VIBRATIONAL BAND SHAPE ANALYSIS AND INTERMOLECULAR INTERACTIONS IN SOME COMPLEX MOLECULES

SOMA DATTA
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

DEDICATED TO MY LOVING PARENTS

whose encouragement and affection has been a constant source of inspiration for this thesis. Any accomplishment of mine is due in no small part to their support.

THE NORTH-EASTERN HILL UNIVERSITY
April, 2006

DECLARATION

I, Soma Datta, 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 Physics.

Soma Datta
(Soma Datta) 21/4/06.

P. Nongkynrih
(Dr. P. Nongkynrih)
Professor & Head
Department of Physics

K Kumar
(Dr. Kamal Kumar)
Professor
Department of Physics

Prof. & Head,
Physics Department,
N.E.H.U, Shillong-793022.

ACKNOWLEDGEMENTS

There are many persons to be thanked for their inspiration and support during this study without whom this work would not have been possible.

First of all, I take the opportunity with immense pleasure, to gratefully acknowledge the enthusiastic supervision of Professor Kamal Kumar, department of physics, NEHU. I am indebted to him for introducing me to the subject and for his support and encouragement during the course of the work.

I am grateful to Professor P. Nongkynrih, Head of the physics department for her interest in this work. I acknowledge my sincere thanks to Mr. A.K. Rathore for his adept assistance in recording the Raman spectra. I would also like to thank the staff of the physics department for their help and cooperation.

I am extremely grateful to Dr. Th. Gomti Devi for the fruitful discussions and valuable suggestions, which helped me in completing this work. A special word of thanks to my friends Sandy and Romolus, for their support and interest in the progress of my work.

Finally, I am forever indebted to my parents and my sister Sweta for their understanding, endless patience and encouragement when it was most required during the course of work.

Soma Datta

(Soma Datta)

CONTENTS

Page

CHAPTER 1

INTRODUCTION

Laser Raman scattering studies of molecules provide an insight into the understanding of vibrational relaxation mechanism in liquids and detailed information about the molecular environment and the specific dynamic processes in liquids [1-10]. Vibrational lineshapes in condensed phases contain the details of the interactions of a normal mode with its environment. These interactions include the important microscopic dynamics and intermolecular couplings.

The study of dynamical behavior in molecular liquids is very difficult since in the liquid state, the molecules are in state of chaotic motion. The importance of liquid phases in chemical reactions has made liquid science an important and rapidly developing field of research. In recent years, there has been a considerable interest in the study of vibrational relaxation in liquids and considerable progress has been made through experiment, theory and computer simulation. The vibrations of a molecule are sensitive probes of local structure and dynamics in molecular liquids. Raman scattering experiment may be used to obtain detailed information about the specific dynamic process in the liquid.

Through a study of vibrational relaxation in molecular liquids, it is possible to gain information about the molecular environment and the main intermolecular forces operative in this state of matter. The processes such as chemical kinetics and solution micro-dynamics can be investigated through a study of vibrational relaxation in molecular liquids. The time resolved experiments have been performed, and these studies have allowed accurate information on dynamics in the solid and liquid states. During the past few decades, vibrational relaxation and molecular reorientation processes in liquids have been studied by analyzing the isotropic and anisotropic profiles of the Raman band of the molecule [1-6]. The isotropic component has contribution only from the vibrational process while the anisotropic component has contributions both from vibrational and reorientational processes. Raman bands of molecules are often observed to be sensitive to various environmental effects such as pressure, temperature, density and solvent concentrations. Precise measurements of isotropic Raman line shapes through continuous Raman scattering have allowed a systematic investigation of these aspects of dephasing in liquids [11].

Since intermolecular interactions depend on orientation and distance, the interactions are inherently time dependent. Thus the eigenvalues and eigenfunctions are time dependent and are constantly fluctuating. These fluctuations are intimately involved in chemical processes, and they are also used to understand dynamics of the solvent and the nature of solute-solvent interactions. The solute-solvent interactions are having implications in drug-drug interactions, adsorption phenomenon, chemical kinetics, ligand-protein interactions, etc.

