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Light Scattering Studies of the Dynamics and Structure of Liquids

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Light scattering studies of the dynamics and structure of liquids

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The polarizability density of a liquid may be expressed in terms of an intrinsic molecular polarizability and a contribution arising from intermolecular interactions. These terms give rise to components of the light scattering spectrum with shapes determined by molecular reorientational motions and by vibrational relaxation, for the intrinsic polarizability, and by motions which alter the relative separation and orientation of molecules, for the interaction-induced term. It is argued that these contributions to the spectrum are separable, provided that the correlation functions of the intrinsic and interaction-induced polarizabilities decay on well separated timescales. The intensities of the separated spectral components give information on the liquid structure. The lineshapes enable the rates of specific single molecule and intermolecular motions to be studied. The shapes and intensities of the interaction-induced and reorientational Rayleigh and Raman spectra of CS_2 and the vibrational relaxation of I_2 and CCl_4 solutions are discussed as examples.

Introduction

The light scattering spectrum gives that information on the liquid structure and dynamics contained in the correlation function of the $\boldsymbol{k}$th Fourier component of the polarizability of the liquid (Fleury & Boon 1973):

$$I_{\alpha\beta}(\omega) \propto \int_0^\infty \mathrm{d}t \exp(-\mathrm{i}\omega t) \langle \alpha_{\alpha\beta}(\boldsymbol{k}, t)\, \alpha_{\alpha\beta}(\boldsymbol{k}, 0)^* \rangle. \tag{1}$$

Here $\boldsymbol{k}$ is the scattering vector and α and β index the polarization of the scattered and incident radiation. By combining spectra with different polarizations, the spectra of the isotropic and anisotropic components of the polarizability density may be separated (Bartoli & Litovitz 1972):

$$I^{\mathrm{an}} = I_{xz}, \tag{2}$$

$$I^{\mathrm{is}} = I_{zz} - \tfrac{4}{3} I^{\mathrm{an}}, \tag{3}$$

where the incident beam defines the x direction and is z-polarized, and the scattering is observed at 90°.

The polarizability density may be written as a sum of the intrinsic molecular polarizabilities and the contribution arising from interactions between molecules

$$\alpha_{\alpha\beta}(\boldsymbol{k}, t) = \sum_{i,\,\mathrm{mols}} \{\alpha^i_{\alpha\beta}(t) + F^i_{\alpha\beta}(t)\} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i(t)]. \tag{4}$$

The time dependences arise from the reorientational, vibrational and relative translational motions of the molecules. The expansion of the intrinsic term, $\alpha^i_{\alpha\beta} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i]$, in the coordinates of these motions is given in table 1 (*a*), together with the spectrum in which each component of the expansion may be observed. Except for the isotropic Rayleigh spectrum, the time dependence of $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i]$ is insignificant compared with that of the other coordinates, because $|\boldsymbol{k}|^{-1}$ is small compared to the range of intermolecular correlations, and is neglected.

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The expansion of $F^i_{\alpha\beta}$ in molecular coordinates is less general, depending on the nature of the molecules and (in the Raman case) the normal coordinate involved. Table 1 (b) gives the expansion for the case when the dipole – induced dipole interaction is dominant, as may be expected for most Rayleigh spectra and strongly allowed Raman spectra. Other mechanisms will be considered later.

TABLE 1(a). EXPANSION OF THE INTRINSIC POLARIZABILITY TERM $\boldsymbol{\alpha}^i \exp(\mathrm{i}\mathbf{k}\cdot\boldsymbol{r}^i)$

isotropic	anisotropic	
$\bar{\alpha} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i(t))$	$\gamma \mathscr{D}_{\alpha\beta}(\Omega^i(t))$	Rayleigh
$\bar{\alpha}' q^i(t)$	$\gamma' q^i(t) \mathscr{D}_{\alpha\beta}(\Omega^i(t))$	Raman

The terms $\bar{\alpha}, \gamma$, $(\bar{\alpha}', \gamma')$ are the molecular isotropic and anisotropic polarizabilities (derivatives), Ω^i is the orientation of molecule i, $\mathscr{D}_{\alpha\beta}(\Omega^i)$ gives the transformation from the molecule to laboratory coordinate frames, q^i is a vibrational normal coordinate of i.

