

Raman spectral study of vibrational relaxation in acetophenone

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Abstract. The isotropic Raman band of the C=O stretching mode of the acetophenone molecule has been recorded in a number of solvents of varying physicochemical properties. The experimental results suggest that dispersion forces are responsible for the observed isotropic frequency shift. The variation in the band shape parameters has been studied as a function of the hydrodynamic properties of the solvents. The effect of solvent viscosity on linewidth (Γ_{iso}) has been studied in detail. The concept of microviscosity is shown to account for the bandwidth of the isotropic component of the Raman band.

Keywords. Raman band; isotropic frequency shift; vibrational relaxation; physico-chemical constants.

1. Introduction

The vibrational relaxation process responsible for the line broadening of an isotropic Raman band can be explained on the basis of two mechanisms (Oxtoby 1979, 1983; Jonas 1983), one involving energy relaxation via inelastic collisions and the other, phase relaxation via quasi-elastic collisional process. The principal theories developed for the dephasing process are the isolated binary collision (IBC) model (Fischer and Lambereau 1975), the hydrodynamic model (Oxtoby 1979a) and the resonant energy transfer model (Doge *et al* 1984). 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 (1975). Oxtoby (1979a) developed a hydrodynamic model to explain the linewidth of the C–I stretching vibration of CH₃I. In this hydrodynamic model, collective effects were included and the vibrating molecule was modelled as a macroscopic body embedded in a viscoelastic continuum. Doge *et al* (1984) showed that resonant energy transfer via transition dipole–transition dipole (TD–TD) interaction is the main intermolecular coupling mechanism for the ν_2 mode of CH₃I. However, the model suggested by Purkayastha and Kumar (1987, 1988) 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. This model has so far been successfully applied for the carbonyl stretching (C=O) band of several ketones (Bhattacharjee *et al* 1994), aldehydes (Bhattacharjee *et al* 1995), amides (Purkayastha and Kumar 1988, 1990) as well as for the C≡N band of nitriles (Bhattacharjee *et al* 1996). Later on, the

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concept of microviscosity instead of dynamic viscosity, was included (Purkayastha and Kumar 1990) so as to incorporate the finer details of solute–solvent systems.

Moreover, the observation of a difference in the peak frequencies of the polarized and depolarized Raman bands of some polar modes, corresponding to intense infrared absorptions, is now a well-established phenomenon and is attributed to orientation-dependent intermolecular potential (Mchale 1981; Schindler *et al* 1982, 1984). Concentration dependence studies have shown that this non-coincidence effect or anisotropy shift decreases with decreasing solute concentration and reduces to zero in the limit of infinite dilution. In our case of acetophenone molecule, the polarized (I_{VV}) and depolarized (I_{VH}) components of the C=O stretching band differ by 5 cm^{-1} and it has been observed that this anisotropy shift decreases with decreasing solute concentration irrespective of the nature of the solvent (Giorgini *et al* 1983).

The purpose of the present work is to study the influence of the solute concentration on the isotropic frequency shifts and vibrational dephasing time of the carbonyl stretching (C=O) band of acetophenone. Raman spectral measurements were carried out in pure liquids and in solvents having varying dipole moments and dielectric constants, as a function of the solute concentration. The validity of the theoretical model has been examined in the interpretation of the experimental results.

2. Experimental

The sample of acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) and the eight solvents (C_6H_{12} , CHCl_3 , CH_2Cl_2 , CCl_4 , CH_3CN , C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_6\text{H}_5\text{Cl}$) were of either spectroscopic or analytical reagent (AR) grade. All these chemicals were obtained commercially and were used without further purification.

The experiments were performed with a Spex Ramalog 1403 double monochromator fitted with 1800 grooves/mm gratings. The 5145 \AA line of a Spectra Physics (model 2020–5) argon ion laser was used as the excitation source. For spectrometer control, data acquisition and analysis, Spex Datamate 1 B was used.

Since our interest is confined to a study of the dephasing mechanism of the C=O stretching vibration of acetophenone, the purely isotropic part of the Raman spectra containing information about vibrational relaxation had to be recorded and in order to obtain this, both the polarized (I_{VV}) and depolarized (I_{VH}) components were measured separately by placing analyser in the path of the scattered radiation. The details of the instrumental setup for polarization measurements have been discussed elsewhere (Bhattacharjee *et al* 1995).