Vibrational dephasing also known as vibrational phase relaxation refers to the loss of coherence by a collection of oscillators coupled to a solvent bath. Imagine an oscillator whose vibrational motion is perturbed by the fluctuating interactions with the surrounding solvent. The phase of the oscillation will soon go random due to the fluctuation in the intermolecular potential. In this phenomenon, both the time scale and magnitude of force fluctuations are important. Vibrational phase relaxation is a sensitive probe of environmental dynamics around a given bond. In recent years, vibrational dephasing has also been investigated directly in the time domain using ultra fast laser spectroscopies as time-resolved coherent anti-Stokes Raman scattering experiments [12-15]. The dephasing times can also be measured from isotropic spontaneous Raman lines [16-18]. More recently, the development of the picosecond and femtosecond lasers has allowed direct time domain measurements of vibrational coherence [19].

The vibrational relaxation process responsible for line broadening of an isotropic Raman band may be influenced by several mechanisms [20-22]. The two dominant ones are the energy relaxation and phase relaxation. The energy relaxation involves inelastic processes and it may occur due to intermolecular transfer of energy between the vibrational degrees of freedom and the bath. The phase relaxation involves only quasi-elastic interactions of the molecules with their surroundings, leading to perturbation of the phase of the vibrational wave function without changing their quantum states. Both mechanisms have been investigated and it has been found that vibrational phase relaxation (dephasing) in liquids occur much faster than energy relaxation. There are three different relaxation times T_1, T_2 and T_2^* associated with each vibrational normal mode [23]. T_1^{-1} is the rate at which energy is dissipated from the vibrations to the surroundings, T_2^{-1} is decorrelation rate of the vibrations, which is sometimes known as the total dephasing rate.

The decorrelation rate can be written as

$$T_2^{-1} = \frac{1}{2}\left[T_1^{-1} + (T_2^*)^{-1}\right]$$

which defines the pure dephasing rate, $(T_2^*)^{-1}$. In many situations the decorrelation is dominated by the pure dephasing term.

Different theoretical models have been used to predict the rate constants for vibrational relaxation process. The theories of vibrational pure dephasing in liquids are based on vibrational-translational coupling and collision induced frequency perturbations and yield results that are related to viscosity. The main theories developed for the dephasing process are the hydrodynamic model [20-22], the isolated binary collision (IBC) model [24], and the model based on resonant energy transfer [25]. Oxtoby [21] has shown that the relaxation time of the random force is responsible for the dependence of the diffusion coefficient. In the IBC model of Fischer and Laubereau, 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. The dephasing time T^*_2 in this model is related to molecular parameters and temperature. The model relates the bandwidth to dephasing collision probability yielding $1/T^*_2 \propto \eta T/\rho$ where T is absolute temperature, η is viscosity and ρ is the density. The hydrodynamic model of Oxtoby obtains results similar to the IBC model, $1/T^*_2 \propto \eta T$. Lynden-Bell [26] relates vibrational dephasing to translational diffusion within the liquid potential and obtains a temperature dependence $1/T^*_2 \propto \rho\eta/T$. In these expressions, the temperature dependence of the viscosity, η, is the dominant factor.

Experimental data related to the C-H / C-D and C-C stretching modes of many molecular liquids have been explained on the basis of the IBC model of Fischer and Laubereau [24]. Oxtoby [20] developed a hydrodynamic model to explain the linewidth of the C-I stretching vibration of CH_3I. In this hydrodynamic model collective effects were included and the vibrating molecule was modeled as a microscopic body embedded in a visco-elastic medium. Döge et al [25] showed that the resonant energy transfer via transition dipole – transition dipole (TD-TD) interaction is the main intermolecular coupling mechanism for the ν_2 mode of CH_3I. The vibrational relaxation rate may be determined using the isotropic Raman band width .The broadening of the bands being due to the vibrational dephasing, the band width is a measure of the relaxation rate. Hence the model suggested by Purkayastha and Kumar [27-28] gives a better picture of the phase relaxation in associated liquids (under the condition of high dilution) where the vibrational relaxation rate has been shown to be function of a parameter related to the hydrodynamic and dispersion forces. This model has so far been successfully applied for the carbonyl-stretching (C=O) band of several amides [28], ketones [29], aldehydes [30], as well as for the C≡N bands of nitriles [31]. Later on, the concept of microviscosity instead of dynamic viscosity was included [32] to incorporate the finer details of the solute-solvent systems and microenvironment. This modification has further supported results in several other molecules, successfully [16-18,31-34].