TABLE 1(b). EXPANSION OF THE INTERACTION-INDUCED POLARIZABILITY $\boldsymbol{F}^i \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}^i)$

$\sum_{j\neq 1} \boldsymbol{\alpha}^i(t)\cdot\boldsymbol{T}^{(2)}(\boldsymbol{r}_{ij}(t))\cdot\boldsymbol{\alpha}^j(t)$	Rayleigh
$\sum_{j\neq 1} q^i(t)\ \boldsymbol{\alpha}^{i\prime}(t)\cdot\boldsymbol{T}^{(2)}(\boldsymbol{r}_{ij}(t))\cdot\boldsymbol{\alpha}^j(t)$	Raman

$\boldsymbol{T}^{(2)}(\boldsymbol{r}_{ij})$ is the interaction tensor $\nabla\nabla(r_{ij}^{-1})$.

The tables show the wide variety of motions which may be observed by light scattering. On substituting the expansion (4) into (1), it can be seen that the correlation functions involved in Rayleigh spectra contain both 'self' and 'distinct' terms, involving the correlation of the polarizability of molecule i with itself and with the polarizability of another molecule respectively. If the interaction between resonant vibrational normal coordinates of different molecules may be neglected (as will often be the case for modes which are not strongly infrared active in pure liquids as well as for dilute solutions) then the distinct correlation $\langle q^i q^j \rangle$ vanishes and it is found that only self terms contribute to a Raman spectrum. The study of molecular motions in liquids is thus further enriched by the possibility of separating single from many molecule correlation functions.

An important simplification of the Raman case occurs when the correlation between the reorientational motion and vibrational relaxation is neglected. That part of the anisotropic Raman spectrum arising from the intrinsic polarizability may then be written:

$$I^{\mathrm{an}}_{\mathrm{Ram}}(\omega) \propto (\gamma')^2 \int_0^\infty \exp(-\mathrm{i}\omega t)\, \langle \mathscr{D}^i_{\alpha\beta}(t)\, \mathscr{D}^{i*}_{\alpha\beta} \rangle\, \langle q^i(t)\, q^i \rangle. \tag{5}$$

The vibrational correlation function may be found from $I^{\mathrm{is}}_{\mathrm{Ram}}$ so that the single molecule reorientational spectrum may be obtained. Although always assumed in Raman work to date, neglect of the vibration–reorientation correlation is certainly not justified when strong intermolecular vibration–vibration interaction is present (Lynden-Bell 1977; Hills & Madden 1978) and is also suspect unless intermolecular motions (determining the rate of change of the force on the normal coordinate) are rapid compared with reorientation.

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The interaction-induced contribution to the intensity

When (4) is substituted into (1) four terms are found; for example, for the particular case of the anisotropic Raman spectrum:

$$I^{\mathrm{an}}_{\mathrm{Ram}}(\omega) \propto \int_0^\infty \mathrm{d}t \exp(-\mathrm{i}\omega t)\{(\gamma')^2\langle \mathscr{D}^i_{xz}(t)\,\mathscr{D}^{i*}_{xz}\rangle + \langle F^{i'}_{xz}(t)\,F^{i'}_{xz}\rangle + \gamma'(\langle F^{i'}_{xz}(t)\,\mathscr{D}^i_{xz}\rangle + \langle \mathscr{D}^i_{xz}(t)\,F^{i'}_{xz}\rangle)\}\langle q^i(t)\,q^i\rangle. \quad (6)$$

