Comparison in the Time Region 0-1.2 ps of Model and Experimental Absorptions of Liquid and Rotator Phases in the Far Infrared

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The Brot–Larkin and Wyllie–Larkin models of permanent-dipolar librational and relaxational molecular motion in the liquid and plastic crystal (rotator) phases are tested in the time domain by comparing the theoretical rotational velocity correlation functions with the Fourier transform of the optical absorption coefficient per unit length [$\alpha(\omega)$]. The discord between model and observation is particularly acute at short times. The Brot–Larkin function does not have the necessary zero slope of the correlation function at $t \to 0$ because of its use of an effectively infinite intermolecular mean square torque. The Wyllie–Larkin treatment also results in an excessive apparent mean square torque, although having the correct short-time zero slope. These features are reflected in the fact that the theoretical curves are too broad in the frequency domain, i.e., do not correctly predict the sharp high frequency fall off in $\alpha(\omega)$. This has the further consequence that the model rotational velocity correlation functions do not show the pronounced short time oscillations of the experimental curves. Qualitative improvements are suggested.

It is by now well established [1,2] that the observed microwave–far infrared bands of simple dipolar molecules in the plastic (rotator) and dense liquid phases are compounded of the following origins. (i) A non-resonant part arising from stochastic diffusion of the permanent dipole, a process approximated by the Debye equations, corrected for inertia,[3] which lead to spectral transparency at about 50-150 cm^{-1} after a period of constancy in $\alpha(\bar{v})$ (the frequency dependent absorption per unit sample path length, in neper cm^{-1}) lasting typically from about 10-100 cm^{-1}, and known as the Debye plateau. (ii) Absorption rising above this plateau generally attributed to the short time process of libration, or torsional oscillation, of the permanent dipole, the restoring torque on which is the derivative of the potential barrier due to the neighbouring molecular fields (the Poley absorption). (iii) Additional absorption due to transient dipoles induced in a molecule by the neighbouring molecular fields and modulated by their motion. This causes absorption in non-dipolar liquids in the region 2-250 cm^{-1}.

(i) and (ii) form the long and short time parts of the same overall process, models for which have been developed by Brot [5] and Wyllie.[6] These have been extended and gradually applied to the plastic and dense liquid phases of progressively aniso-tropic molecules by Larkin *et al.*[7-12] Absorption curves [$\alpha(\bar{v})$] have been computed and matched, in the frequency ($\bar{v}$) domain, with the broad experimental bands using phenomenological parameters which were adjusted for best fit. That such parameters have a statistically valid physical meaning on the molecular scale is illustrated by the fact that a higher mean barrier to libration V (as estimated from both models) is needed as the molecular geometric anisotropy increases.

The aim of this investigation is to compare the correlation function,

$$F(t) = \frac{\langle \dot{u}(0) \cdot \dot{u}(t) \rangle}{\langle \dot{u}(0) \cdot \dot{u}(0) \rangle}$$

(where u is the unit vector along the permanent dipole, and t the time elapsed from an arbitrary $t = 0$) computed from both models with the direct Fourier transform of the observed $\alpha(\bar{v})$ into the time domain. This is carried out for the examples in ref. (7)-(12). This process accentuates the differences between the computed and the observed $\alpha(\bar{v})$ bands, and illustrates directly the dipolar fluctuations and molecular interactions which are the origins of the observed absorptions. From such comparisons as are given here, it is possible to perceive qualitatively what adjustments are needed in these models to evolve a better description of the molecular dynamics, and also to estimate roughly to what extent the bands are distorted by process (iii) above. We first discuss the effect of the internal field on the Fourier transform of $\alpha(\bar{v})$ (experimental) and explain why this refinement of the data is advantageous.

CONTINUUM REPRESENTATIONS OF THE FREQUENCY DATA

If the frequency domain absorptions could be described adequately in terms of transitions between quantised energy levels (e.g. pure rotation of a small molecule in the dilute gas) then the time development of the system would be of secondary interest. However the continuous, broad bands observed in ref. (7)-(12) make assignment of individual transitions impossible. The intensity distribution in $\alpha(\bar{v})$ in these systems is the result of a many-molecule process, and the far infrared spectra can be interpreted more profitably in terms of the Fourier transform of an appropriate time correlation function [13] whose short-time and long-time behaviour may be isolated and discussed separately. (The intensity at any particular frequency includes contributions from the entire time development of a correlation function.) For relatively heavy molecules the correlation function is real, and may be expanded in even powers of time. Neglecting the internal field and the effect of induced dipoles, $\alpha(\bar{v})$ is given by,[13]

$$\alpha(\bar{v}) = \frac{2\pi\bar{v}\varepsilon''(\bar{v})}{n(\bar{v})} = \frac{8\pi^3 N\bar{v}^2 c\mu^2}{3kTn(\bar{v})} \int_{-\infty}^{\infty} \exp(-2i\pi\bar{v}ct)\langle u_1(0)\cdot\sum_i u_i(t)\rangle\,dt$$

where u_i is the unit vector along the permanent dipole μ_i of the ith molecule, $\varepsilon''(\bar{v})$ the loss factor, $n(\bar{v})$ the refractive index, N the molecular number density, T the absolute temperature, and c and k the usual fundamental constants. Using the general relation,

$$\frac{d^2}{dt^2}\langle u_1(0)\cdot\sum u_i(t)\rangle = -\langle \dot{u}_1(0)\cdot\sum_i \dot{u}_i(t)\rangle$$

then

$$\alpha(\bar{v}) = \frac{2\pi N\mu^2}{3ktcn(\bar{v})} \int_{-\infty}^{\infty} \exp(-2\pi i\bar{v}ct)\langle \dot{u}_1(0)\cdot\sum_i \dot{u}_i(t)\rangle\,dt. \tag{1}$$

If cross correlations are neglected, then the correlation function becomes $\langle \dot{u}_1(0)\cdot\dot{u}_1(t)\rangle$.

In principle, both the correlation function $f_0(t) = \langle u_1(0)\cdot\sum_i u_i(t)\rangle$ and $f_2(t) = \langle \dot{u}(0)\cdot\sum_i \dot{u}_i(t)\rangle$ contain the same information, but in practice, frequency data above about 10 cm^{-1} affect $f_0(t)$ very little, and the converse is true for $f_2(t)$, so that the nature of the short-time motion [process (ii) above] is much more clearly visualised with the latter. The value of $f_2(t)$ at zero time ($t = 0$) is a single molecule property which Brot [14] has evaluated as,

$$\langle \dot{u}^2\rangle = kt[(u_y^2+u_z^2)/I_x+(u_z^2+u_x^2)/I_y+(u_x^2+u_y^2)/I_z]. \tag{2}$$

Writing the inverse Fourier transform of eqn (1) and taking it at $t = 0$, one obtains the zeroth moment, or integrated intensity, of the dipolar absorption per molecule,

$$\frac{1}{N}\int_0^\infty \alpha(\bar{\nu})\,\mathrm{d}\bar{\nu} = \frac{2\pi\mu^2}{3c^2}\left(\frac{u_y^2+u_z^2}{I_x}+\frac{u_z^2+u_x^2}{I_y}+\frac{u_y^2+u_x^2}{I_z}\right) \tag{3}$$

which is the sum rule of Gordon,[15] obtained previously using a non-equilibrium method. In practice, the sum (3) is exceeded in dipolar compressed gases,[16, 17] liquids,[18] and plastic phases of molecules, partly because internal field corrections have not been applied to the left-handed side of eqn (3), but mainly because of mechanism (iii) above.

