

Rotational Velocity Correlation Function for assessing Molecular Models for Gas and Liquid Phase Studies

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The rotational velocity correlation function $\langle \dot{\mathbf{u}}(0) \cdot \sum_i \dot{\mathbf{u}}_i(t) \rangle$ (RVCF) is used to assess two analytical models of the molecular motion which gives rise to far infra-red (2-200 cm^{-1}) absorptions in dipolar compressed gases and liquids. These functions are compared with those derived from the experimental data, and the discrepancies attributed largely to induced, temporary dipoles, the short time (< 2 ps) behaviour of which being more clearly reflected in these short time correlation functions than in the corresponding vectorial ones.

The representation of experimental microwave and far infra-red data in the time domain by means of various correlation functions has recently been described.¹⁻⁵ Some articles aimed at developing⁶⁻⁹ model functions for the dynamics of the permanent dipole vector rotation which could later be transformed into the frequency domain using the Kubo formalism.¹⁰ The comparison of theoretical models and experimental data in the time domain as well as the frequency domain is desirable for an analytical assessment of the molecular dynamics, and is profitable when developing statistical averages in time for direct comparison with time domain data.^{6, 11} Part of the aim of the present work is to develop the use of the function :

$$\langle \dot{\mathbf{u}}(0) \cdot \sum_i \dot{\mathbf{u}}_i(t) \rangle$$

recently² used by Gerschel *et al.* and called by them the collective time correlation function for the "rotational velocity" (RCVF) of a unit vector \mathbf{u}_i along the permanent dipole moment μ_i of a molecule. This function is related^{1, 2} to the corresponding vectorial correlation function by :

$$\frac{d^2}{dt^2} (\langle \mathbf{u}(0) \cdot \sum_i \mathbf{u}_i(t) \rangle) = - \langle \dot{\mathbf{u}}(0) \cdot \sum_i \dot{\mathbf{u}}_i(t) \rangle \quad (1)$$

and is damped out to zero in *ca.* 2 ps, thus being the "time domain equivalent" of the far infra-red (2-200 cm^{-1}) region of the frequency domain.

In the liquid phase of polar molecules any model of the molecular motions and interactions which give rise to the absorptions in this region ought to include the effect of induced, temporary dipoles, as well as that of the torsional oscillatory movement of the permanent dipoles. It should also describe accurately the slower, large-amplitude angular motion observed in the microwave region. In the compressed gaseous phase, the collisional, diffusive nature of the molecular interaction dynamics can be described using such models as the M and J representations of Gordon,¹¹ and it is well-known¹² that induced absorption becomes increasingly important with pressure. It is also important that the dynamics giving rise to absorption in the

microwave and far infra-red regions cannot be conveniently separated either in the frequency domain nor in the time domain [only superficially for both by the use of the loss factor $\varepsilon''(\bar{\nu})$ and the absorption coefficient $\alpha(\bar{\nu})$]. Many of these aspects, as well as the discrimination between theoretical models and their comparison with observations, are clearly seen in the RVCF.

Nevertheless, since the use of $\alpha(\bar{\nu})$ in terms of $\bar{\nu}$ for the far infra-red is now widely accepted⁴ [if only because the $\varepsilon''(\bar{\nu})$ against $\bar{\nu}$ representation reduces the whole of the far infra-red to a slightly enhanced absorption intensity in the high frequency tail of the loss curve] then the use of the corresponding time domain representation seems excusable at present. A practical advantage of the RVCF is that it can be calculated to a good approximation using only far infra-red data since the low frequency (microwave) absorption affects only the very weak long-time tail. It does not become indeterminate when calculated from expressions such as that of Cole,¹³ as can be seen from:

$$f_b(t) = \langle \dot{\mathbf{u}}_1(0) \cdot \sum_i \dot{\mathbf{u}}_i(t) \rangle = \frac{2}{\pi} \frac{3kTV}{4\pi N\mu^2} \frac{9(2\varepsilon_0 + \varepsilon_\infty)^2}{(\varepsilon_\infty + 2)^2} c \int_0^\infty \frac{\alpha n \cos \omega t \, d\omega}{(\varepsilon' + 2\varepsilon_0)^2 + \varepsilon''^2} \quad (2)$$

which is derived in ref. (2) from Cole's original result. All experimental RVCFs in this work are derived using (2), which takes into account the "dynamic" Onsager field.