The simultaneous homogenous and inhomogeneous broadening due to the time dependence and the variance of the environments at different reference molecules contribute to the observed line shapes. In binary liquid mixtures, different molecules see different concentrations such that they contribute to the spectrum at different frequencies. The vibrations of neighboring molecules with strong Raman bands arising due to polar bands are coupled by intermolecular interactions. The vibrational relaxation process is mainly responsible for the broadening of the isotropic Raman spectral component. The homogenous and inhomogeneous contribution to the line shape may be separated by time dependent techniques. The two interacting situation, in pure solute and when dissolved in solvents differ markedly. The solvent electric field influences the band shape of a reference mode more significantly. To interpret the experimental results of a study of vibrational relaxation of a particular band in pure liquid, it is useful to perform dilution studies in various solvents with the aim of changing the type of interaction of the active molecules with their neighbors. In this way one can expect to get information about the interaction that influence the band shape in pure liquids.

Solvent induced changes to a solute vibrational spectrum reflect the dynamic aspects of solute-solvent interactions [35-40]. For this reason, vibrational line shape analysis [19,40] and more recently time domain measurements of vibrational relaxation and dephasing [35,37] have been widely used to probe solvation forces [41]. The dynamic aspects of solute-solvent interactions in dense systems remain an active area of present research.

In the vibrational relaxation study of symmetrical modes in polar liquids by means of spontaneous Raman spectroscopic technique, considerable attention has been paid to the non-coincidence effect [16-18,42-55].

In most liquids, the existence of some average orientational structure 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 is observed in the Raman bands of these vibrations through non-coincidence effect (NCE), which is the phenomenon arising due to the difference in the peak wave numbers of anisotropic and isotropic profiles of a Raman band.

The NCE can unambiguously provide information about the molecular coupling mechanisms of short-range orientational order, which arises from the inter- and intra- molecular interactions in dense fluid phase. The phenomenon of NCE is closely related with the occurrence of resonant vibrational interaction, which due to its intermolecular nature can be suppressed by any dilution of the active oscillator. For some polar molecules, the anisotropy shift may be as large as 14 cm^{-1} [16]. Concentration studies have shown that the magnitude of the splitting decreases with increasing concentration of the solvent.

The NCE in solutions have been studied theoretically [42-49]. However there have been limited experimental studies on the dependence of NCE on solvent concentration [50-53]. A few studies have been devoted to the temperature and pressure dependence of NCE in pure liquids [8,10,54-55].

Isotopic dilution experiments [56-58] allow us to isolate the effect of resonant intermolecular vibrational coupling in vibrational bands, when the molar fraction of active molecule is decreased, the RET is gradually eliminated, but the non-resonant interactions are not influenced. It has been experimentally verified [27-34,52-65] that for vibrational modes involving RET, the position of peak frequencies are different for anisotropic and isotropic Raman band component and the corresponding infrared absorption. Wang and McHale [3-4] concluded that local short-range order is not of fundamental importance for NCE, even if its existence can modify the shift between the isotropic and anisotropic maxima. The essential condition for a RET process is the angular dependence of interaction potential. McHale proposed that S = ϵ^{-2} while Mirone corrected the screening factor as S= $[(n^2 + 2)/(2\epsilon+n^2)]^2\epsilon$

. The NCE is assumed to be the result of resonant excitonic transfer of vibrational excitation between the same normal modes of different solute molecules.

Mirone and Fini [43] showed that the separation between the isotropic and the anisotropic maxima of the Raman band of the polar molecule varies with the concentration of the active substance in a manner with a characteristic of the ratio of the static dielectric constant of the solute and the solvent. The data were found to fit in an empirical equation [43]. This behavior suggested that the NCE is related, at least in a first approximation to the interaction between the permanent dipole of the dissolved molecule. Starting from this hypothesis and making the supplementary assumption of a coupling mechanism through the transition dipole McHale derived theoretically the expression for δν

$$\delta\nu = \frac{2\mu^2\left(\frac{\delta\mu}{\delta Q}\right)^2}{25\pi^2 c^2 \nu_0 kTd^3}\frac{N_0}{V_M}\phi\ S$$

