Rotational Dynamics of CH_3Cl and CH_2CF_2 in the Fluid State

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The far infrared absorptions of compressed gaseous and liquid CH_3Cl and CH_2CF_2 (1,1-difluoroethylene) have been measured in the frequency range 2-200 cm^{-1} and the results interpreted in terms of two statistical models of molecular rotational dynamics in fluids. A description based on an extended Langevin equation of Brownian motion reproduces the experimental features adequately using empirical intermolecular torque and width parameters. However, it does not reduce to free rotation in the limit of vanishing torque. The J-diffusion model of collision interrupted rotation in symmetric top molecules reduces to free rotation as the interval between elastic impacts becomes infinite, but fails to predict torsional oscillation at short times in denser fluids, so that it compares badly with the far infrared data for pure liquid CH_3Cl and for a solution in ethane.

In this paper we report some absorption measurements in the 2-200 cm^{-1} region (the far infrared [1]) on two molecules in the compressed gaseous and liquid states, and interpret the results in terms of two models of the molecular movements in the fluid state of matter. In so doing we can see how changes of bandshape and intensity result from the additional constraints which may be imposed on roto-translational freedom in going from gas to liquid. The molecules chosen are the symmetric top CH_3Cl, and the oblate asymmetric top CH_2CF_2. Since one is an ellipsoidal molecule and the other is flat, we can investigate the effect, if any, of physical dimensions of molecules in the far infrared gas/liquid spectra. For CH_3Cl, the symmetry makes it possible to use the recently developed [2] quantum theory of multipole-induced dipole absorption in two-molecule collisions to correct for any effect on the band intensities not due to the motion of the permanent dipole.

One of the models used is McClung's J-diffusion treatment of the motion in symmetric top molecules,[3] where an instantaneous collision randomises the angular momentum of each molecule in both magnitude and direction between periods of free rotation. This analysis has been criticized recently by O'Dell and Berne,[4] whose molecular dynamics model of a rough sphere fluid (with elastic collisions) indicates that J-diffusion cannot represent the motions of these simplest of " molecules " over

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any significant range of densities. Bliot *et al.*[5] have demonstrated that this model is a physical consequence of truncating the Mori continued fraction approximation [6] of the orientational autocorrelation function of the dipole moment, the Fourier transform of the frequency domain absorption. This particular truncation leaves the intermolecular mean square torque,[8] $\langle O(V)^2 \rangle$, undefined since it becomes infinite with each instantaneous change in the angular momentum. Here we use the Mori series, truncated so as to leave $\langle O(V)^2 \rangle$ well defined at all times; this, our second model, is shown to fit the experimental data for both molecules satisfactorily except in the limit of vanishing torque or free rotation. In this limit the weakness built in by truncating the continued fraction of Mori manifests itself the most strikingly.

Another reason for choosing these molecules is that of experimental convenience, since their absorptions fall within our instrumental range.

Measurements were made on pure gaseous CH_3Cl, pure liquid CH_3Cl under the vapour, CH_3Cl+ethane mixtures in both states of matter, and pure gaseous and liquid CH_2CF_2.

EXPERIMENTAL

The spectra were measured with a Grubb–Parsons/N.P.L. Fourier transform spectrometer using amplitude-[9] or phase-modulation [10] of the radiation incident upon a Golay or Rollin [11] detector. The absorption coefficient per unit path length of absorber (α, neper cm^{-1}) was computed from the mean of several interferograms using standard techniques.[12] The uncertainty in α is never more than $\pm 5 \%$ of its value over 90% of the frequency sweep.

Samples of gas or liquid were held in the beam between windows of Z-cut crystalline quartz in a high pressure cell of stainless steel.[13] A variable path length was used to eliminate spectral distortions due to changes in refractive index between sample and background.[10] The cell was thoroughly dried before admission of the gas or gas mixture by distillation from type 3A zeolite at N_2(l) temperatures in a chamber adjoint to the space between the windows. Further purification of the original specimen was achieved by many freeze-pump-thaw cycles.

Number densities (N) were estimated via a Budenberg pressure gauge using generalised tables [14] to calculate the compressibility factor. N is known to about $\pm 3 \%$ of its value.

