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On the calculation of the electric polarizability for the itinerant oscillator model

A comparison of numerical FFT techniques with approximate analytical formulae

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Estimation of the complex polarizability of the itinerant oscillator (I.O.) model of polar fluids has hitherto been based on a truncation of the series expansion of the double transcendental function describing the decay of the dipole moment. The essence of this method is to expand the decay function as a series of single transcendental functions. The resulting series is then Fourier transformed term-by-term by means of the usual response theory formula. The series is generally truncated after the first two terms so as to yield simple analytic formulae analogous to the Rocard equation. Corcoran has developed a numerical algorithm using Fast Fourier Transform techniques which allows the complex polarizability to be calculated to a high degree of precision from the decay function without recourse to any series expansion. The numerical method shows that the analytic approximations to the polarizability which have hitherto been used are quite accurate. Furthermore, if friction does not act on the inner dipole (the form of the model which has hitherto been almost exclusively used to represent spectra), it is found that the moment of inertia of the outer cage should be less than that of the inner dipole in order to achieve a good fit with the experimental data. This conclusion is inconsistent with the physical concept of the I.O., namely a dipole surrounded by a cage of neighbours, and has led to much criticism of the model. On the other hand, when friction acts on the inner dipole and is approximately the same (per unit inertia) as that acting on the outer cage, the model can produce physically realistic spectra for acceptable parameter values. This suggests that the two-friction form of the model should always be used for comparison with experimental spectra.

1. Introduction

Some years ago Calderwood and Coffey made a detailed study [1] of an itinerant oscillator model (I.O.) for molecular motion in liquids. In particular they obtained a simple analytical formula for the polarizability of such a model (equation (59) of [1]). This approach was subsequently generalized to a two-friction I.O.

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model [2, 3] that yielded results that were physically more meaningful in the sense that the observed multi-decade dielectric loss profile was more accurately reproduced. However, extensive comparison of the model with experiment has led to the surprising conclusion that the effective moment of inertia of the outer cage of the I.O. must be *smaller* than that of the inner molecule (dipole) in order to fit measured experimental data. This appears to contradict the basic physical assumptions made in the I.O. [1]. As a consequence the model has been frequently criticized in the literature [3–7].

Recently [8–10] we have given an analysis of a two-friction I.O. or Budó model which shows how the equations of motion of the system may be factorized into two independent modes of motion when the two frictions per unit inertia are equal. It has also been shown [9 (a), (b)] how the mean dipole moment may be calculated both for this particular case and the more general case of two unequal frictions and how this may be Fourier transformed numerically to yield the full polarizability of the system.

In the present work we compare the usual approximate analytic expressions for the polarizability [1, 4] with the full polarizability obtained from a numerical analysis of the system. This indicates that these analytic expressions are quite accurate. We also explain the observations of earlier workers that the outer annulus is smaller than the inner dipole [3–7]. In the light of the present paper and other recent work [8–10] it is evident that the I.O. model must be reconsidered as a useful model of liquid behaviour in the microwave (MW) and far-infrared (FIR) spectral regions.

2. Theoretical background

The basic IO model envisages a molecule of the fluid as being surrounded by a cage of nearest neighbours, supposed as far as the dynamics of the system are concerned to behave as a rigid entity. In what follows, quantities subscripted by a 2 refer to the outer dipole or cage of molecules. This notation is at variance with much of the earlier work but is consistent with [8–10]. The equations of motion of this system when friction acts upon both the dipoles are [10]

$$\ddot{\phi}_1 + \beta_1\dot{\phi}_1 + \omega_0^2(\phi_1 - \phi_2) = g_1(t), \tag{1}$$

$$\ddot{\phi}_2 + \beta_2\dot{\phi}_2 - \Omega_0^2(\phi_1 - \phi_2) = g_2(t), \tag{2}$$

where $I_1 g_1$ and $I_2 g_2$ are white noise torques,

$$\omega_0^2 = \frac{2V_0}{I_1}, \qquad \Omega_0^2 = \frac{I_1}{I_2}\,\omega_0^2.$$

Note that ϕ_1 and ϕ_2 are the angles the dipoles make with an arbitrary unit vector $\mathbf{e}$, while $I_1\beta_1\dot{\phi}_1$ and $I_2\beta_2\dot{\phi}_2$ are the frictional torques. In [9 (a), (b)] we have found it convenient to introduce the parameterization scheme

$$\hat{\alpha} = \sqrt{\left(\frac{kT}{I_1}\right)}, \quad \hat{\gamma} = \frac{V_0}{I_1\hat{\alpha}}, \quad I_r = \frac{I_2}{I_1}, \quad b = \frac{\beta_1}{\beta_2}. \tag{3}$$

where it is useful to note that

$$\omega_0^2 = 2\hat{\alpha}\hat{\gamma}, \quad \frac{V_0}{kT} = \frac{\hat{\gamma}}{\hat{\alpha}}. \tag{4}$$

Now arranging equations (1) and (2) in matrix form, as described in [1, 2, 9(b)], we find that the characteristic equation for the system is $sF(s) = 0$ where

$$F(s) = \{s^3 + \beta_2(1+b)s^2 + [\omega_0^2(1+I_r^{-1}) + \beta_2^2 b]s + \omega_0^2\beta_2(1+bI_r^{-1})\} \qquad (5)$$

and that the Laplace transform of the mean squared displacement of the inner dipole is as follows (the zeros on the angular brackets denote that the ensemble averages are evaluated in the absence of a field):

$$\mathscr{L}\{\langle(\Delta\phi_1)^2\rangle_0\} = \frac{2kT}{I_1}\,\frac{s(s+\beta_2)+\Omega_0^2}{s^2F(s)}, \qquad (6)$$

$$\Delta\phi_1 = \phi_1(t) - \phi_1(0).$$

Since $\phi_1(t)$ and $\phi_1(0)$ are gaussian random variables we have [1]

$$\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 = \tfrac{1}{2}\exp\left[-\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0\right], \qquad (7)$$

and recalling the definition of complex polarizability [11]

$$\frac{\alpha_{\mu_1}(\omega)}{\alpha'_{\mu_1}(0)} = 1 - i\omega\int_0^\infty \frac{\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0}{\langle\cos^2\phi_1(0)\rangle_0}\exp(-i\omega t)\,dt, \qquad (8)$$

it is clear that the task at hand is to Fourier transform equation (7). In their work Calderwood and Coffey [1] followed the approach adopted by Sack [12] to calculate the polarizability of a rigid rotator when inertial effects are included in the analysis.

