

Abstract
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Absorption of Dipolar Liquids in the Far Infrared:

A Sensitive Measure of the Mori Continued Fraction

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Using a specially developed polarising interferometer for the range 2-200 cm^{-1} , the complete rotational type absorptions of some halogenobenzenes and of tertiary butyl chloride have been obtained in the liquid phase at 296 K. The broad experimental bands have contributions from permanent and induced, temporary dipoles; the absorption due to the latter being negligibly small below about 2 cm^{-1} , but (gradually) becoming predominant at the higher wave numbers thereafter. The auto-correlation function of the permanent dipole unit vector (μ) is simulated by a quotient of polynomials obtained by assuming an exponential, Gaussian, $-\langle \dot{\mu}(0) \cdot \dot{\mu}(t) \rangle$ or Lorentzian form for the second memory function $K_1(t) = \langle \dot{\mu}(0) \cdot \mu(t) \rangle / \langle \dot{\mu}(0) \cdot \mu(0) \rangle$. All three theoretical absorptions therefrom reduce to the classical Debye form at low frequencies, but behave very differently in the far infrared, a region particularly sensitive to dynamical events at times shortly after the arbitrary initial $t = 0$. A fairly realistic result is obtained only from the exponential $K_1(t)$, which gives an integrated absorption intensity of about half that observed in the far infrared. The excess is due mainly to collisionally induced absorption, but also in part to the difference between the dynamic internal field and the Maxwell field. $K_1(0)$ is evaluated for the asymmetric top, revealing that it is dependent in general on separable torque and centripetal terms.

If the theoretical method employed here is to be generally successful, then $K_1(t)$ must be simulated more realistically, possibly with the aid of computer molecular dynamics.

In a previous communication¹ a continued fraction series approximation to the orientational autocorrelation function $\langle \mu(0) \cdot \mu(t) \rangle$ was developed and tested against selected experimental data over a limited range of frequencies (10-200 cm^{-1}). Here $\mu(t)$ is the dipole moment. Although the fit of theory to the data was satisfactory, it is by no means certain that it will remain so at the lower (microwave) frequencies, where the a.c.f. becomes exponential, a result predicted by Debye using a model of rotational diffusion.² Indeed, it is valid to attempt a fit of the far infrared band profile³ only with very strongly dipolar molecules, where the phenomenon of interaction induced absorption⁴ is negligibly small in comparison with that of the permanent dipole. As can be shown¹⁷ by a simple application of Gordon's sum rule⁶ (eqn 17) for the total integrated intensity of all rotational modes of motion in the far infrared/microwave. Collision induced dipoles present in all liquids should become negligible at $\bar{\nu} < 1 \text{ cm}^{-1}$ since the induced dipole is short lived and rapidly fluctuating, as is the resultant field due to the motions of neighbouring molecules. Therefore, any approximation to the a.c.f. of the permanent dipole alone should in principle be investigated, as in this paper, with the use of data below 1 cm^{-1} where no experimental technique has been developed which is sufficiently accurate to separate out their contribution to the Cole/Cole semicircle, and the high frequency absorption predicted therefrom.

Accurate data in the decade from 1 to 10 cm^{-1} are very scarce, but in this paper we use a polarising interferometer and a Rollin detector to measure the absorption of some halogenobenzenes and an alkyl halide from 2 to 200 cm^{-1} , thus completing the low frequency work started by Poley.⁵ In general, the Fourier transform of these bands is related to a correlation function $C(t)$ compounded of the following.

$$C(t) = C_p(t) + C_{\text{ind}}(t) + C_{p,\text{ind}}(t), \quad (1)$$

where

$$C_p(t) = C_{\text{sp}}(t) + C_{\text{cp}}(t).$$

Here, $C_{ap}(t) = \langle \mu(0) \cdot \mu(t) \rangle$, the microscopic autocorrelation function of the permanent dipole moment μ ; $C_{cp}(t) = \langle \mu_i(0) \cdot \sum_j \mu_j(t) \rangle$, the microscopic cross-correlation function of the permanent dipole; and $C_{ind}(t) = \sum_{ij} \langle M_i[V(0), 0] \cdot M_j[V(t), t] \rangle$, the cross-correlation function of the interaction induced dipoles $M(V(t), t)$ which are all dependent on the resultant potential at a molecule due to the others at a time t . Unlike μ , M varies in magnitude as well as direction. There is a further contribution $C_{p,ind}(t)$ needed to account for the auto- and cross-correlations between $\mu_i(t)$ and $M_j(t)$.

It is by no means straightforward to relate the macroscopic (observed) correlation function, the Fourier transform of the observed absorption over all frequencies up to $\sim 250 \text{ cm}^{-1}$, to these microscopic functions which sum up to $C(t)$. The attempts at resolving this problem of the dynamic internal field have been reviewed by Brot,⁶ but recently Madden and Kivelson⁷ have greatly simplified the problem by the use of dynamical projection operators to separate the fast variables from the slow in the dynamical set making up a molecular ensemble in the fluid state. A consequence of their theorem is that if a microscopic autocorrelation function were to be expressed in terms of three complex exponentials, such as in our previous paper,¹ the macroscopic cross-correlation function will also be of that same analytical form, but with pre-exponential factors and correlation times proportional to, but different from, ours. Thus the frequency spectrum would be similar in form but different in intensity.