RESULTS

The spectra are described in table 1 and shown in fig. 1 to 4. For the pure gaseous CH_3Cl and CH_2CF_2, table 1 gives the integrated intensity per molecule of each band, defined by :

$$A = \frac{1}{N} \int_{\text{band}} \alpha(\bar{v}) \, d\bar{v}$$

where $\bar{v}$ is the wavenumber. These are compared with the theoretical A of Gordon's sum rule [15] for the total rotational type absorption of a rigid molecule. No value is given for CH_3Cl (liquid), the absorption being too intense for an acceptable estimate of path length difference to be made. Thus we give the spectrum of CH_3Cl(l) in terms of bandshape only as is the more usual practice of presenting infrared spectra. Fig. 1(*a*) is an illustration of the set of $J \rightarrow J+1$ quantum lines of the $\Delta J = 1, \Delta K = 0$ absorptions [2, 13] of freely rotating CH_3Cl molecules, together with results for the gas at 5.8 bar and for a gaseous mixture with ethane of total pressure 39.3 bar. Both experimental bands are broader than the $J \rightarrow J+1$ contour, an observation which may be taken to signify either : (i) the development of collision induced absorption [2] as manifested in a high frequency ($\Delta J = 2$) shoulder to the pure dipolar band ; or (ii) a change of statistics is taking place from that of a Boltzmann distribution of angular velocities as these are perturbed by collision.

The absorption band of liquid methyl chloride is much broader than those above : the peak frequency ($\bar{\nu}_{max}$) is shifted (see table 1), and the spectral distribution is clearly different from the Maxwell–Boltzmann type of the $J \rightarrow J+1$ set of lines. These are unresolved, and it is justifiable to treat it with a classical model. No trace of quantisation is evident in the solution of liquid methyl chloride in liquid ethane [fig. 1(b)], but this band is much more like that of the gas at 5.8 bar. Thus it seems that in the condensed phase, the intermolecular forces between CH_3Cl molecules constrain rotational freedom to a greater degree than do those between CH_3Cl and surrounding ethane.

The corresponding change between CH_2CF_2 gas and liquid is more muted, the $\bar{\nu}_{max}$ remaining approximately static. However, the spectrum of the liquid develops a high frequency tail (fig. 3) so that the corresponding change in the dipolar orientational correlation function [$C(t)$] (the ratio of the autocovarience of the dipole unit vector to its variance) will be a measure of how the molecular dynamics are affected by the change of phase.

DISCUSSION

It is shown in table 1 that the integrated intensities per molecule at different pressures in gaseous CH_3Cl and CH_2CF_2 are those predicted, within experimental uncertainty, by the Gordon sum rule. There is no indication of collision induced absorption. The same is true for CH_2CF_2 liquid. Therefore, it is justifiable to treat these bands with a statistical model of the angular motion of the permanent dipole alone. Such a model should seek to follow the changes in bandshape between the dilute gas and the liquid, and to rationalise these in terms of a limited number of intra- and inter-molecular factors.

TABLE 1.—FAR INFRARED ABSORPTION DATA FOR CH_3Cl AND CH_2CF_2 AT 296 K

	pressure/bar	$10^{20}(A/N)$/cm	$\bar{\nu}_{max}$/cm^{-1}	α_{max}/neper cm^{-1}	(Gordon sum rule) $10^{20}(A/N)$/cm
CH_3Cl	2.7	127	23	2.1	128.9
CH_3Cl	4.4	126	23	3.2	128.9
CH_3Cl	5.8	128	23	4.7	128.9
CH_3Cl+ethane	39.3	—	25	1.0	—
CH_3Cl(l)	—	—	48	—	128.9
CH_3Cl+ethane(l)	—	—	35	4.2	—
CF_2CH_2	11.3	40.7	19.5	11.0	41.6
CF_2CH_2	18.1	40.0	19.5	15.2	41.6
CF_2CH_2	25.0	39.5	19.5	20.0	41.6
CF_2CH_2	31.8	40.6	19.5	24.6	41.6
CF_2CH_2	35.2	39.6	19.5	26.8	41.6
CF_2CH_2(l)	—	42.0	23.0	72.0	41.6

