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Solvent-Induced Vibrational Relaxation in Benzaldehyde

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The Raman band of the C=O stretching vibration of benzaldehyde has been recorded as a function of the concentration in a number of solvents. The experimental results suggest that dispersion forces are responsible for the observed frequency shift. The variation in the band-shape parameters have been interpreted using microviscosity theory.

Vibrational dephasing in liquids has been the subject of intense theoretical and experimental studies in recent years.[1—5] The vibrational phase and energy relaxation are sensitive properties both to potential surfaces and to liquid-state dynamics. Early theoretical studies mainly emphasized the determination of the sources of phase and energy relaxation in liquids, and expressed them in terms of the coupling between a quantum vibrational system to a classical "heat bath" of the rotational and translational degrees of freedom.

Different types of experiments can be performed to observe dephasing in liquids. The simpler approach is to study the isotropic Raman line shape and its dependence on the temperature, pressure and concentration.[3,4,6] Such studies provide information about the structure, molecular dynamics and other basic properties of liquids. Most of these properties are, in turn, related to the intermolecular forces. Although these experiments don't allow the separation of the pure dephasing contribution from the resonant-energy transfer and population-relaxation contributions, experimental evidence suggests that it is the dominant effect.[7]

Moreover, observations of the non-coincidence of the isotropic and anisotropic components of the Raman bands of some polar modes, corresponding to intense infrared absorptions, is now a well-established phenomenon, and is attributed solely to the orientation-dependent intermolecular potential.[4—6] This non-coincidence effect has been shown to decrease with increasing the solvent concentration, and becomes zero in the limit of infinite dilution. The purpose of the present work was to study the influence of the solvent concentration on the anisotropy shifts (non-coincidence splitting), isotropic frequency shifts and vibrational dephasing time of the C=O stretching band of benzaldehyde. The benzaldehyde molecule has a permanent dipole moment of 2.77 D, and its polarised (I_{VV}) and depolarised (I_{VH}) components of the C=O stretching band differ by 5 cm^{-1} (Fig. 1). Raman spectral measurements were carried out in pure liquids and in solvents having various dipole moments and dielectric constants as a function of the concentration. The validity of the theoretical model has been tested by trying to interpret the experimental results.

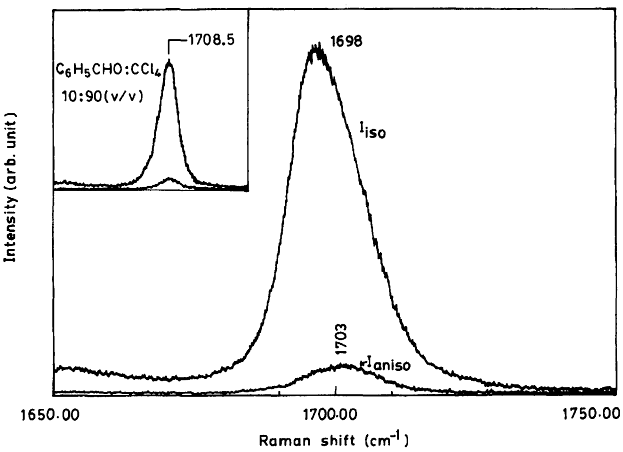

Fig. 1. The I_{iso} and I_{aniso} components of the C=O stretching vibration mode of pure liquid benzaldehyde.

Experimental

The sample benzaldehyde (C_6H_5CHO) and eight solvents (C_6H_{12}, $CHCl_3$, CH_2Cl_2, CCl_4, CH_3CN, C_6H_6, $C_6H_5CH_3$, and C_6H_5Cl) were either of highly pure spectroscopic grade or fairly pure analytical reagent (AR) grade. All of 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/m.m. gratings; the 5145 Å line of a spectra physics (model 2020-5) argon-ion laser was used as the excitation source. For spectrometer control, data acquisition and analysis, a Spex Datamate 1B was used.