Here we represent $C_{ap}(t)$ by a Mori expansion⁸ truncated with: (i) an exponential; (ii) a Gaussian; (iii) a Lorentzian dependence upon time of the second kernel^{1, 4, 7} $K_1(t)$. We fit the data where $C_p(t)$ is experimentally predominant ($\nu < 1 \text{ cm}^{-1}$) and extrapolate the theoretical curves (which are all exponential at long times) to the time origin (through the far infrared frequency region). We find that the short time behaviour of the three curves is quite different, and only another exponential seems capable of producing realistic absorptions from 1 to $\sim 200 \text{ cm}^{-1}$. Where possible, the induced absorption bands for the dipolar monohalobenzenes are separated out from the overall process. They account for well over 50% of the integrated intensity $\left[\int_0^\infty \alpha(\bar{\nu}) d\bar{\nu} \right]$, where $\alpha(\bar{\nu})$ is the absorption coefficient in units of neper cm^{-1} .

EXPERIMENTAL

The power absorption spectra were recorded using a Michelson/NPL interferometer modified to operate in the polarizing mode as described by Martin and Puplett.⁹ In principle the interferometer is that shown in fig. 3 of the above reference.

The Polarizer (P_1) is a circular grid wound with $10 \mu\text{m}$ tungsten wire with $50 \mu\text{m}$ spacing. This grid can be spun about its centre point thus acting as a polarizing chopper blade. A second polarizer (P_2) of similar construction is held in a fixed configuration, *i.e.*, either with the windings perpendicular or horizontal. The beam divider is again of similar construction but in this case the windings are at 45° to those of P_2 .¹⁰ The "roof-top" reflecting mirrors were manufactured to be $90^\circ \pm 1 \text{ arc}$.

A collimated beam is plane-polarized at P_1 in the plane normal to the page. It is then divided by the wire grid polarizer D_1 into a beam A, polarized with its E vector at 45° to the paper and beam B polarized at 90° to A. The "roof-top" reflectors act as polarization rotators and beams A and B are recombined at D. The recombined beam finally passes through polarizer P_2 (the analyser) which has its axis parallel to or at 90° to that direction. The beam reaching the detector is plane-polarized with an amplitude which varies periodically with path-difference in the same way as the normal Michelson interferometer.

For a monochromatic source, *i.e.*,

$$I_p = \frac{1}{2} I_0 [1 + \cos \delta]$$

and

$$I_t = \frac{1}{2} I_0 [1 - \cos \delta]$$

where $\delta = (2\pi/\lambda)x$, (where x is the path difference) and I_0 is the intensity of the plane polarized beam incident on D. The case I_p is for parallel P_1 and P_2 and I_t is for crossed P_1 and P_2 .

Polarizing grids have reflection and transmission coefficients close to 100% for their respective planes of polarization,¹¹ from frequencies close to zero up to $\frac{1}{2}d$ cm⁻¹ where $1/d$ is the spatial frequency of the wires. Grids have the advantage of eliminating "hooping" such as is found with Mylar or Melinex beam-splitters.¹² The response curve for the interferometer should be flat with frequency falling off at $1/(2d)$ cm⁻¹. This, however, does not take into allowance the frequency response of the mercury arc lamp, which rises with increasing frequency, so although we do not see the full benefits of a flat frequency at low frequency we do gain over other far infrared modulation techniques (amplitude and phase modulation) with an increased response at wave numbers ≤ 10 cm⁻¹ plus an increased spectral range with a single beam divider due to the elimination of "hooping".

The interferometer was not evacuable as we were interested in the range 2-50 cm⁻¹ where water vapour absorption is negligible, particularly so below 30 cm⁻¹ which was our main region of interest. The detector was a liquid helium cooled InSb Rollin detector.¹³ The resolution was 2 cm⁻¹ in all cases.

The range above 50 cm⁻¹ was covered with an evacuated, standard Grubb-Parsons Mark III interferometer at Aberystwyth using the same VC-01 variable path length cell as with the above instrument. All solvents were AnalaR or spectroscopic grade, dried over type 3A zeolite baked out at over 673 K.

RESULTS

The present experimental results are shown in fig. 1(b) and 1(c) for bromobenzene and iodobenzene, and in fig. 3 for *t*-butyl chloride. Fig. 1(a) illustrates the data of M. N. Afsar (personal note) for chlorobenzene from 2 to 120 cm⁻¹. We include the microwave results of Poley⁵ for fluorobenzene on fig. 1(d), but no far infrared data are presently available.