Two treatments of the problem of the internal field in a group of intercorrelated molecules constrained in a cavity just large enough for the correlations to be negligible outside have been recently pursued. Using the Lorentz field, Brot[14] has obtained the following equation for $f_2(t)$,

$$f_2(t) = \frac{2}{\pi}\times\frac{3kT}{2N\mu^2}\times 9c^2 \int_0^\infty \frac{\alpha(\bar{\nu})n(\bar{\nu})\cos(2\pi\nu ct)\,\mathrm{d}\bar{\nu}}{[\varepsilon'(\bar{\nu})+2]^2+\varepsilon''(\bar{\nu})^2} \tag{4}$$

where $\varepsilon(\bar{\nu})$ is the frequency dependent permittivity; and using the Onsager field,

$$f_2(t) = \frac{2}{\pi}\times\frac{3kT}{2N\mu^2}\times\frac{9c^2(2\varepsilon_0+\varepsilon_\infty)^2}{(\varepsilon_\infty+2)^2}\int_0^\infty \frac{\alpha(\bar{\nu})n(\bar{\nu})\cos(2\pi\bar{\nu}ct)\,\mathrm{d}\bar{\nu}}{[\varepsilon'(\bar{\nu})+2\varepsilon_0]^2+\varepsilon''(\bar{\nu})^2}. \tag{5}$$

It is fortunate that while the corresponding corrections for $f_0(t)$ give very different results, (4) and (5) give similar curves, because above $\sim 10\ \mathrm{cm}^{-1}$, $n(\bar{\nu})\doteqdot n_0$, the D-line refractive index, $\varepsilon'(\bar{\nu})\doteqdot\varepsilon_\infty$, and $\varepsilon''(\bar{\nu})$ is small [although $\alpha(\bar{\nu})$ is large]. Using these approximations, eqn (4) and (5) both reduce to

$$f_2(t) = \frac{2}{\pi}\times\frac{3kT}{2\pi N\mu^2}\left[\frac{9n_0}{(n_0^2+2)^2}\right]c^2\int_0^\infty \alpha(\bar{\nu})\cos(2\pi\bar{\nu}ct)\,\mathrm{d}\bar{\nu}. \tag{6}$$

In eqn (6) the brackets enclosed the often used [1, 4, 9, 16-18] Polo–Wilson non-dispersive correction. The function we shall use in representing the experimental $\alpha(\bar{\nu})$ data is calculated from eqn (6) and normalised to unity by division with $f_2(0)$ at each t, and is therefore independent of this non-dispersive correction.

THEORETICAL MODELS

In the rotator phase, and perhaps in the liquid phase, the following types of molecular motion could, *a priori*, be taking place.

(*a*) Free rotation,[19] where the absorption would be the envelope of the pure rotational $J\to J+1$ transitions of the gas phase. Among the plastic phases considered in this work are those of the symmetric top molecules $(CH_3)_3CCl$, $(CH_3)_3CNO_2$, and $CH_3 CCl_3$, and that of the linear HCl. For these molecules, it has been shown [17] that for free rotation,

$$f_{\mathrm{fr}}(t) = \langle \dot{u}(0)\cdot\dot{u}(t)\rangle$$
$$\propto \int_0^\infty \sum_{K=-J}^{J}\left[S(I,K)\left(\frac{\bar{\nu}^3}{2B}-2B\bar{\nu}K^2\right)\exp\left(\frac{-|(A-B)|K^2hc}{kT}\right)\right]$$
$$\exp\left(-\frac{Bhc}{kT}\left(\frac{\bar{\nu}}{2B}-1\right)\frac{\bar{\nu}}{2B}\right)\cos(2\pi\bar{\nu}ct)\,\mathrm{d}\bar{\nu} \tag{7}$$

where $J = \bar{\nu}/2B-1$. In eqn (7) $S(I, K)$ is the nuclear spin weighting factor,[16] A

and B the rotational constants, and K the quantum number associated with the component of the angular momentum along the symmetry (threefold) axis.

For freely rotating linear molecules,[14]

$$f_{\mathrm{frl}}(t) = \langle \dot{u}(0) \cdot \dot{u}(t) \rangle$$

$$= \int_0^\infty \omega^3 \exp(-\omega^2/2) \cos \omega t \, d\omega \qquad (8)$$

where $\omega = (I/kT)^{\frac{1}{2}} 2\pi\bar{v}c$.

Eqn (7) is quantum mechanical in origin. but it has been shown [17] that $f_{\mathrm{fr}}(t)$ is practically identical with the corresponding experimental curve obtained from low pressure (1 bar) gas data. The classical equivalent of eqn (7) is given by St. Pierre and Steele.[23] Baise [24] has shown that eqn (8) and its quantised equivalent are identical.
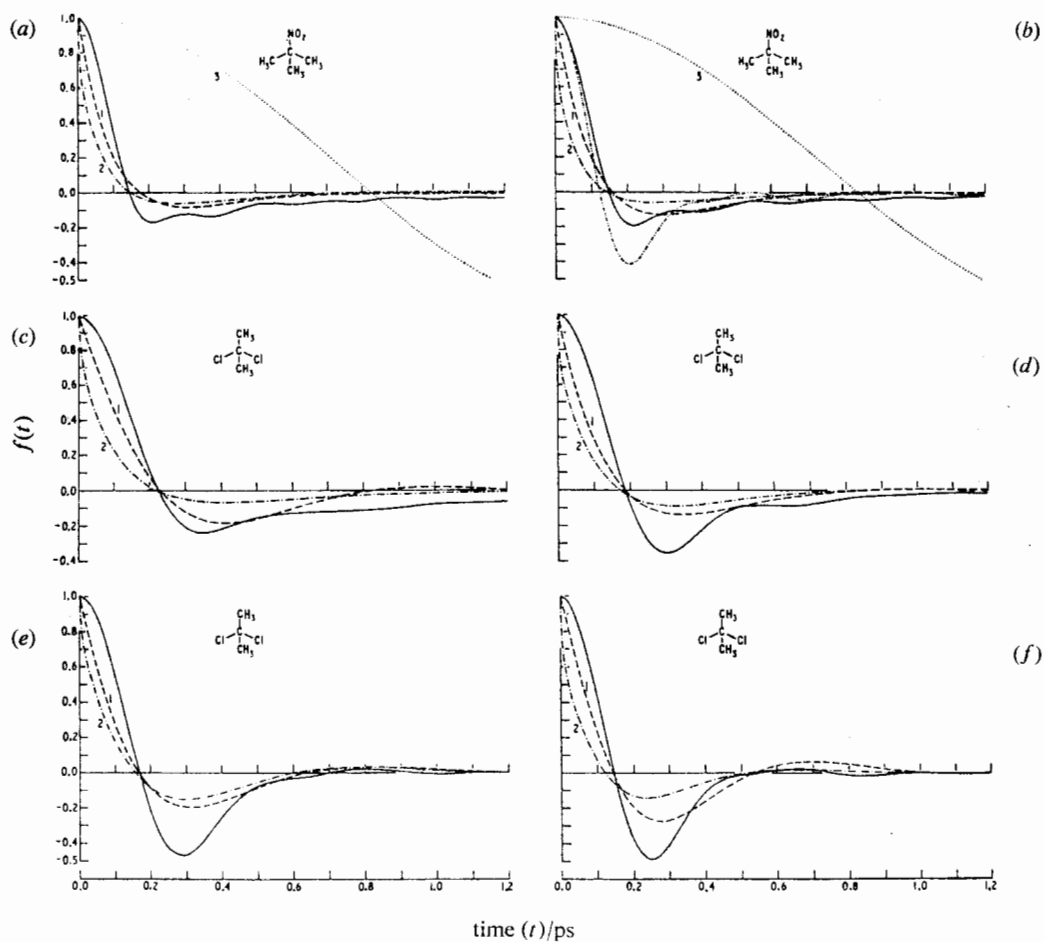