To demonstrate the usefulness of the angular velocity representation, experimental and model functions are compared in the dense liquid phases of 1,1,1-trichloroethane, chlorobenzene, and in the nematic phase of *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA), a sequence chosen to represent the effect of increasing geometric anisotropy on the short time (0.2 ps) behaviour. In addition, the RVCFs of the near linear, dipolar molecule propyne¹⁴ for the compressed gaseous and the dense liquid phases are compared and contrasted; the changes also being represented by model functions which *do not* include the effects of induced dipolar absorption. The differences show that the RVCF is sufficiently discriminating to be used as a possible intermediate representation in the assessment of models which might take account of the induced moments and subsidiary features.

RESULTS AND DISCUSSION

The experimental^{7, 9, 14} RVCFs are shown in fig. 1 where each is normalised to unity at $t = 0$. The Kummer function is computed for the near linear propyne in fig. 1(e) and (f) where is also shown the corresponding experimental curve for the compressed gas at 5.1 bar and 296 K; and also at 25 bar and 376 K. There is appreciable collisional damping at these gaseous number densities.

The free rotation function is hopelessly inadequate to describe the motion of even pseudospherical molecules in the liquid phase as illustrated for 1,1,1-trichloroethane by comparing the experimental and symmetric top free rotor (St. Pierre/Steele¹⁵) vectorial correlation functions (fig. 2). However, Lassier and Brot¹⁶ have recently developed a model based on the classical vectorial correlation function for the angular motion of molecules submitted to thermal collisions in a multi-well potential which has the spectral consequences that an absorption due to the libration of the molecules in the wells is superimposed on a Debye-Kauzmann type absorption, the transparency of the substance being recovered at higher frequencies. This model does *not*, however, include the possible effects of collision induced temporary dipoles. The far infra-red frequency domain band shape predicted by the model has been developed by Larkin *et al.*,⁷⁻⁹ and the properties of the basic correlation function [$F(t)$] in the time

region 0-2 ps can be investigated in detail by straightforward differentiation of the expression for $F(t)$ in ref. (16) giving the corresponding RVCF as:

$$F''(t) = (2\beta^2 - 1) \left[\frac{1}{\tau_r^2} \exp(-t/\tau_r) - \int_0^t \frac{\exp(-t_j/\tau_r)}{\tau_r} H''(t-t_j) dt_j \right] - 2\beta^2 \left\{ \frac{d^2}{dt^2} \left[\exp(-t/\tau_r) V(t) - \int_0^t \frac{\exp(-t_j/\tau_r)}{\tau_r} V(t_j) H''(t-t_j) dt_j \right] \right\} \quad (3)$$

where

$$\begin{aligned} H''(t-t_j) &= 1/\tau_a^2 \exp[-(t-t_j)/\tau_a] [1-(t-t_j)/\tau_a], \\ V(t_j) &= \exp(-t_j/\tau) [\cos(at_j) + \sin(at_j)/a\tau], \quad \text{if } \omega_0 > 1/\tau \\ &= \exp(-t_j/\tau) (1+t_j/\tau), \quad \text{if } \omega_0 = 1/\tau \\ &= \exp(-t_j/\tau) [\cosh(bt_j) + \sinh(bt_j)/b\tau], \quad \text{if } \omega_0 < 1/\tau, \end{aligned}$$

with

$$a = (\omega_0^2 - 1/\tau^2)^{\frac{1}{2}}; \quad b = (1/\tau^2 - \omega_0^2)^{\frac{1}{2}},$$