It is often found, however, that the observed bandshape can be resolved into only two components, a situation analysed by Keyes *et al.* (1971). Their argument can be given a physical interpretation along the following lines. Consider the zz component of the interaction-induced polarizability of a molecule i oriented along the laboratory z direction averaged over the configurations of the neighbouring molecules (which are free except for the constraints imposed by the orientation of i). For the d.i.d. mechanism, and considering only the isotropic intrinsic polarizabilities, we have

$$\overline{F^{i'}_{zz}} = \frac{\bar{\alpha}'\bar{\alpha}}{4\pi\epsilon_0}\frac{1}{2}\overline{\frac{3\cos^2\theta_{ij}-1}{r^3_{ij}}}, \quad (7)$$

where θ_{ij} is the polar angle subtended by $\boldsymbol{r}_{ij}$ with respect to the axis of i and an overbar denotes the average over the neighbour configurations. For a non-spherical molecule the average is non-zero. If, now, i reorients and the neighbour structure instantaneously adjusts to its new orientation, the i will carry $\bar{\boldsymbol{F}}$ with it as an apparent contribution to the molecular polarizability. Under these circumstances it will be convenient to resolve the instantaneous interaction-induced polarizability along the orientation of i:

$$F^i_{\alpha\beta}(t) = \frac{\langle F^{i'}_{\alpha\beta}\mathscr{D}^i_{\alpha\beta}\rangle}{\langle \mathscr{D}^i_{\alpha\beta}\mathscr{D}^i_{\alpha\beta}\rangle}\mathscr{D}^i_{\alpha\beta}(t) + \Delta F^{i'}_{\alpha\beta}(t), \quad (8)$$

where $\Delta\boldsymbol{F}^{i'}$ arises only from fluctuations in the neighbour structure. So long as the neighbour structure relaxes rapidly compared with the orientation of i, this procedure will have projected out of $\Delta\boldsymbol{F}^{i'}$ the part which is correlated with the orientation of i at previous instants. Substituting (8) into (6) we will then obtain

$$I^{\mathrm{an}}_{\mathrm{Ram}}(\omega) \propto \int_0^\infty \mathrm{d}t \exp(-\mathrm{i}\omega t)\{(\gamma'_{\mathrm{eff}})^2\langle \mathscr{D}^i_{xz}(t)\,\mathscr{D}^i_{xz}\rangle + \langle \Delta F^{i'}_{xz}(t)\,\Delta F^{i'}_{xz}\rangle\}\langle q^i(t)\,q^i\rangle, \quad (9)$$

so that the spectrum is simply the sum of a reorientational term and of a fluctuating neighbour interaction-induced term. A similar simplification is found for the isotropic spectra. The two types of contribution to the spectrum will be referred to as the 'intrinsic' and the 'interaction induced' spectra. The polarizabilities appearing in the intrinsic spectra differ from the gas phase molecular polarizabilities; for the example discussed above the effective anisotropy derivative is given by

$$\gamma'_{\mathrm{eff}} = \gamma' + \langle \mathscr{D}^i_{xz}F^{i'}_{xz}\rangle/\langle \mathscr{D}^i_{xz}\mathscr{D}^i_{xz}\rangle. \quad (10)$$

The concepts have recently been put onto a formal basis by the work of Keyes & Ladanyi (1977). By using their techniques, expressions may be derived for γ'_{eff} and the other effective polarizabilities in terms of averages over the equilibrium liquid structure. The liquid structure may thus be studied by integrated intensity measurements on the intrinsic spectra.

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The effective isotropy is found to differ little from its gas phase value so that the ratio of the anisotropic to isotropic integrated intensity, for the intrinsic spectrum, mirrors the dependence on the liquid state of the structural parameters contained in γ'_{eff}:

$$I^{\text{an}}_{\text{Ram}}/I^{\text{is}}_{\text{Ram}} = (\gamma'_{\text{eff}})^2/(\bar{\alpha}'_{\text{eff}})^2. \tag{11}$$

