# Raman Scattering Studies of Vibrational Relaxation in Acetone and 2-Chlorobenzaldehyde

Debajyoti BHATTACHARJEE, Anusree GHOSH (PURKAYASTHA), and T. N. MISRA*
Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta-32, India
(Received October 13, 1993)

The Raman band of the C=O stretching vibration of acetone and 2-chlorobenzaldehyde has been acquired in a number of solvents of varying physicochemical properties. The effect of solute–solvent dispersion forces on the isotropic frequency shifts has been studied in different solvents (polar and nonpolar both). An attempt has been made to estimate the importance of hydrodynamic and dispersion forces in line broadening of the isotropic component, particularly using the theory of microviscosity.

In recent years, the study of vibrational relaxation in liquids has been of considerable interest and significant amount of work has been done through experiment and theory to have a better insight into the different physical processes involved.[1—5] Raman spectroscopy has been successfully used in such studies because it gives information about the structure, molecular dynamics and other basic properties of liquids. Most of these properties are in turn, related to the intermolecular forces. The study of pure molecular liquids involves much complications because of correlation effects. A dilute molecular solution in solvents of varying physicochemical properties, on the other hand, generally gives more information about molecular dynamics.[6—9] The dynamics of vibrational relaxation is closely related to the static frequency shifts. The observation of a difference in the peak frequencies of the polarized and depolarized Raman bands of some polar modes is attributed to orientation dependent intermolecular potential.[4,5,10] Concentration studies have shown that this noncoincidence effect or anisotropy shift decreases with increasing solvent concentration and reduces to zero in the limit of infinite dilution.

The work on temperature and pressure dependence of the Raman band shape of the C=O stretching band of liquid acetone has been done by Jonas and coworkers.[10] However the effect of solvents on the relaxation parameters has not been investigated thoroughly. Acetone molecules exhibit a large dipole moment and the frequencies of the $I_{VV}$ (the polarized component of the scattered light) and $I_{VH}$ (the depolarized light scattering intensity) components differ by several wave numbers. 2-chlorobenzaldehyde molecule also shows large dipole moment and its $I_{VV}$ and $I_{VH}$ components of the C=O stretching band differs by 2.5 $cm^{-1}$.

We have made an extensive study of the solvent dependent vibrational linewidth and the isotropic frequency shift of the C=O band of acetone and 2-chlorobenzaldehyde. The interpretation of the experimental data has been carried out on the basis of various molecular parameters.

## Experimental

The samples of acetone and 2-chlorobenzaldehyde and the solvents $C_6H_{12}$, $CHCl_3$, $CH_2Cl_2$, $CCl_4$, $CH_3CN$, $C_6H_6$, and $C_6H_5CH_3$ are either spectroscopic grade or A.R grade. All these chemicals were obtained commercially and were used without further purification.

The experiments were performed with a Spex Ramalog 1403 double monochromator and the 5145 Å line of a Spectra Physics (model 2020-5) argon ion laser as the Raman excitation source. A Spex Datamate 1B was used for spectrometer control, data acquisition and analysis. The polarized and depolarized components of the scattered Raman radiation were measured by placing an analyzer in the path of the scattered radiation. The intensity of the isotropic ($I_{iso}$) and anisotropic components ($I_{aniso}$) were calculated by using the standard formula;[11]

$$I_{iso}(\bar{\nu}) = I_{VV}(\bar{\nu}) - (4/3)I_{VH}(\bar{\nu}) \quad (1)$$

$$I_{aniso}(\bar{\nu}) = I_{VH}(\bar{\nu}) \quad (2)$$

where $I_{iso}(\bar{\nu})$ gives information about the spherically symmetric part of the intra- and intermolecular forces and $I_{aniso}(\bar{\nu})$ gives information about the anisotropic forces and molecular reorientation.

The error in the measurement of frequency is believed to be $\pm 0.5$ $cm^{-1}$.

## Results and Discussion

In order to interpret the experimental results of the vibrational relaxation for a particular band in the pure liquid, it is useful to perform dilution studies in various solvents, because it changes the type of interaction of the active molecules with their neighbors. Drickamer and co-workers[12,13] developed a theory of solution phase vibrational frequency displacements, in which they showed that (1) the isotropic peak frequency in the liquid phase will be shifted to the high frequency (blue shift) with respect to the gas frequency when the short range, rapidly modulated repulsive force predominates over all other forces, whereas (2) red shift (shift towards low frequency) occurs in case of long range slowly varying attractive forces, which include dispersion, induction, and dipolar interactions.