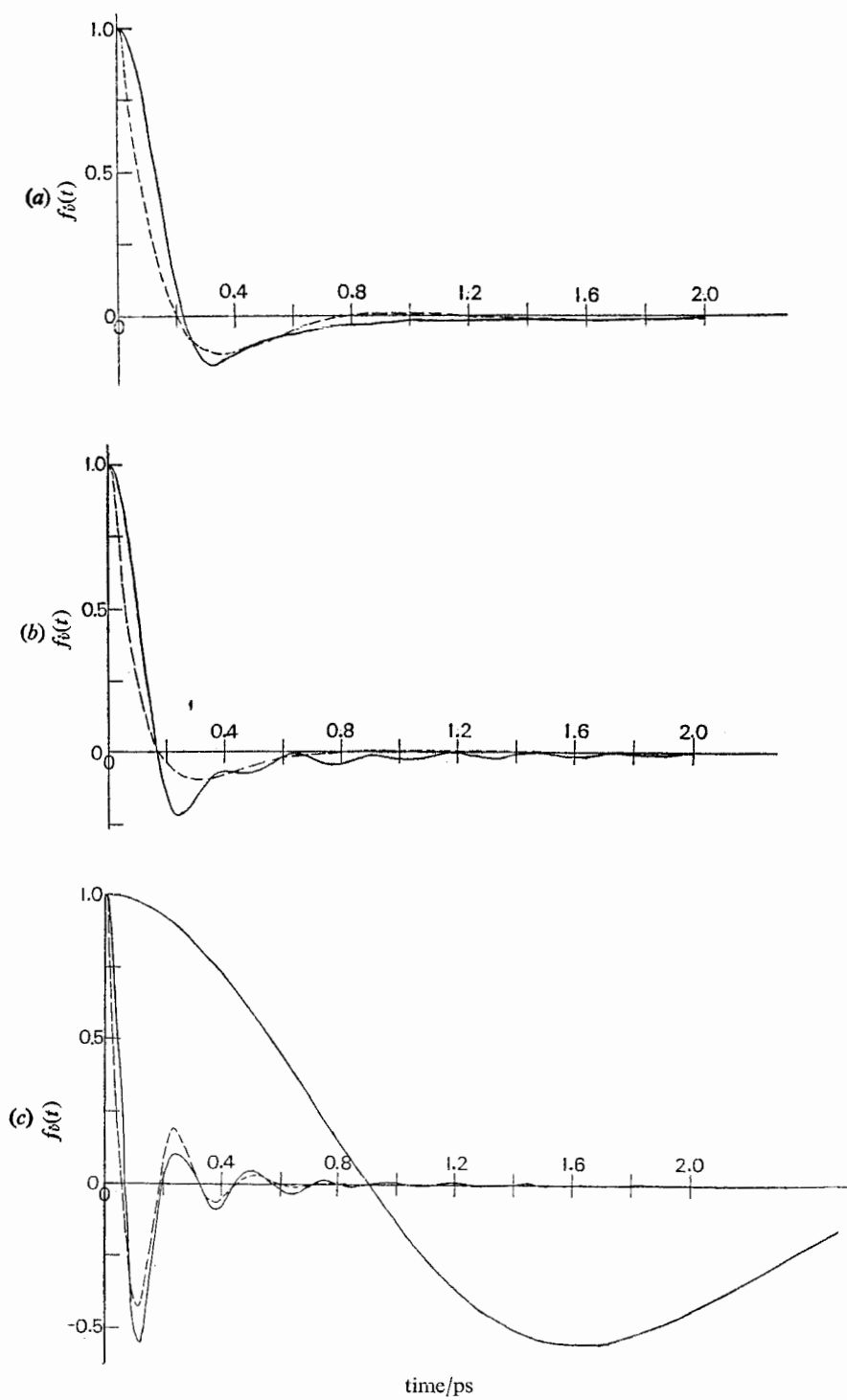
and

$$\begin{aligned} \frac{d^2}{dt^2} [\exp(-t/\tau_r) V(t)] &= \exp[-t(1/\tau_r + 1/\tau)] \{ (1/\tau_r + 1/\tau)^2 [\cos(at) + \sin(at)/a\tau] + 2(1/\tau_r + 1/\tau) [a \sin(at) - \cos(at)/\tau] - [a \sin(at)/\tau + a^2 \cos(at)] \} \quad \text{if } \omega_0 > 1/\tau \\ &= \left\{ \left(\frac{1}{\tau} + \frac{1}{\tau_r} \right) \left[\frac{1}{\tau_r} + \frac{t}{\tau} \left(\frac{1}{\tau} + \frac{1}{\tau_r} \right) \right] - \frac{1}{\tau^2} \right\} \exp[-t(1/\tau + 1/\tau_r)], \\ &\quad \text{if } \omega_0 = 1/\tau \\ &= \exp[-t(1/\tau_r + 1/\tau)] \{ (1/\tau_r + 1/\tau)^2 [\cosh(bt) + \sinh(bt)/b\tau] - 2(1/\tau_r + 1/\tau) [b \sinh(bt) + \cosh(bt)/\tau] + [b \sinh(bt)/\tau + b^2 \cosh(bt)] \}, \quad \text{if } \omega_0 < 1/\tau; \end{aligned}$$