where N_o is Avogadro's number, φ is the volume fraction of the solute, ν_0 is the vibrational frequency of the isolated molecule, d is the maximum intermolecular distance, V_M is the molar volume of the solute, kT is the thermal energy, μ is the dipole moment, Q is the normal coordinate of vibrational mode under consideration and $\frac{\delta\mu}{\delta Q}$ is the transition moment. S is the screening factor which comprises of two factors S_p and S_t related to the interaction of permanent and transition dipoles respectively and are given by the Onsager-Fröhlich model as $S_p = [(n^2 + 2)/(2\epsilon+n^2)]^2\epsilon$ and $S_t = ([(n^2 + 2) / (2 \epsilon_\infty + n^2)]^2 \epsilon_\infty$ where n is the refractive index of the solute, ϵ is the static dielectric constant of the medium and ϵ_∞ is the dielectric constant at infinite frequency.

Giorgini et al [46] studied the effect of composition on the non-coincidence of the isotropic and anisotropic Raman frequencies of the C=O stretching bands of several molecules .The change in anisotropy shift was explained making the assumption that the interaction energy of the dissolved dipoles is described by the above dielectric model. They inferred that even though several approximations were involved in the Onsager-Fröhlich model, the success in interpreting their data of $\delta\nu$ over the whole composition range justified the hypothesis that $\delta\nu$ has the same functional dependence on the dielectric constant of the medium at all concentrations [46].

It was pointed out by Giorgini et al. [46] that this may be due to fortuitous cancellation of errors caused by the different approximation made while deriving the equation. Later Purkayastha and Kumar [16] while studying N,N-dimethylacetamide observed that there is kink around 50% solute concentration and suggested that this may be because the theory is valid for high dilution and different behavior at lower dilution may be expected. Das and Kumar [18,33] showed that for the p-methyl acetophenone and benzaldehyde molecules the data points fit rather well in two straight lines with a sharp discontinuity around 50% concentration. They inferred that it might be due to the reason that below 50% dilution interactions were expected to occur more among solute molecules than between solute and solvents. Further, it was pointed out that to explain the NCE in case of complex molecular systems where the effects of dispersion, induction, multipolar interaction etc are likely to vary from solvent to solvent, the screening effect may not be as effective as envisaged by the Onsager-Fröhlich model. In case of benzaldehyde molecule it was suggested that the structure breaking effects and local fluctuations may also be playing role for the discontinuity observed. Das and Kumar [18,33] have also suggested that repulsive forces are playing role in such molecular systems. However, further work is required in the complex molecular systems to establish the discontinuity and the role of repulsive forces.

The experimental work on Resonance Energy Transfer (RET) assumes that the coupling mechanism is mainly due to transition dipole – transition dipole (TD-TD) interaction [1-5,52-55,59-65].

Owing to the strong interactions between permanent dipoles, this order permits a vibrational coupling through the neighbouring transition dipoles. The phenomenon of NCE is exhibited by liquids to a large extent for the vibrations of molecular groups like C=O which are strongly infrared active. It has been shown [62] that the vibrational exciton approach developed under the assumption of transition dipole coupling mechanism, predicts how the orientational structure of the molecular liquid determines the magnitude and sign of NCE. Giorgini [62] cited that the NCE is large and positive for molecular liquids structured by dipolar forces whereas negative NCE may arise when the liquid structures are dominated by non-dipolar forces. For ring breathing aromatic systems [59] the negative sign of the splitting between anisotropic and isotropic profiles has been attributed to a balance of repulsive and attractive forces. The magnitude of NCE also depends on the thermodynamical state, because it is related to the local structural order in the liquid [63]. Higher absolute NCE values are obtained for molecules with higher steric effects [60]. Torii [61,63] observed anomalous vibrational frequency shift (negative NCE) in some usually used solvents that has a large dipole derivative. He also studied [65] the role of atomic quadrupoles in intermolecular electrostatic interactions and observed that large atomic quadrupolar effect is important for electrostatic interactions around covalent bonded atoms. Thus the phenomenon of non-coincidence can be examined from different point of view.

