

# Rotational Brownian Motion in Liquid and Plastic Crystalline CBr<sub>4</sub> from Far Infrared Induced Absorptions

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*Received 21st April, 1976*

The far infrared induced absorption bands of CBr<sub>4</sub> in the liquid and plastic single crystalline states have been measured in order to study the changes in rotational dynamics brought about by the increased translational constraint and packing symmetry of the solid. Analysis of the band-shapes in terms of rotational Brownian type dynamics suggests that the barrier to such motion is slightly increased on going from the plastic crystal to the liquid a few degrees above the melting point, thus making the change of phase energetically desirable. The integrated intensity per molecule is greater in the liquid, although the macroscopic density is less, which suggests that the spatial disposition of the electrostatic (long range) part of the intermolecular potentials is important in determining the magnitude of the molecular induced dipole moment.

The dipole cross-correlation function corresponding to these bands is compared with that of octopole-induced dipole absorption of a two molecule collision of spherical tops, and with the auto-correlation function for a Maxwellian ensemble of freely rotating molecules of this symmetry. It is found that the mean torque is greater initially in the condensed phases, thereafter, rotational motion is correlated.

The far infrared (20-280 cm<sup>-1</sup>) spectra of CBr<sub>4</sub> in the monoclinic, plastic crystalline, and liquid phases contain information on intra- and intermolecular motions. The latter are responsible for a temporary dipole on each molecule through the interplay of molecular electric fields. This is fluctuating (and weak), consequently the half width of the intermolecular band is considerable in comparison with intramolecular proper modes of band vibration or torsion.<sup>1, 2</sup> The shapes and intensities of these intermolecular bands are sensitive measures of the way its neighbours affect the motion of a reference molecule and distort the symmetry of its electron cloud, producing a small, temporary dipole moment. Each molecule at an instant *t* will have such an induced dipole moment, different in magnitude and direction from any other. The magnitude of this dipole is itself determined by molecular interaction (and thus disorder) which, therefore, affects both bandshape and band intensity. In the plastic crystalline phase,<sup>3</sup> in comparison with the room temperature monoclinic form, each

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molecule is left with a characteristically generous amount of rotational freedom, but translational freedom is limited, though not entirely absent. In contrast, both types of motion are available and strongly coupled in the liquid; the overall molecular dynamics are an amalgam of each. This paper aims to use an infrared absorption dependent only on intermolecular effects to clarify a little the difference between the liquid and plastic crystalline phase, and consequently to illuminate some badly understood facets of the relation between far infrared absorption and intermolecular effects.

### EXPERIMENTAL

The absorptions were measured with a Mark III Grubb-Parsons N.P.L. Fourier transform interferometer incorporating phase modulation<sup>4</sup> of the detected signal (I.R. 50 Golay). The results were reproducible in absolute intensity to within  $\pm 2\%$  over 90% of the frequency range, the maximum resolution<sup>5</sup> being  $2\text{ cm}^{-1}$ . The Golay detector becomes noisy below about  $12\text{ cm}^{-1}$  and the power throughput is low at the peaks of the most intense and sharpest proper modes. Here we estimate the uncertainty from successive interferograms to rise to  $\sim \pm 10\%$ . Systematic uncertainties have been analysed by Chamberlain<sup>4</sup> and, for a convergent beam, are markedly dependent upon sample thickness. However, keeping this constant for liquid and plastic crystal ensures that their absorption cross sections per molecule are accurate relative to each other. Using different interferometric beam dividers with overlapping frequency ranges virtually eliminates any residual systematic uncertainty in bandshape. The correlation functions, being normalised at the origin, depend upon bandshape only, and reflect the latter's small random uncertainty.

A commercial sample of crystalline CBr<sub>4</sub> was purified by zone refining and transferred directly to a thermostatted sample holder. A single crystal of the plastic phase was prepared in this cell by cooling very slowly from the liquid. This eliminates uncertainties in absolute absorption intensity arising from interstitial effects on the dispersion such as those in a powdered disc. Further cooling into the monoclinic configuration at room temperature destroyed the single crystal, but here we were not interested in obtaining accurate absolute absorption intensities, only bandshapes, frequencies and relative intensities, as in a conventional infrared spectrum.