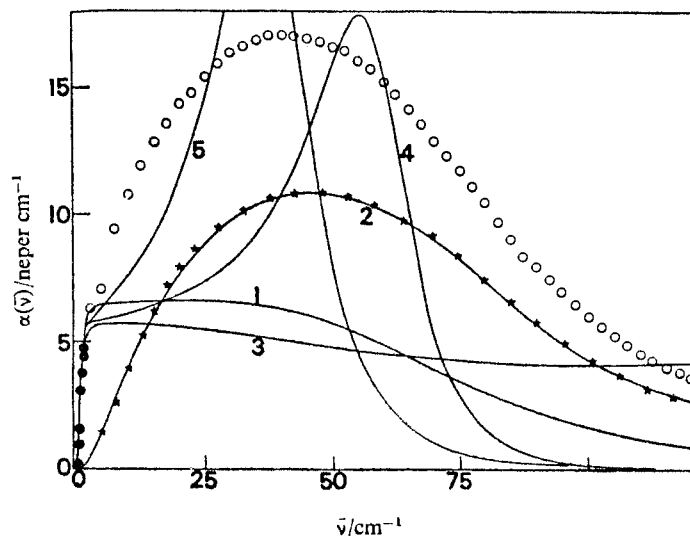
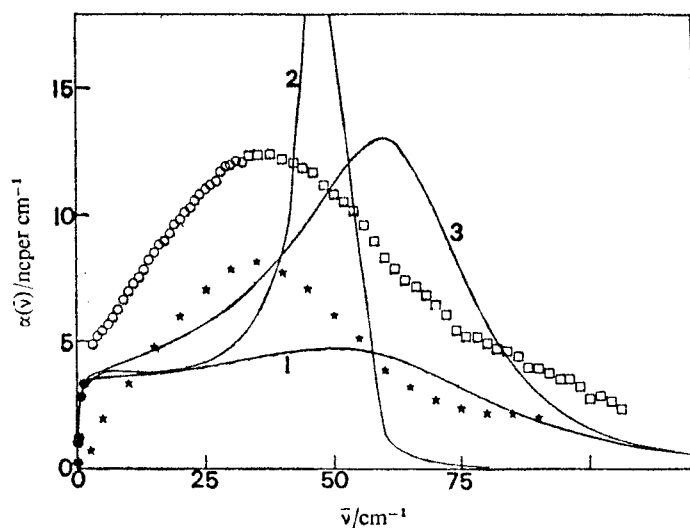
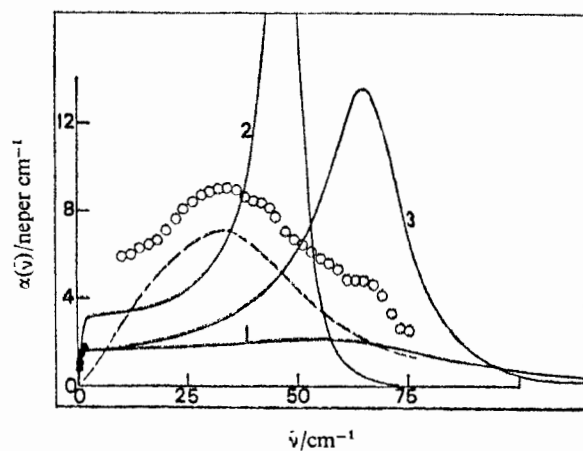


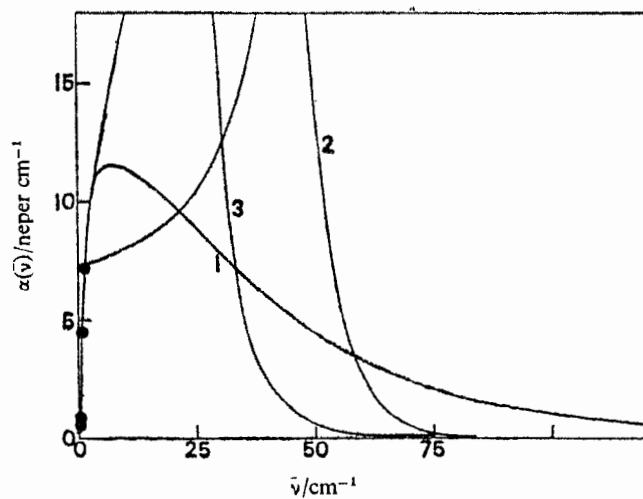
FIG. 1.—(a) ● Microwave results of Poley⁵ for chlorobenzene. ○ Far infrared results of Afsar (personal communication). — (1) Curve for the truncation in eqn (11). * Expt. data with curve (1) subtracted. — (2) Best fit to * of three variable theory.* — (3) Curve from eqn (28). — (4) Curve from eqn (12)—the Gaussian second memory. — (5) Curve from eqn (13)—the Lorentzian second memory.



(b) ● Poley's data⁵ for bromobenzene (klystron frequencies). ○ Polarising interferometer, present investigation. □ Grubb-Parsons "cube" interferometer, present investigation. — (1) Curve from eqn (11). * Expt. data with curve (1) subtracted. — (2) Curve from eqn (12). — (3) Curve from eqn (13).