Later it has been experimentally verified by Hu et al.[14] for the $\nu_4$ vibration of the series $CH_3MCl_3$, with M=C, Si, Ge, Sn, that the long-range slowly varying attractive forces play an important role in shifting the vibrational bands of molecules in condensed phases. They

observed the isotropic frequency shifts in various solvent systems and it was found that the solution shifts were primarily influenced by the solute–solvent dispersion forces (in case of red shift). Now if the net peak frequency displacement in solution is due primarily to solvent dependent dispersion forces, then the fractional shift should be proportional to the solvent's polarizability [proportional to $(n^2-1)/(n^2+2)$].

We have investigated the effect of solvent on the frequency shift of the C=O stretching band of liquid acetone and 2-chlorobenzaldehyde. The anisotropy shift vanishes upon dilution (at around 20% of the sample concentration) in most of the solvents. This indicates that the noncoincidence is due to vibrational resonance coupling between the same vibrational modes of neighboring molecules, the interaction that is removed on dilution. Moreover the isotropic band is shifted to higher frequency with respect to the pure solute systems in case of both acetone and 2-chlorobenzaldehyde. It has been shown earlier by Schindler and Jonas[10] that a shift to higher frequency in going from pure liquid to a solution (in a solvent) occurs due to attractive forces, while repulsive forces result in a shift to lower frequencies. According to Schweizer and Chandler[15] the very large attractive effects in the case of pure acetone are the consequence of the presence of both polarizability and large dipolar interactions. But dipolar forces, although effective in neat liquids, are assumed to be very weak in dilute solutions as the local quasi-crystalline ordering of the solute molecules is destroyed by the solvents. The induction energy, on the other hand is about an order of magnitude smaller than dispersion energy.[16] Hence in this case, solute–solvent dispersion forces should be the more effective parameter for determining frequency shifts in various solvent systems.

We have tried to draw a correlation between the dispersion forces in various solute–solvent systems and the isotropic frequency shifts ($\overline{\nu}_{\mathrm{iso}}$) of the C=O stretching band of both acetone and 2-chlorobenzaldehyde. The experiments were performed at a fixed concentration (20% sample concentration for liquid acetone and 10% for 2-chlorobenzaldehyde) in the seven solvents ($C_6H_{12}$, $CHCl_3$, $CH_2Cl_2$, $CCl_4$, $CH_3CN$, $C_6H_6$, and $C_6H_5CH_3$). In Table 1 we have summarized the molecular parameters of these solvents. The dispersion force is given by[12,13,16,17]

$$U_{\mathrm{dis}} = \frac{-3}{2n^4}\frac{I_1 I_2\,(\alpha_1\alpha_2)}{(I_1+I_2)}\frac{1}{R_{ij}^6} = \frac{-C}{R_{ij}^6} \qquad (3)$$

where '$C$' is the dispersion energy parameter, $I$'s are the ionization potentials, $\alpha$'s are the polarizabilities, and $R_{ij}$ is the distance between the solute and the solvent molecules. The value of dispersion energy parameter '$C$' for both the samples in different solvent systems are shown in Table 2. The variations of $\overline{\nu}_{\mathrm{iso}}$ with '$C$' are shown in Fig. 1a and b.