### RESULTS

The broad bands centred near  $32\text{ cm}^{-1}$  (fig. 1) in both liquid and rotator phase are interpreted as being intermolecular in origin, since they do not correspond to any known difference modes or overtones or fundamentals, and occur at frequencies where such bands are prevalent for non-dipolar molecules.<sup>2, 6</sup> In the  $Th^6(Pa^3)$  monoclinic phase at 298 K this band is replaced by a doublet, both components of which are broader at half peak height than the fundamentals showing up at  $125\text{ cm}^{-1}$ ,  $184\text{ cm}^{-1}$  and  $270\text{ cm}^{-1}$ , doubly, triply and singly degenerate respectively.<sup>7</sup> The fundamental at  $184\text{ cm}^{-1}$  in the monoclinic phase is flanked by well-defined shoulder bands which are again of intermolecular origin.<sup>8</sup> In the plastic crystalline phase at 376 K the fundamental at  $124\text{ cm}^{-1}$  is broadened compared with the monoclinic phase, and considerably so in the liquid.

### CALCULATION

If a CBr<sub>4</sub> molecule whose centre of mass is at the point  $R(r, \theta, \phi)$  is assumed to develop a temporary dipole moment under the influence of the electrostatic fields of its neighbours then the vector sum of these fields at  $R$  at any instant will be determined by the relative positions of all other molecules in the ensemble at that time, and consequently will be a measure of the disorder or ordering in the lattice of molecules near enough for their fields sufficiently to be influential.

With a loss of translational freedom comes a diminution of the resultant field at  $R$ , harnessed to an increased lattice symmetry. This hypothesis is supported by our limited results on  $CBr_4$ , since the intermolecular, induced band in the liquid is the more intense, despite the greater macroscopic density of the plastic crystal. Savoie and Fournier<sup>9</sup> have shown that the maxima of induced bands vary with temperature as  $I^{\frac{1}{2}}$  and not as  $M^{\frac{1}{2}}$  in both the liquid and rotator phase. Here  $M$  is the molecular mass and  $I$  the moment of inertia. They arise, therefore, from intermolecular effects dominated by a rotational type of motion, although gas studies<sup>1, 10</sup> have indicated that translational absorptions ( $\Delta J = 0$ ) are observable also in the far infrared.

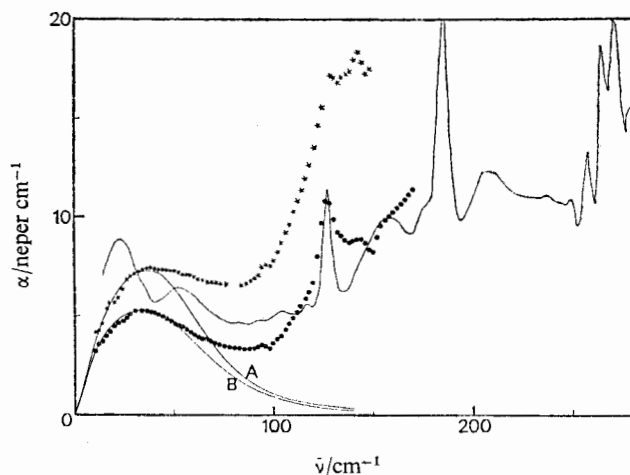


FIG. 1.—Absorption of the  $Th^6(Pa^3)$  monoclinic phase at 298 K. ● Absorption of the plastic (simple cubic) single crystal at 358 K; ★ Absorption of the liquid at 376 K; — (A) and (B), eqn (5) least mean squares best fit to the low frequency experimental data.

The Fourier transform of such an induced band is proportional to a correlation function<sup>10, 11</sup> of the form

$$C(t) = \sum_{ij} \langle \mu_i(0) \cdot \mu_j(t) \rangle = \sum_n (-1)^n a_n \frac{t^{2n}}{(2n)!} \quad (1)$$

where  $\mu_j(t)$  is the dipole vector induced on molecule  $j$  at time  $t$ . It is well known<sup>12</sup> that if the molecules in the liquid are assumed to follow the dynamics of stochastic (Brownian) motion then any statistical correlation function describing that motion can be approximated by an equation of the form

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

where the kernel  $K$  can be looked upon as a response function whose Fourier transform is a frequency dependent "friction coefficient on the microscopic scale".  $K$ , itself a statistical quantity,<sup>13</sup> is the correlation function of the torque on each molecule and in turn can be approximated<sup>14</sup> by equations like (2) linking it to a set of kernels  $K_0, \dots, K_n$

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

Truncating the series at a given  $n = N$ , and solving for the spectral function by Fourier-Laplace inversion<sup>15</sup> gives a convenient analytical spectrum involving the equilibrium averages  $K_0(0), \dots, K_n(0)$ , which are related<sup>12, 15</sup> to the time coefficients  $a_n$  in the even Maclaurin expansion of eqn (1). Naturally, these  $K_n(0)$  coefficients are complicated functions of the phase space averaged resultant molecular electrostatic field at each point  $R$  at equilibrium, but we can suppose that if the environment were such as to constrain rototranslational freedom  $K_n(0)$ , being torque dependent, would change on going from the liquid to the plastic phase. This gives us a quantitative measure of the differences between this phase and the liquid.