The essence of Sack's method is to recognize that the dipole correlation function when inertial effects are included is always a double transcendental function. Such a function can only be Fourier transformed by expressing it as a series of single transcendental functions and then transforming the resulting series of single transcendental functions term by term. In general it is possible to express such a series in several different ways (see equations (3.19 A), (3.19 C) and (3.19 D) of Sack [12]). Such a series may also be expressed as a continued fraction (see equation (4.4) of Sack [12]).

Following this method, we begin by formally inverting equation (6) and inserting the results into equation (7) to obtain

$$\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 = \tfrac{1}{2}\exp[-(K_1 + K_2 t + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4 t) + K_5\exp(-\lambda_5 t)] \qquad (9)$$

where $-\lambda_3$, $-\lambda_4$ and $-\lambda_5$ are the roots of the equation $F(s) = 0$ and K_1, K_2, K_3, K_4, K_5 are the residues at the poles 0, -0, $-\lambda_3$, $-\lambda_4$, $-\lambda_5$ of equation (6). Sack's method as applied by Calderwood and Coffey [1] now requires that $\exp(-K_2 t)$ is factored out of the right-hand side of equation (9) and the remaining terms expanded in series, viz

$$\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 = \tfrac{1}{2}\exp(-K_2 t)$$
$$\times\left\{1 - (K_1 + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4 t) + K_5\exp(-\lambda_5 t)\right.$$
$$\left.+\frac{1}{2!}(K_1 + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4 t) + K_5\exp(-\lambda_5 t))^2\ldots\right\}. \qquad (10)$$

Now before we proceed to the Fourier transform of equation (10) it is useful to note the following (we will work for the moment in the s domain recalling that putting $s = i\omega$ in the resulting formulae will yield the equivalent Fourier transform or frequency domain expressions):

$$\begin{aligned} K_2 &= \lim_{s\to 0} s^2 \mathscr{L}\{\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0\} \\ &= \lim_{s\to 0}\left\{\frac{kT}{I_1}\,\frac{s(s+\beta_2)+\Omega_0^2}{F(s)}\right\} = \frac{kT}{I_2\beta_2}\,\frac{1}{1+bI_r^{-1}}. \end{aligned} \tag{11}$$

Note too that

$$\begin{aligned} \mathscr{L}\{\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0\} &= \frac{G(s)}{sF(s)} + \frac{K_2}{s^2} \\ &= \frac{sG(s) + K_2 F(s)}{s^2 F(s)}, \end{aligned} \tag{12}$$

whence with equations (5), (11)

$$\begin{aligned} G(s) &= \frac{kT}{I_2\beta(1+bI_r^{-1})} \\ &\quad \times [-s^2 - s\beta_2(1+b) - (\omega_0^2 + \Omega_0^2 + \beta_2^2 b)] \\ &\quad + \frac{kT}{I_2}(s+\beta_2) \\ &= \frac{kT}{I_2\beta_2}\,\frac{1}{(1+bI_r^{-1})} \\ &\quad \times \{-s^2 + [I_r\beta_2(1+bI_r^{-1}) - \beta_2(1+b)]s \\ &\quad + [I_r\beta_2^2(1+bI_r^{-1}) - (\omega_0^2 + \Omega_0^2 + \beta_2^2 b)]\} \\ &= \frac{kT}{I_1}\left\{\frac{-I_r^{-1}s^2}{\beta_2(1+bI_r^{-1})} + \left(1 - I_r^{-1}\,\frac{1+b}{1+bI_r^{-1}}\right)s\right. \\ &\quad \left. + \left[\beta_2 - \frac{I_r^{-1}(\omega_0^2 + \Omega_0^2 + \beta_2^2 b)}{\beta_2(1+bI_r^{-1})}\right]\right\}. \end{aligned} \tag{13}$$

The next step in this analysis is to note that

$$\begin{aligned} &\mathscr{L}\{(K_1 + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4(t) + K_5\exp(-\lambda_5 t)\} \\ &\qquad = \mathscr{L}\{\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0 - K_2 t\}. \end{aligned} \tag{14}$$

Noting that $\mathscr{L}\{K_2 t\} = K_2/s^2$, and making use of equation (12), we see that

$$\mathscr{L}\{(K_1 + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4 t) + K_5\exp(-\lambda_5 t)\} = \frac{G(s)}{sF(s)}. \tag{15}$$

It is also necessary in what follows to make use of the shifting theorem of the Laplace transform, namely (h is an arbitrary function of t)

$$\mathscr{L}\{\exp(-at)h(t)\} = H(s+a), \quad H(s) = \mathscr{L}\{h(t)\}. \tag{16}$$

Thus, ignoring all but the first two terms in the series expansion on the right-hand side of equation (10), and using equations (15) and (16), we find that

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = 1 - s\left[\frac{1}{s+K_2} - \frac{G(s+K_2)}{(s+K_2)F(s+K_2)}\right], \tag{17}$$

where K_2, G and F are defined by equations (11), (13) and (5) respectively. This is the analogous result for the two-friction model to equation (54) of Calderwood and Coffey [1] for the one-friction model.

