

Rotational relaxation times from Raman band profiles for benzonitrile in different solvents

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Abstract. The Raman band profiles of two vibrational bands of benzonitrile belonging to the a_1 species (2243 and 1000 cm^{-1}) were analysed by separating the isotropic and anisotropic components. Spectra of benzonitrile were recorded, using argon laser excitation, in solutions of CCl_4 , CS_2 , cyclohexane, cyclohexanol and tertiary butyl alcohol – all having different viscosities. The rotational correlation times were evaluated from the band profiles. The results indicate that (a) the isotropic (and not the anisotropic) linewidth increases with increasing viscosity, which is attributed to the greater effect of intermolecular interactions on vibrational relaxation; and (b) the two modes of the same species give different relaxation times.

Keywords. Rotational relaxation times; benzonitrile; Raman band profiles; vibrational bands; isotropic and anisotropic components.

1. Introduction

Among the techniques available for the study of molecular motions in liquids, the Raman scattering technique has the distinct advantage that it enables simultaneous analysis of both reorientational and non-reorientational processes (Naffie and Peticolas 1972). Using the depolarized spectrum of totally symmetric vibrational bands, a separation of vibrational (isotropic part) and rotational (anisotropic part) contributions to the width of the band can be made. Further, in Raman scattering, the rotational correlation function is essentially a single particle correlation function as the scattering is incoherent and pair correlation contribution to the Raman scattering intensity does not figure in it owing to the random phases of vibrational wavefunctions of different particles.

The correlation functions, $C_v(t)$ (vibrational) $C_{\text{rot}}(t)$ (rotational) and $C_s(t)$ (single particle) are given by

$$C_{\text{iso}}(t) = C_v(t) = \int_{\text{band}} I_{\text{iso}}(\omega) \exp(i\omega t) d\omega, \quad (1)$$

$$C_{\text{aniso}}(t) = C_{\text{rot}}(t) \times C_{\text{iso}}(t) = \int_{\text{band}} I_{\text{aniso}}(\omega) \exp(i\omega t) d\omega, \quad (2)$$

$$C_{\text{rot}}(t) = \frac{C_{\text{aniso}}(t)}{C_{\text{iso}}(t)}, \quad (3)$$

$$C_s(t) = C_{\text{rot}}(t) \exp \left[-t \left(\frac{1}{\tau_{\text{rot}}} - \frac{1}{\tau_{\text{iso}}} \right) \right] \quad (4)$$

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and

$$\tau_{\text{aniso}}^{-1} = \tau_{\text{iso}}^{-1} + \tau_{\text{rot}}^{-1}, \quad (5)$$

where $I_{\text{iso}}(\omega) = I_{\parallel}(\omega) - \frac{4}{3}I_{\perp}(\omega)$ and $I_{\text{aniso}}(\omega) = I_{\perp}(\omega)$, in which I_{\parallel} and I_{\perp} stand respectively for the parallel and perpendicular components of polarization of a Raman band. The above relations are based on the following assumptions (Naffie and Peticolas 1972):

- (i) The vibrational and rotational correlation functions are statistically independent, as given by the product form of these in (2).
- (ii) The correlation functions of both the isotropic and anisotropic parts have the same form of time dependence, namely, exponential decay functions, which implies that

$$e^{-t/\tau_{\text{aniso}}} = e^{-t/\tau_{\text{iso}}} e^{-t/\tau_{\text{rot}}}. \quad (6)$$

- (iii) The band shapes are Lorentzian which implies exponential correlation function in (ii) above and which implies

$$(\Delta\omega_{1/2})_{\text{aniso}} = (\Delta\omega_{1/2})_{\text{iso}} + (\Delta\omega_{1/2})_{\text{rot}}. \quad (7)$$

- (iv) The rotational diffusion constant for rotation of the symmetry axis is given by $D_{\perp} = 1/6\tau$.

The present work is based on the application of the above considerations to the Raman bands of benzonitrile taken in different solvents.

2. Experiment

The Raman spectra were recorded using a Jobin-Yvon Ramanor HG.2S, spectrophotometer. The exciting source used was an argon-ion laser, Coherent Innova model 70, with 4W maximum power operating at 4800 Å and 5145 Å. The spectral slit width was less than 2 cm^{-1} , and the slit effect was corrected according to the equation (Tanabe and Hiraishi 1980a)

$$\delta_t = \delta_a [1 - (S/\delta_a)^2], \quad (8)$$

where δ_t , δ_a and S are the true (corrected) line width (full width at half height, FWHH), the apparent (observed) line width and the spectral width, respectively. The scanning speed was 5 cm^{-1} per minute, and chart speed was 2 or 5 cm^{-1} per minute. A polarizer was placed in the path of the incident beam and also in the scattered beam. The parallel $I_{\parallel}(\omega)$ and perpendicular $I_{\perp}(\omega)$ components were thus recorded independently. The spectra were recorded with slit widths ranging from 150 to 200μ . Spectra of benzonitrile were recorded in solutions of CCl_4 , CS_2 , cyclohexane, cyclohexanol and tertiary butyl alcohol (TBA), having different viscosities.