From these graphs, it is observed that in case of both

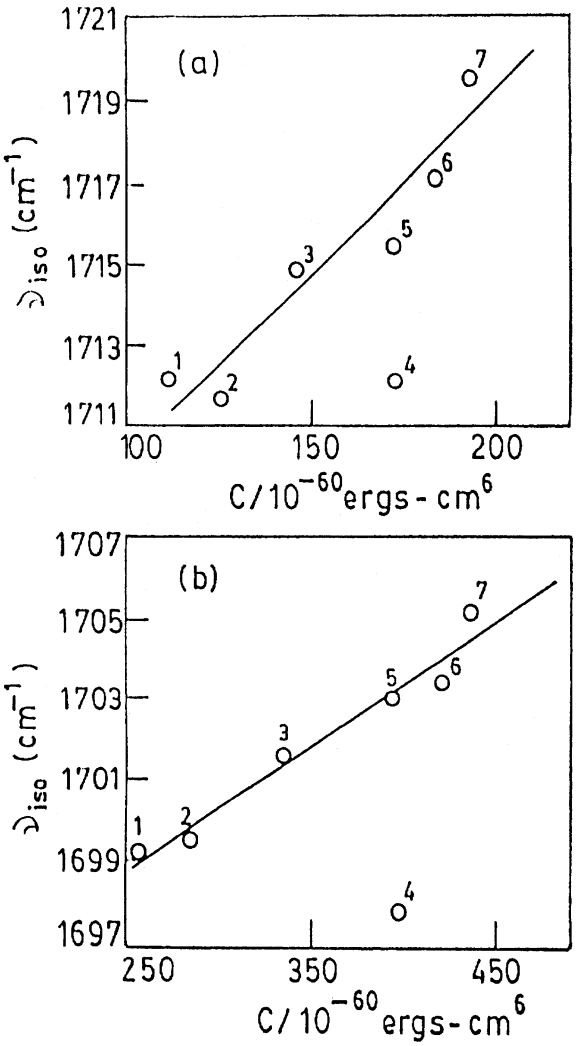


Fig. 1. Variation of the peak frequencies of the isotropic component ($\nu_{\mathrm{iso}}$) as a function of dispersion energy parameter ($C$) for (a) acetone and (b) 2-chlorobenzaldehyde molecules in (1) $CH_3CN$, (2) $CH_2Cl_2$, (3) $C_6H_6$, (4) $CHCl_3$, (5) $C_6H_5CH_3$, (6) $CCl_4$, and (7) $C_6H_{12}$ solvents.

the samples, all the data points, with the exception of data point corresponding to $CHCl_3$ solvent lie almost on a straight line. The apparent decrease in screening in $CHCl_3$ seems to be a result of strong interaction between the C–H bond of $CHCl_3$ and C=O dipole which allows a strong $C^-H^+\cdots O^-{=}C^+$ interaction. Such interactions would lead to large 'red shifts' relative to gas frequency and will mask the effect of screening, although the effect of decoupling would result in a shift into the opposite direction. The correlation coefficients '$R$' for $\overline{\nu}_{\mathrm{iso}}$ vs. '$C$' plots have been calculated to be 0.77 and 0.63 for acetone and 2-chlorohenzaldehyde respectively. However if the data points corresponding to $CHCl_3$ solvent system for both the cases be neglected, the correlation coefficients turns out to be 0.95 and 0.97, respectively, which implies a statistically significant dependence of $\overline{\nu}_{\mathrm{iso}}$ on '$C$'. It should be mentioned in this

Table 1. Molecular Parameters of Various Solvents[a)]

| Solvent | Refractive index | Density | Viscosity | Polarizability | Ionization potential |
|---|---|---|---|---|---|
| | $n$ | $\rho$ / g cm$^{-3}$ | $\eta$ / cP | $\alpha$ / $10^{-24}$ cm$^3$ | $I$ / $10^{-12}$ ergs |
| $C_6H_{12}$ | 1.4266 | 0.7785 | 1.02 | 10.87 | 15.14 |
| $CHCl_3$ | 1.4459 | 1.4232 | 0.580 | 9.5 | 18.29 |
| $CH_2Cl_2$ | 1.4242 | 1.3266 | 0.449 | 7.93 | 18.18 |
| $CCl_4$ | 1.4609 | 1.5940 | 0.969 | 10.5 | 18.37 |
| $CH_3CN$ | 1.3442 | 0.7857 | 0.345 | 4.48 | 19.55 |
| $C_6H_6$ | 1.5011 | 0.8765 | 0.652 | 10.32 | 14.8 |
| $C_6H_5CH_3$ | 1.4961 | 0.8669 | 0.590 | 12.3 | 14.11 |
| $CH_3COCH_3$ | 1.3588 | 0.7899 | 0.316 | 6.4 | 15.52 |
| 2-Chloro benzaldehyde | 1.5662 | 1.2483 | | 14.56[b)] | 15.38 |

a) Ref. 27. b) Calculated using formula $\alpha=\frac{3}{4\pi N_A}\frac{M}{\rho}\frac{(n^2-1)}{(n^2+2)}$. where $N_A$ is the Avogadro's number and the other symbols have their usual meanings. c) 1 cP=0.001 Pa s.