FIG. 1.——— experimental [7-12] curve $f_2(t)$, eqn (6). ————1, Brot–Larkin function, $f_B(t)$, eqn (10); 2, Wyllie–Larkin function, $f_w(t)$, eqn (12); 3, free rotor, eqn (7) or (8).

2-methyl-2-nitropropane (a) (rotator phase 1) at 294 K, (b) at 273 K and 219 K ; 2,2-dichloro-propane (c) (liquid) at 295 K, (d) at 241 K, (e) (rotator phase) at 235 K, (f) at 192 K.

At *very* short times (fig. 7) this description of the molecule's motion in the condensed phase may be justifiable, but obviously not for longer times since eqn (7) is essentially a sum over resonance delta function absorptions ($J \to J+1$, $\Delta K = 0$). In contrast, the microwave absorptions in all the instances considered here follow the Debye (non resonance) pattern, with values of V calculated by Larkin *et al.* always greater than kT.
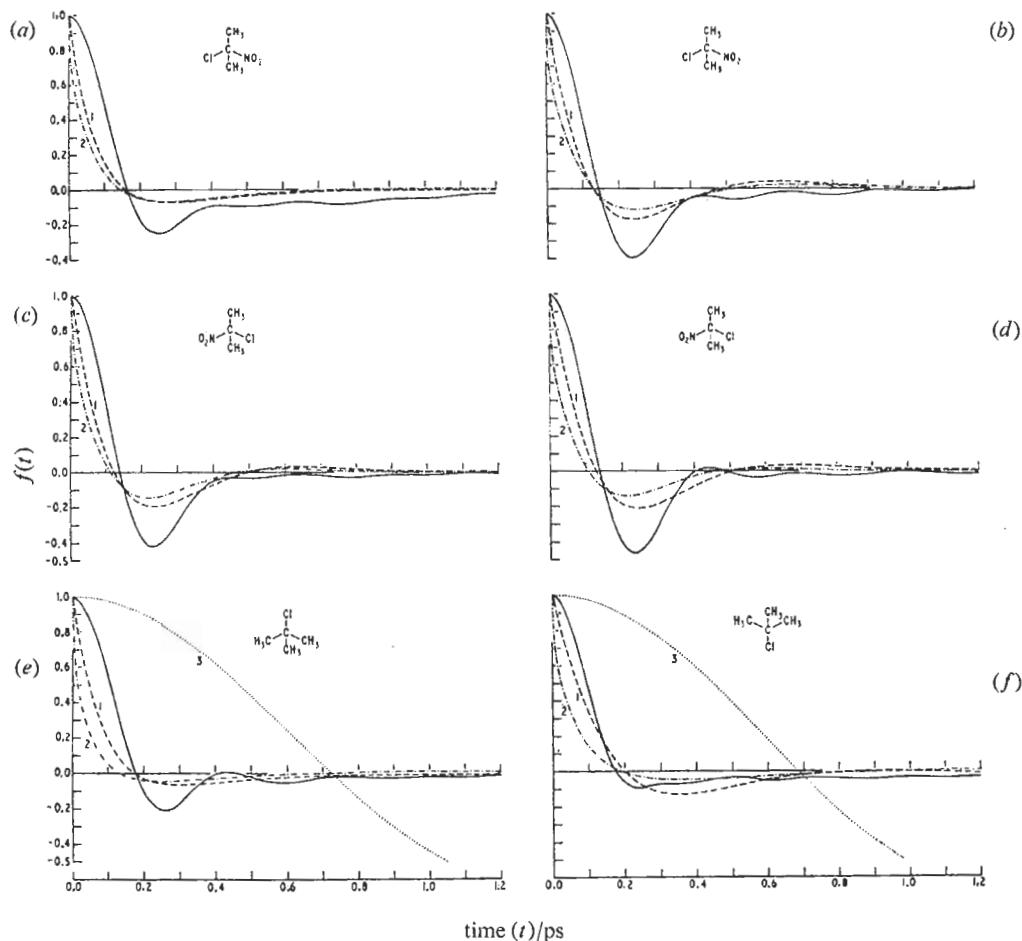

FIG. 2.— ——, and – – – –, as for fig. 1.
2-chloro-2-nitropropane (liquid) (a) at 293 K, (b) at 253 K, (c) (rotator) at 233 K, (d) at 209 K ; t-butyl chloride (rotator) (e) at 238 K (see also fig. 7), (f) (liquid) at 274 K.