The J-diffusion model, which can be used with the symmetric top [2,3] CH_3Cl, achieves this in terms of one parameter only, the mean time between elastic collisions (τ). This model reduces to the free rotor Boltzmann distribution as τ becomes infinite, and to rotational diffusion [7] (infinitesimally small changes of angular momentum, taking place infinitely quickly) as τ approaches zero. A major disadvantage is that it does not represent finite changes in intermolecular torque (the derivative with respect to time of the component of the molecular angular momentum perpendicular to the dipole axis) at each impact, which is assumed to randomise instantaneously, according to a Poisson distribution, the magnitude and direction of the angular momentum. This formalism produces in the far infrared an $\alpha(\omega)$

which is asymptotic as ω^{-2} at high frequencies [16] ($\omega = 2\pi\bar{\nu}c$), a slower return to transparency than that observed.[17]

The related orientational autocorrelation function $C(t)$ is defined by [18]

$$
\begin{aligned}
C(t) &= \langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(t) \rangle \\
&= \frac{3\hbar c}{4\pi^2} \int_{-\infty}^{\infty} \frac{e^{i\omega t}\, \sigma(\omega)}{\omega[1 - \exp(-\hbar\omega/kT)]} \, d\omega \\
&= \sum_{n=0}^{\infty} a_n \frac{t^{2n}}{(2n)_!},
\end{aligned}
\tag{1}
$$

where $\boldsymbol{u}$ is a unit vector in the dipole axis, t the time; $\sigma(\omega) = \alpha(\omega)/N$; and where successive a_n are alternatively positive and negative. Thus $C(t)$, an equilibrium function, contains ideally no odd powers of time in its series expansion.[8] However, the J-diffusion equation [5] for $C(t)$ has a MacLaurin expansion with a term in t^3 and all the odd powers thereafter. Desplanques [19] has shown that for a symmetric top molecule with principal moments of inertia I_A and I_B, the classical $C(t)$ expands as

$$
C(t) = 1 - \frac{kT}{I_B}t^2 + \frac{1}{3}\left(\frac{kT}{I_B}\right)^2 \left(1 + \frac{I_A}{4I_B} + \frac{\langle O(V)^2 \rangle}{k^2 T^2}\right)t^4 - \cdots
$$

The coefficient of t^2 is $\langle \dot{u}(0)^2 \rangle/2!$, and that of t^4 is $\langle \ddot{u}(0)^2 \rangle/4!$, the equilibrium mean square angular velocity and angular acceleration respectively. The latter is made up of the intramolecular centripetal acceleration and a factor $\langle O(V)^2 \rangle$ which is the intermolecular mean square torque, a function of V, the intermolecular potential. The mean square torque is ill-defined in J-diffusion, and as intermolecular effects become important (*i.e.*, as the terms other than the first two in the series become significant) the model will approximate the classical $C(t)$ more and more remotely, especially at short times.[17] At longer times it is less significantly different in overall form, since $C(t)$ then reduces to an exponential (corresponding to the Debye type [7] absorption in liquids).

Our second model succeeds in keeping $\langle O(V)^2 \rangle$ well defined, so that collisions are no longer elastic, by approaching the problem from the viewpoint of Brownian motion.[4-7, 16] The original Langevin equation [20] describing this motion has been extended by Kubo [21] who developed the equation [6, 7, 16]

$$
\dot{C}(t) = -\int_0^t K(t-\tau)C(\tau) \, d\tau.
\tag{2}
$$

Here, K is a response function, whose Fourier transform would be a frequency dependent friction coefficient. It is often called a memory function, and is itself an autocorrelation function (a.c.f.) of the torque, $\Gamma(t)$, randomly imposed on a molecule by the Brownian motion of neighbours of comparable mass.[6, 7] (The original Langevin equation in effect considered the case of a massive particle immersed in a bath of lighter ones.) In simple Langevin theory (which leads to a solution for the molecular motion in terms of rotational diffusion) K is a delta function, since all dynamical coherence (including molecular inertia) is neglected. This has the well-known [22] spectral consequence that $\alpha(\omega)$ exhibits a physically meaningless " Debye plateau " in the far infrared and higher frequencies.

