

MODEL INTERPRETATIONS OF THE FAR INFRARED ABSORPTIONS
IN COMPRESSED GASEOUS AND LIQUID BROMOTRIFLUORO-
METHANE, CBrF_3

Model Interpretations of the Far Infrared Absorptions in Compressed Gaseous and Liquid Bromotrifluoromethane, CBrF_3

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The far infrared (2-100 cm^{-1}) absorption of the symmetric top molecule bromotrifluoromethane (CBrF_3) has been measured for the gas phase in pressure range 1.2-46.2 bar and for the liquid. Whereas the peak of the broad bands observed moves only slightly from 9.8 cm^{-1} at 1.2 bar to 11.0 cm^{-1} in the liquid at the same temperature (295 K), there are pronounced differences in the bandshape which are reflected in considerable damping of the time functions obtained by Fourier transformation of the frequency data. A simple model of bimolecular collision induced dipolar absorption accounts fairly well for the high frequency shoulders which appear in the spectra of the compressed gas. Using this model, preliminary values of the quadrupole (Q) and octopole moment (Ω) of the molecule have been obtained. A mechanism of collision disturbed torsional oscillation of the permanent dipole (μ) within potential wells accounts more satisfactorily for the absorption in the liquid than the J -diffusion model, which assumes free rotation between instantaneous collisions.

Several recent studies¹⁻⁴ of the far infrared (10-200 cm^{-1}) absorption bands of small linear molecules in the compressed gas and liquid states have had the aim of gaining some insight to the liquid state by comparison with the bimolecular collision induced absorption. Present theories^{5, 6} of this latter type of infra-red absorption are restricted by the form of the intermolecular potential $U(R)$ assumed, and since this is still usually approximated by a Lennard-Jones potential,⁷ the experimental absorption is adequately predicted in intensity and bandshape only for the simplest molecules such as⁸ H_2 and N_2 , and then only in the gas phase⁹ where interactions involving more than two molecules are rare. As expected, neglect of the electrostatic part of $U(R)$ (e.g. the quadrupole-quadrupole interaction energy⁴) in highly quadrupolar and anisotropic molecules such as cyanogen⁴ and carbon dioxide³ leads to disagreement between the experimental and predicted frequency of maximum absorption ($\bar{\nu}_{\text{max}}$) and to a fallacious temperature variation³ of the quadrupole moment (Q) when this is regarded as the unknown quantity linking the observation and theory.

However, it is now possible to study larger but "pseudo-spherical" molecules in this way with the help of advances in experimental and theoretical techniques. Frost *et al.*^{10, 11} have recently extended the treatment of bimolecular collision induced absorption to symmetric top molecules which allows this type of study to be made with molecules, other than linear, which contain a permanent dipole moment. The use of a liquid helium cooled Rollin detector with phase-modulated Michelson interferometers has extended the spectroscopic range down to 2 cm^{-1} so that overlap with the "microwave region" is now routine.

The molecule BrCF_3 is well suited to this type of study since it is spheroidal with a small dipole moment (0.65 D), and, by symmetry, a quadrupole moment which is small enough not to affect $U(R)$ adversely, and yet large enough to produce a significant absorption in comparison with that of the permanent dipole. There are at least two classes of information which may be defined. First, values of the apparent quadrupole moment (Q) and the octopole moment (Ω) may be obtained from the integrated intensity of the absorption band with the equation:

$$A = \int_0^\infty \alpha(\bar{\nu}) d\bar{\nu} = A'\mu^2N + (B'\mu^2 + CQ^2 + D\Omega^2)N^2 \quad (1)$$

where $\alpha(\bar{\nu})$ is the experimental absorption coefficient (in neper cm^{-1}) at frequencies $\bar{\nu}$, N the number density (molecule cm^{-3}) and A' , B' , C and D are theoretical constants. (If both Q and Ω are unknown, then (1) must be used in conjunction with frequency or time domain curve fitting, see evaluation section below). The above equation assumes that collisions involving more than two molecules are rare, so that the terms in N^3 etc. are small, that overlap and translational absorptions¹² are small, and that cross terms between the induced dipole moment and the permanent dipole are negligible.