In order to understand the nature of intermolecular interactions and microenvironment, there is a definite need for additional systematic studies on vibrational relaxation and frequency shifts in various liquids. The study of the influence of solvents on the band shape parameters is of paramount importance not only in connection with molecular structure and liquid dynamics but also in connection with solution kinetics. In the present work, the Raman band shapes of Methyl Ethyl Ketone, Acetophenone and Methyl Acetate molecules were chosen for vibrational relaxation studies as these molecules contain C=O bond which is highly polar in nature. These molecules have been studied in different solvents of varying polarity. These solvents were found suitable after considerable screening taking into consideration, no overlapping bands, avoiding strong hydrogen bonding effects. These molecules are of considerable biophysical significance. The solvent dependent studies of Raman band shape parameters may also serve as a model for the environmental effects on the vibrational modes. These studies are therefore expected to throw light on the nature of intermolecular forces playing key role in the interactions of great biophysical significance. The study of the spectral properties of Raman bands has contributed in a major way to our understanding of the various processes involved in liquids. 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. The C=O stretching mode of vibration have been chosen for the present study because its normal mode presents particular characteristics that makes its study of great importance:

(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 a well separated mode for all molecules under study. Therefore, it is particularly suitable for probing the molecular environment and is expected to give detailed information regarding the complex molecular systems.

In case of polar Raman bands such as C=O stretching vibration, it is possible to separate the vibrational relaxation from rotational effects, hence the studies have been limited to the C=O stretching mode of vibration. The choice of solvents was such that solvent molecules were of varying size and shape, different multipolar moments and electrical properties because of which they are important in the study of intermolecular forces in the solute-solvent systems. The benzene and substituted benzene molecules ($C_6H_5CH_3$ and C_6H_5Cl) have significant effects in solute-solvent interactions from the point of view of quadrupole moment and plate like structure. The CH_3CN and CCl_4 molecules have dipole moment and octupole moment respectively. They are also having different shapes. The $CHCl_3$ molecule provides the possibility of hydrogen bonding through C-H bond as hydrogen is slightly acidic. The chloroform molecule also has symmetric top structure. Out of these six solvents, three (CH_3CN, $CHCl_3$ and C_6H_5Cl) solvents belong to the category of dipolar molecules and three (CCl_4, C_6H_6 and $C_6H_5CH_3$) are non-dipolar in nature. The dipolar effects may be studied using CH_3CN, $CHCl_3$ and C_6H_5Cl solvents and they are therefore quite effective in reducing the interactions between the solute molecules. Besides the dipolar interactions, the induction and dispersion forces are also operative and play a significant role in liquid structure. In case of polar molecules all the three types of interactions may be effective. The screening effect due to dielectric constant of the medium may also be investigated using these six solvents, as their dielectric constants are quite different from each other.

REFERENCES:

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

2) G. Fini, P. Mirone, Spectrochim. Acta Part A, **32**, 625 (1976).

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

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

5) W. Schindler, P.T. Sharko, J.Jonas, J.Chem. Phys. **76**, 3493 (1982).

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

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

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

9) B. Hegemann, J. Jonas, J. Chem. phys. **79**, 4683 (1983).

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

11) J. Schroeder, V.H. Schiemann, P.T. Sharko, J. Jonas, J. Chem. Phys. **66**, 3215 (1977) and references therein.

12) G.Seiferet, R.Zuerl, H.Graener, J.Phys.Chem.A,**103**,10749 (1999).

13) D.Biengmenn,A.M.King, F.F.Crim, J.Chem.Phys.**113**,5018 (2000).

14) A Charvat, J. Aβmann, D. Scwarzer, B. Abel, J. Phys. Chem. A, **105**, 5071 (2001).

15) A Charvat, J. Aβmann, B. Abel, D. Scwarzer, K. Henning, K. Luther, J. Troe, Phys. Chem. Chem. Phys, **3**, 2230 (2001).

16) A. Purkayastha, K. Kumar, J. Raman Spectrosc. **22**, 721 (1991).

17) A.Purkayastha,R.Das,K.Kumar,Spectrochim.Acta **47A**,525 (1991).

18) A. Das, K. Kumar, J. Raman Spectrosc. **30**, 563 (1999).

19) A. Morresi, L. Mariani, M.R. Distefano, M.G. Giorgini, J. Raman Spectrosc. **26**,179 (1995).