(b) Certain molecular orientations are energetically less favoured than others, and the intermolecular potential does not have a spherical symmetry.   There are therefore a number of potential wells separated by barriers.   (This is in contrast to Debye's model, where the potential seen by a molecule is spherically symmetrical, but fluctuating interactions with neighbouring molecules manifest themselves as a mean microscopic " friction " coefficient).   Brot [5] has evaluated the classical autocorrelation function of an ensemble of librators subject to random adiabatic collisions on the basis of such potential anisotropy.   The consequences of this treatment are:
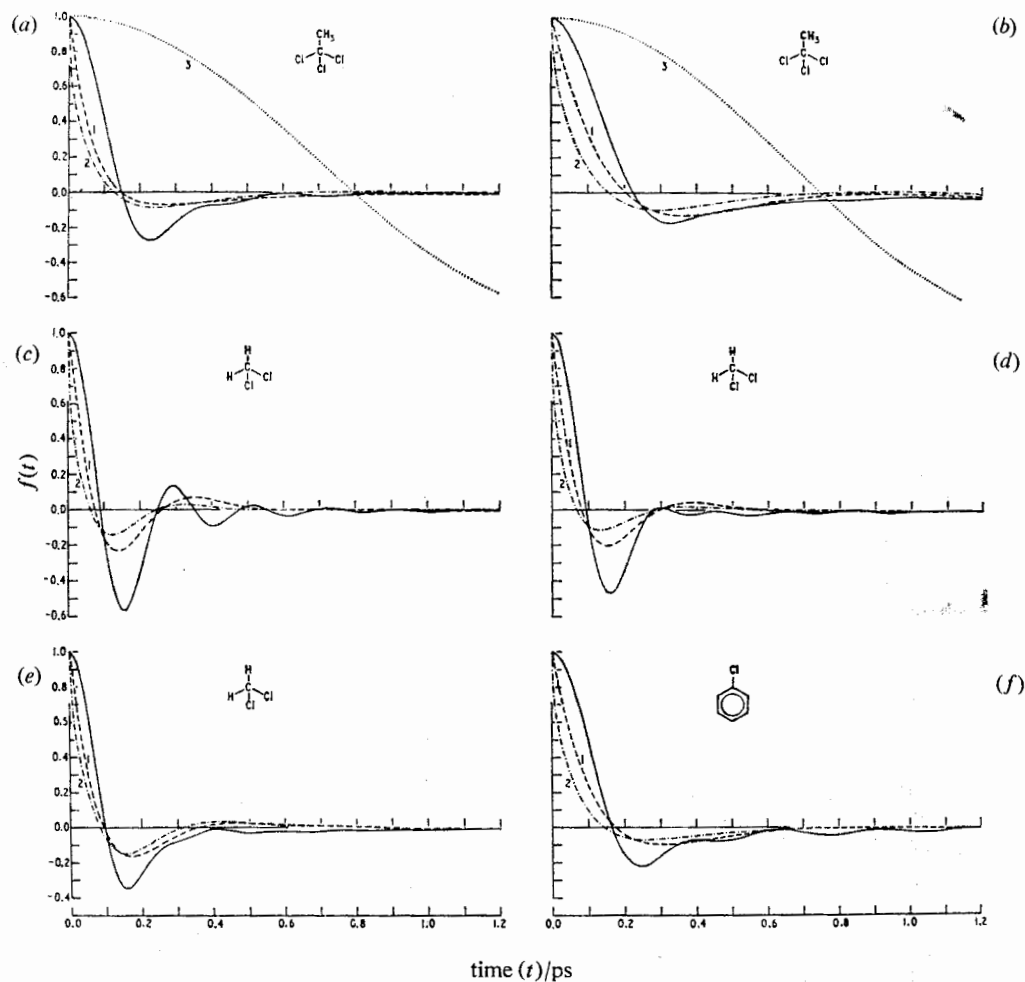
time (t)/ps

FIG. 3.—— ——, and – – – –, as for fig. 1.

1,1,1 trichloroethane (a) (rotator) at 233 K, (b) (liquid) at 293 K ; dichloromethane (c) at 188 K (liquid), (d) at 249 K (liquid), (e) at 298 K (liquid); chlorobenzene (f) (liquid) at 293 K.

(i) the molecules undergo libration for the duration (τ_r) of residence within a potential well;

(ii) the duration of jump (τ_a) from one well to another is not negligible.

The vectorial autocorrelation function predicted by this model and used by Larkin *et al.*[7-12] is,

$$
\begin{aligned}
f_b(t) &= \langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(t) \rangle \\
&= (1-2\beta^2)\left[\exp(-t/\tau_r) + \int_0^t \frac{\exp(-t_j/\tau_r)}{\tau_r} H(t-t_j)\,\mathrm{d}t_j \right] + \\
&\quad 2\beta^2\left[\exp(-t/\tau_r)V(t) + \int_0^t \frac{\exp(-t_j/\tau_r)}{\tau} V(t_j)H(t-t_j)\,\mathrm{d}t_j \right] \quad (9)
\end{aligned}
$$

where $V(t) = e^{-t/\tau} [\cos(at) + \sin(at)/a\tau]$ if $\omega_0 > 1/\tau$

$\qquad = e^{t/\tau} (1 + t/\tau)$ if $\omega_0 = 1/\tau$

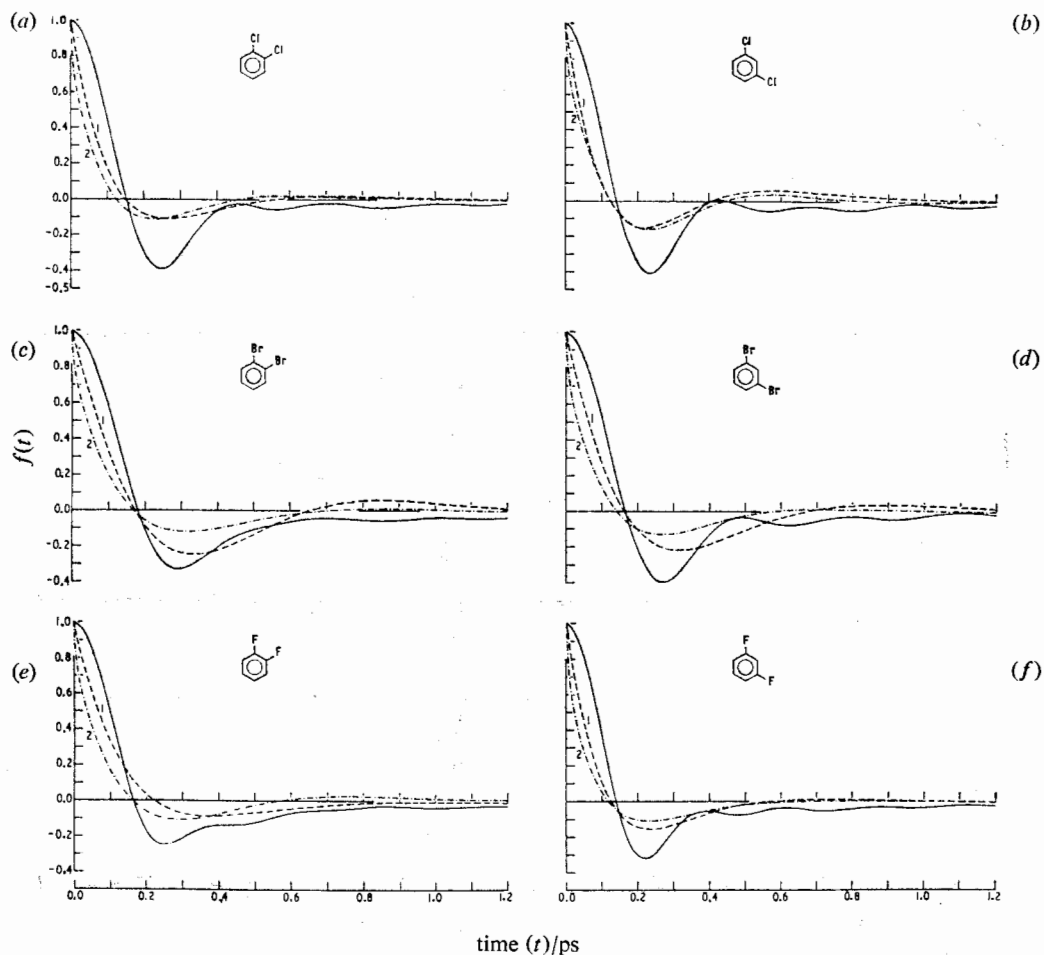$\qquad = e^{t/\tau} [\cosh(bt) + \sinh(bt)/b\tau]$ if $\omega_0 < 1/\tau$

FIG. 4.—──, and – – – –, as for fig. 1.