The intensity of the isotropic (I_{iso}) and anisotropic (I_{aniso}) components were calculated using the standard formula (Tanabe 1984),

$$I_{\text{iso}}(\nu) = I_{VV}(\nu) - (4/3)I_{VH}(\nu),$$

and

$$I_{\text{aniso}}(\nu) = I_{VH}(\nu).$$

The spectral slit width used for recording the Raman spectra was $\approx 3\text{ cm}^{-1}$. The effect of the finite slit width on the observed linewidth was corrected by the usual equation (Tanabe 1984),

$$\Gamma_t = \Gamma_a \left[1 - \left(\frac{S}{\Gamma_a} \right)^2 \right],$$

where Γ_a and Γ_t are the apparent and true Raman linewidth (full width at half maximum intensity, FWHM) respectively and S is the spectral slit width in cm^{-1} .

For measuring the bandwidth and the isotropic frequency shift accurately, we followed the method of Chen and Schwartz (1985). Each spectrum was recorded three times; the values of the bandwidth (full width at half maxima) represent the average of the three runs. The standard deviations for the three runs were typically 0.1 to 0.2 cm^{-1} . However, considering possible systemic errors resulting from the slit width correction, the error estimated for the FWHM is 0.5 cm^{-1} . The peak frequencies were interpolated to the nearest 0.1 cm^{-1} by a linear regression algorithm (Chen and Schwartz 1985) using nine points in the vicinity of the maximum. The band centres in the solutions were compared to values obtained here for the neat liquids. The precision of the measured peak positions was ± 0.1 – 0.2 cm^{-1} , based on the deviation between runs. However, a reasonable error estimated for the peak position is taken as 0.5 cm^{-1} .

3. Results and discussions

The acetophenone molecule has been studied by Mirone and co-workers (Giorgini *et al* 1983), who observed that the anisotropy shift or noncoincidence splitting of the C=O stretching band of acetophenone decreases with decreasing solute concentration in different solvent systems. This anisotropy shift, however, reduces to zero at a certain volume fraction in most of the solvents.

Here we carried out a detailed study of the isotropic frequency shift and linewidth of the C=O stretching band of acetophenone in solvents of varying physico-chemical constants as a function of the concentration and solvents used.

3.1 Solvent-dependent isotropic frequency shift

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 neighbours. When the peak frequencies of the isotropic and anisotropic parts of the bands are extrapolated to infinite dilution in the given solvent, the two frequencies coincide and then the TD–TD (transition dipole) interactions responsible for the non-coincidence effect in pure liquid vanish. Under this condition, the maximum shift of the isotropic peak frequency with respect to a pure liquid, may be a measure of the strength of the potential field perturbing the vibration since the solute molecule is assumed to be in a cage of solvent molecules.

We have investigated the effect of solvent on the frequency shift of the C=O stretching band of acetophenone at high dilution. When the band is extrapolated to infinite dilution, it is found that the isotropic band is shifted to higher frequency with respect to that in pure solute. It has also been shown earlier by Schindler and Jonas (Schindler *et al* 1984) that a shift to higher frequency in going from pure liquid to a solution (in a solvent) occurs due to attractive forces between solute molecules. These attractive forces include dispersion, induction and dipolar interactions. The 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 (Schindler and Jonas 1981). Hence solute–solvent dispersion forces should be the more effective parameter for determining the frequency

shifts in various solvent systems. It has been shown before that there is a good correlation between the dispersion forces in various solute-solvent systems and the isotropic frequency shift (ν_{iso}) of the C=O stretching band of acetone and 2-chlorobenzaldehyde (Bhattacharjee *et al* 1994) as well as in benzaldehyde (Bhattacharjee *et al* 1995). In this report we make a similar correlation between the dispersion forces in various solute-solvent systems and the isotropic frequency shifts (ν_{iso}) of the C=O stretching band of acetophenone under the condition of high dilution (10% sample concentration) in the eight solvents mentioned above. The molecular parameters of these solvents are summarized in table 1. The dispersion force is given by (Benson and Drickamer 1957; Wiederkehr and Drickamer 1958; Langbien 1974),

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

where C is the dispersion energy parameter, the I 's are the ionization potentials, the α 's are the polarizabilities, n is the refractive index of the solvent and R_{ij} is the distance between the solute and the solvent molecule. Subscripts 1 and 2 represent solute and solvent respectively. The values of the dispersion energy parameter (C) for acetophenone (solute) in different solvent systems are summarized in table 2. From the variation of ν_{iso} with C (figure 1), it is clear that in the case of acetophenone also, there is a linear dependence of ν_{iso} on C . However, the data-point for CHCl_3 is far away from the correlation line. As mentioned previously (Bhattacharjee *et al* 1994, 1995) 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 the C=O dipole which allows a strong $\text{C}^-\text{H}^+\cdots\text{O}^-=\text{C}^+$ interaction. Such interactions would lead to large 'red shifts' relative to gas frequency and mask the effect of screening, although the effect of decoupling would result in a shift into the opposite direction. The correlation coefficient for ν_{iso} vs C plot was calculated to be 0.52. However, if the data-point corresponding to the CHCl_3 solvent system be neglected, then the correlation coefficient turns out to be 0.89, which implies a statistically significant dependence of ν_{iso} on C .

