Effect of Electric Fields on the Far Infrared Absorption Cross-section of Liquid Aniline

By Gareth J. Evans and Myron W. Evans*

Chemistry Department, University College of Wales, Aberystwyth SY23 1NE

Some electric field induced intensity changes in the far infrared spectrum of liquid aniline are interpreted qualitatively in terms of the dynamical internal field theory of Lobo *et al.*, based on the concept of dielectric friction. Several of the relevant models of molecular motion are inter-related for ease of interpretation.

Far infrared reflectance spectra of nitromethane have been used recently by Ascarelli [1] to discuss collective modes in liquids with sufficiently high dipole moments and therefore pronounced intermolecular interaction. The mathematical foundation for the existence of these collective modes (transverse and longitudinal) comes from a theory by Lobo *et al.*[2] based on the treatment of internal (or reaction) field due to Nee and Zwanzig.[3] Here the reaction field does not follow the motion of the dipole instantaneously but in a " retarded " fashion, due to what is termed dielectric friction.

The existence of electric field induced infrared intensity changes has emerged from the analysis of Lippert and Michel [4] of pure liquid acetonitrile. Some bands are sensitive to the application of external electric fields, their absorption intensity cross-section being considerably depleted. This effect is opposite to that of temperature. The purpose of this paper is two-fold : (i) to present some far infrared spectra of aniline as a function of applied electric field ; (ii) to coordinate the theories of the far infrared available in the literature in preparation for a more detailed analysis of the experimental data.

The paper is developed as follows. Firstly we interrelate the theories. It emerges that the equations used by Lobo *et al.*[2] are those of Evans *et al.*,[5] or alternatively of Kivelson and Madden [6] corrected for the dynamical internal field using the concept of dielectric friction, introduced by Scaife,[7] Fatuzzo and Mason[8] and Nee and Zwanzig.[3] The work of Kivelson and Madden [6] allows us to relate the single particle auto-correlation function ($C_u(t) = \langle u(t) \cdot u(0) \rangle$, where u is the dipole vector) to the full (multi-particle) cross-correlation function $C_m(t)$ observable experimentally. Although Lobo *et al.*[2] speak of collective modes, both transverse and longitudinal, their theory is concerned only with $C_u(t)$, *i.e.*, with the autocorrelation function. The macro–micro theorem of Kivelson and Madden [6] states that $C_m(t)$ has the same mathematical dependence on t as $C_u(t)$, although the constants of the equation are different.

Secondly, the experimental arrangement and results are described and lastly the results are discussed in terms of collective response to the applied electric field.

THEORETICAL REMARKS

The expression devised for $C_u(t)$ by Nee and Zwanzig [3] may be written as :

$$\mathcal{L}_a[-\dot{C}_u(t)] = \left[1-i\omega\tau_0-\left(1-\frac{n^2}{\varepsilon(0)}\right)\left(\frac{\varepsilon^*(\omega)-\varepsilon(0)}{2\varepsilon^*(\omega)+n^2}\right)\right]^{-1} \tag{1}$$

where τ_0 is the microscopic relaxation time, inversely proportional to the rotational diffusion constant (or friction coefficient), n is the refractive index at the end of the far infrared dispersion (which is not ε_∞) and $\varepsilon^*(\omega)$ is the complex permittivity. $\mathcal{L}_a$ is the Laplace-transform operator. The relaxation time τ_0 is due to the van der Waals and not the long-range dipole–dipole and other types of electrodynamic interactions. When there is no internal field correction, or when $[\varepsilon(0)-n^2]$ is small, we have :

$$\mathcal{L}_a[-\dot{C}_u(t)] \to (1-i\omega\tau_0)^{-1}, \tag{2}$$

the Debye equation. Eqn (1) may be rewritten as :

$$\mathcal{L}_a[-\dot{C}_u(t)] = [1-i\omega\tau(\omega)]^{-1} \tag{3}$$

where $\tau(\omega) = \zeta(\omega)/(2kT)$ and is memoryless in the sense that ζ_0 defined by :

$$\zeta(\omega) = \zeta_0+\zeta_D(\omega)$$

is independent of frequency. Here $\zeta_D(\omega)$ is the dielectric friction term and ζ_0 the hydrodynamic.