Eqn (2) has the advantage that the set of memory functions $K_0(t), \ldots, K_n(t)$ forms an infinite series of Volterra equations [6] such that

$$
\frac{\partial}{\partial t} K_{n-1}(t) = -\int_0^t K_n(t-\tau)K_{n-1}(\tau) \, d\tau.
\tag{3}
$$

This is simply repeating the relation [eqn (2)] of $C(t)$ to $K(t)$, since the latter is itself a correlation function. These equations may be solved approximately by truncating the infinite series at a given $n = N$ with a suitable empirical form for $K_N(t)$, an exponential or a Gaussian.[7] The resulting spectrum $\alpha(\omega)$ is then known in terms of equilibrium averages $K_0(0), \ldots, K_N(0)$. These are related [6,7,16] to the a_n of eqn (1), e.g.,

$$K_0(0) = -a_1 = 2kT/I_B;$$
$$K_1(0) = a_1 - a_2/a_1.$$

A simple form such as [23]

$$K_1(t) = K_1(0) \exp(-\gamma t), \tag{4}$$

where γ^{-1} is an empirical correlation time related [1] to the Debye relaxation time by

$$\tau_D^2 = \frac{(K_0(0) + K_1(0))^2 - 2K_0(0)\gamma^2}{K_0^2(0)\gamma^2}, \tag{5}$$

can be used to derive $\alpha(\omega)$ analytically. The equilibrium average $K_1(0)$ is proportional to $\langle 0(V)^2 \rangle$ by Desplanques's expansion given above, and is well defined at all times. In this paper we regard $\langle O(V)^2 \rangle$, i.e., $K_1(0)$, as empirical, along with γ, and evaluate them by least mean squares fitting of the analytical $\alpha(\omega)$ to the experimental data. It can be shown that eqn (4) leads to

$$\alpha(\omega) \propto \frac{K_0(0)K_1(0)\gamma\omega^2}{\gamma^2(K_0(0)-\omega^2)^2 + \omega^2\{\omega^2 - [K_0(0) + K_1(0)]\}^2} \tag{6}$$

for the bandshape, so that the curve is asymptotic as ω^{-4} at high frequencies. The corresponding $C(t)$ has been evaluated analytically [24] by Fourier transform, and is even up to t^4 in its series expansion, but contains all the odd powers of time thereafter.

In the limit of vanishing torque in gaseous CH_3Cl, this model reduces to the truly free rotor [3,25] $C(t)$ [fig. 2(a)] at short times only, when the free rotor Maclaurin series is approximated adequately by its first few terms. In the frequency domain [fig. 1(a)] the contour of the $J \to J+1$ lines is fitted with the $K_1(0)$ and γ of table 2. Ideally, for $\langle O(V)^2 \rangle = 0$, $K_1(0) = 4kT/I_B$. A typical fit to the CH_3Cl compressed gas is shown in fig. 1(a), together with that for the gaseous mixture. The torque dependent term in the latter is almost twice that needed to fit the free rotor contour. The fit for the pure liquid is good [fig. 1(c)] with $K_1(0)$ considerably increased. The time factor γ^{-1} decreases but is not compatible with an interval between collisions since it is finite in the free rotor limit. In the liquid mixture [fig. 1(b)], $K_1(0)$ is surprisingly small, and the band surprisingly narrow, with the half width reflected in the low value of γ needed for best fit (table 2). Within the limitations imposed by our model, we may take this to indicate that CH_3Cl molecules surrounded by ethane are allowed a greater degree of angular freedom of movement, so that jumps through large angles are statistically significant. This is seen reflected in the form of $C(t)$ [fig. 2(c)], which becomes exponential at long times only, in contrast to the a.c.f. of the pure liquid, which exhibits logarithmic decay very quickly. Since rotational diffusion by infinitely small angular displacements corresponds to a purely exponential form $C_D(t) = \exp(-t/\tau_D)$, the above is an indication that angular freedom is very much more restricted in pure CH_3Cl than in the ethane solution.