Secondly, information about the fluctuation in space with time of the molecular permanent dipole moment vector (\mathbf{u}) (i.e., a unit vector along the permanent dipole) may be obtained following the effect of progressive compression and liquefaction of the macroscopic sample on the far infrared bandshapes. A convenient function which can be used for this purpose is

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

where t denotes time elapsed from an arbitrary point $t = 0$ and the angular brackets denote ensemble averaging. $f(t)$ is proportional¹³ to the Fourier transform of $\alpha(\bar{\nu})$:

$$f(t) \propto \int_{-\infty}^{\infty} \frac{\bar{\nu}\alpha(\bar{\nu}) \exp(2\pi i\bar{\nu}ct) d\bar{\nu}}{[1 - \exp(-hc\bar{\nu}/kT)]} \quad (2)$$

if cross-correlations (vector products of \mathbf{u} between different molecules) are neglected and the internal field factor¹⁴ is considered static (independent of $\bar{\nu}$). "Dynamic" internal field factors have been reviewed by Brot¹⁵ and are important only for large μ in the liquid phase.

Eqn (2) is valid only if the absorption due to the permanent dipole¹⁶ is Fourier transformed. Given accurate estimates of $|Q|$ and $|\Omega|$, it would be possible to subtract the induced dipolar absorption in the gas phase using eqn (1). However, in the liquid phase eqn (1) no longer applies (because of many body collisions) and the relative contributions of permanent and induced dipole to the bandshape are usually very difficult to estimate.¹⁷ [Gordon's sum rule¹⁸ may be used¹⁹ to estimate the contribution to the integrated intensity (A) of all rotational modes (microwave and far infrared) of the permanent dipole. In liquids such as chlorobenzene¹⁹ the excess over this sum is of the order of 30–50% of the total observed A .]

Experimentally, CBrF_3 is convenient because the rotational contribution of the permanent dipole peaks at 9.8 cm^{-1} , so that the whole band is situated in the measurable range $2\text{--}100 \text{ cm}^{-1}$. Finally, the critical properties make it straightforward to study the liquid in equilibrium with several atmospheres pressure of vapour and also to obtain high gas number densities by heating to above the critical temperature.

EXPERIMENTAL

Submillimetre wavelength measurements²⁰ were carried out at Dollis Hill with two interferometers evacuated to remove water vapour and modified to cover the spectral ranges (i) 2 to 31 cm^{-1} ; (ii) 20–100 cm^{-1} . In both cases the air-cooled lamp-housing was replaced by a more efficient water-cooled unit and phase-modulation^{21, 22} was incorporated. The apparatus was left switched on to ensure maximum stability. Over the range 20–100 cm^{-1} , where a quartz Golay detector was used, signal to noise ratios²¹ as great as 1000 were obtained.²³ Resolution in this region was 4 cm^{-1} .

For the range 2 to 31 cm^{-1} a Rollin InSb, liquid helium cooled detector²⁴ was employed together with a 4 mm black-polyethylene filter. Signal to noise ratios as great as 10 000 were obtained, whilst the reproducibility of three consecutive runs was estimated to be of the order of 0.1%. The resolution was 2 cm^{-1} .

The spectra of the compressed gas and liquid were taken in a high pressure cell¹ having 7 mm *Z* cut crystalline quartz windows, and with an adjustable path length. The spectrum of the detected power was computed for a number of interferograms for two thicknesses of the given gas or liquid sample, and the power coefficient was calculated from the ratio of the averages. Surface and internal-reflection effects were thus almost eliminated.²⁵

The absorption of the lower density vapour was measured with a fixed path length (147.6 mm) cell consisting of a gold-plated copper light pipe with poly-(4-methylpent-1-ene) windows embedded in a stainless steel sheath. The radiation was focused onto the detector with a light cone.

The nominal purity of the sample (Matheson Ltd.) of CBrF_3 used was 99.0 mole % (minimum), the main contaminants being other freons and air. The specimen was distilled onto type 3-A zeolite at liquid nitrogen temperature in adjoint chambers of either cell to remove moisture as far as possible. The CBrF_3 was thereafter stored in these chambers as a liquid under its own vapour pressure at room temperature (295 K). High pressures were obtained by heating the assembly above the critical temperature (340 K). The liquid absorption was observed at 295 K after distillation into the optical path.

The pressure, as monitored by a Budenberg gauge, was constant to within $\pm 2\%$ of its value once equilibrium was obtained. *N* was calculated with generalised compressibility curves²⁶ at each pressure and its uncertainty is estimated to be $\sim \pm 3.5\%$.

RESULTS

The far infrared spectra of gaseous CBrF_3 at low and high pressure and of the liquid in equilibrium with the vapour at 295 K are illustrated in figs. 1, 3, 5 and 7. The experimental *A* values are shown in table 1, together with the relevant observed $\bar{\nu}_{\text{max}}$, the wavenumber corresponding to α_{max} , the maximum in each absorption band.