Table 2. Solute–Solvent Dispersion Energy Parameter '$C$' and $f_m$ for Various Solvent Systems, of the Two Samples, Acetone and 2-Chlorobenzaldehyde

| Solvent | Sample | | | |
|---|---|---|---|---|
| | Acetone | | 2-Chlorobenzaldehyde | |
| | Dispersion energy parameter $C$ / $10^{-60}$ ergs-cm$^6$ | $f_m$ | Dispersion energy parameter $C$ / $10^{-60}$ ergs-cm$^6$ | $f_m$ |
| $C_6H_{12}$ | 193.25 | 1.5734 | 437.29 | 1.57 |
| $CHCl_3$ | 173.20 | 2.5610 | 396.60 | 3.17 |
| $CH_2Cl_2$ | 125.21 | 0.9281 | 286.60 | 1.08 |
| $CCl_4$ | 184.13 | 2.2765 | 421.46 | 2.64 |
| $CH_3CN$ | 112.90 | 0.6269 | 257.95 | 0.627 |
| $C_6H_6$ | 146.20 | 1.1617 | 334.81 | 1.162 |
| $C_6H_5CH_3$ | 172.70 | 0.7207 | 394.57 | 0.721 |

context, that we should search for a better fit parameter which would account well the hydrogen bonding and other associative factors which reduce the screening effect on dilution. Moreover the repulsive force contribution to vibrational frequency shift has to be included for understanding the wide variety of experimental observations.

Line width measurements may be of considerable value for understanding the dynamics of a molecular system. There are both homogeneous and inhomogeneous contributions to the line widths.[18)] When the vibrational frequency of a molecule is perturbed by its interaction with other molecules, there is a fluctuation in energy levels of the states involved in the transition, which leads to modulation of the vibrational frequency and therefore line broadening occurs. This mechanism of line broadening is called pure dephasing.[2)]

The line broadening mechanisms may be inhomogeneous (slow modulated) or homogeneous (fast modulated)) depending upon whether $<\Delta\omega^2>\tau_c\gg1$ or $<\Delta\omega^2>\tau_c\ll1$, where $\Delta\omega$ is frequency displacement of the instantaneous transition frequency and $\tau_c$ is the correlation time. Lorentzian line shape occurs in case of homogeneous broadening and non-Lorentzian lines are often attributed to inhomogeneous broadening. In the rapid modulation limit where the line is narrowed to a Lorentzian, the vibrational relaxation time is defined as:[2)]

$$\tau_v^{-1} = \pi c \Gamma_{iso} \tag{4}$$

where $\Gamma_{iso}$ is the FWHM of the isotropic component of the Raman band and '$c$' is the velocity of light.

For an isolated transition, phase relaxation leading to broadening of the isotropic Raman spectral component arises mainly due to life time broadening, pure dephasing and resonant energy transfer. In case of dilute solution the most important contribution to line broadening is generally considered to be from pure dephasing. A number of theories have been proposed to explain the dephasing phenomena, some of the important ones are the isolated binary collision (IBC) theory of Fischer and Laubereau,[19)] hydrodynamic theory of Oxtoby,[20)] and molecular dynamics simulations on liquid nitrogen using the quantum perturbation theory.[21,22)] The general conclusion reached was that the dephasing process is very sensitive to the details of the interaction potentials and attractive forces (e.g. dispersion, quadrupolar) play an important role but do not lead to the inhomogeneous broadening of the vibrational line.[15)] Although these theoretical models are able to explain the experimental data of a few specific systems, a general understanding of the dependence of dephasing process on solvent, thermodynamic state and molecular parameters is lacking. The model suggested by Purkayastha and Kumar,[23,24)] however, gives a better picture of the phase relaxation in associated liquids (under the conditions of high dilution) where the vibrational relaxation rate has been shown to be a function of a parameter related to the hydrodynamic and dispersion forces. According to this model the vibrational relaxation rate is

given by,

$$\tau_v^{-1} = C_m f(\rho, \eta, n) \quad (5)$$

where

$$f(\rho, \eta, n) = \rho n \left[\frac{n^2-1}{2n^2+1}\right]^{-1} \quad (6)$$

and $C_m$ is a constant depending mainly on the solute properties. $\rho$ $\eta$, and $n$ are the density, dynamic viscosity, and refractive index of the solvent, respectively. Although this parameter, $f(\rho,\eta,n)$ is able to explain the important role played by hydrodynamic and dispersion forces, hydrogen bonding, and other associative factors are not included in this parameter. It has been shown recently,[24] that the concept of microviscosity instead of dynamic viscosity may be used to incorporate the finer details of the solute–solvent systems. The modified parameter $f_m$ which takes into account the discrete nature of the viscoelastic medium is given by,

$$f_m = \rho\eta_m \left[\frac{n^2-1}{2n^2+1}\right]^{-1} \quad (7)$$

Here, the microviscosity $\eta_m$ is given by: —

$$\eta_m = \eta\gamma = \eta\,[0.16 + 0.4(a/b)]\,.$$

where $\gamma$ is the microfriction parameter, and '$a$' and '$b$' correspond to sample and solvent radii respectively. Calculations of $f_m$ for acetone and 2-chlorobenzaldehyde corresponding to various solvents are given in Table 2.