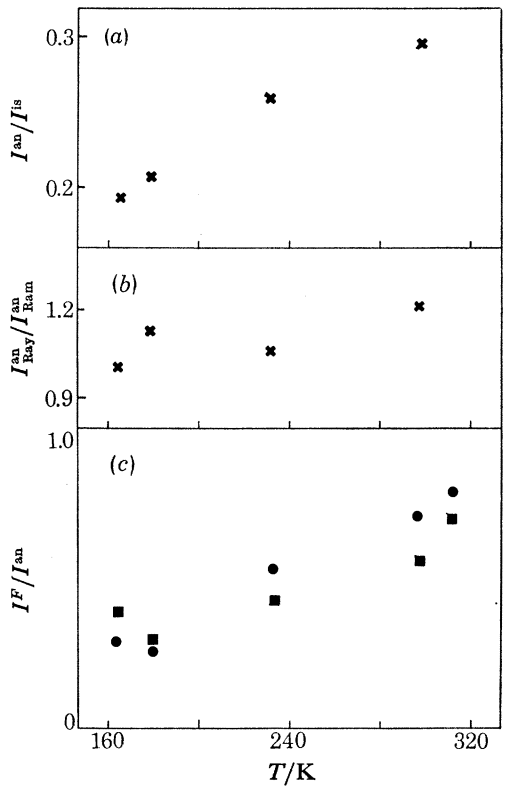

FIGURE 1. Integrated intensities for CS_2. (*a*) Ratio of Raman (ν_1) anisotropic to isotropic intensities. (*b*) Ratio of anisotropic Rayleigh to anisotropic Raman intensities. (*c*) Ratio of interaction-induced to intrinsic intensities of anisotropic spectra. ●, Rayleigh; ■, Raman.

The dominant terms in this ratio are found to be

$$I^{\text{an}}_{\text{Ram}}/I^{\text{is}}_{\text{Ram}} = (\gamma'/\bar{\alpha}')^2\,(1 + C\langle r_{12}^{-3}\rangle_2), \tag{12}$$

where $\langle r_{12}^{-3}\rangle_2$ is the mean value of the inverse cube of the intermolecular separation averaged over that component ($g_2(r_{12})$) of the pair distribution function ($g(\Omega_1, \Omega_2, \boldsymbol{r}_{12})$) which has the angle subtended by the intermolecular separation vector with respect to the axis of molecule 1 (θ_{12}) distributed as a second order Legendre polynomial, i.e.

$$\langle r_{12}^{-3}\rangle_2 = \int \mathrm{d}r_{12}\, r_{12}^2\, g_2(r_{12})\, r_{12}^{-3}, \tag{13}$$

$$g_2(r_{12}) = \int \mathrm{d}\theta_{12}\, P_2(\theta_{12}) \int \mathrm{d}\phi_{12}\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2\, g(\Omega_1, \Omega_2, \boldsymbol{r}_{12}). \tag{14}$$

Here Ω_i is the orientation of molecule i with respect to the laboratory z axis. In figure 1 (*a*) the temperature dependence of the intensity ratio for the ν_1 band of CS_2 is shown (Cox & Madden 1979).

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Since similar properties of the liquid structure affect γ'_{eff} and γ_{eff} it might be expected that their ratio is insensitive to the thermodynamic state of the liquid; this can be shown to be the case. The ratio of the anisotropic intrinsic Rayleigh and Raman integrated intensities,

$$I^{\text{an}}_{\text{Ray}}/I^{\text{an}}_{\text{Ram}} = (\gamma_{\text{eff}}/\gamma'_{\text{eff}})^2\,(1+f_2), \tag{15}$$

which is plotted in figure 1 (*b*) for CS_2, with the Raman ν_1 (Cox & Madden 1979), can then be used to follow variations in the orientational correlation parameter

$$f_2 = \frac{1}{N}\sum_{j\neq 1}\frac{\langle P_2(\Omega_1)\,P_2(\Omega_j)\rangle}{\langle P_2(\Omega_1)^2\rangle}. \tag{16}$$

The temperature dependence of $1+f_2$ is weak, in agreement with the results discussed by Flygare (this Symposium).

Provided that there is a large timescale separation between the intramolecular motions and the intermolecular motions, the spectra of these two contributions to the time dependence of the polarizability density may be separated. This leads to a dependence of the Raman and Rayleigh intensities on the thermodynamic state of the liquid.