TABLE 1.—FAR INFRARED ABSORPTIONS OF CBrF_3 GAS AND LIQUID

phase	temp./K	pressure/ bar	$10^{21}N/molecule\ cm^{-3}$	<i>A</i> /neper cm^{-2}	$\bar{\nu}_{\text{max}}/\text{cm}^{-1}$
gas	295	1.2	0.03	0.57	9.8
gas	295	3.3	0.08	2.05	9.8
gas	357	28.4	0.77	36	10.7
gas	357	46.2	1.94	204	11.0
liquid	295	—	6.22	388	11.0

In the figures, the bars denote the theoretical frequencies and relative intensities corresponding to the $J \rightarrow J+n$ ($n = 1, 2, 3$) absorption due to rotation of the permanent dipole ($n = 1$), dipole induced ($n = 1$); quadrupole induced ($n = 2$); and octopole induced ($n = 3$) dipole absorptions.

Qualitatively, it is apparent that the envelope of the pure rotational lines observed at 1.2 bar and 3.3 bar develops an extended high frequency tail at 28.4 bar, which is

more significant at 46.2 bar and relatively less so in the liquid. The overall integrated intensity A is linearly dependent on N at the lowest pressures but increases as a higher power of N thereafter. In the liquid, A/N is relatively much smaller than in the

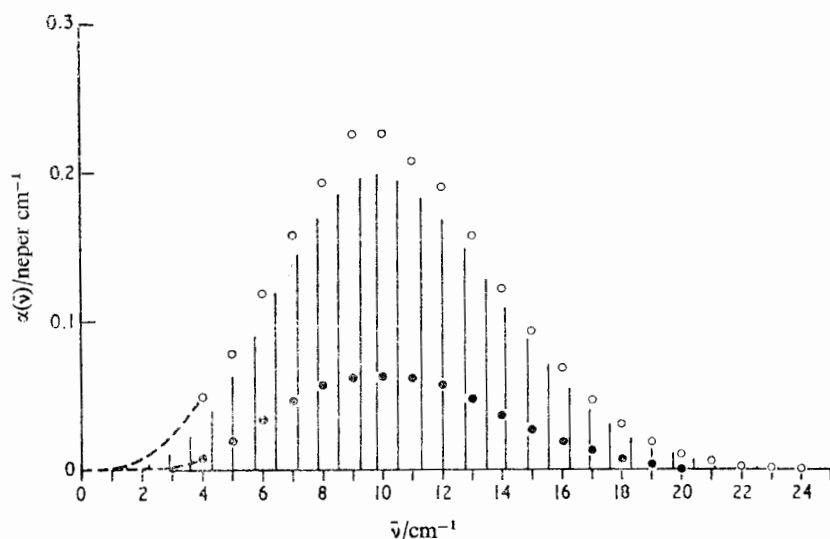


FIG. 1.—Measured absorption at 1.2 bar and 3.3 bar, 295 K (○). The bars represent the frequencies and relative integrated intensities of some $J \rightarrow J+1$ pure rotational absorptions.

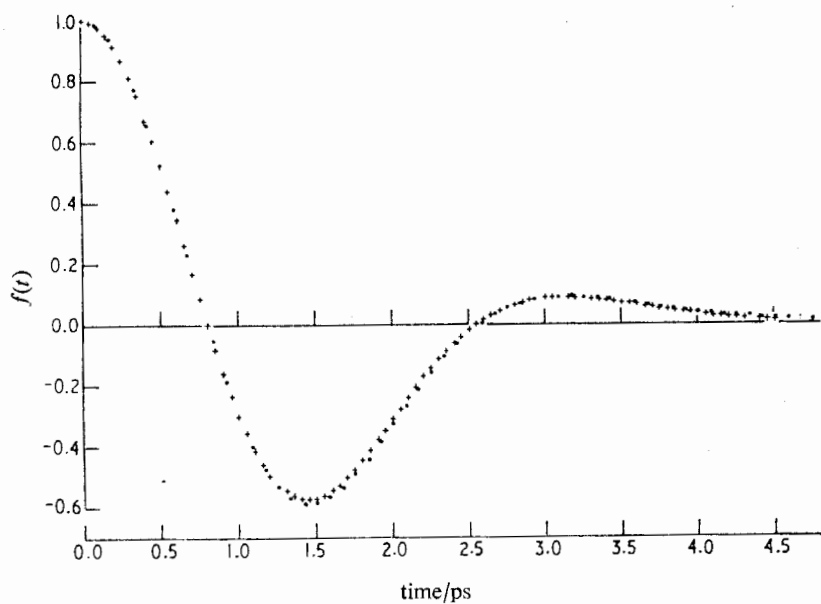


FIG. 2.—Plot of $f_{\text{exp}}(t)$ for the 1.2 bar experimental absorption (+) and $f_{\text{th}}(t)$ from eqn (6) (●).