Table 1. Molecular parameters of various solvents^a.

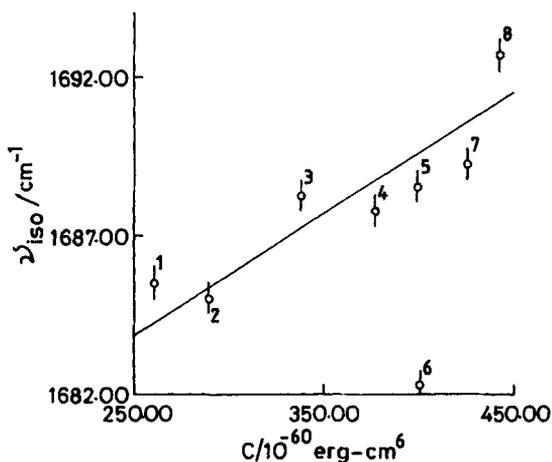
Solvent	Refractive index n	Density ρ (g cm^{-3})	Viscosity ^b η (cP)	Polarizability α (10^{-24} cm^3)	Ionization potential $I(10^{-12})$
C_6H_{12}	1.4266	0.7785	1.020	10.87	15.14
CHCl_3	1.4459	1.4832	0.580	09.50	18.29
CH_2Cl_2	1.4242	1.3266	0.449	07.93	18.18
CCl_4	1.4609	1.5940	0.969	10.50	18.37
CH_3CN	1.3442	0.7857	0.345	04.48	19.55
C_6H_6	1.5011	0.8765	0.652	10.32	14.80
$\text{C}_6\text{H}_5\text{CH}_3$	1.4961	0.8669	0.590	12.30	14.11
$\text{C}_6\text{H}_5\text{Cl}$	1.5241	1.1058	0.799	12.35	14.51
Aceto-phenone	1.3442			15.00	14.832

^aWeast (1986-87)

^b1 cP = 0.01 poise

Table 2. Solute-solvent dispersion energy parameter C , $f(\rho, \eta, n)$ and f_m for various solvent systems, for the sample of acetophenone.

Solvent	Dispersion energy parameter		
	C (10^{-60} erg-cm ⁶)	$f(\rho, \eta, n)$ (10^{-2} gm ² -cm ⁻⁴ -s ⁻¹)	f_m (10^{-2} gm ² -cm ⁻⁴ -s ⁻¹)
C ₆ H ₁₂	442.40	3.8893	1.5700
CHCl ₃	400.54	4.0868	2.5620
CH ₂ Cl ₂	289.46	2.9289	1.8350
CCl ₄	425.63	7.1745	2.2765
CH ₃ CN	260.37	1.5499	0.6270
C ₆ H ₆	338.79	2.5108	1.1617
C ₆ H ₅ CH ₃	399.43	2.2618	0.7207
C ₆ H ₅ Cl	377.72	3.7707	1.1965

**Figure 1.** Variation of the peak frequencies of the isotropic component (ν_{iso}) as a function of dispersion energy parameter (C) in (1) CH₃CN, (2) C₆H₅CH₃, (3) C₆H₆, (4) CH₂Cl₂, (5) C₆H₅Cl, (6) C₆H₁₂, (7) CHCl₃ and (8) CCl₄.

3.2 Solvent dependence of dephasing time

The study of the dynamics of pure molecular liquids is very complicated because it involves correlation effects. Dilute molecular solutions in solvents of varying physicochemical properties, on the other hand, give more information about the molecular dynamics as there is change in the type of interactions of the active molecules with their neighbours.

Linewidth measurements may be of considerable value for understanding the dynamics of a molecular system. The linewidth of an isotropic Raman band is dependent on the vibrational phase relaxation and for a well-separated vibrational transition (no overlapping with hot band or other transitions) there are three primary sources of such line broadening as below.

(i) Life-time broadening: Because of the finite life time of a quantum state, there is broadening due to the uncertainty principle. However, it generally makes a rather small contribution to the linewidth.

(ii) Resonance energy transfer or excitonic broadening which appears only in pure liquids and is absent in dilute solution.