Reorientational dynamics

When the vibrational normal coordinates of different molecules are uncorrelated, the anisotropic Raman spectrum may be used to study reorientational motions. For many liquids, especially when interest is confined to the region out to a few half widths from the band centre, the following assumptions may be made: the vibration–reorientation interaction is negligible, vibrational relaxation takes place in the fast modulation limit (discussed in the next section) and the reorientational process is diffusional. The intrinsic Raman lineshapes then take the simple forms (Hills & Madden 1978):

$$I^{\text{is}}_{\text{Ram}}(\omega) \propto \Delta/((\omega-\omega_0)^2+\Delta^2), \tag{17}$$

$$I^{\text{an}}_{\text{Ram}}(\omega) \propto (\Delta+\tau_{\text{s}}^{-1})/((\omega-\omega_0)^2+(\Delta+\tau_{\text{s}}^{-1})^2), \tag{18}$$

where ω_0 is the mode frequency, Δ a vibrational relaxation frequency and τ_{s} is the correlation time for reorientation of a single molecule:

$$\tau_{\text{s}} = \int_0^\infty \mathrm{d}t\langle \mathscr{D}^1_{xz}(t)\,\mathscr{D}^1_{xz}\rangle/\langle|\mathscr{D}^1_{xz}|^2\rangle. \tag{19}$$

The term τ_{s} can be found from the difference of the anisotropic and the isotropic linewidths. Under the same rotational diffusion condition the intrinsic anisotropic Rayleigh spectrum is also Lorentzian, with a width given by the inverse decay time of the many molecule reorientational correlation function, which includes both self and distinct orientational correlation

$$\tau_{\text{m}} = \int_0^\infty \mathrm{d}t\sum_j \langle \mathscr{D}^1_{xz}(t)\,\mathscr{D}^j_{xz}\rangle/\sum_j \langle \mathscr{D}^1_{xz}\,\mathscr{D}^j_{xz}\rangle. \tag{20}$$

The assumptions used in obtaining these expressions are found to be appropriate to the description of the ν_1 Raman band of CS_2 (Cox & Madden 1979). In figure 2 (*a*) the value for τ_{s}, obtained from Raman ν_1, is compared with a value from n.m.r. (Speiss *et al.* 1971) relaxation measurements. (The close agreement between these two sets of results would have been

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lost if the interaction-induced background had not been subtracted from the spectra before the fit to (18) was made.)

The difference between τ_s and τ_m in figure 2(*a*) is experimentally significant (as they were obtained by using identical instruments and fitting procedures). The ratio of these times is given by (Keyes & Kivelson 1972)

$$\tau_s/\tau_m = (1+j_2)/(1+f_2), \tag{21}$$

where j_2 is a parameter that vanishes unless the angular velocities of different molecules are correlated. The temperature dependence of the ratio is shown in figure 2(*b*) and, in view of the insensitivity to temperature of f_2 discussed in the last section, appears to show that j_2 is non-zero.

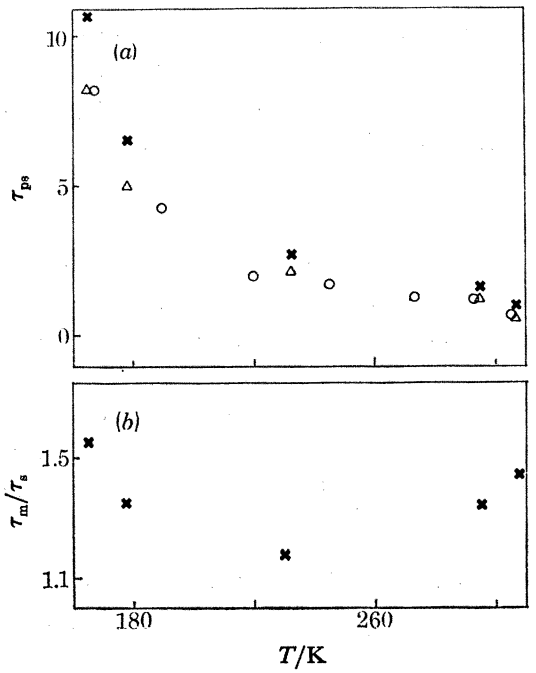

FIGURE 2. Reorientational dynamics for CS_2. (*a*) △, τ_s Raman (ν_1); ○, τ_s n.m.r.; ×, τ_m Rayleigh. (*b*) τ_m/τ_s.