compressed gas, as for nitrous oxide¹ and the non-dipolars carbon dioxide³ and cyanogen.⁴ The non linear dependence of A upon N suggests that induced dipolar absorption involving two or more molecules is occurring in addition to rotational

absorption of individual permanent dipoles. In the following evaluation of the results the induced dipole is assumed to arise from the effect of a second molecule (expanded in point multipoles and modulated by its rotational motion) in inducing a

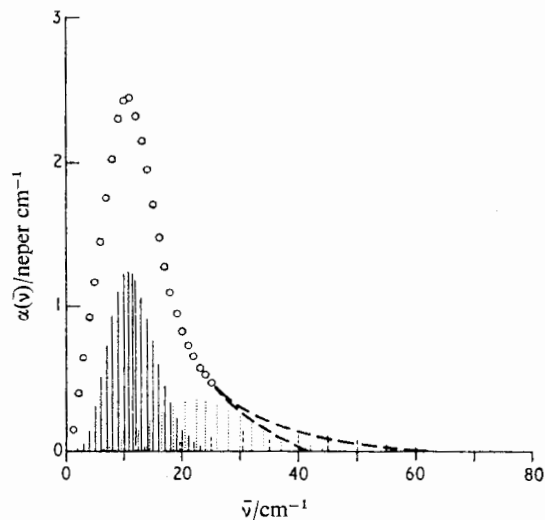


FIG. 3.—Measured absorption at 28.4 bar, 357 K (O). ---, Alternative extrapolations of high frequency necessary because of low power throughput in this region. —, Frequencies and relative intensities of $J \rightarrow J+1$ (pure dipolar and dipole-induced dipole) absorptions; --- as above for quadrupole-induced dipole ($J \rightarrow J+2$) lines; ··· octopole-induced ($J \rightarrow J+3$) lines.

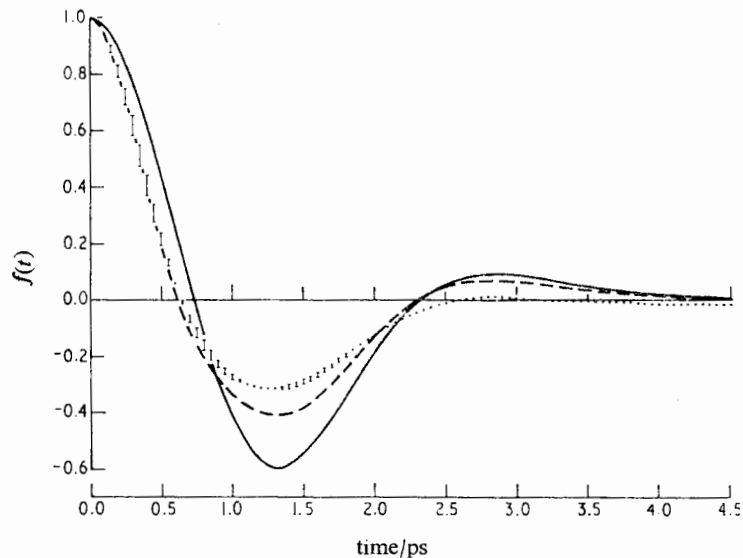


FIG. 4.—Plot of $f_{\text{exp}}(t)$ (●, I) (with uncertainty bars due to high frequency extrapolation at 28.4 bar and 357 K). —, free rotor function $f_{\text{th}}(t)$ [eqn (6)] at 357 K; ---, eqn (7) with $|Q| = 4.0 \times 10^{-26}$ e.s.u., $|\Omega| = 10 \times 10^{-34}$ e.s.u.

dipole in the first in a bimolecular collision. Interactions involving more than two molecules are neglected, which has the consequences that the apparent values of $|Q|$

(the quadrupole moment) and $|\Omega|$ (the octopole moment) needed to account for the experimental liquid A/N using this model [eqn (1)] will be less than the corresponding constants derived from the gas phase data. This reflects the reduced efficacy of