It is theoretically possible to calculate the next term of this series for the polarizability, but in practice it becomes extremely hard because of the difficulty of expressing the residues as a function of the roots and in turn in terms of the coefficients of the equation for $F(s)$. In order to find a tractable expression for the polarizability Calderwood and Coffey [1] then simply assumed that equation (17) adequately approximated the exact polarizability. Moreover they assumed that equation (17) could be further approximated by

$$1 - s\left[\frac{1}{s+K_2} - \frac{G(s)}{(s+K_2)F(s)}\right], \tag{18}$$

so that

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = \frac{1}{s+K_2}\,\frac{[K_2F(s)+sG(s)]}{F(s)}, \tag{19}$$

$$K_2 = \frac{kT}{I_2\beta_2}\,\frac{1}{1+bI_r^{-1}}, \tag{20}$$

or

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = \frac{\left[\dfrac{kT}{I_1}\,s(s+\beta_2) + \dfrac{kT}{I_2}\,\omega_0^2\right]}{\left[s + \dfrac{kT}{I_2\beta}\,\dfrac{1}{1+bI_r^{-1}}\right]\{s^3+\beta_2(1+b)s^2 + [\omega_0^2(1+I_r^{-1})+\beta_2^2 b]s + \omega_0^2\beta_2(1+bI_r^{-1})\}}. \tag{21}$$

If $b = 0$, i.e. stochastic torques on the dipole are ignored, which is the original version of the model as described by Calderwood and Coffey [1] we find that equation (21) reduces to equation (59) of their paper, i.e.

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = \frac{\dfrac{kT}{I_1}\,s(s+\beta) + \dfrac{kT}{I_2}\,\omega_0^2}{\left(s + \dfrac{kT}{I_2\beta}\right)[s^3+\beta s^2+\omega_0^2(1+I_r^{-1})s+\omega_0^2\beta]}. \tag{22}$$

This is the formula that was used extensively by Reid [5, 6] to compare experimentally-observed spectra with the calculated ones. Equation (21) on the other hand has been used by M. W. Evans *et al.* [4, p. 506]. It should be noted that I_1 and I_2 are interchanged in this calculation in order to concur with the notation of Coffey, Corcoran and Evans [10], and Coffey, Corcoran and Vij [9(a), (b)]. As we mentioned, these simple formulae were suggested by Sack's method of deriving the Rocard equation (12). If Sack's equation (3.9 D) is truncated at the second term of the series or if his continued fraction (his equation (4.4)) is truncated at the second convergent, then one always finds that the complex polarizability in the freely-rotating disk model is well described by the (Rocard) equation

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = \frac{1}{1 + s\tau_0 + s^2 \dfrac{\tau_0}{\beta}}, \qquad \tau_0 = \frac{I\beta}{kT}. \tag{23}$$

In the present work it is shown that equation (21) closely approximates the polarizability of the I.O. so providing a simple analytic formula analogous to the Rocard equation (23).

Before proceeding we note that if $b = 1$ equation (22) becomes

$$\frac{\alpha_{\mu_1}(s)}{\alpha'_{\mu_1}(0)} = \frac{\dfrac{kT}{I_1} s(s+\beta) + \dfrac{kT}{I_2}\omega_0^2}{\left(s + \dfrac{kT}{I_2\beta}\dfrac{1}{1+I_r^{-1}}\right)(s+\beta)[s^2 + \beta s + \omega_0^2(1 + I_r^{-1})]}, \tag{23 a}$$

so that the natural frequency of oscillation Ω_N is given by (Ω_{FIR} = FIR peak frequency)

$$\Omega_N^2 = \omega_0^2(1 + I_r^{-1}) \simeq \Omega_{FIR}^2.$$

The Q factor is

$$\sqrt{(\omega_0^2(1 + I_r^{-1}))}\beta^{-1}.$$

The Debye time is

$$\tau_0 = \frac{I_2\beta}{kT}(1 + I_r^{-1}).$$

Note that the non-resonant part of (23 *a*) has the form of the Rocard equation.

3. Parametric form of the polarizability

For a comparison of the model with experimental data we are most interested in evaluating $\alpha''_{\mu_1}(\omega)$ which is proportional to the dielectric loss $\varepsilon''(\omega)$ and the power absorption coefficient $A(\omega)$. To this end equation (19) must be rearranged by writing $s = i\omega$ and separating it into real and imaginary parts. The end result of this algebraic manipulation has been given on page 506 of [4]. In terms of the parameter scheme defined by equation (3) of the present work this should be rewritten as

$$\begin{aligned} x_1 &= \frac{\hat{\alpha}^2 I_r^{-1}}{\beta_2(1 + bI_r^{-1})} = K_2, \\ x_2 &= \beta_2(1 + b), \\ x_3 &= 2\hat{\alpha}\hat{\gamma}(1 + I_r^{-1}) + \beta_2^2 b, \\ x_4 &= 2\beta_2\hat{\alpha}\hat{\gamma}(1 + bI_r^{-1}), \end{aligned} \tag{24}$$

which define

$$\begin{aligned} x &= \omega^2(\omega^2 - x_3) + x_1(x_4 - x_2\omega^2), \\ y &= \omega[x_4 + x_1(x_3 - \omega^2) - x_2\omega^2]. \end{aligned} \tag{25}$$

This allows the imaginary part of the polarizability to be simply written as

$$\frac{\alpha''_{\mu_1}(\omega)}{\alpha'_{\mu_1}(0)} = -\hat{\alpha}^2\left[\frac{\omega\beta_2 x - y(2\hat{\alpha}\hat{\gamma}I_r^{-1} - \omega^2)}{x^2 + y^2}\right], \tag{26}$$

while the real part is given by

$$\frac{\alpha'_{\mu_1}(\omega)}{\alpha'_{\mu_1}(0)} = \hat{\alpha}^2\left[\frac{x(2\hat{\alpha}\hat{\gamma}I_r^{-1} - \omega^2) + \omega\beta_1 y}{x^2 + y^2}\right]. \tag{27}$$