(a) o-dichlorobenzene; (b) m-dichlorobenzene; (c) o-dibromobenzene; (d) m-dibromobenzene; (e) o-difluorobenzene; (f) m-difluorobenzene. All liquid, at 293 K.

and $a^2 = -b^2 = \omega_0^2 - 1/\tau^2$, $\beta = kT/I\omega_0^2$, where ω_0 is the proper libration frequency and τ the mean time between adiabatic collisions. The correlation function of the molecules in a state of jump is taken arbitrarily [5] to be; $H(t - t_j) = \exp[-(t - t_j)/\tau_a][1 + (t - t_j)/\tau_a]$ the Fourier–Laplace transform of which is analytically known.

The second derivative of $f_b(t)$ has been evaluated [2] giving,

$$-f_b''(t) = \langle \dot{u}(0) \cdot u(t) \rangle = f_B(t). \qquad (10)$$

The consequences of assuming adiabatic (instantaneous) collisions in Brot's model

can be seen in the incorrect short time behaviour $f_B(t)$. Gordon [20] has shown that the classical autocorrelation function has the following expansion in powers of t;

$$\langle u(0) \cdot u(t) \rangle = 1 - \frac{kTt^2}{I} + O(t^4) - \cdots$$

$$\langle \dot{u}(0) \cdot \dot{u}(t) \rangle = \frac{2kT}{I} - O(t^2) + \cdots$$
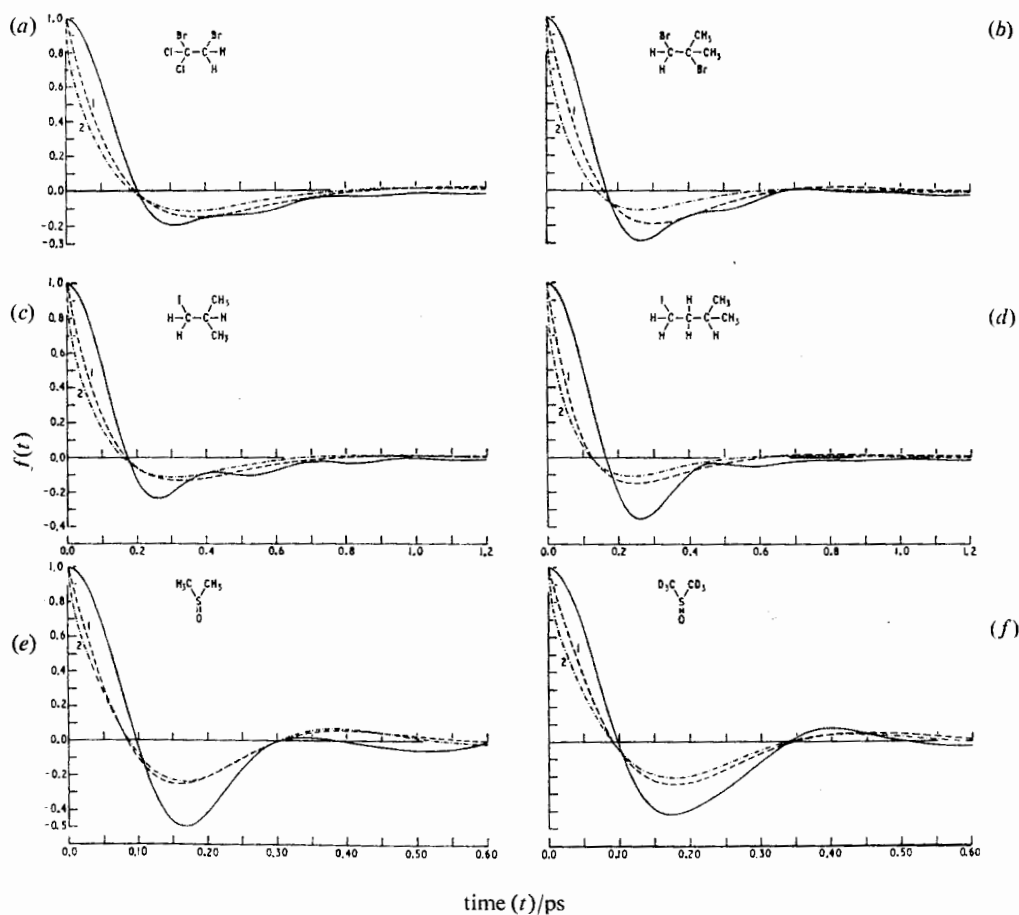
(11)

with zero slope at $t = 0$ in both cases.

FIG. 5.—— ——, and – – – – as for fig. 1.

(a) 1,2-dibromo-1,1-dichloroethane at 295 K ; (b) 1,2-dibromo-2-methylpropane at 295 K ; (c) 1-iodo-2-methylpropane at 295 K ; (d) 1-iodo-3-methylbutane at 295 K ; (e) [^{1}H$_6$]dimethylsulphoxide at 293 K ; (f) [^{2}H$_6$]dimethylsulphoxide at 293 K. All liquid.

In contrast, it may be established from eqn (9) that ;

$$f'_B(0) = \frac{(1-2\beta^2)}{\tau_r^3} - 2\beta^2 \left[\left(\frac{1}{\tau} + \frac{1}{\tau_r} \right)^2 \left(\frac{2}{\tau} - \frac{1}{\tau_r} \right) + a^2 \left(\frac{2}{\tau} + \frac{3}{\tau_r} \right) \right] \text{ if } \omega_0 > 1/\tau$$

$$= \frac{(1-2\beta^2)}{\tau_r^3} - 2\beta^2\left[\left(\frac{1}{\tau}+\frac{1}{\tau_r}\right)^2\left(\frac{2}{\tau}-\frac{1}{\tau_r}\right)\right] \text{ if } \omega_0 = 1/\tau$$

$$= \frac{(1-2\beta^2)}{\tau_r^3} - 2\beta^2\left[\left(\frac{1}{\tau}+\frac{1}{\tau_r}\right)^2\left(\frac{2}{\tau}-\frac{1}{\tau_r}\right) - b^2\left(\frac{2}{\tau}+\frac{3}{\tau_r}\right)\right] \text{ when } \omega_0 < 1/\tau$$