Below $t^* = (kT/I_B)^{\frac{1}{2}}t = 1$, $C(t)$ for $CH_3Cl(l)$ exhibits oscillatory behaviour. This shows up in the far infrared as the Poley absorption [22] of [fig. 1(c)], the high frequency extension of the microwave absorption. The short time behaviour of $C(t)$ reflects the torsional oscillatory, or librational motion of u about an axis which is
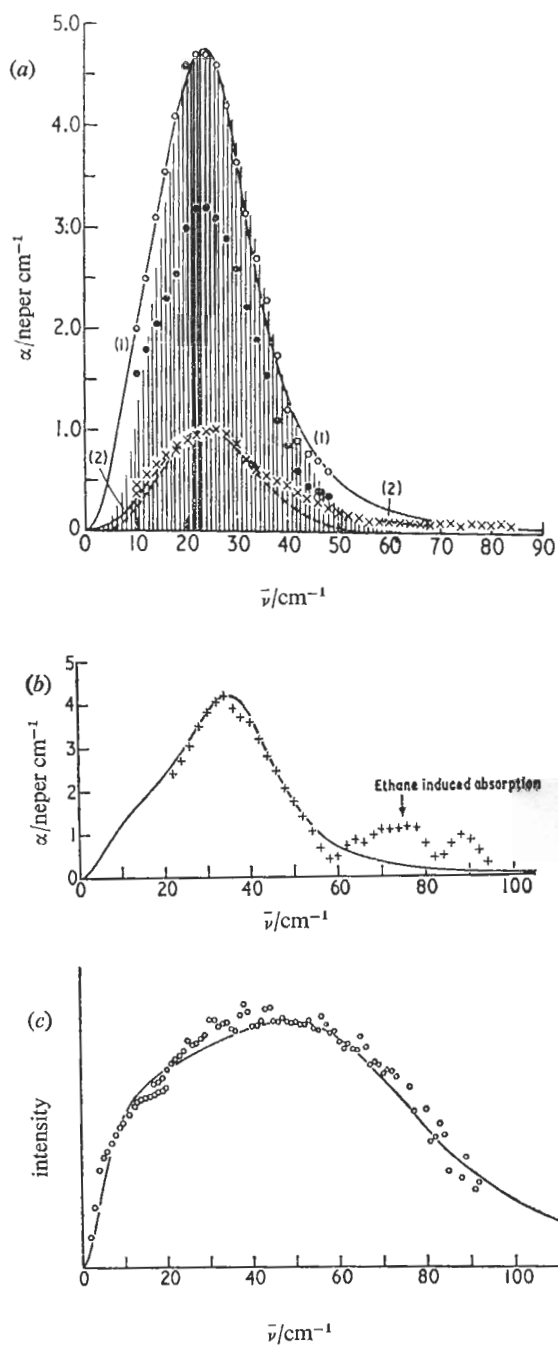
FIG. 1.—(a) ○ Absorption of CH_3Cl at 5.8 bar, 296 K ; ● absorption of CH_3Cl at 4.4 bar, 296 K ; × absorption of CH_3Cl+ethane at a total pressure of 33.5 bar, 296 K. | Set of $\Delta J = 1$ lines for quantum free rotation. The $\Delta K = 0$ lines are not drawn in. — (1) Eqn (6) for the tabulated parameters γ and $K_1(0)$; (2) best, least mean squares, fit to the data. − − − Contour of the $J \to J+1$ lines. (b) + Absorption of CH_3Cl+ethane (liquid) at 296 K. — Eqn (6) best fit. (c) ○ Absorption of liquid CH_3Cl at 296 K. — Eqn (6) best fit.
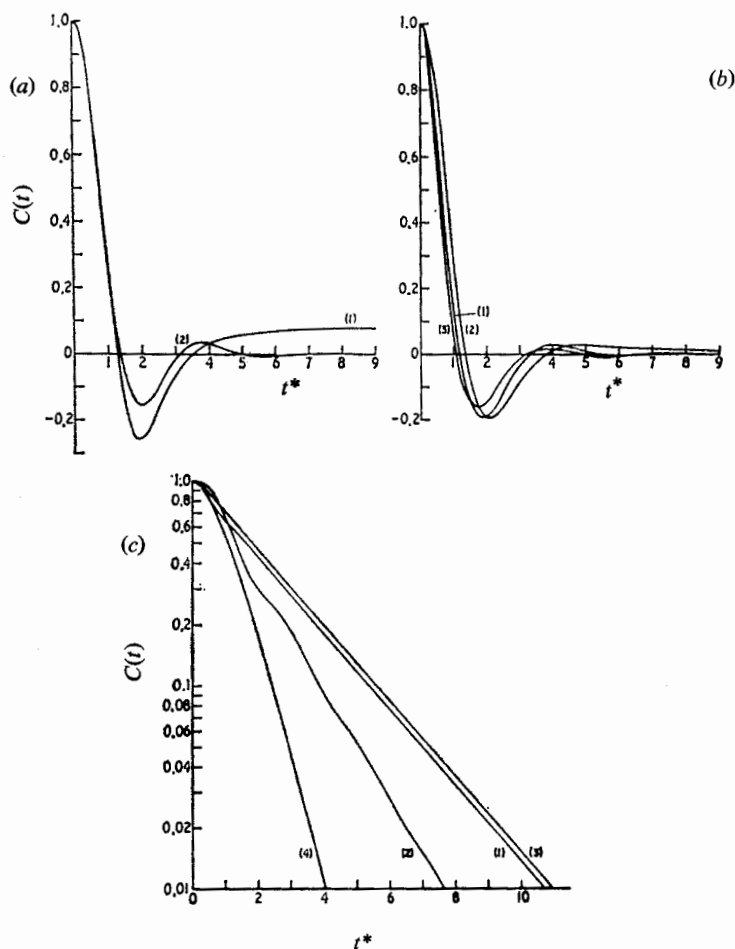
FIG. 2.—(a) $t^* = (kT/I_B)^{\frac{1}{2}}t$. (1) True free rotor orientational autocorrelation function for CH_3Cl at 296 K; (2) best fit of eqn (6) to the $J \rightarrow J+1$ contour, the equivalent correlation function $[C(t)]$. (b) (1) $C(t)$ for $CH_3Cl(g)$ at 5.8 bar, 296 K; (2) J-diffusion model with $\tau^* = (kT/I_B)^{\frac{1}{2}}\tau = 4.0$; (3) $C(t)$ for $CH_3Cl+ethane(g)$ at 33.5 bar, 296 K. (c) (1) $C(t)$ for $CH_3Cl(l)$ at 296 K; (2) $C(t)$ for CH_3Cl+ ethane (l) at 296 K; (3) J-diffusion model with $\tau^* = 0.2$; (4) J-diffusion model with $\tau^* = 0.5$.