In deriving eqn (1) the assumptions are made that : (i) The Euler equations are linearised in the angular velocity ω. In general all three components of ω are coupled. (ii) The Liouville equation for the conditional probability density function $f[u(t) ; u(0), t_0]$ is solved in a Gaussian approximation.

Now we may introduce inertial and memory effects by one of two means. Firstly, following Lobo et al. we may write the Langevin equation for the Cartesian components of the angular velocity ω, i.e., for each component :

$$I\dot{\omega} = -\int_0^t d\tau \, K_\omega(t-\tau)\omega(\tau)+N_T(\tau). \tag{4}$$

Here $N_T(t)$ is a random torque due to van der Waals interactions (short-ranged). If the torque autocorrelation function is assumed to be exponentially decaying then for each component :

$$\langle N_T(t)N_T(0)\rangle = \langle N_T^2\rangle \exp(-t/\tau) \tag{5}$$

then it follows that eqn (1) is modified to :

$$\mathcal{L}_a[-\dot{C}_u(t)] = 1-i\omega\mathcal{L}_a C_u(t)$$

$$= \left[1-\frac{I^*\omega^2}{2kT}-\frac{i\omega}{1-i\omega\tau}\frac{\langle N_T^2\rangle\tau}{2(kT)^2}-\left(1-\frac{n^2}{\varepsilon(0)}\right)\left(\frac{\varepsilon^*(\omega)-\varepsilon(0)}{2\varepsilon^*(\omega)+n^2}\right)\right]^{-1}. \tag{6}$$

The rotational dynamics of an asymmetric top are complicated but the exact asymptotic expansion of $E^*(\omega)$ depends only on a weighted average of the inverse of the inertial tensor. This is :

$$\frac{1}{I^*} = \frac{1}{2}\left(\frac{1}{I_1}+\frac{1}{I_2}\right) \tag{7}$$

where I_2 and I_2 are the principal moments of inertia about axes normal to the dipole moment. Eqn (7) is that for I^*, the effective moment of inertia to be used in a spherical equivalent of an asymmetric top. Secondly, we note that the r.h.s. of eqn (6) may be written as ($p = -i\omega$)

$$\frac{p^2 + p(1/\tau) + (2kT/I^*)\langle N_T^2\rangle/2(kT)^2}{p^3 + p^2(1/\tau) + (2kT/I^*)\left(1 + \frac{\langle N_T^2\rangle}{2(kT)^2}\right)p + \frac{1}{\tau}\frac{2kT}{I^*}} \tag{8}$$

when electrodynamical field corrections are neglected. This term is exactly the form used by Evans et al.[5] to describe the zero-THz absorption of gases, liquids, rotator phase and mesophases. In the notation of these papers:

$$\gamma \equiv 1/\tau; \quad K_0(0) \equiv 2kT/I^*; \quad K_1(0) \equiv \langle N_T^2\rangle/I^*kT.$$

The term (8) is therefore also subject to the geometrical constraints of linearisation in the Euler angles, i.e., the diffusing asymmetric top is treated as a spherical top. The effect of this approximation is small when memory effects are neglected, but in the nematic phase where the molecules are pronouncedly aspherical, this mathematical convenience might give rise to some trouble. The question of extending the Zwanzig/Lobo formalism to the nematic phase is under consideration.

The complete expression derived by Lobo et al. for the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ (their definition) is therefore equivalent to the expression (8) corrected for dielectric friction, as envisaged by Nee and Zwanzig. With this correction the permittivity is governed by:

$$[\varepsilon^*(\omega) - n^2]\left[1 - \frac{I^*\omega^2}{2kT} - \frac{i\omega\tau_0}{1 - i\omega\tau} - \left(1 - \frac{\varepsilon_0}{n^2}\right)\left(\frac{\varepsilon^*(\omega) - \varepsilon(0)}{2\varepsilon^*(\omega) + n^2}\right)\right]$$
$$= \frac{3\varepsilon^*(\omega)}{2\varepsilon^*(\omega) + n^2}\frac{4\pi(N/V)\mu^2}{3kT}g_K(\omega) \tag{9}$$

where $\tau_0 = \langle N_T^2\rangle\tau/2(kT)^2$ or, solving for $\varepsilon^*(\omega)$, after Lobo et al.,