and since $a^2 = -b^2 = \omega_0^2 - 1/\tau^2$, the slope is the same for all ω_0 at $t = 0$, and is *non-zero* generally, as for all collisional models of this kind.
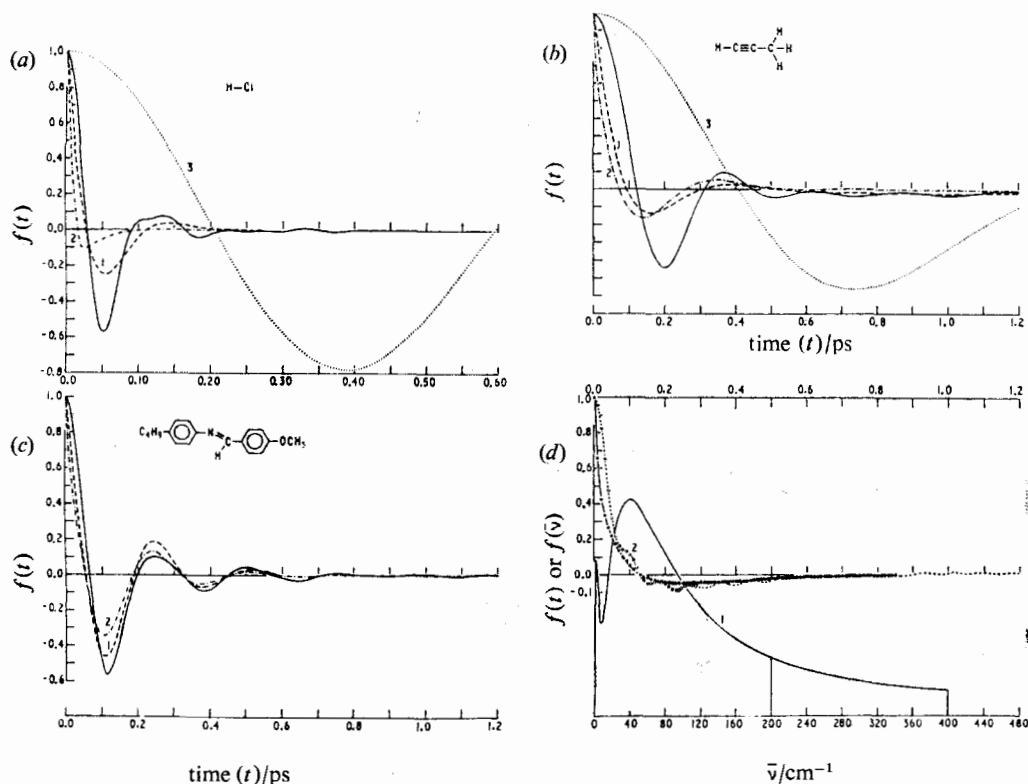

FIG. 6.—(a)-(c) ——, and – – – –, as for fig. 1.

(a) HCl (rotator phase) at 100 K; (b) propyne (liquid) at 293 K; (c) p-methoxybenzylidene-p-N-butylaniline (MBBA) in the nematic phase at 296 K; (d) curve 1. Frequency domain curve of $\alpha(\bar{\nu})$ predicted by the Wyllie–Larkin model at 238 K for the rotator phase of t-butyl chloride. Integration of this curve up to 400 cm^{-1} produces the spurious oscillations of curve 2, which is the $f_w(t)$ function. These disappear upon integrating to 3000 cm^{-1}.

Considerable use has been made [7-12] of Wyllie's [6] itinerant oscillation model of molecular motion and interaction in the condensed phase. This model considers a librator of moment of inertia I constrained within a cage of Z nearest neighbours of moment of inertia I_c. The damping (r) of the librator is assumed not to be of a collisional nature, but to arise from lack of rigidity of the cage. Debye relaxational absorption occurs through the cooperative diffusional reorientation of the cage molecules about the centres of mass against a resistance ζ.

Larkin,[10] in his extension, considered both inertial and damping effects, then solved the ensuing equations of motion to give the Fick diffusion equation, from which

a solution of the dipole moment distribution function is obtained. The mean dipole moment parallel to the field (and hence the frequency dependent polarisability) then gives the optical coefficient $\alpha_w(\bar{v})$ as

$$\frac{\bar{v}_r^2 K/(1+\bar{v}_r^2 K^2)}{[1-\bar{v}_r^2+\mathscr{I}\bar{v}_r^2/(Z^2+\bar{v}_r^2)]^2+(\mathscr{I}\bar{v}_r Z/(Z^2+\bar{v}_r^2)+r\bar{v}_r)^2} \times$$

$$\left\{ \frac{\mathscr{I}zK}{Z^2+\bar{v}_r^2}+\left(\frac{\mathscr{I}z}{Z^2+\bar{v}_r^2}\right)^2-\left(1-\frac{\mathscr{I}}{Z^2+\bar{v}_r^2}\right)\left(1-\bar{v}_r^2+\frac{\mathscr{I}\bar{v}_r^2}{Z^2+\bar{v}_r^2}\right)+ \right.$$

$$\left. r\left[\frac{\mathscr{I}z}{Z^2+\bar{v}_r^2}+\bar{v}_r^2 K\left(1-\frac{\mathscr{I}}{Z^2+\bar{v}_r^2}\right)\right]\right\}$$

where $K = 2\pi\bar{v}_0 c\tau_D$, τ_D being the Debye relaxation time and $\bar{v}_0$ the proper frequency of libration;

$$Z = \zeta/(2\pi\bar{v}_0 cI_c); \quad \mathscr{I} = I/I_c; \quad \text{and } \bar{v}_r = \bar{v}/\bar{v}_0.$$

Thus

$$f_w(t) = \langle \dot{u}(0) \cdot \dot{u}(t)\rangle \propto \int_0^\infty \alpha_w(\bar{v})\cos{(2\pi\bar{v}ct)}\,d\bar{v}. \tag{12}$$

In this case, $f'_w(t) = 0$ when $t = 0$, and thus Wyllie's model conforms with Gordon's law [eqn (11)].
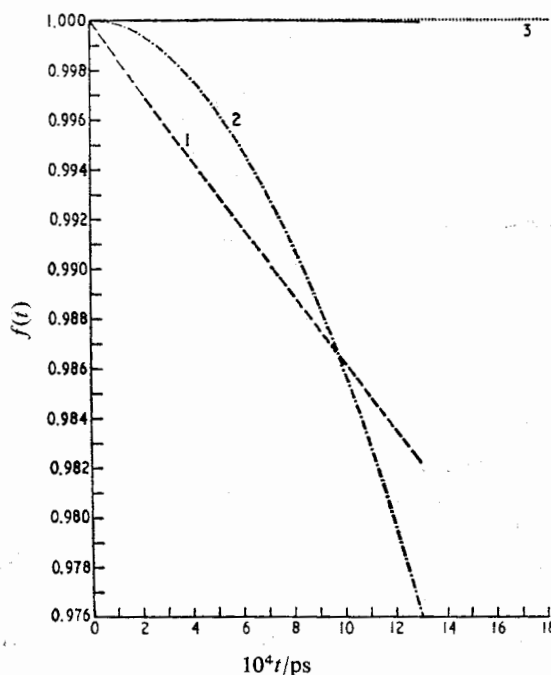

FIG. 7.—Behaviour of $f_2(t)$, $f_w(t)$, $f_B(t)$ and $f_{fr}(t)$ for t-butyl chloride (rotator phase) at 238 K as $t \to 0$; ——, and - - - -, as in fig. 1.