Power absorption spectra may also be calculated from equations (26) and (27). We first make the assumption that

$$\varepsilon''(\omega) \simeq (\varepsilon_s - \varepsilon_\infty)\frac{\alpha''(\omega)}{\alpha'(0)}. \tag{28}$$

Now, while this approximation is not always valid, it is adequate for the qualitative discussion which we shall give in the next section. The power absorption $A(\omega)$ is defined as

$$A(\omega) = \frac{\omega\varepsilon''(\omega)}{n(\omega)c}\ \mathrm{Np\,cm^{-1}} \tag{29}$$

where $n(\omega)$ is the real part of the refractive index of the dielectric material and c is the velocity of light. The $n(\omega)$ function is related to $\varepsilon(\omega)$ by [15]

$$n(\omega) = \sqrt{\left(\frac{\varepsilon'(\omega)}{2}\right)}\sqrt{\left\{1 + \sqrt{\left[1 + \left(\frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}\right)^2\right]}\right\}} \tag{30}$$

and $\varepsilon'(\omega)$ is given by [16]

$$\varepsilon'(\omega) = \varepsilon_s - \omega(\varepsilon_s - \varepsilon_\infty)\int_0^\infty \langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 \sin\omega t\, dt \tag{31}$$

So from equation (8) we see that

$$\varepsilon'(\omega) \simeq \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{\alpha'_{\mu_1}(\omega)}{\alpha'_{\mu_1}(0)}. \tag{32}$$

Note that these results are obtained by writing the exp $(-i\omega t)$ function in equation (8) as

$$\exp(-i\omega t) = \cos\omega t - i\sin\omega t$$

and then equating the real and imaginary parts of equation (8). Thus we may calculate both $\varepsilon''(\omega)$ and $\varepsilon'(\omega)$ from our approximate formula and evaluate $n(\omega)$. The power absorption spectrum may then be obtained from equation (29). Finally we should mention that our numerical method involves approximating the integral of equation (8) using the Fast Fourier Transform algorithm. The $\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0$ function may also be calculated numerically for the general two-friction case, $\beta_1 \neq \beta_2$. These methods have been detailed elsewhere [9 (a), (b)].

4. Results and discussion

The results of our analysis are illustrated in figures 1 to 5. The numerical methods used to calculate the polarizability spectrum of the I.O. have been

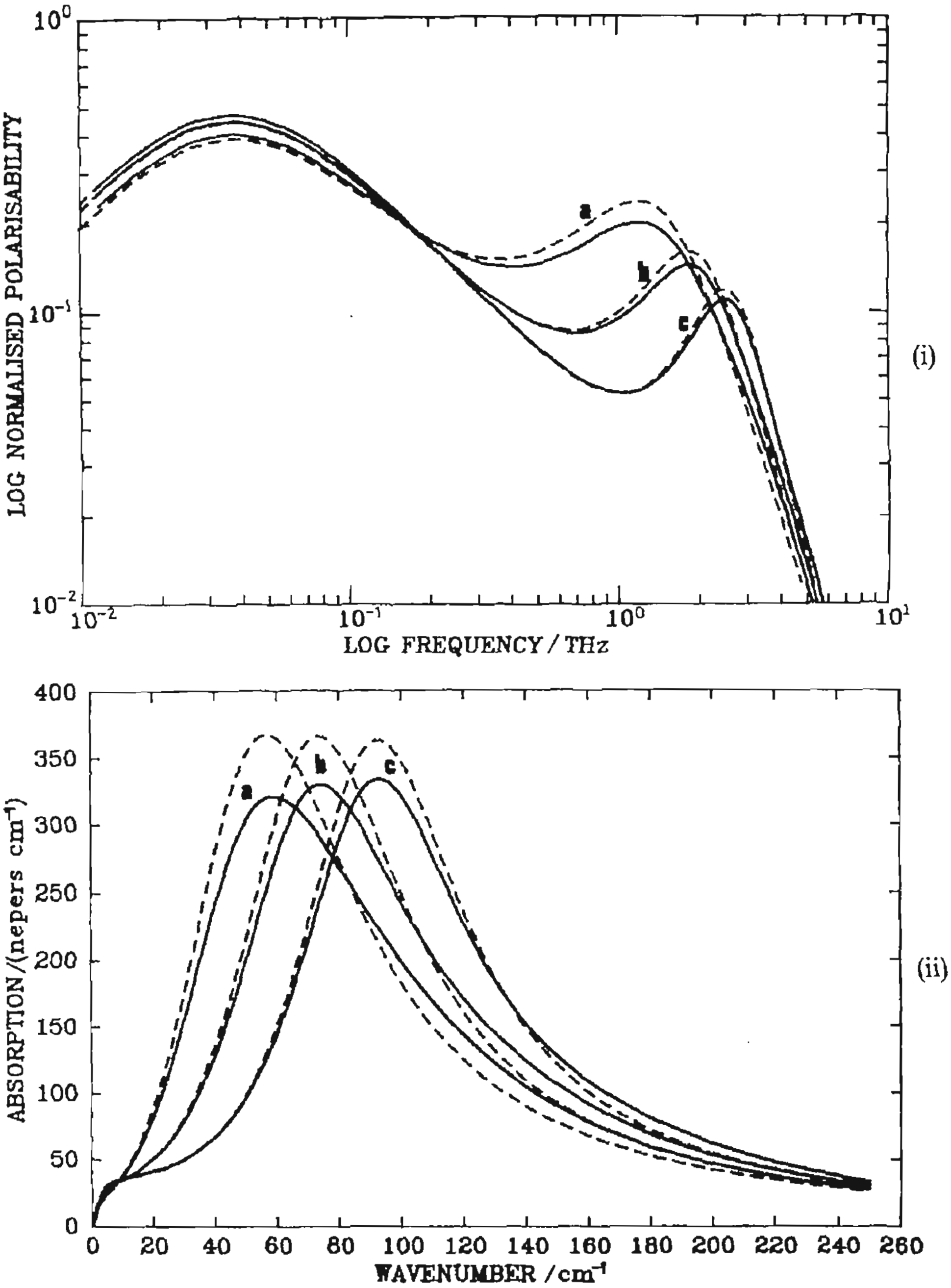
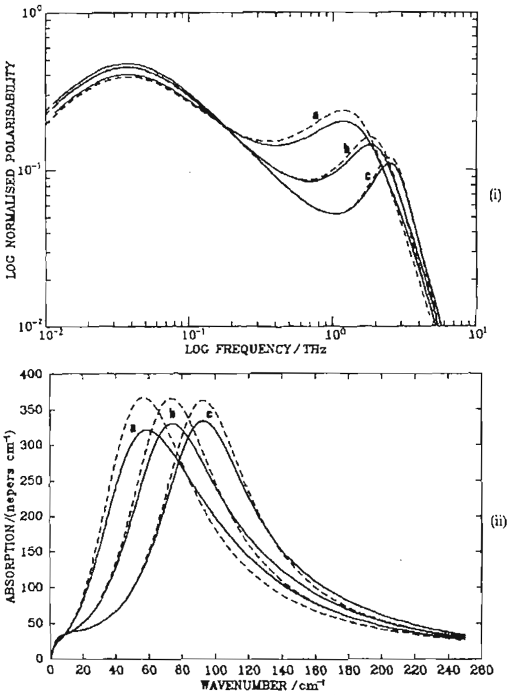