It is practical only to use a truncated form of the series [eqn (3)] otherwise there would be too many factors  $K_n(0)$  whose relation to the fundamental molecular constants would be unknown, and thus would remain empirical. The equation<sup>15</sup>

$$K_1(t) = K_1(0) \exp(-\gamma t) \quad (4)$$

is a compromise which avoids premature truncation while retaining three coefficients  $K_0(0)$ ,  $K_1(0)$  and  $\gamma$  whose dimensions and general characteristics are known but can be determined numerically only by a least mean squares fit to the experimental absorption bands. Eqn (4) renders  $K_1(t)$  a Markovian process.<sup>12</sup>  $K_0(0)$  and  $K_1(0)$  are related to equilibrium ensemble averages (in position and momentum subspaces) of angular momenta derivatives (intermolecular torques) and their derivatives in turn.<sup>15</sup> They have the units of  $s^{-2}$ .  $\gamma^{-1}$  is a correlation time, and is conceptually a distant relative of the Debye time of dipolar liquids. Use of eqn (2)-(4) gives the power absorption coefficient per unit path length of absorber (neper  $cm^{-1}$ ) as

$$\alpha(\omega) = \frac{\Lambda \omega^2 \gamma K_0(0) K_1(0)}{\gamma^2 [K_0(0) - \omega^2]^2 + \omega^2 \{\omega^2 - [K_0(0) + K_1(0)]\}^2} \quad (5)$$

Here  $\Lambda$  is a proportionality constant dealing with the dispersion ( $\epsilon_0 - \epsilon_\infty$ ) and the small internal field correction in these very low absorbers.

In order to estimate absolutely the degree of rotational freedom retained in these condensed phases it is profitable to compare the correlation functions of fig. 2 with those estimated using models of rotational motion in the gas phase. The correlation function for the free rotation of a Maxwellian distribution of spherical tops<sup>16</sup> [ $C_{FR}(t)$ ] is given by

$$C_{FR}(t) = \frac{2}{3} \left( 1 - t^2 \frac{kT}{I} \right) \exp \left( -t^2 \frac{kT}{2I} \right) + \frac{1}{3} \quad (6)$$

This is illustrated for CBr<sub>4</sub> at 376 K in fig. 2 and decays much more slowly than the functions  $C(t)$  of the condensed phases. Thus the effect of intermolecular forces is clearly seen in the time domain. It is well known<sup>17</sup> that spherical top molecules in the dense gas phase exhibit a far infrared rotational band reflecting via its angular movement the distortion of a molecular electron field during and after a bimolecular collision. The electrostatic and overlap contributions to this band are treated separately, the former being developed in point multipole moments, of which the first in a spherical top is the octopole ( $\Omega$ ). The overlap absorption is regarded as less important and treated empirically<sup>18</sup> or ignored, since multipole theory is capable of producing the experimental broad band acceptably well for simple molecules such as CH<sub>4</sub> and CF<sub>4</sub> in the gas phase.<sup>17</sup>

It is shown in the appendix that the multipole-induced band produces in the classical limit<sup>19</sup> a correlation function  $C_\Omega(t)$  which can be compared with  $C_{FR}(t)$  and  $C(t)$  (fig. 2).

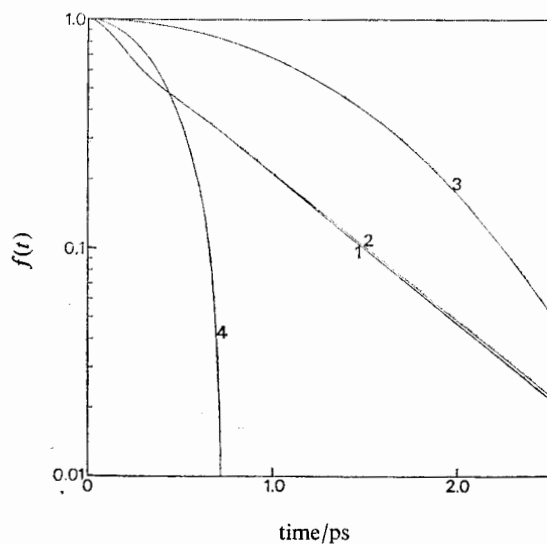


FIG. 2.—Correlation functions for  $\text{CBr}_4$  from induced far infrared bands. (1)  $C(t)$  for the liquid, (2) for the plastic crystal, (3)  $C_\Omega(t)$ ; (4)  $C_{\text{FR}}(t)$ .