(c) ● Poley's data ⁵ for iodobenzene. ○ Grubb-Parsons "cube", present investigation. — (1) Curve from eqn (11). --- Exptl. data with curve (1) subtracted. — (2) Curve from eqn (12). — (3) Curve from eqn (13).



(d) Poley's data ⁵ for fluorobenzene. — (1) eqn (11); — (2) eqn (12); — (3) eqn (13).

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Fig. 2 compares Poley's data with each of the theoretical curves from eqn (11) to (13) (below) on a Cole-Cole plot, with special emphasis on the theoretical high frequency curve of eqn (11) which shows significant deviations from the semicircular. Each of these theoretical plots reduce to the same semicircle up to about 1 or 2 cm^{-1} , but behave differently thereafter.

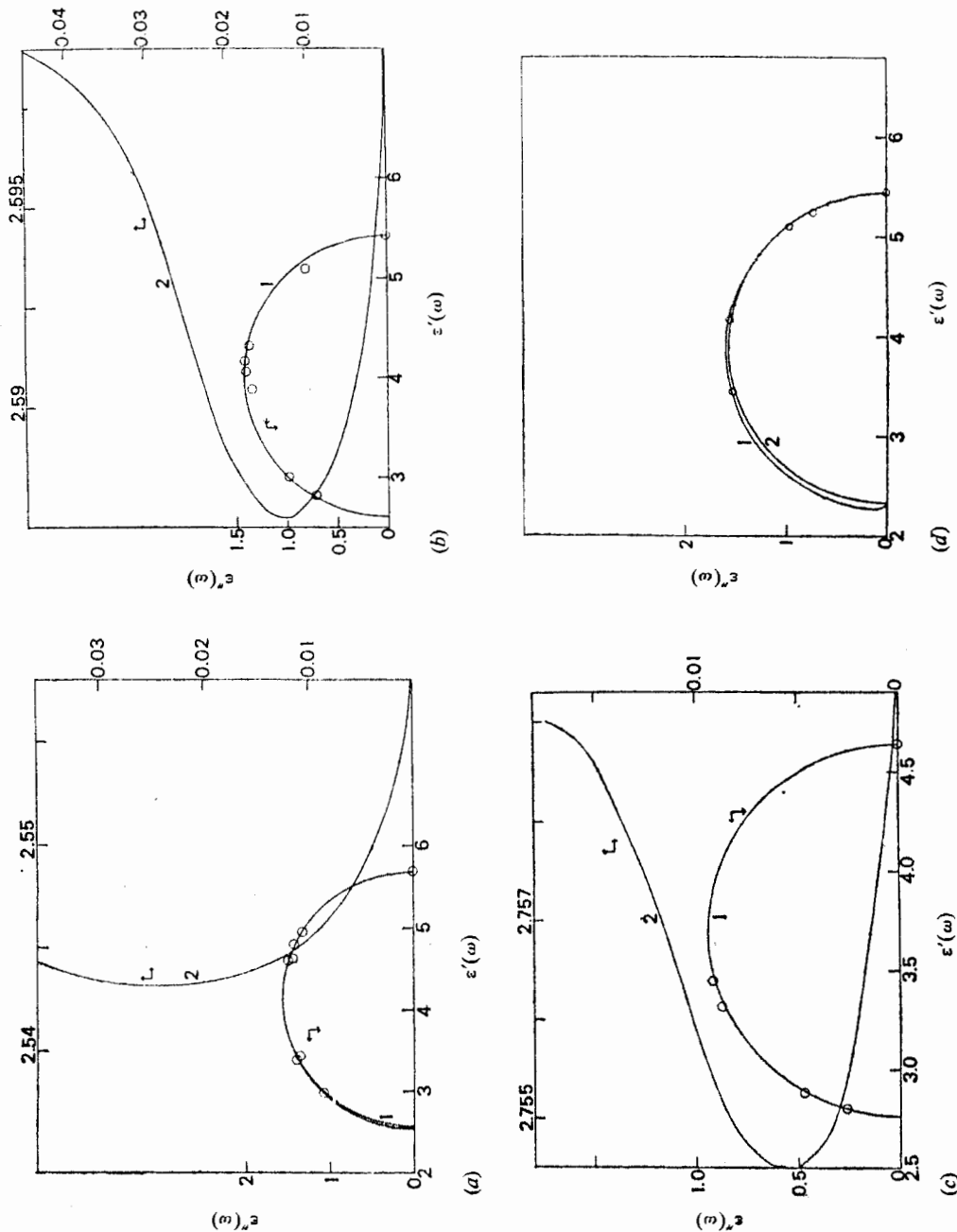


Fig. 2.—(a) \circ Collected microwave data for chlorobenzene.⁵ — eqn (27) l.m.s. best fit. (1) — Semicircular function at high frequencies. (2) — eqn (27) at far infrared frequencies (exponential memory).