COMPUTATIONAL DETAILS

The functions $f_2(t)$, $f_B(t)$ and $f_w(t)$ have been computed from eqn (6), (10) and (12) for the molecules given in fig. 1-6. The curves are illustrated in fig. 1-7, being normalised to unity at $t = 0$. The free rotor functions $f_{fr}(t)$ and $f_{fr1}(t)$, calculated from

eqn (7) and (8) are also displayed for the molecules listed above. Each curve was computed with : (1) a Cooley–Tukey fast Fourier transform algorithm ; (2) Simpson's rule ; except in the direct evaluations from eqn (10) where no Fourier transform is necessary. Any aliasing effects were thus eliminated, since the computation was

TABLE 1.—PARAMETERS USED IN EVALUATING $f_B(t)$ AND $f_w(t)$

molecule	T/K	τ/ps	τ_a/ps	τ_r/ps	τ_D/ps	$\dfrac{10^{40} I}{g\,cm^2}$	Z	r	$\dfrac{\zeta(2kT)^{-1}}{ps}$	$\bar{\nu}_0/cm^{-1}$
$(CH_3)_3CNO_2$	294	0.15	0.24	10.0	8.0	370	12	2.4	12.0	30.8
$(CH_3)_3CNO_2$	273	0.16	0.24	21.0	14.0	370	12	2.4	28.0	32.4
$(CH_3)_2CCl_2$	295	0.30	0.25	5.7	6.5	373	12	2.4	8.0	21.2
$(CH_3)_2CCl_2$	241	0.20	0.29	15.6	13.0	373	12	1.8	14.0	30.3
$(CH_3)_2CCl_2$	235	0.22	0.29	16.0	15.0	373	12	1.2	14.0	37.7
$(CH_3)_2CCl_2$	192	0.23	0.31	35.0	28.0	373	12	1.2	51.0	47.8
$(CH_3)_2CNO_2Cl$	293	0.13	0.24	17.0	12.0	494	12	2.2	16.0	32.9
$(CH_3)_2CNO_2Cl$	253	0.16	0.27	20.0	20.0	494	12	1.4	18.0	43.5
$(CH_3)_2CNO_2Cl$	233	0.16	0.27	31.0	30.0	494	12	1.2	41.0	51.5
$(CH_3)_2CNO_2Cl$	209	0.17	0.29	42.0	40.0	494	12	1.2	72.0	53.1
$(CH_3)_3CCl$	238	0.14	0.24	8.3	7.4	269	12	2.8	7.8	30.8
$(CH_3)_3CCl$	274	0.22	0.24	4.7	5.4	269	12	3.0	4.4	21.8
$CH_3 \cdot CCl_3$	233	0.11	0.12	21.5	14.2	338	12	1.8	22.0	39.8
$CH_3 \cdot CCl_3$	293	0.22	0.24	6.2	5.9	338	12	1.8	8.2	32.9
CH_2Cl_2	188	0.11	0.15	17.9	20.0	208	12	1.1	22.9	89.7
CH_2Cl_2	249	0.11	0.13	15.2	11.5	208	12	1.4	13.3	77.5
CH_2Cl_2	298	0.11	0.19	9.3	8.5	208	12	1.2	9.1	69.0
C_6H_5Cl	293	0.16	0.19	20.4	12.0	693	6	2.0	29.7	35.0
$o\text{-}C_6H_4Cl_2$	293	0.15	0.23	36.8	23.9	1300	6	1.36	40.7	46.2
$m\text{-}C_6H_4Cl_2$	293	0.15	0.26	36.4	16.0	1630	6	1.04	59.9	49.5
$o\text{-}C_6H_4Br_2$	293	0.26	0.46	57.2	38.5	1740	6	1.36	63.8	34.8
$m\text{-}C_6H_4Br_2$	293	0.22	0.54	109.0	37.5	2700	6	1.28	116.0	41.4
$o\text{-}C_6H_4F_2$	293	0.19	0.20	13.2	10.5	670	6	1.44	14.2	35.8
$m\text{-}C_6H_4F_2$	293	0.14	0.20	19.9	7.6	302	6	1.52	29.8	46.9
$C_2Cl_2Br_2H_2$	295	0.22	0.44	49.0	26.5	1500	8	1.5	49.0	30.0
$C_4H_8Br_2$	295	0.20	0.24	64.0	20.0	1200	8	1.5	55.0	40.0
C_4H_9I	295	0.18	0.29	34.0	14.5	800	8	1.5	30.0	35.0
$C_5H_{11}I$	295	0.14	0.39	59.0	29.0	1200	8	1.5	58.0	45.0
$(CH_3)_2SO$	293	0.13	0.15	8.4	8.0	118	8	0.76	9.5	75.9
$(CD_3)_2SO$	293	0.14	0.16	9.5	7.5	118	8	0.88	12.3	69.6
HCl	100	0.04	0.08	46.7	50.1	36.8	12	1.96	51.8	221.4
$CH_3C \equiv CH$	293	0.14	0.12	2.9	2.8	98.1	8	1.04	3.5	81.0
MBBA	296	0.14	0.19	250.0	250.0	470	6	0.54	295.8	130.0

repeated until the curves obtained by both methods from the same set of data $\alpha(\bar{\nu})$ were indistinguishable. It was found necessary to integrate eqn (12) up to ~ 3000 cm^{-1} before smooth $f_w(t)$ curves were obtained. The functions given here were computed with an upper limit to the integral of twice this value. Fig. 6(d) shows the oscillations induced in $f_w(t)$ by integrating up to 400 cm^{-1} only. The oscillations observed in almost every $f_2(t)$ function are thus not due to computational artefacts since the integration in eqn (6) was always carried out to the point when $\alpha(\bar{\nu}) = 0$ on the high frequency side. The parameters necessary for the evaluation of $f_B(t)$ and $f_w(t)$ are shown in table 1, and those for $f_{fr}(t)$ and $f_{fr1}(t)$ given in table 2.

TABLE 2.—PARAMETERS USED IN CALCULATING f_{fr} AND f_{fr1}

molecule	A/cm^{-1}	B/cm^{-1}	I	T/K
$(CH_3)_3CCl$	0.177	0.100 6	0	238, 274
$(CH_3)_3CNO_2$	0.177	0.075 6	0	273, 294
CH_3CCl_3	0.056	0.079 5	$\frac{3}{2}$	233, 293
$CH_3C \equiv CH$	5.100	0.285 2	$\frac{1}{2}$	293
H—Cl	0	10.35	—	100

DISCUSSION

The discord between the predicted and experimental functions at extremely short times is particularly acute (fig. 7), an example is shown for $(CH_3)_3CCl$ in the rotator

phase at 238 K. Within the time scale shown in fig. 7, a single molecule has time enough to rotate through a small fraction of a radian only. The free rotor function shows a negligibly small loss of correlation, as does the experimental function $f_2(t)$, which means that very little molecular motion or interaction has taken place within such a short interval. However, $f_w(t)$ falls off much too rapidly, although it does have the required zero slope at $t = 0$. The function $f_B(t)$ is virtually linear in this range, and is unrealistic, at these very short times.