$$\frac{\varepsilon^*(\omega)}{n^2} = \frac{1}{4}\left[\frac{z_p^2 - z^2(\omega)}{z_t^2 - z^2(\omega)}\right] + \frac{3}{4}\left[\frac{[z_1^2 - z^2(\omega)][z_p^2 - z^2(\omega)]}{[z_t^2 - z^2(\omega)][z_t^2 - z^2(\omega)]}\right]^{\frac{1}{2}} \tag{10}$$

$$z_1^2 = 1 + \frac{n^2}{\varepsilon_0} - \frac{\varepsilon_0}{n^2}; \quad z_t^2 = \frac{1}{2}\left(1 + \frac{n^2}{\varepsilon_0}\right);$$

where

$$z_p^2 = \varepsilon_0/n^2; \quad z^2(\omega) = \omega^2\frac{I^*}{2kT} + \frac{i\omega\tau_0}{1 - i\omega\tau}.$$

The effect of dielectric friction on the far infrared spectrum of eqn (8) is illustrated in fig. 1 for various values of $\varepsilon(0)$ and n^2.

We remark to close this section that the equivalent of eqn (8) has been derived by Kivelson and Madden; their three variable macro–micro correlation theorem linking the single particle autocorrelation theorem $C_u(t)$ to the multiparticle cross-correlation function $C_m(t)$. In their notation:

$$\tilde{C}_u(i\omega) = \tau_{S\theta}\left[1 + \left(\frac{\omega^*}{\omega_\theta^*}\right)^2[(\omega_\theta^* + \omega_T^*)^2 - 2] + \left(\frac{\omega^*}{\omega_\theta^*}\right)^4[1 - 2\omega_T^*(\omega_\theta^* + \omega_T^*)] + \left(\frac{\omega^*}{\omega_\theta^*}\right)^6\omega_T^{*2}\right]^{-1}.$$

This expression is identical with the three variable theory of Quentrec and Bezot,[9] developed by Evans *et al.*[5] We have

$$\tau \equiv \gamma^{-1} \equiv \tau_{ST};$$

$$\frac{\langle N_T^2 \rangle}{2(kT)^2} \equiv \frac{K_1(0)}{K_0(0)} \equiv \left[\frac{\langle (d^2 \cos \theta_1/dt^2) \rangle}{(kT/I)^2} - 1 \right].$$

Here τ_{ST} is a single-particle correlation time associated with intermolecular torques. It is related to a single particle orientational correlation time $\tau_{S\theta}$ by:

$$\tau_{S\theta} = \left[\frac{\langle d^2 \cos \theta_1/dt^2 \rangle}{(kT/I)^2} - 1 \right] \tau_{ST}.$$
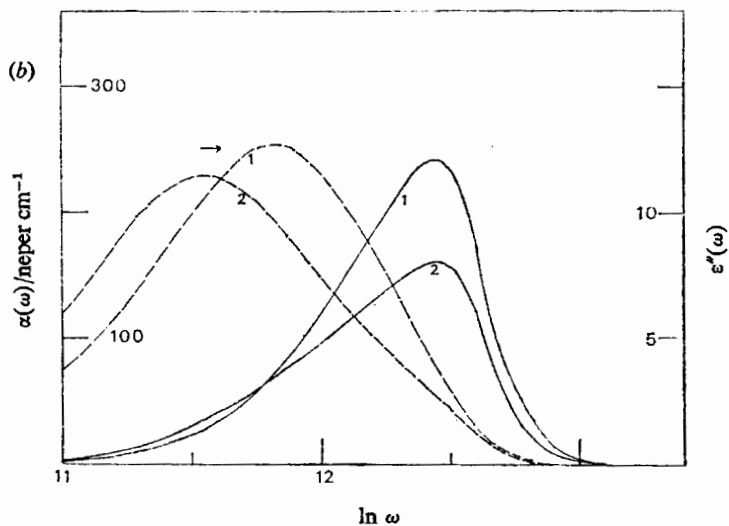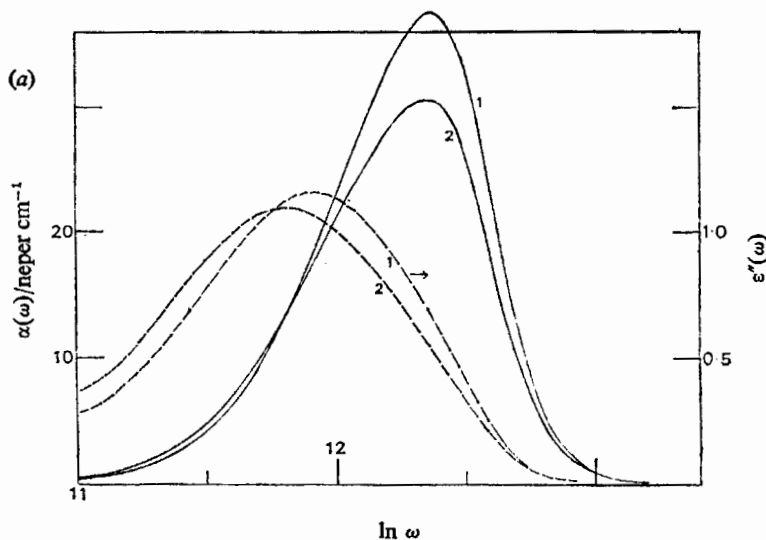