All solutions used in this work were prepared using 1 ml by volume of each solvent and ten percent by volume of each solute. The benzonitrile bands studied were the totally symmetric vibrations 2243 and 1000 cm^{-1} , with a small depolarization factor. For the analysis, the high frequency side of each band of the solute in a given solvent was folded to give a symmetric peak.

3. Results and discussion

(i) The normalized intensity distribution $I_{iso}(\omega)$ and $I_{aniso}(\omega)$ for the isotropic and anisotropic components of the benzonitrile 2243 cm^{-1} ($C \equiv N$) stretch band are given in figures 1 and 2 and those for the 1000 cm^{-1} (ring breathing) band in figures 3 and 4 in the various solvents. The solvents have been chosen in such a way that the solvent bands do not interfere with solute bands.

(ii) In figures 5 and 6, the rotational correlation function $C_{rot}(t)$ is plotted as a function of t for the above two bands in different solvents. The solvent viscosities η are indicated against each plot.

(iii) The half-widths $\Delta\omega_{1/2}$ of the bands for the isotropic and anisotropic components and the difference between the two which gives $(\Delta\omega_{1/2})_{rot}$ as per (7) are given for various solvents in table 1.

(iv) The τ_{rot} values calculated from $(\Delta\omega)_{1/2}$ and from the $1/e$ th value of $C_{rot}(t)$ at $t = 0$ are listed in table 2, together with the rotational diffusion constant (D_{\perp}) for all the solvents.

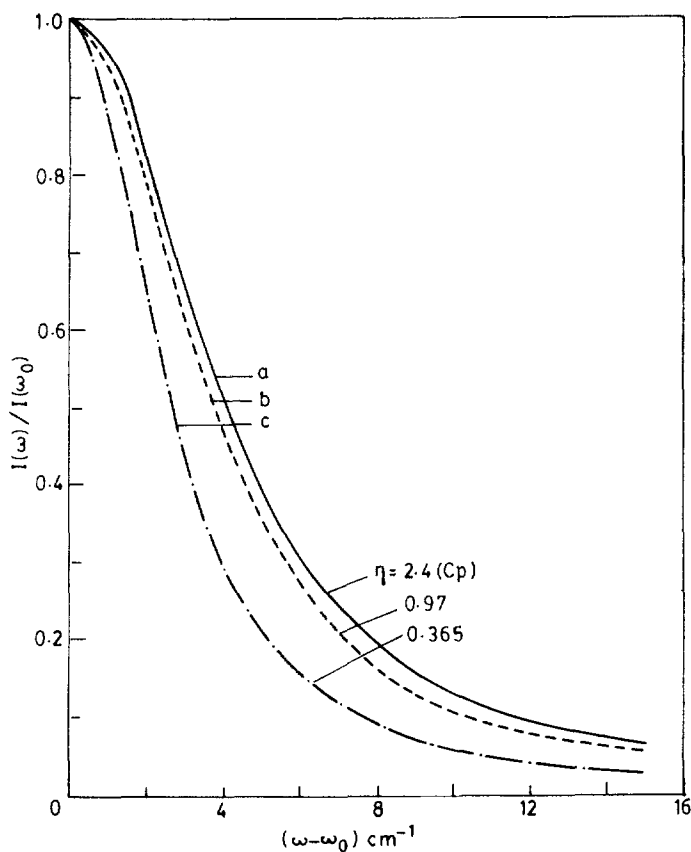


Figure 1. Normalized line shapes of $I_{iso}(\omega)$ for the 2243 cm^{-1} band of benzonitrile in (a) TBA, (b) CCl_4 and (c) CS_2 .