Since our interest was confined to a study of the dephasing mechanism of C=O stretching vibration of benzaldehyde, the purely isotropic part of the Raman spectra containing information about vibrational dephasing had to be recorded. In order to obtain the isotropic part of the Raman spectra corresponding to C=O stretching vibration in benzaldehyde, both the polarised (I_{VV}) and depolarised (I_{VH}) components were measured separately by placing an analyzer in the path of the scattered radiation. The instrumental set up was put in an appropriate condition for polarisation measurements. For this purpose, three test runs were taken for CCl_4 by scanning the 185—350 cm^{-1} range for both the polarised (I_{VV}) and depolarised (I_{VH}) components of the Raman intensity. During the test runs, the Raman spectra were recorded with a data step size of 0.2 cm^{-1}, an integration time of 0.5 second and a spectral slit width of 2 cm^{-1}. The polarisation of the incident laser light was carefully adjusted so as to produce a depolarization ratio (I_{VH}/I_{VV}) of 3/4 for the bands of CCl_4 at 215 and 314 cm^{-1}, which are depolarised Raman lines. The I_{VV} and I_{VH} components of the Raman-scattered intensity were subsequently recorded without altering the slit setting or disturbing the polarization.

The intensity of the isotropic (I_{iso}) and anisotropic (I_{aniso}) components were calculated using the standard formula,[8]

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

and

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

The spectral slit width used for the Raman spectra was ca 2 cm^{-1}. No finite slit width corrections are required, since the line width is large compared with the slit width (slit width <0.25× apparent band width).

Regarding the accuracy of measuring the band width and isotropic frequency shift, we followed the method of Schwartz et al.[9] Each spectra were recorded three times; the values of the band width (full width at half maxima) shown in Table 1 represent the average of three runs. The standard deviations for the three runs were typically 0.1—0.2 cm^{-1}. However, a reasonable error estimate for the FWHM presented in Table 1 is 0.5 cm^{-1}.

Results and Discussion

The benzaldehyde molecule has been studied by Yarwood and Arndt,[10] who observed that the I_{VV} component of the C=O stretching mode gives an asymmetric shape, whereas the I_{VH} component is almost symmetric with its maximum shifted to higher wavenumbers. For a 98 mole percent dilution of benzaldehyde in a carbondisulfide solvent the I_{VV} component narrows to a symmetric band, and its peak frequency coincides with the I_{VH} component. The asymmetry of the I_{VV} component (or anisotropy shift) is explained as being due to transition dipole–transition dipole (TD–TD) interactions. Upon dilution, the effects of a resonant transfer of vibrational energy due to TD–TD interactions on the band shape are reduced as the benzaldehyde molecules become separated. Isotopic dilution studies of benzaldehyde in benzaldehyde-d_6 show that with increasing dilution the anisotropy shift decreases from about 4.5 to 1 cm^{-1} in the most dilute solution.[10]

Table 1. Peak Frequencies, and FWHM[a] in Solutions

Solvent	Dipole moment μ Debye	Isotropic frequency shift ν_{iso} cm^{-1}	FWHM[a] Γ_{iso} cm^{-1}
C_6H_{12}	0.00	1709.0	11.44
CCl_4	0.00	1708.5	12.94
C_6H_6	0.00	1706.5	9.95
$C_6H_5CH_3$	0.36	1707.0	11.94
C_6H_5Cl	1.69	1706.5	9.45
CH_2Cl_2	1.60	1705.5	9.95
CH_3CN	3.92	1704.0	9.95
$CHCl_3$	1.01	1703.5	10.45

a) FWHM: Full width at half maxima.

Here, we carried out a detailed study of the anisotropy shift (non-coincidence effect), isotropic frequency shift and line width of the C=O stretching band of benzaldehyde in solvents of varying physico-chemical constants as a function of the concentration and solvents used.

Effect of the Concentration on Non-Coincidence Effect: The anisotropy shift (or non-coincidence effect) has been related, to a first approximation, to the permanent dipoles of the dissolved molecules. It has been shown that an anisotropy shift is caused by a resonant-energy transfer due to TD–TD interactions. This assumption is supported by the experimental results as the anisotropy shift decreases with increasing concentration of the solvent, irrespective of the nature of the solvent (Fig. 2).