Figure 1. (i) Normalized polarizability spectra, $\alpha''_{\mu_1}(\omega)/\alpha'_{\mu_1}(0)$ for $\hat{\alpha} = 5$, $\beta = 12$, $b = 1$, $I_r = 8$ and (a) $\hat{\gamma} = 8$, (b) $\hat{\gamma} = 15$, (c) $\hat{\gamma} = 25$. The dashed lines show spectra obtained from the formulae described in § 3, while the solid lines are the results of our numerical calculations. This is the equal-frictions form of the I.O. (ii) Power absorption spectra for the same parameter values as curves (a), (b) and (c) of (i). We have taken $\varepsilon_\infty = 2$ and $\varepsilon_s - \varepsilon_\infty = 8$, for all the calculations of power absorption spectra in this paper.

described in detail elsewhere [9 (b)]. The first set of spectra we illustrate are for the $\beta_1 = \beta_2$, I.O. model and are given in figure 1 (i) (polarizability spectrum) and 1 (ii) (absorption spectrum). The dashed lines are the spectra obtained from the formulae of § 3 while the solid lines show the numerical results. In figure 2 (i), (ii), spectra are given for two intermediate values of the friction ratio b, i.e. $b = 0{\cdot}25$ and $b = 0{\cdot}75$. From these diagrams it is evident that both methods of calculating spectra for the I.O. model are in close agreement.



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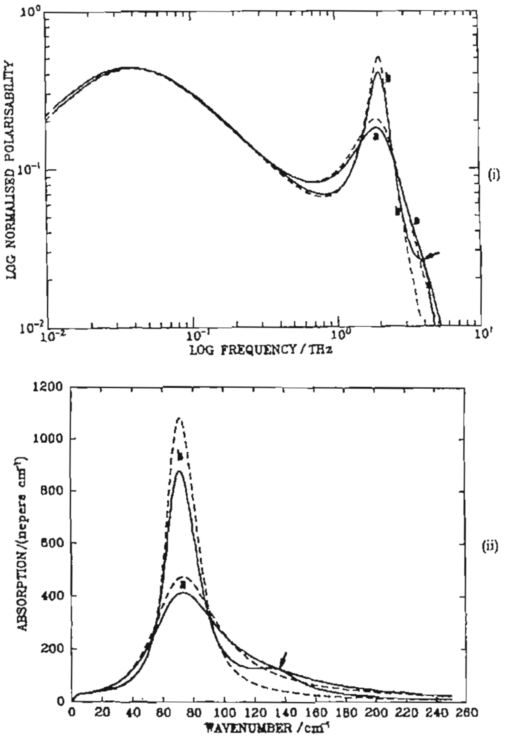

Figure 2. (i) Normalized polarizability spectra, $\alpha''_{\mu_1}(\omega)/\alpha'_{\mu_1}(0)$, for $\hat{\alpha} = 5$, $\beta = 12$, $\hat{\gamma} = 15$, $I_r = 8$ and (a) $b = 0{\cdot}75$, (b) $b = 0{\cdot}25$. Again, the dashed lines are calculated from the formulae of § 3, while the solid lines are our numerical results. Note the appearance of a second harmonic structure in this spectrum for $b = 0{\cdot}25$. Also note the sharpening of the FIR resonance peak as the friction ratio, b, is reduced. (ii) Power absorption spectra of curves (a) and (b) of (i). Note how the shoulder-like structure of (*a*) has developed into a distinct maximum. This feature is not reproduced in the spectrum calculated from the analytical formula of § 3 because the polarizability series is truncated after the first two terms.

It is interesting to remark on the occurrence of a secondary peak or shoulder which for $b = 0{\cdot}25$ is in evidence in the polarizability spectrum. The shoulder is marked by an arrow in figure 2 (i), (ii). In the absorption spectrum this feature becomes more pronounced, and indeed as the friction on the inner dipole tends to zero ($b \to 0$), a multi-peaked harmonic structure may be observed [13]. This spectral feature of the I.O. cannot be reproduced by the analytical formula given in this paper because the method by which it is derived takes only the first two terms in the relevant series expansion into account (cf. equation (10)).

The results exhibited in figures 1 and 2 clearly indicate that our analytical formula agrees closely with the results of our numerical method of calculating the spectra. Now, in conjunction with other recent work [9 (a), (b)], it would seem that the I.O. does in fact offer a reasonable theoretical approach to modelling the behaviour of molecular liquids. Our findings conflict, however, with earlier work in the literature [4, 14] where it has been often noted that for a fitting of the model to experimental data the moment of inertia of the cage tends to be somewhat less than that of the inner dipole, contrary to what one would expect. We shall now attempt to rationalize the findings of earlier authors.