TABLE 2.—PARAMETERS OF THE BROWNIAN MODEL FOUND BY A LEAST MEAN SQUARES FIT TO EXPERIMENTAL DATA

	pressure/bar	$2kT\,K_1(0)/I_B$	$(2kT/I_B)^{\frac{1}{2}}\gamma$	$10^{40}\,I_B$ /g cm^2
CH_3Cl	5.8	3.61	3.74	
$CH_3Cl+ethane$	39.3	4.21	3.74	63.12
$CH_3Cl+ethane(l)$	—	4.00	1.90	63.12
$CH_3Cl(l)$	—	14.39	4.29	63.12
CF_2CH_2	35.2	3.67	3.86	80.45
$CF_2CH_2(l)$	—	6.15	3.91	80.45
CH_3Cl $(J \rightarrow J+1)$ contour	—	2.51	2.54	63.12

itself diffusing through the fluid, the itinerant oscillator.[7]   As [fig. 2(c)] shows, the J-diffusion model (e.g., the curve for $\tau^* = 0.2$) is incapable of reproducing this oscillating form of $C(t)$ at short times, a form which predominates experimentally [17] for a whole series of liquids.   In CH_3Cl+ethane(l), the oscillation is much more pronounced, and much longer lived.
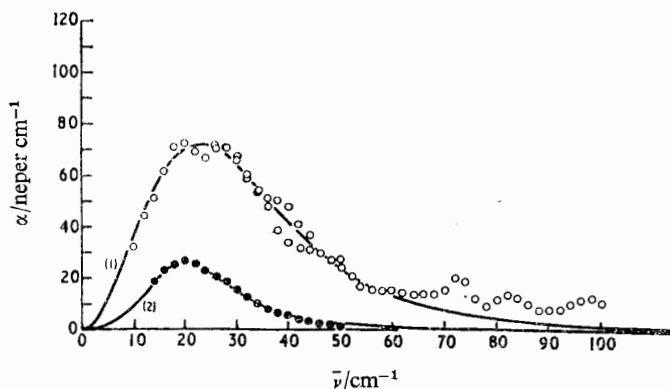