FIG.1—(See caption opposite).
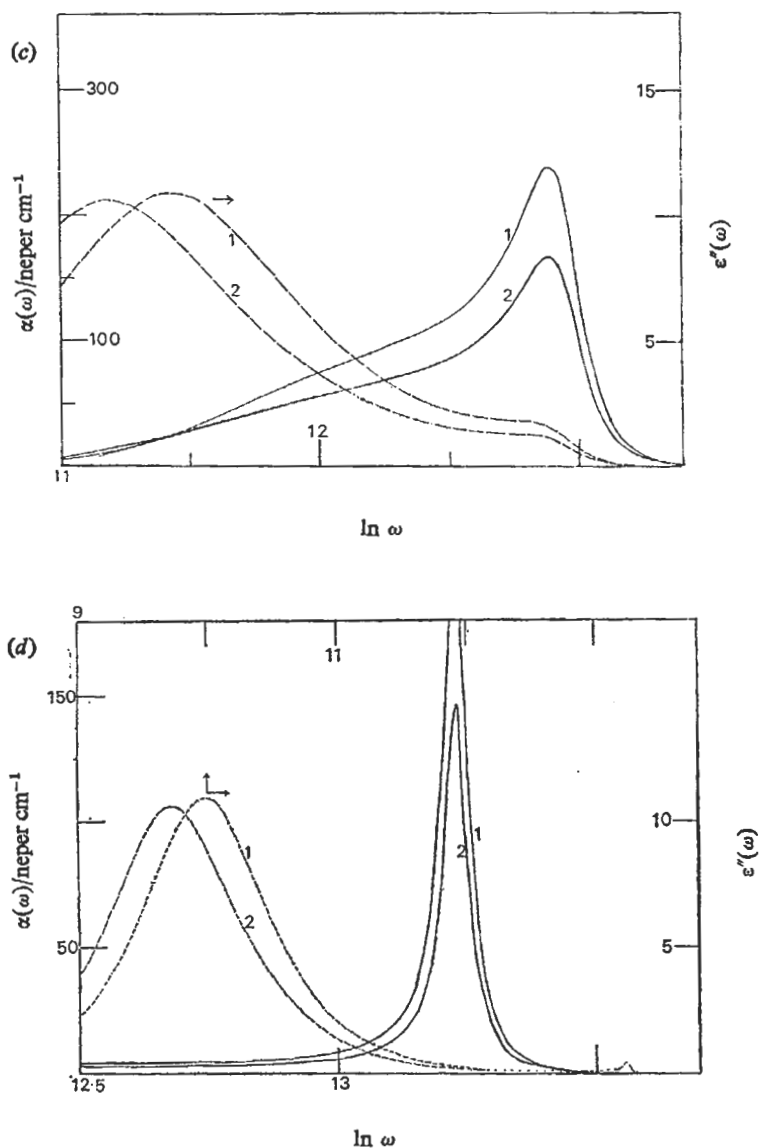
FIG. 1.—(a) Effect of dielectric friction on the far infrared power absorption coefficient $[\alpha(\omega)]$ and dielectric loss $[\varepsilon''(\omega)]K_0(0) = 2 \times 10^{24} \, s^{-2}$; $K_1(0) = 17 \times 10^{24} \, s^{-2}$, $\gamma = 6 \times 10^{12} \, s^{-1}$. $\varepsilon_0 = 4.0$; $n^2 = 2.0$. (1) Evans *et al.*, three variable theory (no internal field); (2) Lobo *et al.* [eqn (10)]; (——) $\alpha(\omega)$; (- - -) $\varepsilon''(\omega)$. The intensity decrease due to the internal field, interpreted in terms of dielectric friction, mirrors that in fig. 3, induced by an *external* electric field. (b) $\varepsilon_0 = 25.0$; $n^2 = 3.0$; $K_0(0) = 1.43 \times 10^{24} \, s^{-2}$; $K_1(0) = 15 \times 10^{24} \, s^{-2}$; $\gamma = 6 \times 10^{12} \, s^{-1}$. The greater is the difference $\varepsilon_0 - n^2$, the greater is the relative decrease in absorption cross-section. (c) $\varepsilon_0 = 25.0$; $n^2 = 3.0$, $K_0(0) = 2.89 \times 10^{24} \, s^{-2}$; $K_1(0) = 72.25 \times 10^{24} \, s^{-2}$; $\gamma = 6.8 \times 10^{24} \, s^{-1}$. (d) $\varepsilon_0 = 25.0$; $n^2 = 3.0$, $K_0(0) = 1.12 \times 10^{24} \, s^{-2}$; $K_1(0) = 288 \times 10^{24} \, s^{-2}$; $\gamma = 2.4 \times 10^{12} \, s^{-1}$.