VIBRATIONAL RELAXATION

The shape of the isotropic intrinsic Raman spectrum, in the absence of intermolecular vibrational interactions, is determined by the correlation function $\langle q^i(t)\, q^i\rangle$. The oscillator–medium interaction has two effects: the oscillator exchanges energy with the medium and the oscillator frequency is modulated. The line broadening can be explained by analogy with radio, the two effects being amplitude modulation (a.m.) and frequency modulation (f.m.) of the oscillator. The Raman spectrum in the absence of interactions occurs at a sharp (carrier) frequency; in the liquid the signal is broadened in a way characteristic of the a.m. and f.m. processes.

Consider a probe molecule i with a harmonic normal mode (frequency ω_0) whose interaction with the molecules of the liquid gives a potential V. The oscillator–medium interaction may be represented by

$$V_{\text{o.m.}} = V' q^i + \tfrac{1}{2} V'' q^{i2}. \tag{22}$$

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The probe may be thought of as 'jumping' between 'sites' in the liquid, each characterized by different values of V' and V'', with a time constant τ_j. (The 'sites' and 'jumps' are only a semantic convenience to describe the fluctuations in neighbour structure.) The time duration of the scattering event is the reciprocal of the bandwidth (Δ); if

$$\Delta^{-1} \gg \tau_j, \tag{23}$$

the probe will sense many sites during the observation (this is the fast modulation condition mentioned in the last section). In this limit the lineshape may be found from perturbation theory to be given by (Madden & Lynden-Bell 1976)

$$I^{is}_{Ram}(\omega) \propto \Delta/((\omega-\omega_0)^2+\Delta^2), \tag{24}$$

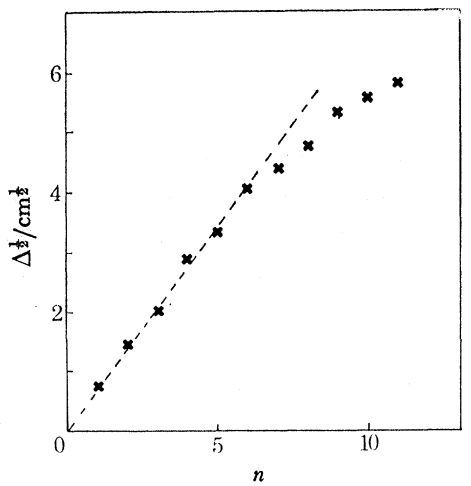

FIGURE 3. Isotropic linewidths (square root) for the overtones of I_2/CCl_4 against overtone order n.

where, for the nth overtone ($n = 1$ for the fundamental),

$$\Delta = n\Delta_{a.m.} + n^2\Delta_{f.m.}, \tag{25}$$

with $\Delta_{a.m.}$ and $\Delta_{f.m.}$ the contributions arising from the a.m. and f.m. processes:

$$\Delta_{a.m.} \propto \int_0^\infty dt \exp(-i\omega_0 t)\langle V'(t)V'\rangle = \langle V'^2\rangle/(\tau_j\omega_0^2), \tag{26}$$

$$\Delta_{f.m.} \propto \int_0^\infty dt \langle V''(t)V''\rangle = \langle V''^2\rangle\tau_j. \tag{27}$$

Notice that the a.m. process requires power in the V' spectrum at the oscillator frequency ω_0.

To investigate the relative importance of the a.m. and f.m. processes it is convenient to make use of the fact that long overtone progressions are observed in resonance Raman scattering (Kiefer & Bernstein 1973; Battaglia & Madden 1978). The resonance Raman linewidth has been shown to be determined by the relaxation of the molecule in its electronic ground state, and hence by the same processes as for the off resonance case (Madden & Wennerström 1976). A plot of the square root of the width against overtone order n is shown in figure 3 for a 10^{-2} M I_2/CCl_4 solution. It is clear from this figure (see equation (25)) that the f.m. process is dominant, the unimportance of the (presumably) larger V' term in equation (22) in the broadening is

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because the site jump frequency is so small relative to ω_0 that there is no power to drive the energy relaxation.