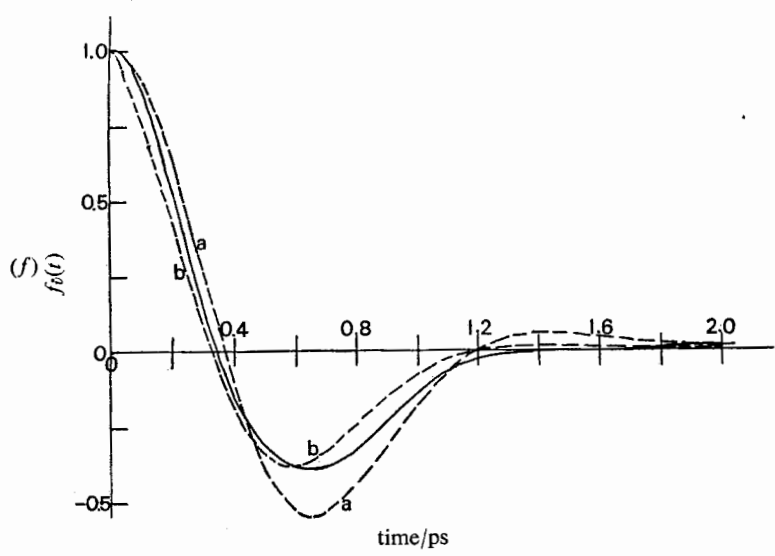
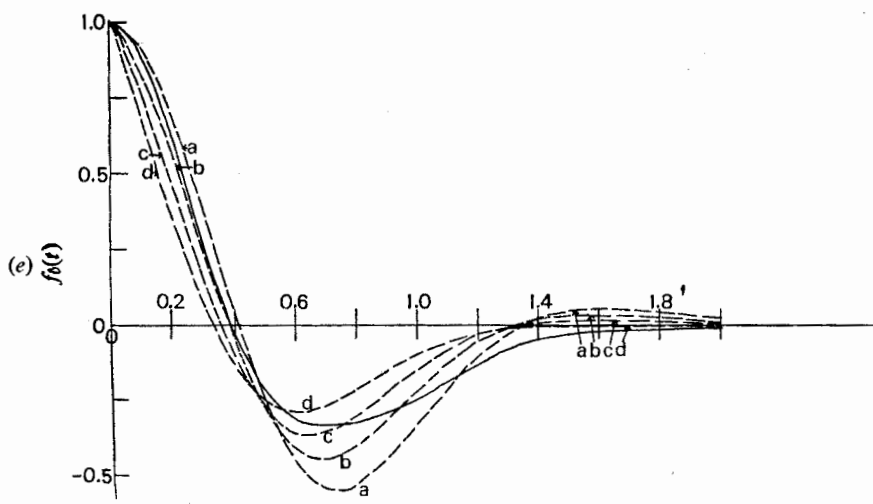
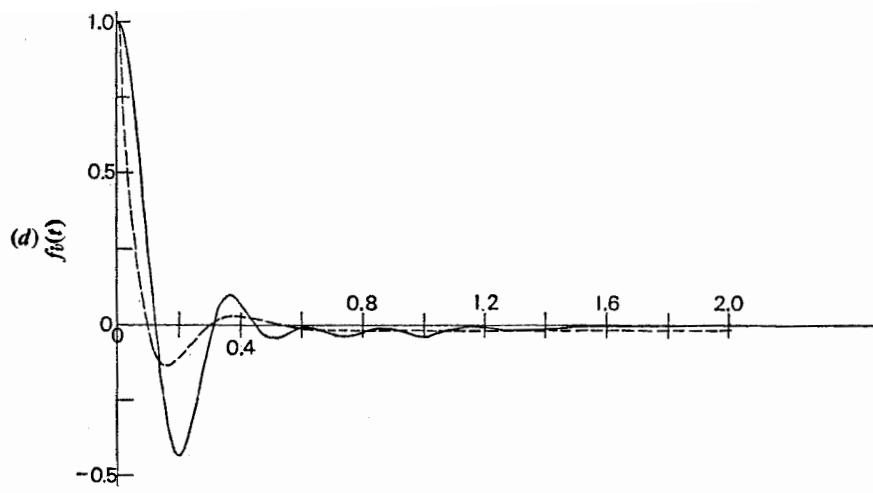
where $\beta^2 = kT/I\omega_0^2$, I is the moment of inertia about an axis perpendicular to that containing the dipole and ω_0 is the degenerate angular frequency of libration.