II—22

The use of the three variable models with a Fatuzzo/Mason type of internal field correction is equivalent to the theory of Lobo *et al.*   These models are known [5] to break down under certain limits; the experimental case of highly viscous or glassy media is one of these and another is the approach to free rotation.   However, the predicted frequencies of the longitudinal (ω_p) and transverse (ω_t) " collective " modes are:

$$\omega_p^2 = \omega_t^2 + \omega_0^2$$

where

$$\omega_0^2 = 4\pi(N/V)(\mu_V^2/I^*)(n^2+2)^2/9n^2$$

and

$$\omega_t^2 = (kT/I^*)(1+2\tau_0/\tau).$$

Ascarelli has made use of the fact that the longitudinal mode does not couple to a transverse electromagnetic wave incident normal to the surface, in order to identify ω_t and ω_p experimentally.   The longitudinal wave can be picked up when the electromagnetic wave has an oblique angle of incidence on the surface of the liquid specimen. The values for ω_T and ω_p are in agreement with those calculated from the theory of Lobo *et al.*   Ascarelli also discovered by means of reflectivity a significant effect of an external electric field on the "collective" electrodynamical modes.   The effect of an externally applied electric field favours the growth of clusters or aggregation of dipoles in the liquid so that the local dipole density may differ very much from its average value.   The resultant value of ω_p then has a distribution which depends on the local dipole density.   Even in as dilute a solution as 10 % nitromethane in carbon tetrachloride observed ω_p shifts from ≈ 30 to $\approx 60 \text{ cm}^{-1}$.   In the sections below we present some electric field affected far infrared spectra of the hydrogen-bonded system, aniline, and qualitatively assess their significance in the light of these remarks.

EXPERIMENTAL

The standard interferometric techniques of far infrared power absorption spectroscopy were used with an N.P.L./Grubb–Parsons " cube " spectrometer.   The electric field cell was constructed from poly(4-methyl-pent-1-ene) and was designed for field application perpendicular to measuring electromagnetic radiation.   Electric fields (both static and alternating) were applied.   Alternating fields of up to 3 kV at 1 kHz were used and static fields of up to 8 kV, across an electrode gap of 25 mm in a cell otherwise constructed solely of poly(4-methyl-pent-1-ene).

Conductivity measurements were made on all the samples employed.   There does not appear to be a correlation between this quantity and the electric field effects.   The response of the integrated absorption intensity to the field application is illustrated in fig. 2.   This could be roughly measured to less than a second with the means at our disposal.

RESULTS

When a static or alternating electric field is applied perpendicularly to the measuring, electromagnetic beam the far infrared absorption (fig. 3) decreases, as observed for a liquid CH_3CN near infrared band by Lippert and Michel.[4]   In the nematogenic state it has been previously reported that application of an alternating field produces an effect identical with that of a static field of comparable strength.