### CONCLUSIONS

Eqn (5) has been used here to describe the absorption around  $35\text{ cm}^{-1}$  for both liquid and plastic crystalline phases of  $\text{CBr}_4$ . The best fit is shown in fig. 1 with the parameters tabulated below. It is clear from the table that the rotational motion is slightly less hindered in the plastic phase given the above hypothesis. The correlation functions corresponding  $^{11}$  to  $\alpha(\omega)$  are displayed in fig. 2 and 3, together with their related kernels  $K$  [linked by eqn (2)].

TABLE 1.—LANGEVIN PARAMETERS FOR  $\text{CBr}_4$  ( $I = 1.33 \times 10^{-37}\text{ g cm}^2$ )

	$\left(\frac{2kT}{I}\right)K_0(0)$	$\left(\frac{2kT}{I}\right)K_1(0)$	$\left(\frac{2kT}{I}\right)^{\frac{1}{2}}\gamma$	$T/K$
liquid	$21 \pm 0.4$	$247 \pm 5$	$21 \pm 0.4$	$376 \pm 1$
rotator	$20 \pm 0.4$	$227 \pm 5$	$20 \pm 0.4$	$358 \pm 1$

The function  $C_\Omega(t)/C_\Omega(0)$ , displayed in fig. 2, looks very little like the correlation functions of the condensed phase bands, which fall off initially faster and thereafter exponentially and more slowly. The octopolar function becomes negative after 0.7 ps, exhibits a minimum at 1.2 ps and is damped to zero after  $\sim 5.0$  ps. At very short times, these correlation functions all take the form

$$C(t) = 1 - \frac{a_1 t^2}{2!} + \dots$$

and the fact that  $C_\Omega(t)/C_\Omega(0)$  falls off faster than  $C_{\text{FR}}(t)$  means that  $a_2$  is affected in some way by molecular interaction, *i.e.*, it is torque dependent. From fig. 2 it is clear that  $\text{CBr}_4$  molecules in both the liquid and plastic crystalline phase experience a torque almost immediately after the arbitrary  $t = 0$ . This is greater in magnitude than that in a bimolecular collision of octopole fields since  $C(t)$  falls off faster initially than  $C_\Omega(t)/C_\Omega(0)$ . Rotational motions are then correlated in the condensed phases, and after  $\sim 0.7$  ps both  $C(t)$  become exponential and decay relatively slowly compared

with  $C_{\Omega}(t)/C_{\Omega}(0)$ . O'Dell and Berne have discovered recently<sup>20</sup> that rotational motion is freer in the solid just below the melting point in rough hard sphere ensembles. This seems to be the case here, since  $C(t)$  for the liquid falls off initially a little faster.

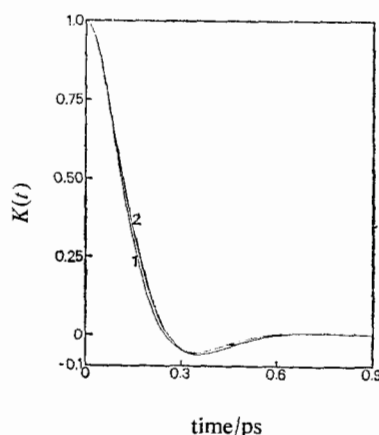


FIG. 3.—Memory functions for CBr<sub>4</sub>, (1) liquid, (2) plastic crystal.

The greater initial torque in the condensed phases can be explained superficially in terms of the greater packing density since the intermolecular potential would be much greater on average with van der Waals radii overlapping (repulsive domain) for a greater percentage of the time. However, this is too simple a view, since the packing density in the plastic solid is the greater while the mean torque is smaller. This can only mean that symmetry of packing and the resultant restriction on molecular diffusion is a factor which is important in determining the ease of rotational movement in the plastic phase.

At some density in the liquid, rotation is bound to become easier than in the plastic solid, but near the melting point it seems that lack of packing symmetry makes rotation a statistically more energetic process than in the solid, resulting, naturally, in the phase transition itself.

To fit eqn (7) to our experimental integrated absorption intensity per molecule in the liquid and plastic crystal is clearly indicated as a recondite exercise by fig. 2. In fact  $|\Omega|$  for the liquid using this procedure is  $59 \times 10^{-34}$  e.s.u. and  $42 \times 10^{-34}$  e.s.u. for the solid. These compare with the value of  $31 \times 10^{-34}$  e.s.u. calculated by Ewool and Strauss.<sup>21</sup> Vapour phase studies for CBr<sub>4</sub> would yield a truer estimate of the octopole moment.