At high n, the quadratic dependence of bandwidth on n breaks down. This arises because the fast-modulation condition used to derive equation (25) is violated. Since Δ^{-1} (the observation time) is decreasing as n^{-2} the condition (23) must eventually fail. It then becomes more appropriate to describe the observation as made on a molecule at a single site (the slow modulation limit). The observed spectrum is then a superposition of site spectra and its shape is determined by the probability of obtaining a given value of the site shift V''. Typically, the spectrum is Gaussian with a width which varies linearly with n (Battaglia & Madden 1978). The changeover from n^2 to n behaviour occurs roughly when $\Delta \sim \tau_j^{-1}$ (Battaglia & Madden 1978), i.e. (from (27)) when $n^2\langle V''^2\rangle \tau_j \approx \tau_j^{-1}$. Consequently, from the width for $n = 1$ and at the changeover point the jump time (*ca.* 5×10^{-13} s) and r.m.s. site frequency shift $\langle V''^2\rangle^{\frac{1}{2}}$ (*ca.* 4 cm^{-1}) may be determined.

Interaction-induced spectra

It was shown earlier that a Rayleigh or allowed Raman line will have a background due to the modulation of the d.i.d. polarizability by the fluctuations in the local liquid structure. For a u symmetry mode of a centrosymmetric molecule the intrinsic polarizability derivative vanishes and the whole Raman spectrum is interaction-induced, the fluctuations destroying the molecular inversion symmetry.

The mean square amplitude of these fluctuations may be monitored by comparing the integrated intensities of the interaction-induced and intrinsic components of a band. Such a comparison is shown in figure 1 (*c*) for the Rayleigh and Raman ν_1 anisotropic spectra of CS_2. The intrinsic isotropic Raman linewidth also depends on the mean square amplitude of the fluctuation of a function of the intermolecular coordinates (equation (27)). The width of the ν_1 isotropic spectrum of CS_2 shows a similar temperature dependence to that of the integrated intensity of the d.i.d. scattering.

To construct a theory of the lineshape for liquids of anisotropic molecules is very difficult, although a theory exists for spherical molecules, which provides some guidance (Madden 1978). In the absence of a general theory, an empirical approach to understanding the dynamical behaviour of the intermolecular coordinates must be adopted. For liquid CS_2 (Cox & Madden 1976), insight is gained from a comparison of the Raman spectra of the u symmetry ν_2 and ν_3 modes and interaction induced parts of the Rayleigh and Raman ν_1. The polarizability for the latter arises from the d.i.d. mechanism and depends on the intermolecular separation vector through the interaction tensor $\boldsymbol{T}^{(2)}(\nabla\nabla r_{12}^{-1})$. The d.i.d. mechanism cannot contribute to the polarizability derivative for ν_2 and ν_3; instead it has been proposed that the mechanism responsible for light scattering by ν_2 and ν_3 is the action of the quadrupolar field of a neighbour on the hyperpolarizability derivative (Cox & Madden 1976):

$$F_{\alpha\beta}^{i'} = \sum_{j\neq 1} q^i \beta_{\alpha\beta\gamma}^{i'} T_{\gamma\delta\phi}^{(3)}(\boldsymbol{r}_{ij})\, \Theta_{\delta\phi}^{j} \quad \text{(for } \nu_2 \text{ and } \nu_3\text{)}, \tag{28}$$

where $\Theta_{\alpha\beta}^{j}$ is a component of the quadrupole of molecule j and

$$T_{\alpha\beta\gamma}^{(3)}(\boldsymbol{r}_{ij}) = \nabla_\alpha\nabla_\beta\nabla_\gamma(r_{ij}^{-1}) \tag{29}$$