(iii) The third and most important contribution to vibrational phase relaxation may be referred to as "environmental broadening". It arises from the fact that when the vibrational frequency of a molecule is perturbed by its interaction with other molecules, there is fluctuation in energy levels of the states involved in the transition, which in turn leads to modulation of the vibrational frequency and eventually line broadening. This mechanism of line broadening is also called pure dephasing.

The isotropic Raman line shape, as discussed by Oxtoby (1979) is given by the Fourier transform of the vibrational co-ordinate autocorrelation function $\langle Q_i(t)Q_i(0) \rangle$ where the angular brackets define an ensemble average. The vibrational co-ordinate Q_i at time t differs from $Q_i(0)$, by a phase factor $\exp(i[\phi_i(t) - \phi_i(0)])$ where the phase difference is given by,

$$\phi_i(t) - \phi_i(0) = \int_0^t dt' \cdot \omega_i(t') = \bar{\omega}t + \int_0^t dt' \cdot \Delta\omega_i(t'),$$

where $\bar{\omega}$ is the average vibrational transition frequency in the liquid and $\Delta\omega_i(t)$ gives the fluctuations in frequency due to the environment. The vibrational phase relaxation is then given by,

$$\langle Q_i(t)Q_i(0) \rangle = \left\langle \exp \left[i \int_0^t dt' \cdot \Delta\omega_i(t') \right] \right\rangle$$

and depends on the statistical properties of $\Delta\omega_i(t)$. A characteristic time τ_c may now be defined as,

$$\tau_c = \int_0^t dt \frac{\langle \Delta\omega_i(t)\Delta\omega_i(0) \rangle}{\langle \Delta\omega_i^2 \rangle}$$

where $\langle \Delta\omega_i(t)\Delta\omega_i(0) \rangle$ is the autocorrelation function of $\Delta\omega_i(t)$. The nature of the lineshape depends on the relative magnitude of the two characteristic frequencies $\langle \Delta\omega_i^2 \rangle^{1/2}$ and τ_c^{-1} . When $\langle \Delta\omega_i^2 \rangle^{1/2}\tau_c \gg 1$, we have the "static" limit considered above, while when $\langle \Delta\omega_i^2 \rangle^{1/2}\tau_c \ll 1$, we have the rapid modulation limit where the line is narrowed to a Lorentzian.

Under the condition of rapid modulation limit, the vibrational relaxation time is defined as (Schindler and Jonas 1981);

$$\tau_V = (\pi c \Gamma_{\text{iso}})^{-1}$$

where Γ_{iso} is the FWHM of the isotropic components of the Raman band and c is the velocity of light.

In the model suggested by Purkayastha and Kumar (1987, 1988) 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 related to the PK parameter $f(\rho, \eta, n)$ as,

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

where

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

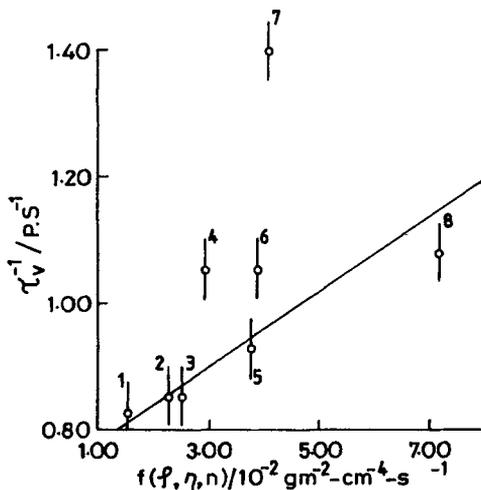


Figure 2. Vibrational relaxation rate (τ_v^{-1}) dependence as a function of the parameter $f(\rho, \eta, n)$ for acetophenone in solvents (1)–(8) as in figure 1.

and C_m is a constant depending mainly on solute properties ρ , η and n , the density, dynamic viscosity and refractive index respectively of the solvent. However, hydrogen bonding and other associative factors are not included in this parameter.

The variation in the vibrational relaxation rate (τ_v^{-1}) as a function of $f(\rho, \eta, n)$ is shown in figure 2. It is seen in the figure that all the data points except the two corresponding to the CHCl_3 and CH_2Cl_2 solvent systems lie almost on a straight line. Especially in the case of the CHCl_3 solvent system the point is far above the straight line. This discrepancy is due to the fact that hydrogen bonding of the type $\text{C}^-\text{H}^+\cdots\text{O}^-\text{C}^+$ would be formed between the solute and solvent molecules. The hydrogen atom present in the CHCl_3 molecule is acidic in nature, which may form a strong hydrogen bond with the $\text{C}=\text{O}$ dipole of the sample molecule. However, in case of CH_2Cl_2 , a weak hydrogen bond is formed, which is quite evident from figure 2. In this context, it should be mentioned that this weak hydrogen bonding in the CH_2Cl_2 solvent system does not affect the isotropic frequency shift appreciably while the strong hydrogen bonding in CHCl_3 contributes appreciably to the shift. This is observed in figure 1 and discussed in the previous section.

