of effective van der Waals' volume. The non-coincidence effect has been studied in p-methylacetophenone and benzaldehyde molecules by taking into account the screening factor related to permanent and transition dipoles. The isotropic band width of Raman band and the dephasing process have also been studied for the two molecules to develop a microscopic picture of the processes involved in liquids. The anisotropic component of the Raman band gives information about the angular dependence of intermolecular potentials. Therefore the anisotropic band width has been studied for the molecules p-methylacetophenone (PMA), benzaldehyde (BH), cyclohexanone (CH), N,N-dimethylacetamide (DMA), N,N- dimethylformamide (DMF) using different solvents by considering the van der Waals' volume of the sphere of influence in solution. The study of the spectral properties of Raman bands has contributed in a major way to our understanding of the processes involved.

REFERENCES

1. G. Fini and P. Mirone, *J. Chem. Soc., Faraday Trans.2,* **70,** 1776 (1974).

2. E. W. Knapp and S. F. Fischer. *J. Chem. Phys.,* **76,** 4730(1982)

3. W. Schindler, P.T. Sherko and J. Jonas, *J. Chem. Phys.* **76,** 3439(1982).

4. C. H. Wang and J. McHale, *J. Chem. Phys.,* **72,** 4039(1980)

5. J. McHale, *J. Chem. Phys.* **75,** 30(1981).

6. W. Schindler and J. Jonas, *J. Chem. Phys.,* **72,** 5019(1980).

7. J. Schroeder and J. Jonas, *J. Chem. Phys.,* **34,** 11(1978)

8. T. W. Zerda, S. Perry and J. Jonas, *Chem. Phys. Lett.,* **83** , 600(1981)

9. D. W. Oxtoby, *J. Phys. Chem.,* **87,** 3028(1983).

10. W. Schindler. T. W. Zerda and J. Jonas, *J. Chem. Phys.,* **81,** 4306(1984).

11. J. Jonas, *Acc. Chem. Res.,* **17,** 74(1984).

12. L. A. Nafie and W. L. Peticolas, *J. Chem. Phys.,* **57,** 3145(1972).

13. S. F. Fischer and A. Lauberau, *Chem. Phys. Lett.,* **35,** 6(1975).

14. D. W. Oxtoby and S. A. Rice, *Chem. Phys. Lett,* **42,** 1(1976).

15. D. W. Oxtoby, *J. Chem. Phys.*, **70,** 2605(1979).

16. R. Ouillon, V. Sergiescu and R. J. D'Leon, *Mol. Phys.*, **49,** 151(1983).

17. P. S. Dardiaw, R. I. Culier, *J. Chem. Phys.*, **89,** 4415(1988).

18. W. Rothschild, *J. Chem. Phys.*, **62,** 1253(1975).

19. W. Rothschild, *J. Chem. Phys.*, **65,** 455(1976).

20. G. Döge, Z. Nabrforsch, *Jeil, A,* **28,** 419(1973).

21. G. Fini and P. Mirone, *Spectrochim. Acta.* **32A,** 625 (1976).

22. P. Mirone and G. Fini, *J. Chem. Phys.*, **71,** 2241 (1979).

23. M. G. Giorgini, G. Fini and P. Mirone, *J. Chem. Phys.*, **79,** 639 (1983).

24. D. Schiebe and G. Döge, *Ber. Bunsenges. Phys. Chem.*,**85,** 520 (1981).

25. D. Scheibe, *J. Raman Spectrosc.*, **13,** 103 (1982).

26. F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56,** 404(1972).

27. G. Fini, P. Mirone and B. Fortunato, *J. Chem. Soc., Faraday Trans 2.*,**69,** 1243 (1973).

28. W. Schindler, T. W. Zerda and J. Jonas, *J. Chem. Phys.*,**81,**

4306 (1984).

29. A. Purkayastha and K. Kumar, *Spectrochim. Acta,* **42A,** 1379 (1986).

30. A. Purkayastha and K. Kumar, *Spectrochim. Acta,* **43A,** 1269 (1987).

31. A. Purkayastha and K. Kumar, *J. Raman Spectrosc.,* **19,** 249 (1988).

32. V. M. Shelly, A. Talintyr, J. Yarwood and R. Buchner, *Faraday Dissc. Chem. Soc.,***85** 211 (1988).

33. J. Dybal and B. Schneider, *Spectrochim. Acta,* **41A,** 691 (1985).

34. T. F. Sun, J. B. Chan, S. N. Walen and J. Jonas, *J. Chem. Phys.,* **94,** 7486 (1991).

35. G. Döge, D. Schneider and A. Morresi, *Mol. Phys.,***80,** 525 (1993).