Solvent Dependent Isotropic Frequency Shift: Table 1 shows the coinciding values of the peak frequencies for the isotropic and anisotropic parts of the band extrapolated to infinite dilution in the given solvent. The maximum shift, with respect to a pure liquid, decreases with increasing polarity of the solvent, which 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 the solvent molecules. The relatively small frequency shift in benzene (compared to other non-polar solvents) may be interpreted by assuming the specific interaction possibilities of benzene resulting from its delocalized π-electron cloud. $CHCl_3$ forms hydrogen bonds with the C=O group, which leads to a very small shift.

The shift of the isotropic band to higher frequencies with respect to pure benzaldehyde indicates that attractive forces play an important role in determining a solvent-induced vibrational frequency shift.[6,11] The dipolar forces are negligible in the case of dilute solutions (especially in the case of non-polar solvents); since the induction forces are very weak it is the dispersion force which accounts for any variation of the frequency shifts in different solvents. It has been shown 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-chloro-benzaldehyde.[12] In this report we try to make a

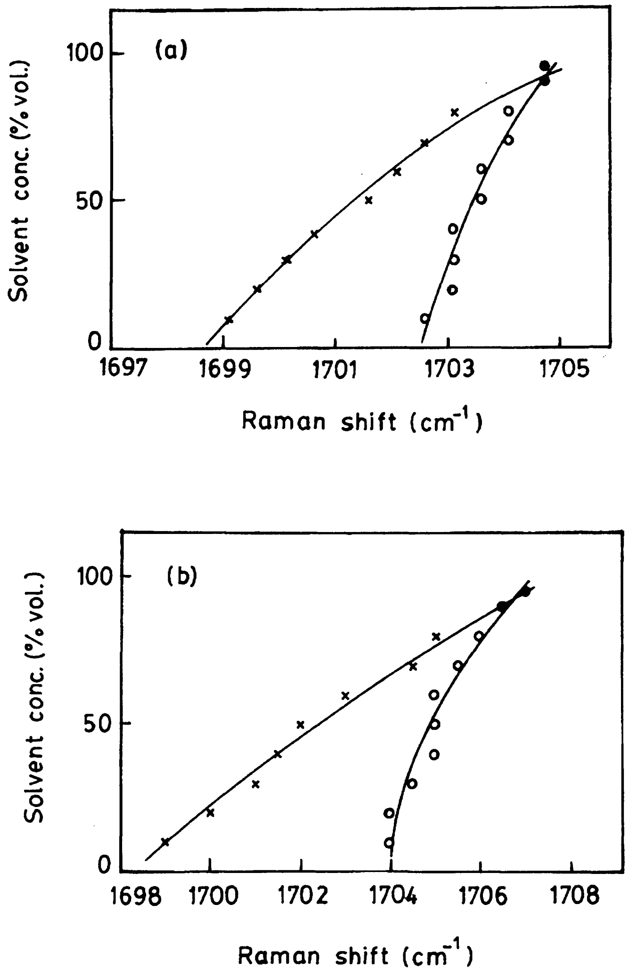

Fig. 2. The variation of isotropic (×) and anisotropic (O) maximum frequencies as a function of solvent (s) concentration. Solvents: (a) CH_2Cl_2 and (b) C_6H_6.

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 benzaldehyde under the condition of a high-dilution (10% sample concentration) in the eight solvents mentioned above. The molecular parameters of these solvents are summarized in Table 2. The dispersion force is given by[13,14)]

$$U_{dis} = -\frac{3}{2n^4}\frac{I_1I_2(\alpha_1\alpha_2)}{(I_1+I_2)}\frac{1}{R_{ij}^6} = -\frac{C}{R_{ij}^6}, \tag{3}$$

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 molecules. The values of the dispersion energy parameter (C) for benzaldehyde (solute) in different solvent systems are summarized in Table 3. From the variation of ν_{iso} with C (Fig. 3), it is clear that also in the case of benzaldehyde 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 earlier, this may be due to the fact that $CHCl_3$ forms hydrogen bonds with the C=O dipole of benzaldehyde. This leads to a large red shift relative to the gas frequency, although the effect of screening should lead to a shift to a higher frequency. The correlation coefficient (R) for ν_{iso} vs. C plots was calculated to be 0.70. However, if we neglect the data point corresponding to $CHCl_3$, the correlation coefficient becomes 0.97, which shows a statistically significant dependence of ν_{iso} on C.