#### APPENDIX

The total integrated intensity of an octopole-induced dipole absorption band is given by Ozier and Fox<sup>17</sup> as

$$A = \sum_{J \neq J'} A(J, J') \quad (7)$$

where

$$A(J, J') = \frac{(8\pi)^4 N^2 \Omega^2 \alpha_0^2}{280 hcZ} \int_0^\infty R^{-8} \exp(-U(R)/kT) dR \times \bar{\nu}(J, J')(2J+1)(2J'+1)[e^{-aJ(J+1)} - e^{-aJ'(J'+1)}],$$

with  $a = Bhc/kT$ ,  $\bar{\nu}(J, J') = B[J'(J'+1) - J(J+1)]$ , and where  $\Delta J = J' - J = 0, 1, 2, 3$  are allowed.

Here  $N$  is the molecular number density,  $\alpha_0$  the polarisability,  $B$  the rotational constant ( $\text{cm}^{-1}$ ) and  $Z$ , the rotational partition function

$$Z = \sum_J (2J+1)^2 \exp[-aJ(J+1)].$$

Thus the overall band is the sum of the individual transition intensities  $A(J, J+1)$ ,  $A(J, J+2)$ , and  $A(J, J+3)$ . The correlation function is thus given by

$$C_{\Omega}(t) \propto \int_0^{\infty} \frac{A(J, J+1) \cos 2\pi\bar{\nu}ct \, d\bar{\nu}}{({}^{(1)}\bar{\nu})[1 - \exp(-h({}^{(1)}\bar{\nu}c/kT)]} + \\ \int_0^{\infty} \frac{A(J, J+2) \cos 2\pi\bar{\nu}ct \, d\bar{\nu}}{({}^{(2)}\bar{\nu})[1 - \exp(-h({}^{(2)}\bar{\nu}c/kT)]} + \\ \int_0^{\infty} \frac{A(J, J+3) \cos 2\pi\bar{\nu}ct \, d\bar{\nu}}{({}^{(3)}\bar{\nu})[1 - \exp(-h({}^{(3)}\bar{\nu}c/kT)]}$$

with  $({}^{(1)}\bar{\nu}) = 2B(J+1)$ ;  $({}^{(2)}\bar{\nu}) = 2B(2J+3)$ ;  $({}^{(3)}\bar{\nu}) = 6B(J+2)$ . It is easy to show that:

$$A(J, J+1) \propto ({}^{(1)}\bar{\nu}) \cdot (2J+1)(2J+3) \exp[-aJ(J+1)] \\ \times [1 - \exp(-hc({}^{(1)}\bar{\nu})/kT)];$$

$$A(J, J+2) \propto ({}^{(2)}\bar{\nu}) \cdot (2J+1)(2J+5) \exp[-aJ(J+1)] \\ \times [1 - \exp(-hc({}^{(2)}\bar{\nu})/kT)];$$

$$A(J, J+3) \propto ({}^{(3)}\bar{\nu}) \cdot (2J+1)(2J+7) \exp[-aJ(J+1)] \\ \times [1 - \exp(-hc({}^{(3)}\bar{\nu})/kT)];$$

the proportionality constant being in each case the  $J$ -independent part of eqn (7). We have, finally, in the classical limit,<sup>19</sup>

$$C_{\Omega}(t) \propto \int_0^{\infty} \left[ \left( \frac{\bar{\nu}}{B} - 1 \right) \left( \frac{\bar{\nu}}{B} + 1 \right) \exp \left[ -a \left( \frac{\bar{\nu}}{2B} - 1 \right) \left( \frac{\bar{\nu}}{2B} \right) \right] + \right. \\ \left. \left( \frac{\bar{\nu}}{2B} - 2 \right) \left( \frac{\bar{\nu}}{2B} + 2 \right) \exp \left[ -a \left( \frac{\bar{\nu}}{4B} - \frac{3}{2} \right) \left( \frac{\bar{\nu}}{4B} - \frac{1}{2} \right) \right] + \right. \\ \left. \left( \frac{\bar{\nu}}{3B} - 3 \right) \left( \frac{\bar{\nu}}{3B} + 3 \right) \exp \left[ -a \left( \frac{\bar{\nu}}{6B} - 2 \right) \left( \frac{\bar{\nu}}{6B} - 1 \right) \right] \right] \cos 2\pi\bar{\nu}ct \, d\bar{\nu}.$$

The S.R.C. is thanked for a postgraduate studentship for G. J. E., a postdoctoral fellowship for M. W. E. and an equipment grant. The director of research at the Post Office is thanked for permission to publish to G. J. D.

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