This behaviour can be investigated quantitatively for the linear HCl molecule [fig. 6(a)] whose short time behaviour of $f_2(t)$, $f_w(t)$ and $f_B(t)$ is similar to that of $(CH_3)_3CCl$ and typical of that of the other molecules studied here. Gordon[21] has expanded the classical autocorrelation function for linear molecules at short times to the fourth power in t, from which;

$$f_c(t) = \frac{\langle \dot{u}(0) \cdot \dot{u}(t) \rangle}{\langle \dot{u}(0) \cdot \dot{u}(0) \rangle} = 1 - \frac{1}{I}\left(2kT + \frac{\langle (ov)^2 \rangle}{4kT}\right)t^2 + O(t^4) \qquad (13)$$

where $\langle (ov)^2 \rangle$ is the mean squared torque on a molecule due to the other molecules. Whereas the initial curvature of the vectorial correlation function $\langle u(0) \cdot u(t) \rangle$ depends only on the temperature of the system and the molecular moment of inertia I, the effect of intermolecular forces determines that of $f_c(t)$. For a free rotor, $\langle (ov)^2 \rangle$ is negligible and

$$\frac{f_{fr1}(t)}{f_{fr1}(0)} = 1 - \frac{2kTt^2}{I} + O(t^4). \qquad (14)$$

The curve $f_{fr1}(t)$ consequently falls off less rapidly [fig. 6(a)] than $f_2(t)$, in which $\langle (ov)^2 \rangle$ is positive. The rapid fall off in $f_w(t)$ can be explained in terms of eqn (13) only if it is assumed that the apparent mean square torque generated by this model is much larger than the experimental value of 300-400 cm^{-1} rad^{-1}. Since the torque is the angular derivative of the mean intermolecular potential energy, given empirically by Larkin[10] as,

$$U(\theta) = V \sin^2\left(\frac{\pi\theta}{2\xi}\right), \qquad (15)$$

eqn (13) can be rewritten as,

$$f_c(t) = 1 - \frac{1}{I}\left[2kT + \left\langle \frac{\pi^2 V^2}{16kT\xi^2} \sin 2\left(\frac{\pi\theta}{2\xi}\right)\right\rangle\right]t^2 + O(t^4) \qquad (16)$$

where ξ is the half angular aperture of a potential well as determined from X-ray diffraction. In Larkin's approach, V, the mean barrier height to libration, being a phenomenological parameter, is determined directly from the observed $\bar{v}_{max}$ by solving harmonically[10] for small θ. The term in t^2 in eqn (16) found by this method is clearly too large, and the choice of a barrier V to fit $\bar{v}_{max}$ takes no account of the shape of the absorption band. The difficulty arises simply because Wyllie's model which is not a collisonal one, treats the molecular environment as a continuum with an opposing viscous drag ζ, and does not treat the form of $U(\theta)$ explicitly. The equivalent discord in the frequency domain is the extremely long high frequency tail predicted by this model [fig. 6(d)], whereas the experimental absorption falls sharply[7-12] off to zero at ~200-300 cm^{-1}.

Brot's model goes to the extreme of instantaneous collisions, with the torque $\langle (ov)^2 \rangle$ tending to infinity as t tends to zero thereby ensuring that $f_B(0)$, the slope of $f_B(t)$ at $t = 0$, can never attain the required value of zero. Clearly a model involving the vague concept of " soft collisions " is desirable.

The oscillations (fig. 1-7) observed in almost every $f_2(t)$ are real (for reasons set out above) and qualitatively related to the form of $\alpha(\bar{v})$ at higher frequencies. The extreme case of a vertical drop in $\alpha(\bar{v})$ is shown in fig. 6(d), where regular, short time oscillations are induced in the equivalent time function [which happens to be $f_w(t)$ in this case]. This oscillation is not a single molecule property which could be linked to a simple parameter such as the inertia. First, there is no detectable relation between the moment of inertia and the periodic time of these oscillations, and for the same molecule, they are more pronounced in certain environments than in others [e.g. fig. 3(c)-3(e)]; secondly they have practically disappeared in some of the examples studied [fig. 1(c), 1(e), 2(c), 2(f) and 3(b)]. Their origin is therefore multi-molecular.

Before going into a more detailed discussion of this phenomenon it must be re-called that in terms of molecular motion and interaction at longer times (up to ~ 1 ps), the experimental curves $f_2(t)$ involve cross-correlations, and are distorted by induced dipolar absorption. There is the additional uncertainty of the form of the internal field, largely avoided by using $f_2(t)$ but which ought to be treated accurately with eqn (4) or (5). The non-dispersive Polo–Wilson type correction of eqn (6) does not affect $f_2(t)/f_2(0)$. At present, there is a total lack of $\alpha(\bar{v})$ data in the critical region 1-10 cm^{-1} and no $n(\bar{v})$ in the whole range of interest.

The problem of the induced dipolar contribution of $f_2(t)$ is unsolved, the only previous attempts have been by comparing [14] molecules such as CS_2 and OCS, and taking the absorption of the former as the induced absorption of the latter. The induced contribution to the integrated intensity per molecule can be estimated [18] from eqn (3). This is small in the molecule CHF_3 [22] where pronounced short time oscillations in $f_2(t)$ were observed in the liquid phase. This suggests that they originate in the movement of the permanent molecular dipoles. It will be interesting to see whether these effects are observed in functions equivalent to $f_2(t)$ calculated from time of flight neutron scattering data, where problems of induced absorption and the internal field are eliminated.

Gordon's sum rule was derived for the total optical absorption due to a system of rigid molecules of arbitrary mass and charge distribution, and which have random orientations in space. This predicts a zero time value of $2kT/I$ (for linear and symmetric top molecules) for the function $f_2(t)$. However, the behaviour of $f_2(t)$ after $t = 0$ is determined by intermolecular torque forces of which the Gordon sum rule takes no account, it being essentially a first approximation to the total integrated intensity in the liquid phase where molecules are not oriented randomly with respect to each other. Recent approximations to the orientational time-correlation function of the permanent dipoles of simple molecules in the liquid phase [25] using the repeated fraction representation of Mori have been successful in reproducing almost precisely the observed bandshapes in the far infrared. Therefore, on this evidence, the bandshape with which we are primarily concerned in this paper, does not seem to be sensitive to induced-dipolar effects, the Gordon sum rule being no more than an approximation to the integrated absorption intensity of rigid dipolar molecules.

INDIVIDUAL MOLECULES

The oscillations are least pronounced in CH_3CCl_3 in the liquid phase at 293 K [fig. 3(b)], and most marked in the nematogen MBBA at 296 K [fig. 6(c)]. Com-paring fig. 1-3 with fig. 4-6 it can be seen that they become more pronounced as molecular anisotropy increases.

In addition they appear to become more significant as the temperature is lowered

within a given phase. Fig. 3(c)-(e) for CH_2Cl_2 illustrate this trend the most clearly. Such changes have been observed by Gerschel [22] in liquid CHF_3, and attributed to increased " structuring " in the liquid phase as the temperature is lowered. They also seem to become more marked as the temperature of a rotator phase is lowered [fig. 1(a), 1(b), 2(c), 2(d)]. Reference to fig. 1(b) and 1(a) and 1(c)-1(f), and comparison of fig. 2(a) and 2(b) with 2(c) and 2(d), fig. 2(e) with 2(f), and 3(a) with 3(b) reveal that they are more marked in the rotator phase than in the corresponding liquid.

Free rotor curves calculated from eqn (7), are plotted in fig. 1(a), 1(b), 2(e), 2(f), 3(a), 3(b), 6(a) and 6(b), and emphasize the substantial torque forces present in these condensed phases. These are responsible for the rapid fall off in $f_2(t)$.

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