DISCUSSION

Note that the " collective " mode predicted theoretically is also a resonance of the single-dipole motion.   For H_2O, HCl and $CHCl_3$ liquids Lobo *et al.* estimate collective mode frequencies in the 300-600 cm^{-1} region.   However,
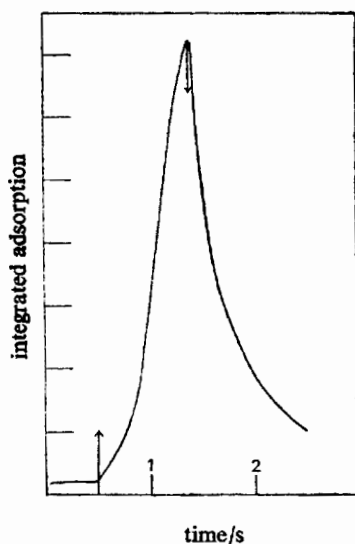
FIG. 2.—Decrease and subsequent increase of integrated absorption intensity of aniline with application of an external electric field.
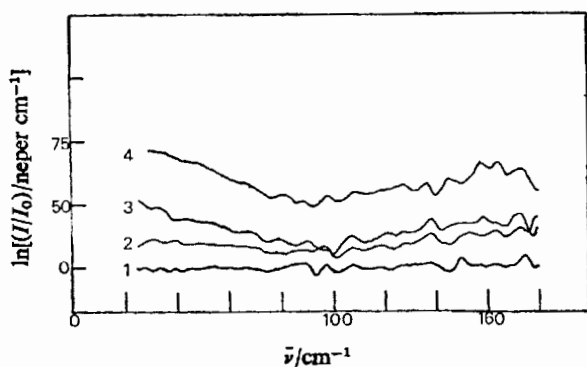

FIG. 3.—Plot of ln (I/I_0) against $\bar{\nu}$ for liquid aniline. Here I_0 is the absorption intensity in the absence of an electric field and I that with an electric field applied. (1) [0, (2) 3.5, (3) 5.0, (4) 7.0 kV cm^{-1}.

our results do not substantiate the prediction of collective modes at 0.5-5.0 cm^{-1} for a number of simple benzene derivatives. If this is due to quantitative deficiencies in the Nee–Zwanzig evaluation then the use of structural and electrical characteristics rather than field equations might improve the agreement between theory and experiment.

Lippert and Michel observed their effects in liquid acetonitrile, using static electric fields of up to 5×10^5 V cm^{-1}. With increase in the electric field a rapid decrease of intensity can be observed in the 2250 cm^{-1} band, while the other mid and near infrared bands show effects similar to that of heating. A similar phenomenon can be observed in the far infrared for aniline (fig. 3) where the integrated intensity rapidly falls with the application of the field and then rapidly regains its original level when the field is switched off. In acetonitrile the field effect was interpreted in terms of excitation of the π-electrons. Indeed Lippert and Michel have suggested the existence of a " pre-solid " state of matter on this and related evidence,

such as the sudden increase in the maximum intensities of the normal modes coupled with a sudden decrease in the coordination modes. The state is due to cooperative dynamic phenomena originating from a coupling of molecular oscillations. The cooperative oscillation reduces the distance between the molecules, destroys individual rotational freedom and leads to the characteristic interactions and dynamics of the solid state. To support this conjecture in liquid acetonitrile these authors cite as evidence the local asymmetry in the structure of liquid acetonitrile, revealed by X-ray analysis. There is an asymmetry in the perpendicular intermolecular distances despite the fact that the perpendicular potentials are symmetric.

At this stage it is relevant to discuss the role of the wave vector k in a zero-THz spectrum. If for some reason this remains finite in such an experiment then the spectrum would be capable of yielding information on density fluctuations, or large scale collective motions propagated electrodynamically. If we deal with a Kirkwood correlation sphere containing a large number of molecules the relevant zero-THz correlation function is in fact :[2]

$$\frac{1}{k^2\mu^2}\langle k \cdot \mu_1(t) \exp\left[ik \cdot r_1(t)\right] \sum_j k \cdot \mu_j(0) \exp\left[-ik \cdot r_j(0)\right]\rangle$$