The other parameters in eqn (3) have been estimated phenomenologically by frequency domain curve fitting^{7, 9, 14} (see table 1): τ_r is the mean time of residence in a librational well, τ_a is the Brot's parameter for the state of jump correlation function $H(t)$ and $1/\tau$ is the width of the librational absorption. The model function (3) was evaluated using Simpson's rule on an Elliot 4130 computer (program available on request). In each case the zero time^{1, 2} value of $F(t)$ was found to be $\approx kT/I$ to within 1 %, this value being thereafter conveniently normalised to unity for direct comparison [fig. 1(a)-(d)] with the corresponding experimental functions.

The discrepancies between experimental and theoretical functions at very short times (less than 0.2 ps) are regarded as real, there being corresponding^{7-9, 14} ones in the frequency domain, where they are observed as *sharper* high frequency fall-offs of the experimental bands. In performing the Fourier transform of the experimental data with Lassier's program CHINT, the integration of the $\alpha(\bar{\nu})$ against $\bar{\nu}$ band was carried out in each case using high frequency data extrapolated where necessary to $\alpha(\bar{\nu}) = 0$, i.e. to the point where higher frequency contributions would be negligible.



(Caption for fig. 1 on p. 1625).



(Caption for fig. 1 on p. 1625).

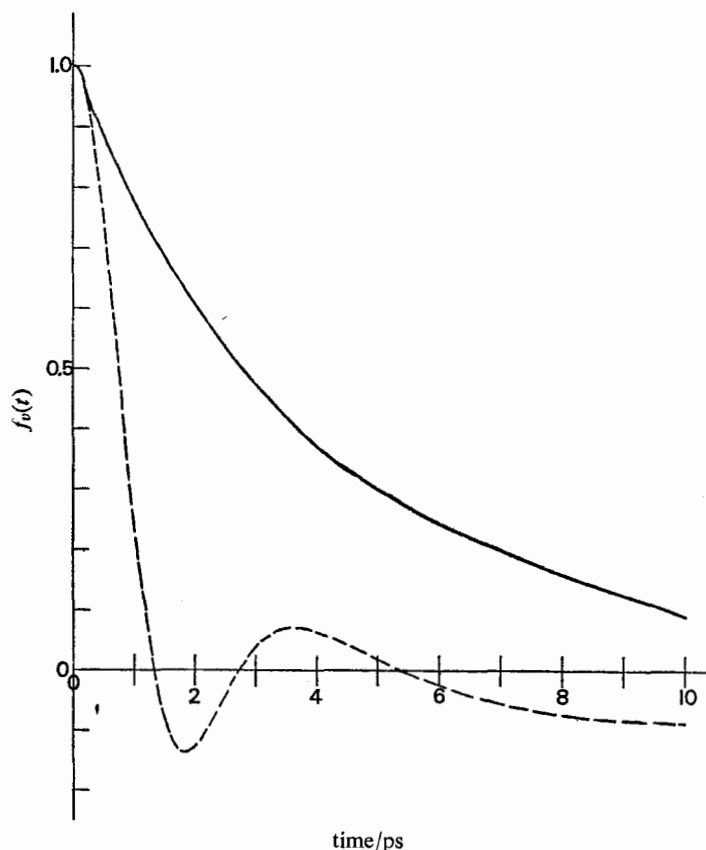


Fig. 2.—Vectorial correlation function ² for 1,1,1-trichloroethane at 293 K. —, experimental ^{1, 2}; ---, St. Pierre/Steele ¹⁵ correlation function for freely rotating symmetric top molecules applied to 1,1,1-trichloroethane taking the —CH₃ group as an unit of mass 15 proton units.