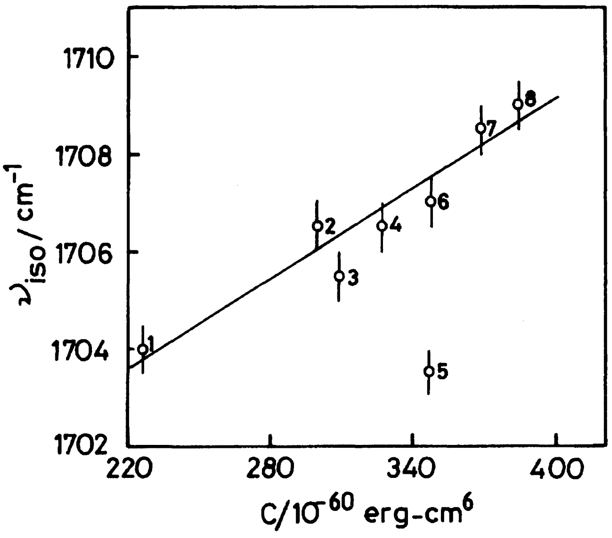

Fig. 3. Variation of the peak frequencies of the isotropic component (ν_{iso}) as a function of dispersion energy parameter (C) in (1) CH_3CN, (2) C_6H_6, (3) CH_2Cl_2, (4) C_6H_5Cl, (5) $CHCl_3$, (6) $C_6H_5CH_3$, (7) CCl_4, and (8) C_6H_{12} solvents.

Solvent Dependence of Dephasing Time: A large number of theories have been proposed to treat various aspects of dephasing phenomena.[15—18)] However, no unified quantitative theory that simultaneously predicts the role of various forces in determining the density, temperature, and solvent dependence of the dephasing of polyatomic molecules in liquids exists. The general conclusion is that the attractive forces play an important role in dephasing phenomena. To understand this dephasing process, line-width measurements may be of considerable value. For an isolated transition, phase relaxation leading to a broadening of the isotropic Raman spectral component arises mainly due to lifetime broadening, pure dephasing and a resonant-energy transfer. However, in the case of a dilute solution, the most important contribution to line broadening is generally considered to be from pure dephasing. 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 Γ_{iso} is the FWHM of the isotropic component of the Raman band and c is the velocity of light.

In order to have a better picture of the phase relaxation in associated liquid (under the condition of high

Table 2. Molecular Parameters of Various Solvents[a)]

Solvent	Refractive index n	Density ρ	Viscosity[c)] η	Polarizability[b)] α	Ionization potential I
		g cm^{-3}	cP	10^{-24} cm^3	10^{-12} erg
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
$C_6H_5CH_3$	1.4961	0.8669	0.590	12.30	14.11
C_6H_5Cl	1.5241	1.1058	0.799	12.35	14.51
C_6H_5CHO	1.5463	1.0415		12.80[b)]	15.23

a) Ref. 23. 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 =0.01 Poise.

Table 3. Solute–Solvent Dispersion Energy Parameter 'C' and 'f_m' for Various Solvent Systems, for the Sample Benzaldehyde

Solvent	Dispersion energy parameter C	f_m
	10^{-60} erg cm^6	10^{-2} g m^{-2} cm^{-4} s^{-1}
C_6H_{12}	383.19	1.57
$CHCl_3$	346.80	2.56
CH_2Cl_2	306.70	0.93
CCl_4	368.50	2.28
CH_3CN	225.52	0.63
C_6H_6	299.81	1.16
$C_6H_5CH_3$	345.25	0.72
C_6H_5Cl	326.54	1.20

dilution), Purkayastha and Kumar[19)] have derived a model in which the vibrational relaxation rate is shown to be function of a parameter (PK 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