(b) \circ Collected microwave data for bromobenzene.⁵ (1) — eqn (27), l.m.s. best fit. (2) — Details of the Cole-Cole plot at far infrared frequencies, with the exponential memory of eqn (11).

(c) \circ Microwave data for iodobenzene.⁵ (1) — eqn (27), l.m.s. best fit. (2) — Details of the Cole-Cole plot at far infrared frequencies, exponential memory.

(d) \circ Microwave data for fluorobenzene.⁵ (1) — eqn (27), l.m.s. best fit. (2) — Semicircular function.

In each available complete spectrum the agreement between the data from free-space Michelson/Rollin interferometry down to 2 or 4 cm⁻¹ and that from the klystron measurements⁵ is good. At the high frequency end [*e.g.*, for bromobenzene in fig. 1(b)], there is an equally satisfactory overlap between the P.O. polarising interferometer and an Aberystwyth phase modulated cube interferometer. Thus it seems that any systematic uncertainty between different klystrons and interferometers is acceptably small.

DISCUSSION

For coherence we recall some formalism of Berne, Boon and Rice¹⁴ concerning the general time evolution of the autocorrelation function [$C(t)$] of a dynamical operator (vector) U in phase space Γ :

$$C(t) = Z_N^{-1} \int d\Gamma_N U(\Gamma_N) \exp(it\mathcal{L}^{(N)}) U(\Gamma_N) \exp(-H^{(N)}/kT). \quad (2)$$

Here Z_N is the canonical partition function for the N molecule system, and $\mathcal{L}^{(N)}$, $H^{(N)}$ are the corresponding Liouville operator and hamiltonian. Denoting by $\langle \alpha \rangle$ the canonical average of α we have $\langle U \rangle = 0$, $\langle U^2 \rangle = 1$. Differentiation of eqn (2) twice, followed by integration by parts, leads directly to:

$$\ddot{c}(t) = -\langle \dot{u}(0)\dot{u}(t) \rangle = \phi(t) \quad (3)$$

the Laplace transformation of which, together with an algebraic identity for $C(p)$ yields the fundamental relation

$$\dot{c}(t) = \int_0^t K(t-\tau)c(\tau)d\tau \quad (4)$$

with

$$\bar{K}(p) = \bar{\phi}(p)/[1 - \bar{\phi}(p)/p]. \quad (5)$$

It is important to note that eqn (4) embodies no assumptions other than those inherent in eqn (2), and is true for *any* operator U whose expectation vanishes and for which $\dot{c}(t) = \langle u(0)\dot{u}(0) \rangle = 0$. Eqn (4) can be rederived independently by the use of linear regression theory¹⁴ and transport coefficients,¹⁵ and is a general theorem of statistical mechanics.

Defining a projection operator \hat{P} onto a well-behaved function of the phase Γ_N , $G(\Gamma_N)$, as:

$$\hat{P}G(\Gamma_N) = U(\Gamma_N) f_{\text{eq}}^{(N)} \int d\Gamma'_N U(\Gamma'_N) G(\Gamma'_N)$$

where $f_{\text{eq}}^{(N)} = Z_N^{-1} \exp(-H^{(N)}/kT)$; it follows that

$$K(t) = \langle \dot{u} \exp[it(1 - \hat{P})\mathcal{L}^{(N)}] \dot{u} \rangle \quad (6)$$

showing that the kernel K is related to the dynamical coherence, or memory, of the N particle ensemble. It is indeed possible¹⁶ to define a set of kernels, or memory functions, $K_0(t), \dots, K_n(t), \dots$, such that:

$$K_n(t) = \langle f_n \exp(i\mathcal{L}_n t) f_n \rangle \quad (7)$$

where the dynamical quantities f_n are defined so that $f_0 = U$ and $f_n = (1 - \hat{P}_{n-1})_t \mathcal{L}_{n-1} U_{n-1}$. This leads directly to the equations:

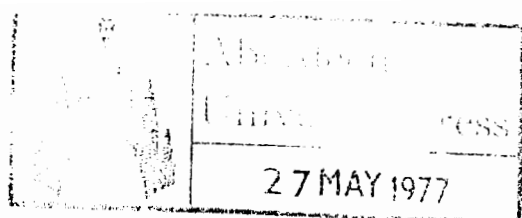
$$\frac{\partial}{\partial t} K_{n-1}(t) = - \int_0^t K_n(t-\tau) K_{n-1}(\tau) d\tau \quad (8)$$

first derived by Mori.⁸ In Laplace space, this is a continued fraction representation of $C(t) = \langle U(0)U(t) \rangle$, and implies that all $K_n(t)$ have even, real expansions in time (t), given that

$$C(t) = \sum_{n=0}^{\infty} (-1)^n \gamma_{2n} t^{2n} / (2n)!;$$

where

$$\gamma_{2n} = \langle U^{(n)} U^{(n)} \rangle.$$



If a property $F(t)$ is defined such that :

$$F(t) = (\{\exp i(1-\hat{P})\mathcal{L}t\})\mathcal{L}u \quad (9)$$

then it follows that :

$$\frac{\partial u}{\partial t} = - \int_0^t K(\tau)U(t-\tau) d\tau + F(t) \quad (10)$$

and from the definition (9) $K(t) = \langle F(0)F(t) \rangle$ and $\langle UF(t) \rangle = 0$. Eqn (10) is known as a generalised Langevin equation, but can be derived without any assumptions about Brownian motion *per se*. It is valid for any operator U which can be defined with an equation such as (2).