The best agreement between (2) and (3) is expected for 1,1,1-trichloroethane, which forms a rotator phase, and with which, among others, the Brot-Larkin model was developed. The agreement is acceptable (neither function showing short time oscillations) but reflects the fact that for this molecule the experimental integrated intensity: $x \int_{\text{band}} \alpha(\bar{\nu}) d\bar{\nu}$ (where x is the Polo-Wilson ¹⁸ correction for internal field

Fig. 1.—Rotational velocity correlation functions. (a) 1,1,1-trichloroethane. —, experimental ⁷ [eqn (2)]; ---, eqn (3) with ⁷ $\omega_0 = 6.2 \times 10^{12} \text{ rad s}^{-1}$; $\tau = 2.22 \times 10^{-13} \text{ s}$; $\tau_a = 2.57 \times 10^{-13} \text{ s}$; $I = 3.45 \times 10^{-38} \text{ g cm}^2$; $T = 293 \text{ K}$. (b) Chlorobenzene. —, experimental ⁷ [eqn (2)]; ---, eqn (3) with ⁷ $\omega_0 = 7.2 \times 10^{12} \text{ rad s}^{-1}$; $\tau = 1.6 \times 10^{-13} \text{ s}$; $\tau_a = 1.87 \times 10^{-13} \text{ s}$; $\tau_r = 2.04 \times 10^{-11} \text{ s}$; $I = 6.79 \times 10^{-38} \text{ g cm}^2$; $T = 293 \text{ K}$. (c) MBBA. —, experimental ⁹ [eqn (2)]; ---, eqn (3) with ⁹ $\omega_0 = 2.45 \times 10^{13} \text{ rad s}^{-1}$; $\tau = 1.43 \times 10^{-13} \text{ s}$; $\tau_a = 1.92 \times 10^{-13} \text{ s}$; $\tau_r = 2.5 \times 10^{-10} \text{ s}$; $I = 4.7 \times 10^{-38} \text{ g cm}^2$; $T = 296 \text{ K}$. The broad full curve is that for the "equivalent linear free rotor" (see text). (d) Liquid propyne.¹⁴ —, experimental ¹⁴ [eqn (2)]; ---, eqn (3) with ¹⁴ $\omega_0 = 1.45 \times 10^{13} \text{ rad s}^{-1}$; $\tau = 1.09 \times 10^{-13} \text{ s}$; $\tau_a = 1.17 \times 10^{-13} \text{ s}$; $\tau_r = 2.9 \times 10^{-12} \text{ s}$; $I = 9.816 \times 10^{-39} \text{ g cm}^2$; $T = 293 \text{ K}$. (e) Gaseous propyne ¹⁴ at 5.1 bar and 296 K. —, experimental ¹⁴ [eqn (2)]; ---, (A) Kummer function, (B) eqn (4) with $\tau = 1.20 \times 10^{-12} \text{ s}$, (C) eqn (4) with $\tau = 0.60 \times 10^{-12} \text{ s}$, (D) eqn (4) with $\tau = 0.40 \times 10^{-12} \text{ s}$. (f) Gaseous propyne ¹⁴ at 25.3 bar and 376 K. —, experimental ¹⁴ [eqn (2)]; ---, (A) Kummer function, (B) eqn (4) with $\tau = 0.59 \times 10^{-12} \text{ s}$.

effects) is about 16 % greater than the total theoretical absorption expected on the basis of Gordon's sum rule¹⁹ for the rotation of the permanent dipole. (Although it is widely used, the Polo-Wilson correction was not derived for the type of band in

TABLE 1.—LARKIN'S ESTIMATES OF THE BROT PARAMETERS

molecule	T/K	$I \times 10^{45}/$ kg m ²	$10^{-12}\omega_0/$ rad s ⁻¹	τ_r/ps	τ/ps	τ_a/ps
chlorobenzene	293	6.79	7.2	20.4	0.16	0.19
1,1,1-trichloroethane	293	3.45	6.2	6.2	0.22	0.26
MBBA	296	4.7	24.5	25.0	0.14	0.19
propyne (<i>l</i>)	293	0.9816	14.5	2.9	0.11	0.12

question. However, some estimate of the order of magnitude of this factor would perhaps be more helpful than its complete neglect.) The more asymmetric chlorobenzene has¹⁷ a corresponding excess of *ca.* 30 % which is reflected in fig. 1(*b*), where the experimental against theoretical comparison is not so satisfactory and indicates a basic line shape discrepancy in the frequency domain. It is relevant that the quadrupolar benzene molecule is more heavily²⁰ absorbing in the far infra-red region than the octopolar CCl₄, where the mechanism of the absorption is believed in each case to be due to near neighbour field induction of the absorbing molecular dipole. These molecules may be thought of as the non-dipolar "symmetric analogues" of 1,1,1-trichloroethane and chlorobenzene, and illustrate the important role of molecular symmetry in induced dipole absorption.