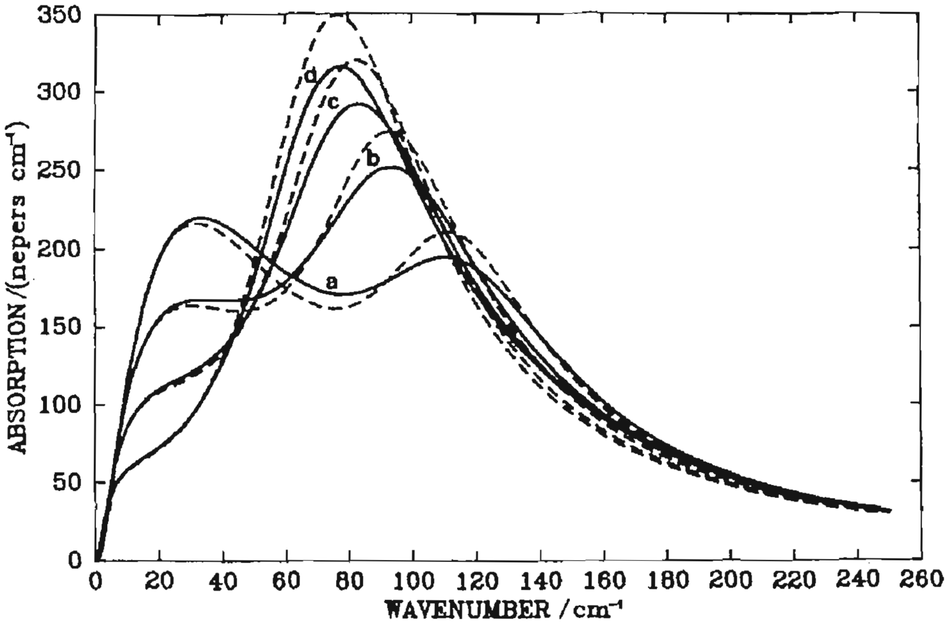

Figure 3. Power absorption for $\hat{\alpha} = 5$, $\beta = 12$, $\hat{\gamma} = 15$, $b = 1$ with $\varepsilon_\infty = 2$, $\varepsilon_s - \varepsilon_\infty = 8$ and for $I_r =$ (a) 0·5, (b) 1·0, (c) 2·0, (d) 4·0. This illustrates the fact that for $I_r \leqslant 1{\cdot}0$, much of the broadening of the FIR absorption spectrum is due to a shifting of the MW (Debye) peak to higher frequencies. Note the predominant left-hand peak for $I_r = 0{\cdot}5$.

To this end, power absorption spectra are shown in figure 3 for the $\beta_1 = \beta_2$ model for several values of the I_r parameter. The most significant feature of this diagram is the occurrence of two peaks in the power absorption spectrum for $I_r = \frac{1}{2}$. For $I_r = 1$ (i.e. the equal dipoles–equal friction case), there is still a distinct shoulder in the MW wave. As I_r is increased, this MW shoulder is strongly suppressed and, indeed, is hardly noticeable for $I_r = 4$ or larger. Now this MW shoulder is, in fact, due to the shift of the microwave absorption to higher frequencies as the moment of inertia ratio, I_r, is reduced. This phenomenon can be readily understood by recalling that the Debye time for the equal frictions case is given by [9 (b)]

$$\tau_D = \frac{2\beta}{a_2 \hat{\alpha}^2}, \qquad a_2 = \frac{2I_1}{I_1 + I_2} = \frac{2}{1 + I_r}. \tag{33}$$

Now the microwave absorption will reach its Debye plateau value for $f \geqslant f_D$ where

$$f_D = \frac{1}{2\pi} \frac{a_2 \hat{\alpha}^2}{2\beta}. \tag{34}$$

Evidently a_2 will get larger as we reduce the value of I_2, a fact which holds good for $I_r < 1$ as well as $I_r > 1$. *Thus much of the broadening of the power absorption spectrum in curves* (*a*) *and* (*b*) *of figure 3 is due to a shifting of the MW peak to higher frequencies.* It is *not* caused by a FIR libration mechanism. On the other hand, the spectra described by curves (c) and (d), i.e. $I_r = 2$ and $I_r = 4$, respectively, exhibit a clear-cut resonance broadening.

As we have already mentioned, earlier workers have found in their analysis of experimental data using the I.O. that the best fits of the model to experiment have been for $I_r \leqslant 1{\cdot}0$. In this context it is important to note that *almost all the work on the I.O. has been based on the single-friction version of the model* although the two-friction version has been available for some time [4, p. 506]. Now the single-friction I.O. tends to be sharply peaked in the FIR region of the spectrum for physically reasonable values of the parameters, in contrast to the equal frictions ($\beta_1 = \beta_2$) I.O. [9 (b)]. It is possible to reduce the sharpness of the FIR peak to some extent by reducing the moment of inertia of the outer annulus. For reasons which we have just given, this also tends to shift the MW peak to higher frequencies thus enhancing the contribution of the relaxational (Debye) process to the absorption spectrum.

By way of illustration of this point, we show in figure 4 (i) power absorption plots derived from our analytic formula for the single friction I.O. model. Note that for $I_r = 1$ this spectrum has an unacceptably sharp peak. Reducing I_r to 0·5 or 0·25 reduces this sharply-peaked structure. We note, however, that this reduction of I_r produces two distinct peaks in the power absorption spectrum, a structure which may be observed in the work of earlier authors [4, 14]. If we turn our attention to the equivalent polarizability plots given in figure 4 (ii), it becomes clear that the low-frequency shoulder or peak of the absorption spectrum is, in fact, due to relaxational motion in the MW region. There is not, therefore, *any broadening of the power absorption spectrum due to FIR libration for* $I_r < 1$. This is emphasized by curve (e) which shows the Debye process equivalent to curve (c). The effect in the single-friction model of reducing I_r is chiefly to dampen the excessively sharp FIR resonance which is observed in this form of the I.O. model. A reduction of I_r does not affect the MW peaks as significantly as in the equal-frictions case of the I.O.