20) D.W. Oxtoby, Adv. Chem. Phys, **40**, 1 (1979).

21) D.W. Oxtoby, Ann. Rev. Phys. Chem. **32**, 77 (1981).

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

23) S.F.Fischer, A.Laubereau, Chem. Phys. Lett. **55**, 189 (1978).

24) S.F. Fischer, A. Laubereau, Chem. Phys. Lett. **36**, 6, (1975).

25) G. Döge, R. Arndt, J. Yarwood, J. Mol. Phys. **52**, 399 (1984).

26) R.M. Lynden-Bell, Mol. Phys. **33**, 907 (1977).

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

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

29) D. Bhattacharjee, A. Ghosh, T.N. Mishra, Bull. Chem. Soc. Jpn. **67**, 1221 (1994).

30) D. Bhattacharjee, A. Ghosh, T.N. Mishra, Bull. Chem. Soc. Jpn. **68**, 1269 (1995).

31) D. Bhattacharjee, A. Ghosh, T.N. Mishra, S.K. Nandy, J. Raman Spectrosc. **27**, 457 (1996).

32) A. Purkayastha, K. Kumar, Spectrochim. Acta **46A**, 1545 (1990).

33) A. Das, K. Kumar, Spectrochim. Acta **54A**, 793 (1998).

34) Th.G. Devi, K. Kumar, J. Raman. Spectrosc. **35**, 835 (2004).

35) T. Elsaesser, W. Kaiser, Annu. Rev. Phys. Chem. **42**, 83 (1991).

36) D.W. Miller, S.A. Adelman, Int. Rev. Phys. Chem. **42**, 83 (1991).

37) J.C. Owrutsky, D. Raferty, R.M. Hochstrasser, Annu. Rev. Phys. Chem. **45**, 519 (1994).

38) R.M. Stratt, M. Maroncelli, J. Phys. Chem. **100**, 12981 (1996).

39) E.J. Hutchinson, D. Ben-Amotz, J. Phys. Chem. B **102**, 3354 (1998).

40) J. Chesnoy, G.M. Gale, Adv. Chem. Phys. **70**, 297 (1998).

41) F. Seifert, K.L. Oehme, G. Rudakoff, W. Hölzer, W. Carius, O. Schrötter, Chem. Phys. Lett. **105**, 635 (1984).

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

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

44) P. Mirone, J. Chem. Phys. **77**, 2704 (1982).

45) J. McHale, J. Chem. Phys. **77**, 2705 (1982).

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

47) D.E. Logan, Chem. Phys. **103**, 215 (1986).

48) D.E. Logan, Mol. Phys. **58**, 97 (1986).

49) D.E. Logan, Chem. Phys. **131**, 199 (1989).

50) M. Kamoun, P. Mirone, Chem. Phys. Lett. **75**, 287 (1980).

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

52) V.M. Shelly, A. Talintyre, J. Yarwood, R. Buchner, Farady Discuss. Chem. Soc. **85**, 211 (1988).

53) V.M. Shelly, J. Yarwood, Chem. Phys. **137**, 277 (1989).

54) H.D. Thomas, J. Jonas, J. Chem. Phys. **90**, 4144, 4632, (1989).

55) T.F. Sun, J.B. Chan, S.L. Wallen, J. Jonas, J. Chem. Phys. **94**, 7486 (1991).

56) G. Döge, Z. Naturforsch, Teil A. **28**, 919 (1973).

57) P.C.M. Van Woerkom, J. de Bleyser, M. de Zwart, J.C. Leyle, Chem. Phys. **4**, 236 (1974).

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

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

60) A. Morresi, M. Paolantoni, P. Sassi, R.S. Cataliotti, G. Paliani, J. Phys.: Condens. Matter **12**, 3631 (2000).

61) H. Torii, J. Chem. Phys. **119**, 2192 (2003).

62) M.G. Giorgini, Pure and Applied Chemistry **76**, 261 (2004).

63) H. Torii, J. Phys. Chem. A **108**, 2103 (2004).

64) M.G. Giorgini, M. Musso, H. Torri, J. Phys. Chem. A, **109**, 5846 (2005).

65) H. Torri, M. Musso, M.G. Giorgini, J. Phys. Chem. A, **109**, 7797 (2005).