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is an interaction tensor. Note that $\boldsymbol{T}^{(3)}$ is a more rapidly varying function of r_{ij} and of the orientation of $\boldsymbol{r}_{ij}$ than is $\boldsymbol{T}^{(2)}$. If the relative translational motions of the molecules, which change the length and orientation of $\boldsymbol{r}_{ij}$, are very rapid, the lineshape of a particular band will depend only on the order of the interaction tensor involved in the induced polarizability for that band. The dependence of the interaction-induced polarizability on the orientation of the molecules with respect to $\boldsymbol{r}_{ij}$ is specific to the particular mode and polarization studied, so that if these reorientational motions were very rapid every line in the spectrum would be expected to have a different shape. The observed lineshapes at high temperature are compared in figure 4. The bands ν_2 and ν_3 are found to have the same lineshape as have ν_1 and the Rayleigh line. The spectra are found to be independent of polarization. These conclusions show that the observed lineshapes are determined by the dynamical behaviour of $\boldsymbol{r}_{ij}$ and not molecular orientation.

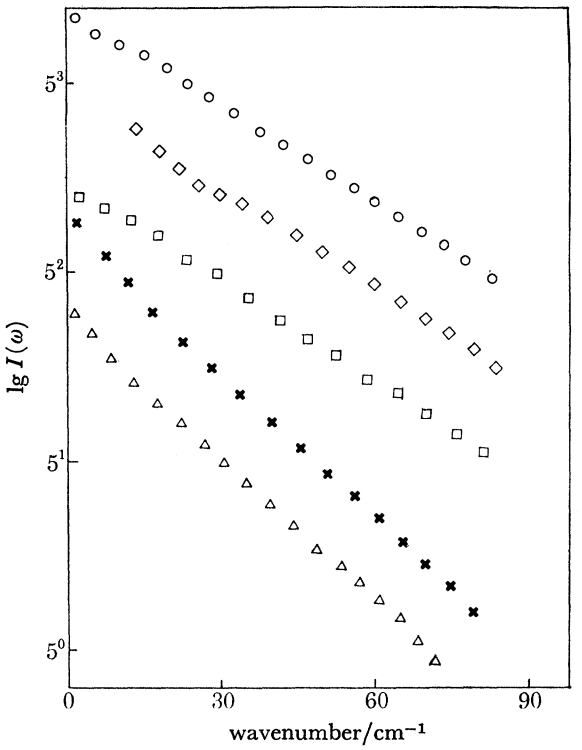

FIGURE 4. Interaction-induced spectra of CS_2 at 295 K; △, Raman (ν_1); ×, Rayleigh; ○, Raman ($\nu_2 \pi_u$); ◇, f.i.r. (Davies & Chamberlain 1973); □, Raman ($\nu_3 \epsilon_u^+$).

Since $\boldsymbol{T}^{(3)}$ is a more rapidly varying function of $\boldsymbol{r}_{ij}$ than is $\boldsymbol{T}^{(2)}$ we would expect its correlation functions to be more rapidly decaying in time, and thus that the ν_2, ν_3 spectra would be broader, as is indeed observed. Also shown in the figure is the f.i.r. (Davies & Chamberlain 1973) absorption lineshape. On the basis of the same multipole expansion used to obtain (28), the interaction-induced dipole responsible for this spectrum is given by:

$$\mu_\alpha^i = \alpha_{\alpha\beta}^i T_{\alpha\beta\gamma}^{(3)}(\boldsymbol{r}_{ij})\, \Theta_{\beta\gamma}^j. \tag{30}$$

When the translational motions dominate the time dependence of the polarizabilities, the f.i.r. lineshape should agree with the ν_2 and ν_3 lineshapes, as is found.

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Conclusion

In order to realize all the information contained in light scattering it is important to recognize the existence of the interaction-induced polarizability. In the studies described here emphasis has been on the importance of comparing the intensities and shapes of related spectra. Theoretical work should be concentrated on showing the existence of and defining the limitations for such relationships. Experimental work should be designed to draw out the similarities in the behaviour of related systems.

I should like to acknowledge the contributions of T. I. Cox (CS_2) and M. R. Battaglia (resonance Raman) to the experimental studies that I have described.

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