It is quite evident from the foregoing discussion that much of the previous criticism in the literature of the I.O. model is unfounded. A substantial part of the work of earlier authors is misleading because they concentrated upon the single-friction I.O. For example, in [4] almost all the work of Chapters 4 and 7 is based on the single-friction I.O. model, and although the two-friction model is presented on

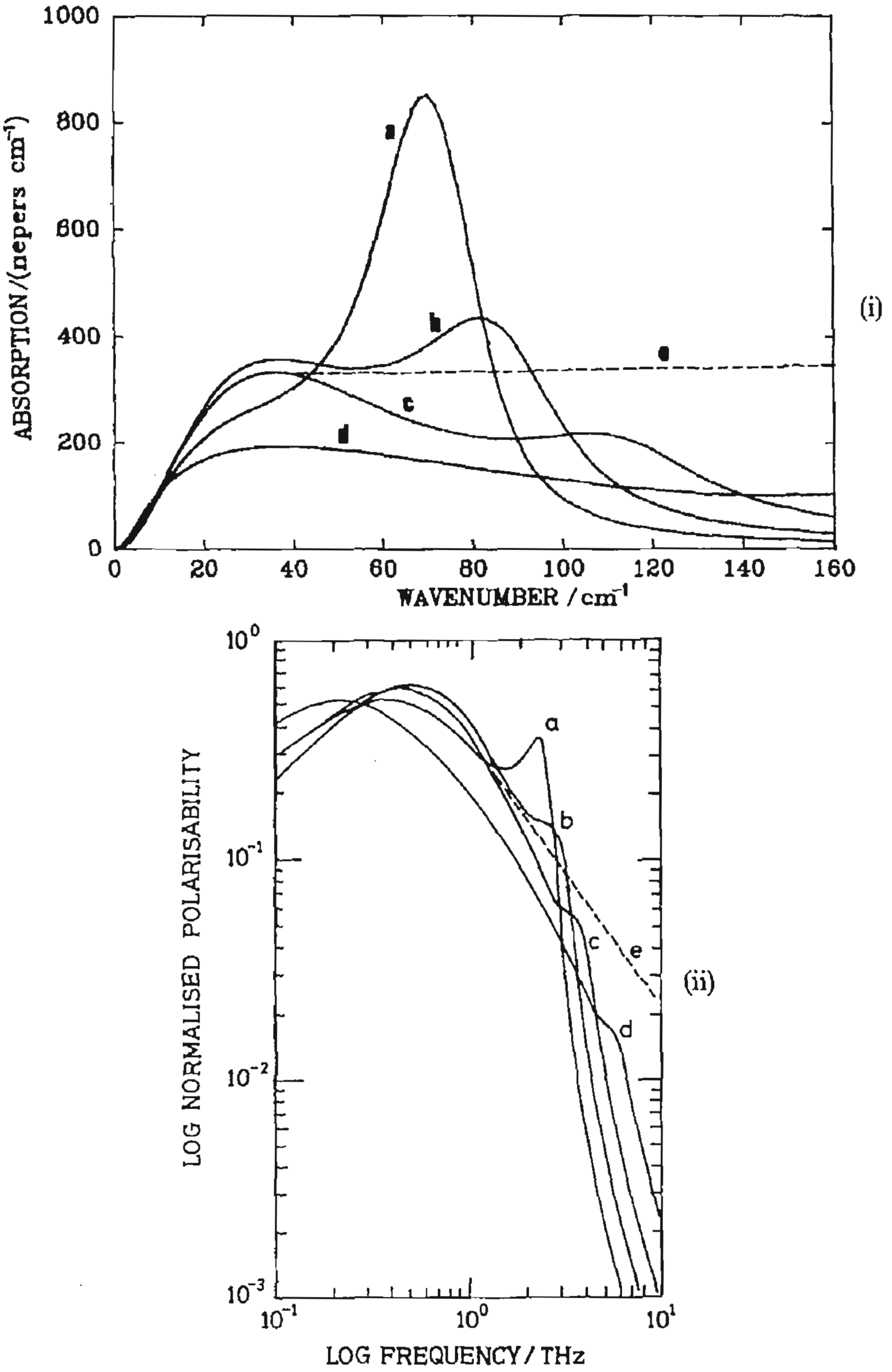

Figure 4. (i) Power absorption spectra for the single-friction model, i.e. $b = 0$, with $\hat{\alpha} = 5$, $\hat{\beta} = 12$, $\hat{\gamma} = 15$ and (a) $I_r = 1{\cdot}0$, (b) $I_r = 0{\cdot}5$, (c) $I_r = 0{\cdot}25$, (d) $I_r = 0{\cdot}1$. Note how reducing I_r suppresses the very sharp FIR peak of curve (a). Curve (e) shows the Debye process, i.e. purely relaxational behaviour, equivalent to curve (c). (ii) Polarizability spectra for the same parameters as (i). Evidently most of the power absorption spectra in (i) are produced by MW relaxation rather than FIR libration of the inner dipole of the I.O. See the text for a more detailed discussion.

page 506 of this reference, it was not used very extensively in comparison with experimental data.