It has been shown recently (Purkayastha and Kumar 1990) that the concept of microviscosity instead of dynamic viscosity may be used to incorporate the finer details of the solute–solvent interactions. The modified parameter f_m which takes into account the discrete nature of the visco-elastic medium is given by (Purkayastha and Kumar 1990),

$$f_m = \rho\eta_m \left[\frac{n^2 - 1}{2n^2 + 1} \right]^{-1}.$$

Here the microviscosity η_m is defined as,

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

where γ is the microfriction parameter, and a and b correspond to sample and solvent radii respectively. Calculations for f_m for acetophenone in various solvents are given in table 2.

Considering the different types of interactions between solute-solvent molecules viz. $\pi-\pi^*/n-\pi^*$ type interaction in the 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 value of the solute radius was chosen to be 1.4 \AA , the C=O bond length. Now, in the case of $CHCl_3$ solvent molecule, the value of the solvent radius (b) was chosen to be 1.2 \AA , the van der Waal's radius for an H atom (Bondi 1964). This is due to the fact that the hydrogen atom present in the $CHCl_3$ molecule is acidic in nature and, hence, it may form a hydrogen bond with the C=O dipole of the solute molecule. Moreover, in case of CH_2Cl_2 solvent, there is also a possibility of forming a hydrogen bond with the C=O group of acetophenone, which appears to be reasonable from the relatively large bandwidth (FWHM) in this solvent. But the effect is quite small, since it is not observable in the case of isotropic frequency shift as discussed previously. Then in this case also, the solvent radius (b) is taken as 1.2 \AA . However, other chlorinated solvents (CCl_4 and C_6H_5Cl) are non-hydrogen bonded systems and in the second case the interactions may be considered through the C-Cl bond. Therefore, the distance of closest approach is the sum of the van der Waal's radius of the 'Cl' atom (1.8 \AA) and the C-Cl bond distance (1.76 \AA for CCl_4 and 1.77 \AA for CH_2Cl_2). In the case of the CH_3CN molecule, so far as the C-C \equiv 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 \AA) and the van der Waal's radius of the 'H' atom (1.2 \AA). In case of cyclohexane (C_6H_{12}) molecule also, the solvent radius is taken as 2.29 \AA , i.e. the sum of the C-H bond distance (1.09 \AA) and the van der Waal's radius of the 'H' atom (1.2 \AA).

In case of benzene molecule, b is chosen to be 1.85 \AA ($1/2$ thickness of the benzene ring), whereas for toluene, the interaction is through the CH_3 group. In this case, the distance of closest approach is 3.53 \AA (2.0 \AA , the van der Waal's radius for the CH_3 group + 1.53 \AA for C=C bond length) (Bondi 1964).

The variation in the vibrational relaxation rate (τ_v^{-1}) as a function of f_m is shown in figure 3. This is clearly a linear variation; the fitting of the parameter in case of the eight

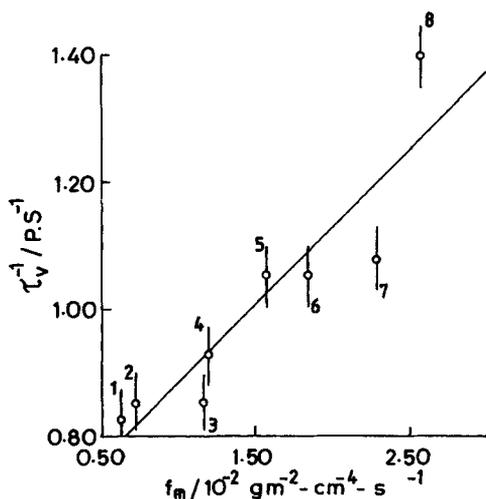


Figure 3. Vibrational relaxation rate (τ_v^{-1}) dependence as a function of the parameter f_m for acetophenone in solvents (1)–(8) as in figure 1.

solvents at 90% solvent concentration is quite good. The correlation coefficient for the τ_v^{-1} against f_m has been calculated to be 0.97. This shows the validity of the expression and the assumptions involved in deriving it for determining the Raman band shape in the case of dilute solutions of acetophenone.

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