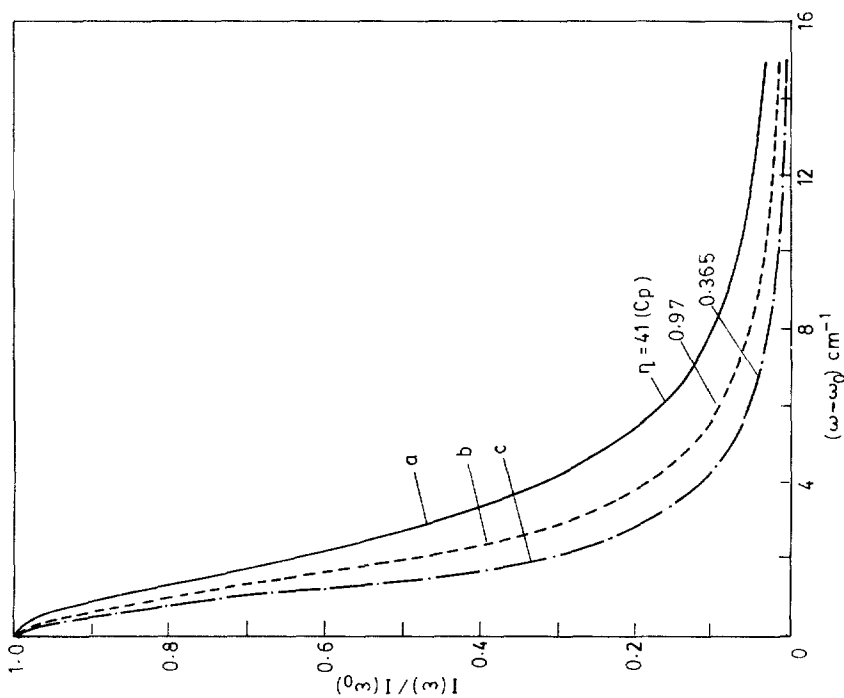


Figure 2. Normalized line shapes of $I_{anisotropic}(\omega)$ for the 2243 cm^{-1} band of benzonitrile in (a) TBA, (b) CCl_4 and (c) CS_2 .

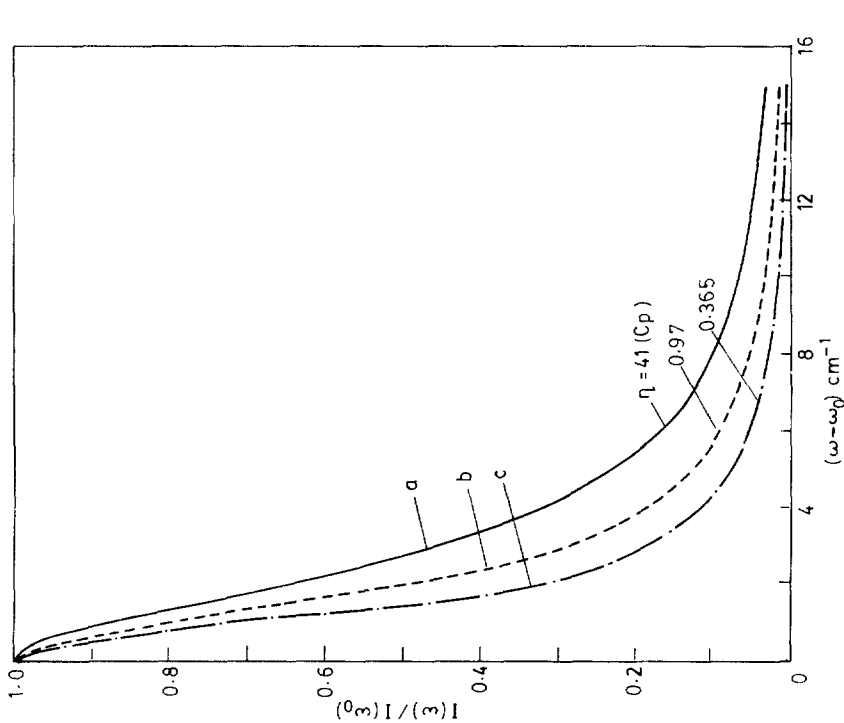


Figure 3. Normalized line shapes of $I_{anisotropic}(\omega)$ for the 1000 cm^{-1} band of benzonitrile in (a) cyclohexanol, (b) CCl_4 and (c) CS_2 .