The value of the solute radius '$a$' was chosen as 1.4 Å for acetone molecule for the calculation of $\eta_m$ as the interactions are through the '$O$' atom. This value is chosen because of the possibility of $\pi$–$\pi^*$/$n$–$\pi^*$ type interaction in case of $C_6H_6$ and $C_6H_5CH_3$ solvent systems and dipole–dipole types of interactions in the case of other polar solvents. The contribution of dipole–octupole or dipole–induced dipole interactions to the line broadening may be neglected because they are very weak. In case of 2-chlorobenzaldehyde, the value of the solute radius '$a$' is taken as 1.4 Å for the solvents $C_6H_{12}$, $CH_3CN$, $C_6H_6$, and $C_6H_5CH_3$. But for the solvents $CHCl_3$, $CH_2Cl_2$, and $CCl_4$, due to the presence of chlorine atom in the benzene ring of the sample molecule, the solute radius '$a$' is taken as 1.85 Å (1/2 thickness of the benzene ring)[25] which is the distance of closest approach.

Now in the case of $CHCl_3$, the hydrogen atom present in $CHCl_3$ molecule is of acidic nature, which may form a hydrogen bond with the C=O bond of solute molecule. Hence in this case, hydrogen bonding may be the main interaction for the $CHCl_3$–solute molecule system. Therefore, for $CHCl_3$, the value of '$b$' was taken as 1.2 Å, the van der Waals' radius for a H atom.[25] Other chlorinated solvents $CH_2Cl_2$ and $CCl_4$ are non-hydrogen-bonded systems where the interactions may be considered through the C–Cl bond. Therefore the distance of closest approach is the sum of the van der Waals' radius of the 'Cl' atom (1.8 Å) and the C–Cl bond distance[26] (1.76 Å for $CCl_4$ and 1.77 Å for $CH_2Cl_2$), as these molecules are tetrahedral. In case of $CH_3CN$ molecule, so far as the C–C≡N portion is concerned, a plate like structure may be considered. Hence the distance of closest approach is limited by the $CH_3$ group of the symmetric top structure of the $CH_3CN$ molecule and the value of '$b$' is taken as the sum of the C–H bond distance (1.09 Å) and the van der Waals' radius of the H atom (1.2 Å). In the case of benzene molecule, '$b$' is chosen as 1.85 Å (1/2 thickness of the benzene ring), whereas for toluene, due to the presence of methyl group, the interaction will be through the $CH_3$ group and in this case, the distance of closest approach is 3.53 Å (2.0 Å, the van der Waals' radius for $CH_3$ group +1.53 Å for C=C bond length).[26]

From the correlation of $\tau_v^{-1}$ with $f_m$ [Figs. 2a and 2b] it appears that within the scatter of the data points there is no significant deviation from a single straight line. This is also supported from the value of the correlation coefficients, which are 0.99 and 0.98 for acetone and 2-chlorobenzaldehyde respectively. This shows the validity of the expression and the assumptions involved in deriving it for determining the Raman band shape in case of dilute solutions of acetone and 2-chlorobenz-