A further point which should be clarified is the effect of including contributions to the polarizability due to the a.c.f. of the outer annulus and the a.c.f. between the

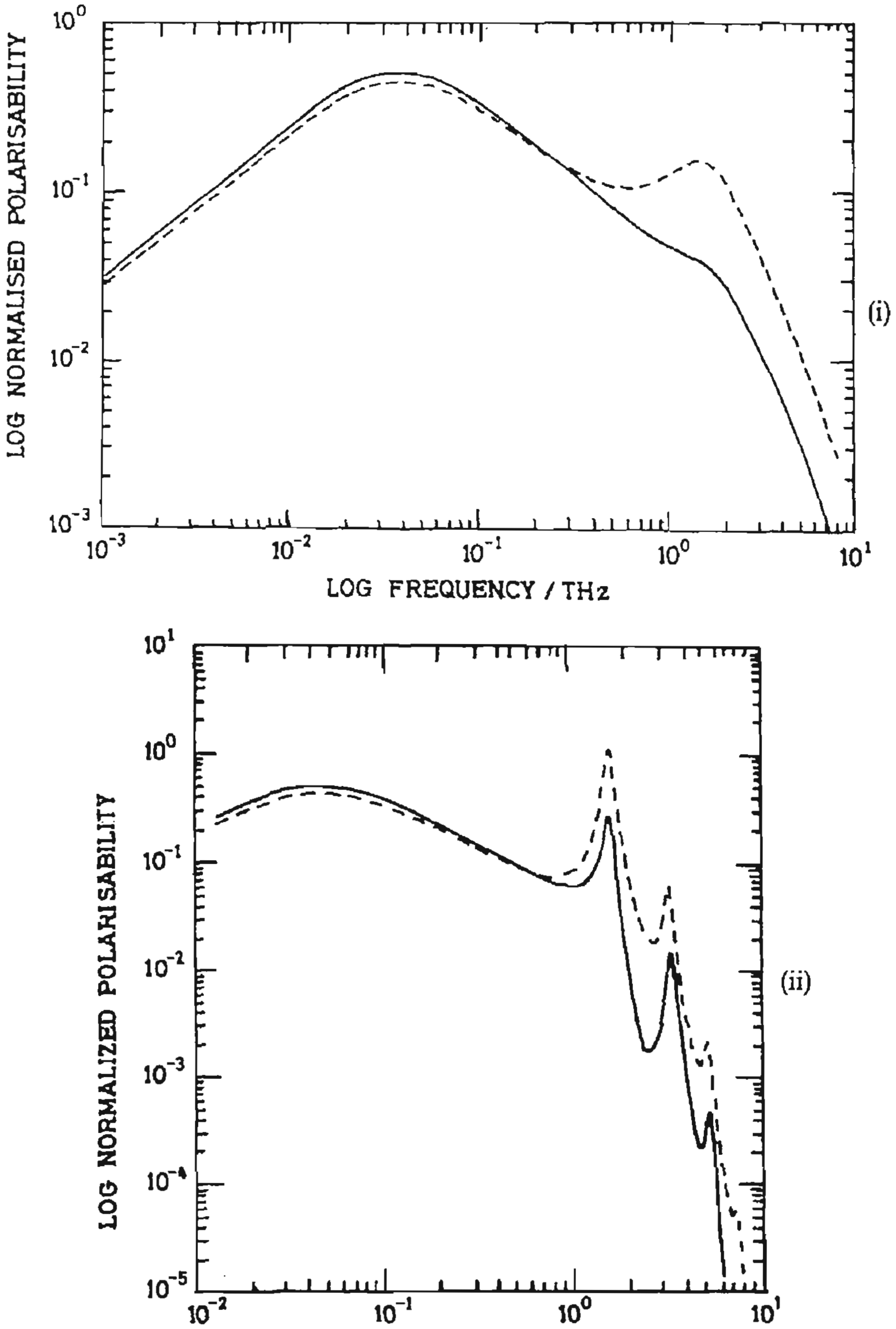

Figure 5. (i) The polarizability, calculated numerically, when contributions due to the a.c.f. of the outer dipole and the c.c.f. between the two dipoles are included (solid line) compared with the polarizability, calculated numerically, when only the a.c.f. of the inner dipole is taken into account (dashed line). Parameter values are $\hat{\alpha} = 5$, $\beta = 12$, $\hat{\gamma} = 12{\cdot}75$, $b = 1$ and $I_r = 6$. (ii) As for (i), but $b = 0$. Note the appearance of harmonic peaks due to ignoring the friction on the inner dipole.

two dipoles. We have included both these terms in our earlier work [9 (a), (b), 10] but not in figure 1 of the present work because we wished to compare equations (24) to (26) with their exact numerical equivalent. We will now show the effect of including these additional terms, that is we write (using the gaussian properties of ϕ_1 and ϕ_2) (see [9 (b), 10] for more detail)

$$\begin{aligned}
&\frac{\mu^2}{kT}\{\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0+2\langle\cos\phi_1(0)\cos\phi_2(t)\rangle_0\\
&\qquad+\langle\cos\phi_2(0)\cos\phi_2(t)\rangle_0\}\\
&\quad=\frac{\mu^2}{2kT}\{\exp[-\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0]+2\exp[-\tfrac{1}{2}\langle\Delta^2_{\phi_1\phi_2}\rangle_0]\\
&\qquad+\exp[-\tfrac{1}{2}\langle(\Delta\phi_2)^2\rangle_0]\},\\
&\quad\Delta\phi_i=\phi_i(t)-\phi_i(0),\qquad\Delta_{\phi_1\phi_2}=\phi_1(t)-\phi_2(0),
\end{aligned}\tag{35}$$

and it is this quantity which is Fourier transformed numerically to yield the polarizability of the system. As may be seen from figure 5, the effect of including these terms is to reduce the relative contribution of the far-infrared peak in the polarizability spectrum. This is interesting physically because it indicates that if the 'cage' of surrounding molecules envisaged in the I.O. tends to break and re-form on a slightly longer time scale than that of the far-infrared oscillations, it may well be that their contributions to the polarizability should be ignored. This assumption would tend to broaden the far-infrared peak even more than indicated in earlier work [9 (a), (b), 10]. For a more detailed discussion, the reader is referred to [9 (a), (b)].

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