In this paper we define U as the unit vector u in the direction of the molecular dipole moment μ , and evaluate the far infrared/microwave absorption spectrum obtained by approximating $C_{ap}(t) = \langle u(0) \cdot u(t) \rangle$ with a truncated version of eqn (8). We justify the neglect of cross-correlation [$C_{cp}(t)$] on the following grounds :

(i) The observed far infrared bandshapes³ of many pure liquids change very little upon dilution in a non-dipolar solvent. In very dilute solutions the correlation function of the permanent dipole is truly a single molecule dot product. (ii) It can be shown theoretically⁷ that the shapes of these absorption bands will be insensitive to cross-correlations, although the absolute intensities may be heavily dependent upon them. This is particularly true at short times.¹⁷

We truncate the series of eqn (8) in three ways :

$$K_1(t) = K_1(0) \exp(-\gamma_1 t) \quad (11)$$

$$K_1(t) = K_1(0) \exp(-\gamma_2^2 t^2) \quad (12)$$

$$K_1(t) = K_1(0)/(1+\gamma_3^2 t^2) \quad (13)$$

where $K_1(t)$ is the memory function of $K_0(t)$, the memory function of $C_{ap}(t)$. Eqn (12) and (13) have even-powered Taylor series, whereas eqn (11) has all the odd terms as well, so that here $C_{ap}(t)$ will be well defined only up to the t^4 coefficient.¹ Physically, we are assuming that $K_1(t)$ might decay in a far simpler way than $C_{ap}(t)$ itself, and that this decay might be exponential, Gaussian, or Lorentzian, and in this way we hope to represent the complex N -body fluid molecular dynamics by a simple analytical function.

It follows from the general properties of projection operators,¹⁶ that the equilibrium statistical averages $K_0(0)$ and $K_1(0)$ are defined as :

$$K_0(0) = \langle [\dot{u}(0)]^2 \rangle \quad (14)$$

$$K_1(0) = \frac{\langle [\ddot{u}(0)]^2 \rangle}{\langle [\dot{u}(0)]^2 \rangle} - \langle [\dot{u}(0)]^2 \rangle \quad (15)$$

so that $K_1(t)$ has the units of the autocorrelation function :

$$K_1(t) = \frac{\langle \ddot{u}(0) \cdot \ddot{u}(t) \rangle}{\langle \dot{u}(0) \cdot \dot{u}(0) \rangle} \quad (16)$$

In general, for an asymmetric top, Brot has shown¹⁷ that

$$\langle \ddot{u}^2(0) \rangle = kT \left[\frac{(U_y^2 + U_z^2)}{I_x} + \frac{(U_z^2 + U_x^2)}{I_y} + \frac{(U_x^2 + U_y^2)}{I_z} \right] \quad (17)$$

where $|u| = (U_x^2 + U_y^2 + U_z^2)^{1/2} = 1$; and I is the moment of inertia tensor. The a.c.f. $\langle \ddot{u}(0) \cdot \ddot{u}(t) \rangle$ can be related to the angular velocity, ω , by the equations :

$$\dot{u} = \omega \times u \quad (18)$$

$$\ddot{u} = \dot{\omega} \times u + \omega \times (\omega \times u). \quad (19)$$

Using these, and the general property $u \cdot \dot{u} = 0$ for a vector of constant magnitude, it is possible to show that :

$$\langle \ddot{u}^2 \rangle = \langle \dot{\omega}_\perp^2 \rangle + \langle (\omega_\perp \cdot \omega_\perp)^2 \rangle. \quad (20)$$

In eqn (20) ω_\perp is the component of the angular velocity mutually perpendicular to u and \dot{u} . Thus $K_1(0)$ is related directly to the mean square angular acceleration, $\langle \dot{\omega}_\perp^2 \rangle$ which consists of a centripetal part and a component due to the mean square torque $\langle T_M^2 \rangle$ imposed on the molecule by its surroundings. For a symmetric top, Desplanques¹⁸ has evaluated eqn (20) to be :

$$\langle \ddot{u}^2 \rangle = 2 \left(\frac{2kI}{I_B} \right)^2 \left(1 + \frac{I_B}{I_A} \right) + \frac{\langle T_M^2 \rangle}{I_B^2} \quad (21)$$

where I_A and I_B are inertia components in the standard notation. The autocorrelation function $\langle \ddot{u}(0) \cdot \ddot{u}(t) \rangle$ has the units of angular acceleration in general asymmetric top reorientation, and its general form at $t = 0$ is similar.