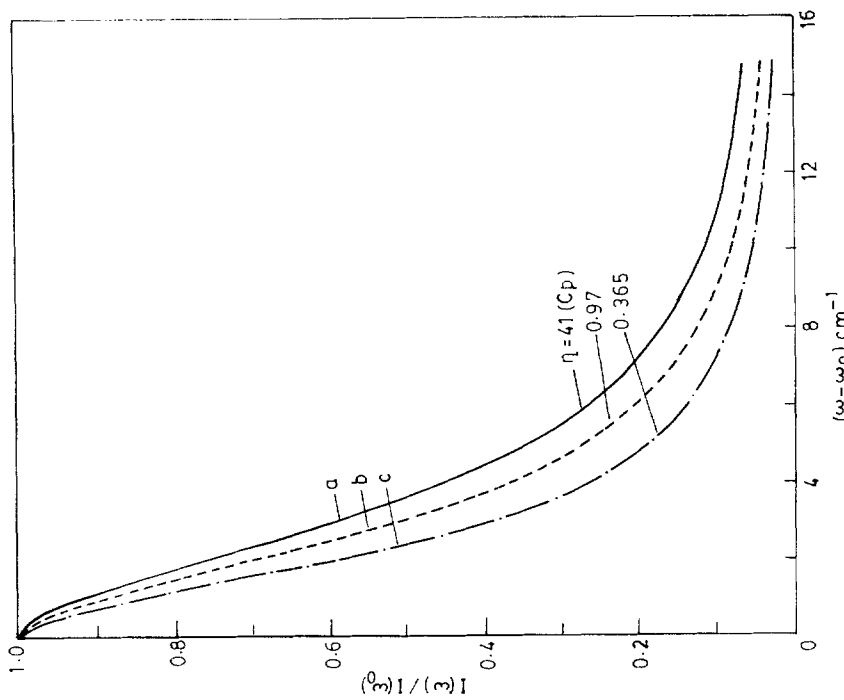


Figure 4. Normalized line shapes of $I_{\text{aniso}}(\omega)$ for the 1000 cm^{-1} band of benzonitrile in (a) cyclohexanol, (b) CCl_4 and (c) CS_2 .

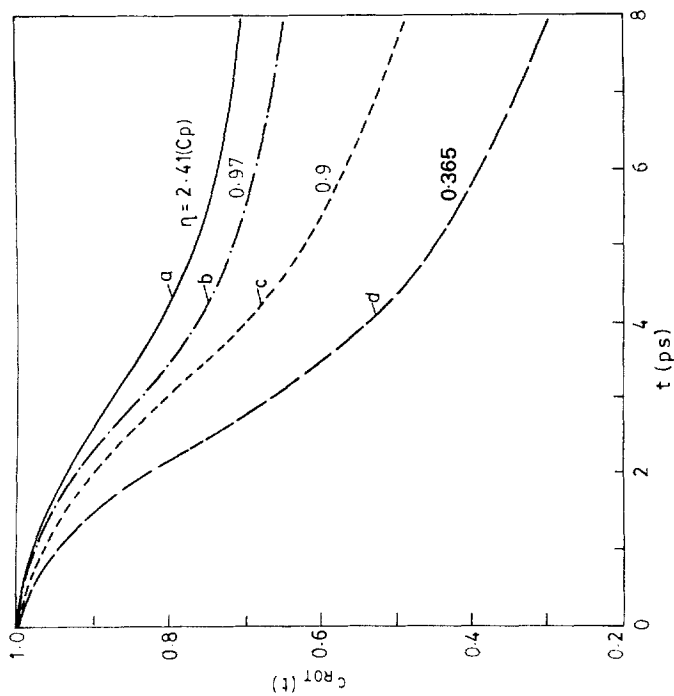


Figure 5. The plots of the $C_{\text{rot}}(t)$ for the 1000 cm^{-1} band of benzonitrile in (a) TBA, (b) CCl_4 , (c) cyclohexane and (d) CS_2 .