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

where

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

and C_m is a constant which depends mainly on the solute properties; ρ, η, n are the density, dynamic viscosity, and refractive index of the solvent, respectively. However, hydrogen bonding and other associative factors are not included in this parameter. The concept of the microviscosity instead of the dynamic viscosity has recently been included[20)] so as to incorporate finer details of solute–solvent systems. Then, the modified PK parameter $f(\rho,\eta,n)$ takes the form

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

Here, the microviscosity (η_m) is given by

$$\eta_m = \eta\gamma = \eta[0.16+0.4(a/b)], \tag{8}$$

where γ is the microfriction parameter and a and b are the sample and solvent radii, respectively. The values of f_m for different solvent systems are given in Table 3.

Considering the different types of interactions between solute–solvent molecules viz a π–π^*/n–π^* 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 Å, the C=O bond length.

Now, in the case of a $CHCl_3$ solvent molecule, the value of the solvent radius (b) was chosen to be 1.2 Å, the van der Waal's radius for an H-atom.[20)] This is due to the fact that the hydrogen atom present in a $CHCl_3$ molecule is acidic in nature, and, hence, it may form a hydrogen bond of the type $C^-H^+\cdots O^-{=}C^+$ with the C=O dipole of the solute molecule. Other chlorinated solvents (CH_2Cl_2, CCl_4, and C_6H_5Cl) are non-hydrogen bonded systems, in which 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 Å) and the C–Cl bond distance[21)] (1.76 Å for CCl_4 and 1.77 Å for CH_2Cl_2). The value of the solvent radius (b) is 2.29 Å for CH_3CN. It represents the sum of the C–H bond length (1.09 Å) and the van der Waal's radius for the H atom (1.2 Å).

In case of the benzene molecule, b is chosen to be 1.85 Å (1/2 the 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 Å (2.0 Å, the van der Waal's radius for the CH_3 group +1.53 Å for C=C bond length).[22)]

The variation in the vibrational relaxation rate (τ_v^{-1}) as a function of f_m is shown in Fig. 4. This is clearly a linear variation; the fitting of the parameter in case of the eight solvents at 90 % solvent concentration is quite

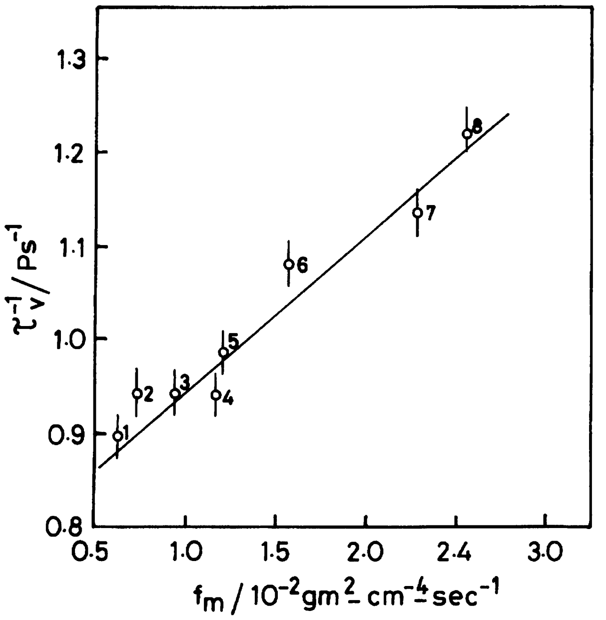

Fig. 4. Vibrational relaxation rate (τ_v^{-1}) dependence as a function of the parameter f_m for benzaldehyde in (1) CH_3CN, (2) $C_6H_5CH_3$, (3) CH_2Cl_2, (4) C_6H_6, (5) C_6H_5Cl, (6) C_6H_{12}, (7) CCL_4, (8) $CHCl_3$.

good.

The correlation coefficient (R) 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 benzaldehyde.

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