Given that $K_1(t) = K_1(0)f(t)$ in general, where $f(t)$ is a continuous, differentiable function of time, then it can be shown that the real and imaginary parts of $C_{ap}(-i\omega)$, the spectral Fourier transform of $C_{ap}(t)$ are given by:

$$\text{Re}[c(-i\omega)] = K_0(0)K_1(0) \int_0^\infty f(t) \cos \omega t / D; \quad (22)$$

$$\text{Im}[C(-i\omega)] = [A(\omega)(k_1(0) \int_0^\infty \sin \omega t dt - \omega) + \omega B(\omega)] / D \quad (23)$$

where

$$A(\omega) = K_0(0) + \omega K_1(0) \int_0^\infty f(t) \sin \omega t dt - \omega^2; \quad B(\omega) = K_1^2(0) \left(\int_0^\infty f(t) \cos \omega t dt \right)^2$$

with

$$D = A^2(\omega) + \omega^2 B(\omega).$$

Making no correction for the internal field, then the dielectric loss (ϵ'') and permittivity (ϵ') are given by:

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) \text{Re}[C(-i\omega)] \quad (24)$$

$$\epsilon' = \epsilon_0 - (\epsilon_0 - \epsilon_\infty) \omega \text{Im}[C(-i\omega)] \quad (25)$$

with ϵ_0 as the static permittivity and ϵ_∞ that at $\sim 250 \text{ cm}^{-1}$. The optical absorption coefficient ($\alpha(\bar{\nu})/\text{neper cm}^{-1}$) is then related to ϵ'' and ϵ' by the Maxwell equation

$$\alpha(\bar{\nu}) = \frac{2\sqrt{2}\pi\epsilon''\bar{\nu}}{[(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon']^{1/2}} \quad (26)$$

The method employed here to investigate the spectral consequence of the truncations represented by eqn (11)-(13) is to make a least squares fit to the theoretical expression:

$$\frac{\epsilon_0 - \epsilon'}{\epsilon''} = \frac{A(\omega) \left[K_1(0) \int_0^\infty f(t) \sin \omega t dt - \omega \right] + \omega B(\omega)}{K_0(0)K_1(0) \int_0^\infty f(t) \cos \omega t dt} \quad (27)$$

for the experimental data below $\sim 2 \text{ cm}^{-1}$ and extrapolate to the far infrared using eqn (26) for comparison with $\alpha(\bar{\nu})$ observed. We iterate on $K_1(0)$ and the correlation times γ_n^{-1} , but keep $K_0(0)$ fixed at $2kT/I_B$, which by equipartition is the mean square angular velocity for a linear or symmetric top molecule. The integrals can be evaluated numerically to any required accuracy.

The results are shown in fig. 1 to 3. Using this method, eqn (27) produces the same low frequency Cole-Cole plot for all $f(t)$, initially semicircular, but approaching the $\epsilon'' = 0$ axis horizontally in the high frequency limit (fig. 2). However, eqn (11)-(13) yield very different results at $\bar{\nu} > 2 \text{ cm}^{-1}$, the Gaussian [eqn (12)] being particularly unrealistic. This diversification means that the form of $K_1(t)$ must be accurately defined since the far infrared provides critical discrimination for short-time behaviour. In comparison, the far wings of the Rayleigh depolarised spectrum, for example, would represent $\alpha(\omega)/\omega^2$, or, to a very good approximation $\epsilon''(\omega)/\omega$, and as a consequence any deviation from the low frequency Lorentzian is difficult to observe. In the $\epsilon''(\omega)$ representation, the whole of the far infrared is already reduced to a slight high frequency deviation³ from the classical Debye form.²

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A Lorentzian decay for $K_1(t)$ produces only slightly more realistic results, but the exponential form is by far the best behaved although, paradoxically, this contains physically unacceptable odd powers of time in its series expansion, not in the other functions. For some of the roughly symmetric top pure liquid monohalogenobenzenes at room temperature a smooth curve is obtained by subtracting this theoretical absorption from the experimental data (fig. 1), a curve which can be simulated closely in turn as shown by Davies and Evans,⁴ *i.e.*, by using eqn (22)–(26) with $K_0(0)$ a free variable and torque dependent; this may be taken as perhaps matching the induced absorption band in these fluids. The integrated intensities of these latter are close to those estimated by Pardoe²² using the sum rule [eqn (17)] for the total rotational integrated intensity expected from the permanent dipole alone.

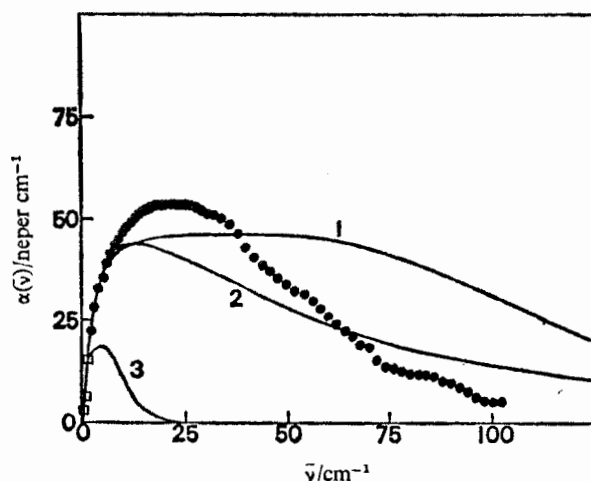


FIG. 3.—□ Poley's microwave data⁵ for t-butyl chloride. ● Polarising interferometer, present investigation. — (1) eqn (11); (2) eqn (28); (3) eqn (12).