where the sum runs over all molecules within the Kirkwood sphere, centred on $r_1(0)$, the position vector of the centre of mass of molecule 1. The $k \cdot \mu$ signifies that it is the polarisation charge density which responds to a scalar probe, not the polarisation, as is usually tacitly assumed. Reduction to the classical Kirkwood theory is possible only for $k \to 0$, the hydrodynamic limit,

$$\frac{1}{3\mu^2}\langle \mu_1(0) \cdot \sum_j \mu_i(t)\rangle.$$

In a fluid made up of ions, of course, we may define a charge density *via* the Poisson equation :

$$\nabla \cdot E = 4\pi q\delta\rho$$

where q is the particle charge and E an external applied electric field. If we then use hydrodynamic equations to describe the liquid a term proportional to $E(r, t)$ must be added to the Navier–Stokes equation. When solved this leads directly to a plasma frequency $\omega_p^2 = 4\pi\rho q^2/m$, where m is the particle mass. The frequency of collective oscillations does not vanish as $|k| \to 0$ in this case, but $\to \omega_p$. This collective oscillation in the ionic fluid is called the plasmon and may be simulated by computer molecular dynamics.[10] If we substitute for the charge density the polarisation charge density then it is clear that zero-THz spectroscopy with finite k leads to information on " plasmons " in dipolar but molecular (as opposed to ionic) fluids.

As $|k| \to 0$ in an ionic fluid, the density fluctuations are dominated by the plasma oscillations. In some cases (*e.g.*, molten salts) it is possible to separate and identify the fluctuations in density and those in charge density. The former determine sound wave propagation and the latter the plasmons, or plasma oscillations. These are liquid-state analogues of the acoustic and optic longitudinal phonons in an ionic crystal. These show up in the far infrared for both ionic and molecular crystals. Obviously the plasmon frequency of polarisation charge density fluctuations in a molecular fluid is the liquid-state analogue of the longitudinal optical phonon mode in the far infrared of the molecular crystal. All these propagative modes depend on the mutual interaction of molecular rotation and translation, the molecular crystal phonon modes being of course classifiable into those of translational and those of rotational origin.

The spectra therefore corroborate the evidence put forward by Ascarelli and Lobo *et al.* for internal field propagated intensity changes (fig. 1 in liquids where dipole–dipole interaction is strong). The formalism of Lobo *et al.* is identical with that extensively used by Evans *et al.*, provided the latter's equations are modified using the dynamic internal field, or dielectric friction concept of Nee and Zwanzig.

The effect of including the internal field theoretically is to decrease the integrated absorption intensity when expressed in terms of $\alpha(\omega)$, the power absorption coefficient, and to shift the peak in $\varepsilon''(\omega)$ to lower frequencies (fig. 1). The correction of Lobo *et al.* introduces no significant new feature into the three variable theory of Evans *et al.* or of Madden and Kivelson. This is to say that the poles $\varepsilon^*(\omega) \to 0$ and $\varepsilon^*(\omega) \to \infty$ labelled by these authors as plasmons are not specifically electrodynamic in origin but are rather natural spectral consequences of the particular Mori approximant used.

[1] G. Ascarelli, *Chem. Phys. Letters*, 1976, **39**, 23.
[2] R. Lobo, J. E. Robinson and J. Rodrigues, *J. Chem. Phys.*, 1973, **59**, 5992.
[3] T. W. Nee and R. Zwanzig, *J. Chem. Phys.*, 1970, **52**, 6353.
[4] H. Michel and E. Lippert, in *Organic Liquids: Structure, Dynamics and Chemical Properties*, ed. A. D. Buckingham, E. Lippert and S. Bratos (Wiley, Chichester, 1978).
[5] M. W. Evans, in *Dielectric and Related Molecular Processes* (Specialist Periodical Report, The Chemical Society, London, 1977), vol. 3, p. 1.
[6] D. Kivelson and P. Madden, *Mol. Phys.*, 1975, **30**, 1749.
[7] *Complex Permittivity*, ed. B. K. P. Scaife (English Univ. Press, London, 1971).
[8] E. Fatuzzo and P. R. Mason, *Proc. Phys. Soc.*, 1967, **90**, 741.
[9] B. Quentrec and P. Bezot, *Mol. Phys.*, 1974, **27**, 879.
[10] I. R. McDonald and J. P. Hansen, *Theory of Simple Liquids* (Academic Press, New York, 1976).