The Brot-Larkin model was modified slightly⁹ in treating MBBA, in that the simple $\sin^2 \theta$ function for the shape of the potential barrier to libration was modified to give broad barriers and narrow wells. The resulting phenomenological curve fitting yielded acceptable values (table 1) of τ , τ_a and τ_r which give quite good agreement between (2) and (3) [fig. 1(*c*)] despite the extreme asymmetry and unfavourable conditions for the application of the model. Future theoretical induced-dipole-inclusive treatments may produce a vectorial correlation function which may be difficult to transform into the frequency domain, but the far infra-red band shape can be checked in the time domain using the RVCF. As a slight aside, the Kummer function for a hypothetical freely rotating linear molecule with the same moment of inertia as that about the long axis of MBBA, which would be a first approximation to a freely semiaxially rotating nematic phase molecule, is shown in fig. 1(*c*). Even this facsimile is enough to show that free rotation about the long axis of a nematic phase molecule such as MBBA is highly improbable.

The poor agreement [fig. 1(*d*)] for propyne may indicate a major effect on the lineshape by induced dipoles,¹⁴ but it must be considered that increasing molecular symmetry does not favour the model, and that the number of nearest neighbour molecules^{9, 14} in propyne is not known with any degree of certainty.

An estimate of the mean time between collisions and of the success or otherwise of Gordon's M diffusion model¹¹ for linear dipolar molecules in describing short time molecular behaviour can be made by double differentiation of the analytical expression³ for the vectorial correlation function derived from this model. It can be shown that:

$$F''_M(t) = \exp(-t/2\tau) \int_0^\infty \omega \exp(-\omega^2/2) \{ \omega^2 \cosh[t(1-\beta)^{1/2}/2\tau] + \frac{[(1-\beta)^{1/2} - (1-\beta)^{-1/2}]}{4\tau^2} \sinh[t(1-\beta)^{1/2}/2\tau] \} d\omega, \quad \text{when } \beta < 1$$

$$\begin{aligned}
&= \exp(-t/2\tau) \int_0^\infty \frac{\omega \exp(-\omega^2/2)}{4\tau^2} \left(1 - \frac{t}{2\tau}\right) d\omega, \quad \text{when } \beta = 1 \\
&= \exp(-t/2\tau) \int_0^\infty \omega \exp(-\omega^2/2) \left\{ \omega^2 \cos[t(\beta-1)^{\frac{1}{2}}/2\tau] - \right. \\
&\quad \left. \frac{[(\beta-1)^{\frac{1}{2}} + (\beta-1)^{-\frac{1}{2}}]}{4\tau^2} \sin[t(\beta-1)^{\frac{1}{2}}/2\tau] \right\} d\omega, \quad \text{when } \beta > 1; \quad (4)
\end{aligned}$$

where $\beta = 4\omega^2\tau^2$, τ is the mean time between collisions and ω is normalised by multiplication by $(I/kT)^{\frac{1}{2}}$. From (4):

$$(i) F_M''(0) = \int_0^\infty \omega^3 \exp(-\omega^2/2) d\omega = 2 \quad (\text{normalised})$$

$$(ii) \text{ as } \tau \rightarrow \infty, F_M''(t) \rightarrow \int_0^\infty \omega^3 \exp(-\omega^2/2) \cos \omega t d\omega$$

i.e., the normalised Kummer function for the RVCF of a freely rotating linear molecular system.

The comparison of (2) and (4) is given in fig. 1(e) and (f) for propyne at two different gaseous number densities. The effect of varying τ is shown, the value for best agreement being ca. 0.6 ps at 5.1 bar, 296 K, and ca. 0.55 ps at 25 bar and 376 K. In the curve fitting, both (2) and (4) are again normalised to unity at $t = 0$, bearing in mind that the M diffusion model will not be strictly valid² at $t = 0$ due to the inherent assumptions¹¹ of instantaneous collision. This example illustrates the usefulness of testing analytical models in the short-time domain.

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