FIG. 3.— ○ Absorption of CH_2CF_2 liquid at 296 K ;   ● absorption of CH_2CF_2 gas at 35.2 bar, 296 K.   — (1), (2) Eqn (6), best fits.
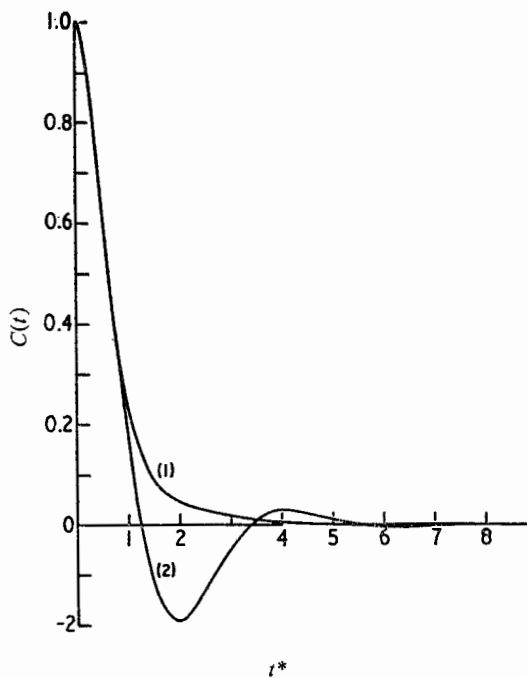

FIG. 4.— ——(1) $C(t)$ for the liquid CH_2CF_2 ; (2) $C(t)$ for the gas at 35.2 bar.

Illustrated in [fig. 2(b)] are the a.c.f. values from both models describing the gas phase data of [fig. 1(a)].   Both show a negative overshoot in $C(t)$, which means that angles of greater than 90° are traversed on average between collisions.   In this case

the *J*-diffusion model is likely to be an adequate description of the molecular dynamics, *i.e.*, those of periods of rotation separated by hard collisions. The $C(t)$ of the Brownian model is more damped in the mixture at 39.3 bar than in the pure gas at 5.8 bar, because the collision frequency is higher.

The Brownian model reproduces experimental features in CH_3Cl gas/liquid spectra adequately: the variations in the empirical terms $K_1(0)$ and γ are in accord with physical expectation, *i.e.*, a higher $\langle O(V)^2 \rangle$ as the fluid becomes denser. In the liquid, the corresponding $C(t)$ succeeds in reproducing oscillatory behaviour [17] at short times, and experimental [22] at long, while in the gas, negative overshoot is apparent. It fails to reproduce free rotor behaviour in the limit where the torque becomes zero. On the other hand, the *J*-diffusion model reduces to the free rotor as $\tau^* \rightarrow \infty$, but fails to predict torsional oscillation, so that it compares badly with experimental data in the far infrared.

In the asymmetric rotor CH_2CF_2, no formalism akin to that of McClung [3] is available, so that we have only our Brownian model. Fig. 3 shows the absorption in CH_2CF_2 gas at 35.2 bar and in the liquid. The difference between them is seen more clearly in terms of $C(t)$ [fig. 4]. Although still enjoying a great degree of angular freedom, the liquid a.c.f. is damped at longer times and never becomes negative. It is exponential at very long times. In the gas, there is a large negative part to the $C(t)$ since collisions are rarer.

The difference in behaviour of CH_2CF_2 and CH_3Cl liquids is pronounced and remarkable. In the former, $\bar{\nu}_{max}$ is hardly changed from that of the compressed gas, in striking contrast to the shift of $\sim 25\ cm^{-1}$ in CH_3Cl. It may be true that CH_2CF_2 enjoys a great deal of rotational freedom in its plane, *i.e.*, about an axis perpendicular to that containing the resultant dipole, although a degree of antiparallel alignment might be anticipated from dipole-dipole interactions ($\mu = 1.37\ D$). This might be a reason for the apparent lack of angular freedom in $CH_3Cl(l)$ ($\mu = 1.87\ D$). However, it is relevant to note that under our experimental conditions, we are dealing with a liquid of greater macroscopic density in CH_3Cl, so that the corresponding amount of free volume is smaller.

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