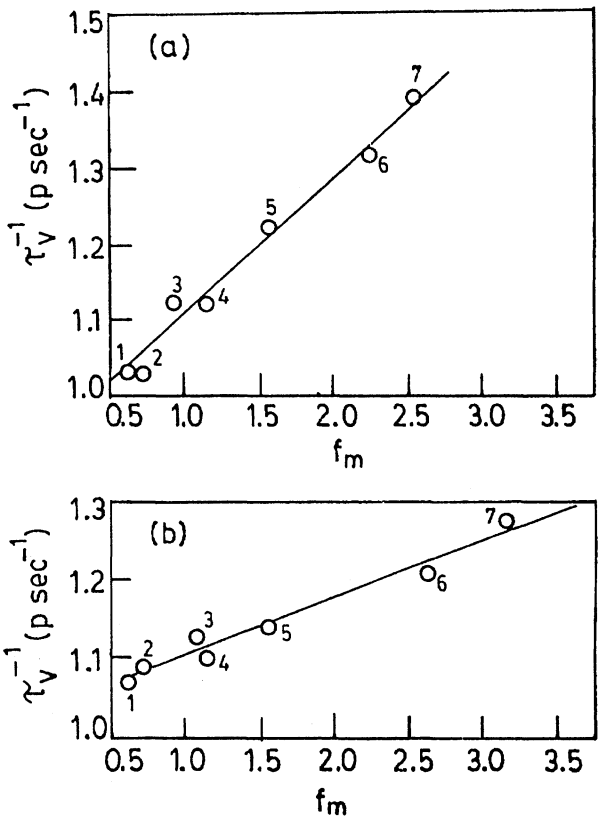


Fig. 2. Vibrational relaxation rate ($\tau_v^{-1}$) dependence as a function of the parameter $f_m$ for (a) acetone and (b) 2-chlorobenzaldehyde molecules in (1) $CH_3CN$, (2) $C_6H_5CH_3$, (3) $CH_2Cl_2$, (4) $C_6H_6$, (5) $C_6H_{12}$, (6) $CCl_4$, and (7) $CHCl_3$ solvents.

aldehyde. The model therefore can provide a good description of dephasing in molecular liquids. More systematic studies of similar molecules under a wide range of physicochemical conditions are on progress.

The authors D.B and A.G are grateful to C.S.I.R, New Delhi, for providing financial support. Thanks are also due to Department of Science and Technology, Govt. of India, for supporting laser facilities.

## References

1) D. Schiebe, *J. Raman Spectrosc.*, **13**, 103 (1982).
2) D. W. Oxtoby, *J. Phys. Chem.*, **87**, 3028 (1983).
3) G. Doge, R. Arndt, and J. Yarwood, *Mol. Phys.*, **52**, 399 (1984).
4) J. L. McHale, *J. Chem. Phys.*, **75**, 30 (1981).
5) W. Schindler, T. W. Zerda, and J. Jonas, *J. Chem. Phys.*, **81**, 4306 (1984).
6) M. Kamoun and P. Mirone, *Chem. Phys. Lett.*, **75**, 287 (1980).
7) G. Fini and P. Mirone, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1776 (1974).
8) T. Bien and G. Doge, *J. Raman Spectrosc.*, **12**, 82 (1982).
9) E. W. Knapp and S. F. Fischer, *J. Chem. Phys.*, **76**, 4730 (1982).
10) W. Schindler, P. T. Sharko, and J. Jonas, *J. Chem. Phys.*, **76**, 3493 (1982).
11) K. Tanabe, *Spectrochim. Acta, Part A*, **40A**, 437 (1984).
12) A. M. Benson, Jr., and H. G. Drickamer, *J. Chem. Phys.*, **27**, 1164 (1957).
13) R. R. Wiederkehr and H. G. Drickamer, *J. Chem. Phys.*, **28**, 311 (1958).
14) W. P. Hu, A. A. Rodriguez, and M. Schwartz, *Spectrochim. Acta, Part A*, **45A**, 929 (1989).
15) K. S. Schweizer and D. Chandler, *J. Chem. Phys.*, **76**, 2296 (1982).
16) W. Schindler and J. Jonas, *J. Chem. Phys.*, **73**, 3547 (1980).
17) D. Langbien, in "Theory of van der Waals' Attraction: Springer Tracts in Modern Physics," ed by G. Hohler, Springer, Berlin (1974), Vol. 72.
18) E. W. Knapp and S. F. Fischer, *J. Chem. Phys.*, **74**, 89 (1981).
19) S. F. Fischer and A. Lauberau, *Chem. Phys. Lett.*, **35**, 6 (1975).
20) D. W. Oxtoby, *J. Chem. Phys.*, **70**, 2605 (1979).
21) D. W. Oxtoby, D. Levesque, and J. J. Weis, *J. Chem. Phys.*, **68**, 5528 (1978).
22) D. Levesque, J. J. Weis, and D. W. Oxtoby, *J. Chem. Phys.*, **72**, 2744 (1980).
23) A. Purkayastha and K. Kumar, *J. Raman Spectrosc.*, **19**, 249 (1988).
24) A. Purkayastha, R. Das, and K. Kumar, *Spectrochim. Acta, Part A*, **46A**, 1545 (1990).
25) A. Bondi, *J. Phys. Chem.*, **64**, 441 (1964).
26) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca (1960), p. 229.
27) R. C. Weast, "CRC Handbook of Chemistry and Physics," 67th ed, CRC press, Boca Raton (1986—1987).