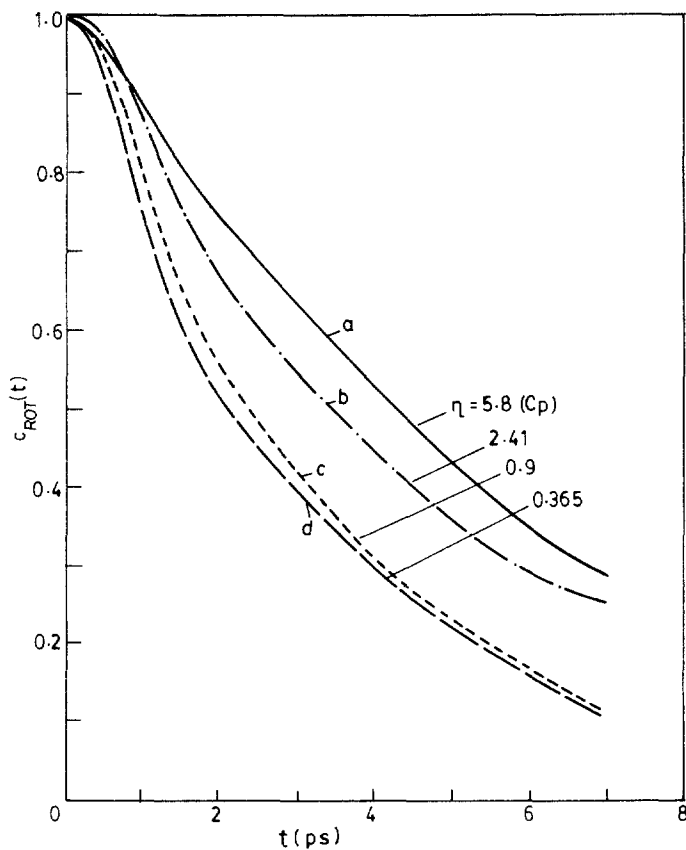


Figure 6. The plots of the $C_{rot}(t)$ for the 2243 cm^{-1} band of benzonitrile in (a) benzyl alcohol, (b) TBA, (c) cyclohexane and (d) CS_2 .

Table 1. Halfwidths of Raman bands of benzonitrile in different solvents. All values in cm^{-1} .

Solvents	2243 cm^{-1}			1000 cm^{-1}		
	$\Delta\omega_{\text{aniso}}$	$\Delta\omega_{\text{iso}}$	$\Delta\omega_{\text{rot}}$	$\Delta\omega_{\text{aniso}}$	$\Delta\omega_{\text{iso}}$	$\Delta\omega_{\text{rot}}$
CS_2	7.75	6.00	1.75	1.88	1.37	0.51
Cyclo-hexane	7.75	6.25	1.50	1.98	1.53	0.45
CCl_4	8.25	7.00	1.25	2.21	1.83	0.38
TBA	9.75	8.68	1.07	2.44	2.10	0.34
Benzyl alcohol	10.50	9.50	1.00	—	—	—
Cyclo-hexanol	10.75	10.00	0.75	2.88	2.58	0.30

Table 2. τ_{rot} in units of 10^{-12} s and D_{\perp} in units of 10^{12} s $^{-1}$ for benzonitrile in different solvents.

Solvents	2243 cm $^{-1}$			1000 cm $^{-1}$		
	τ_{rot} calculated from FWHH	Diffusion constant D_{\perp}	τ_{rot} calculated from 1/eth of C_{rot}	τ_{rot} calculated from FWHH	Diffusion constant D_{\perp}	τ_{rot} calculated from 1/eth of C_{rot}
CS $_2$	3.03	0.0550	4.37	10.40	0.0160	10.85
Cyclo-hexane	3.54	0.0471	4.77	11.79	0.0141	15.97
CCl $_4$	4.24	0.0393	5.76	13.96	0.0119	17.41
TBA	4.96	0.0336	7.16	15.60	0.0107	17.98
Benzyl alcohol	5.30	0.0314	7.37	—	—	—
Cyclo-hexanol	7.07	0.0236	10.21	17.69	0.0094	23.70

The following observations and conclusions can be made from the results obtained.

- (i) Figures 1 to 4 indicate that both the isotropic and anisotropic components of the Raman bands of benzonitrile are narrow for the CS $_2$ solution and much larger for the TBA or cyclohexanol solutions, with the curves for CCl $_4$ or cyclohexane lying in-between. This trend is in conformity with the viscosities of the solvents – the higher the viscosity, the more the widening of both the isotropic and anisotropic components.
- (ii) Figures 5 and 6 indicate that the C \equiv N stretching mode at 2243 cm $^{-1}$ and the ring breathing mode at 1000 cm $^{-1}$, both belonging to the a_1 symmetry, have different correlation functions – the decay being much faster for the ring breathing mode. This happens for all the solvents. Detailed work on similar molecules is being carried out to understand why this happens.
- (iii) $C_{\text{rot}}(t)$ falls faster as the viscosity decreases.
- (iv) Table 1 shows that, in general, the isotropic line width increases as the viscosity of the solvent increases, whereas the anisotropic line width does not show significant variations. Tanabe and Hiraishi (1980b) have found similar results while studying solvent effects on chloroform. The larger variations for isotropic line widths are attributed to the increase in intermolecular interactions which affects the vibrational contribution to a greater extent than the rotational contribution.
- (v) In table 2, the τ_{rot} values obtained from the 1/eth value of $C_{\text{rot}}(t)$ at $t = 0$ are usually higher than those obtained from $\Delta\omega_{1/2}$. This shows that a strict exponential decay can not always be assumed.
- (vi) The diffusion constants D_{\perp} pertain to the rotational diffusion of the two-fold symmetry axis in benzonitrile as the bands considered, being of the a_1 species, arise from vibrations parallel to this axis.

References

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