For pure liquid t-butyl chloride at 295 K (fig. 3), even the exponential produces a very unsatisfactory result, but taking another term in the Mori series via:

$$K_2(t) = K_2(0) \exp(-\gamma_4 t) \quad (28)$$

iterating on $K_2(0)$, $K_1(0)$ and γ_4 , produces a significant improvement. Nonetheless, these curves, necessarily identical in the microwave region, show up a disappointing lack of convergence in the far infrared. This is especially true, for example, in chlorobenzene, where the use of eqn (28) produces a *more unrealistic* curve than that from eqn (11). The conclusion is that not one of the forms of eqn (11) to (13) is acceptable. The only "direct" source of information about this autocorrelation function at present available comes from the numerical technique of "molecular dynamics", where the Newton equations are solved numerically for a group of about 10^2 particles with a given intermolecular potential (such as the Lennard-Jones with added electrostatic terms, such as the quadrupole-quadrupole). Only very simple "molecules" are yet computed, but little or no work has been done on the autocorrelation of \dot{u} , although it is known¹⁶ that the autocorrelation of \mathbf{J} , the total molecular angular momentum, is complicated, sometimes oscillatory, and definitely non-exponential.

It seems on the slender experimental evidence available that the empirical eqn (11) reproduces far infrared *induced* absorption bands in non-dipolar fluids adequately, but satisfactorily only *some* of the data available for dipolar dense liquids.

For some other fundamental reasons which may explain in part the inability of theory to match satisfactorily the experimental results given here we refer the reader to Deutch,²³ whose recent assessment indicates the theoretical and practical difficulties that are encountered in dielectric measurements of molecular motion. He concluded that differences in the predictions of the various models became more pronounced at short times (far infrared) and the underlying assumptions about the effects of intramolecular motions and polarisabilities become more uncertain.

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- ¹ G. J. Evans and M. Evans, *J.C.S. Faraday II*, 1976, **72**, 1169.
- ² P. Debye, *Polar Molecules* (Chemical Catalog Co., N.Y. 1929); *Polare Molekeln* (S. Hirzel Verlag, Leipzig, 1929).
- ³ M. Davies, *Ann. Report*, 1971, **67**, 65.
- ⁴ G. J. Davies and M. Evans, *J.C.S. Faraday II*, 1976, **72**, 1194, 1206; *Chem. Phys. Letters*, 1976, **41**, 521.
- ⁵ J. Ph. Poley, *J. Appl. Sci. B*, 1955, **4**, 337.
- ⁶ C. Brot, in *Dielectric and Related Molecular Processes* (Chemical Soc., London, 1972), vol. II, p. 1.
- ⁷ P. Madden and D. Kivelson, *Mol. Phys.*, 1975, **30**, 1749.
- ⁸ H. Mori, *Progr. Theor. Phys.*, 1965, **33**, 423; G. Wyllie, ref. (6).
- ⁹ D. H. Martin and E. Puppelt, *Infrared Phys.*, 1969, **10**, 105.
- ¹⁰ D. G. Vickers, E. I. Robson and J. E. Beckman, *Appl. Optics*, 1971, **10**, 682.
- ¹¹ A. E. Coxley and J. M. Ward, unpublished work at N.P.L.
- ¹² P. L. Richards, *J. Opt. Soc. Amer.*, 1964, **54**, 1478.
- ¹³ P. E. Clegg and J. S. Huizinga, *I.E.R.E. Conf. Infrared Techniques* (Reading, 1971).
- ¹⁴ B. J. Berne, J.-P. Boon and S. A. Rice, *J. Chem. Phys.*, 1966, **45**, 1086.
- ¹⁵ R. Zwanzig, *J. Chem. Phys.*, 1964, **40**, 2527.
- ¹⁶ B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 106.
- ¹⁷ A. Gerschel, I. Darmon and C. Brot, *Mol. Phys.*, 1972, **23**, 317.
- ¹⁸ P. Desplanques, *These d'Etat* (Univ. of Lille, 1974).
- ¹⁹ H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (van Nostrand, N.Y., 1962), p. 286.
- ²⁰ J. O. Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.
- ²¹ M. R. Spiegel, *Theory and Problems of Vector Analysis* (Schaum, N.Y., 1959), p. 51.
- ²² G. W. F. Pardoe, *Thesis* (Univ. of Wales, 1969).
- ²³ J. M. Deutsch, *Faraday Symp. Chem. Soc.*, 1976, **11**.

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