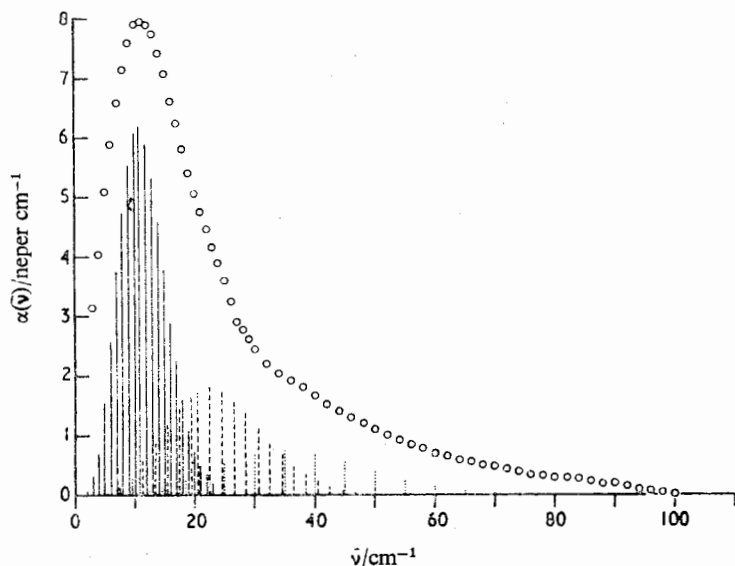


FIG. 5.—As for fig. 3 with data at 46.2 bar, 357 K, no extrapolation being necessary.

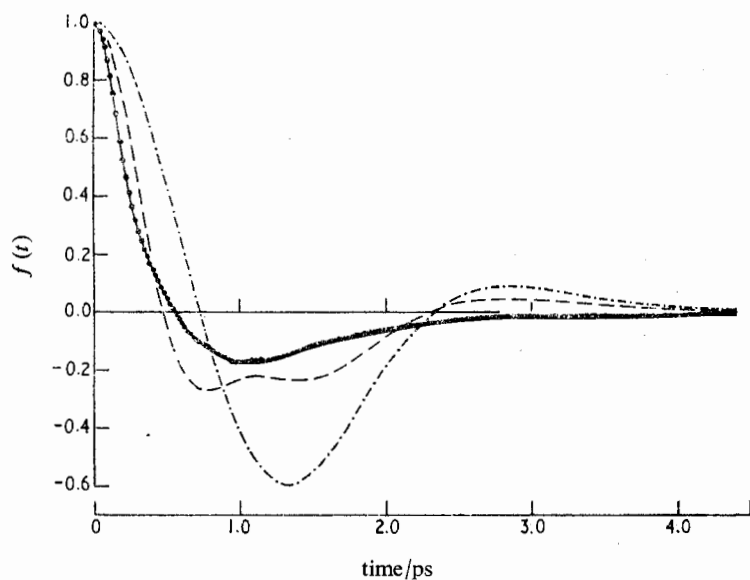


FIG. 6.—Plot of $f_{\text{exp}}(t)$ computed with two different algorithms from the experimental $\alpha(\bar{\nu})$ of fig. 5 (—○—○—); $f_{\text{th}}(t)$ at 357 K (---); eqn (7) with $|Q| = 4.2 \times 10^{-16}$ e.s.u., $|\Omega| = 11 \times 10^{-34}$ e.s.u. (—).

multibody interactions in the liquid in generating induced dipoles, and the breakdown of the bimolecular model.

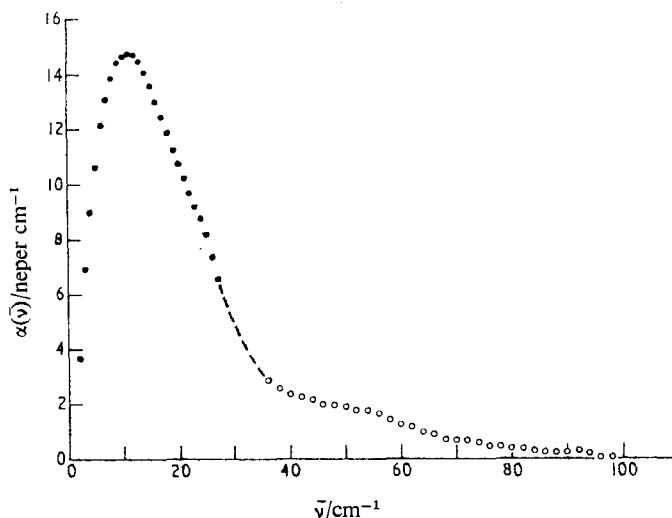


FIG. 7.—The far infrared absorption of $\text{CBrF}_3(l)$ at 295 K.

EVALUATION OF THE RESULTS

GAS AT 1.2 AND 3.3 bar

At these low pressures, the linear dependence of A upon N suggests that the observed bands, each peaking at 9.8 cm^{-1} , arise from rotational absorption of the permanent dipole, and that we are observing the Boltzmann envelope of the $J \rightarrow J+1$ transitions (separated by $2B = 0.13996 \text{ cm}^{-1}$ and thus well outside our resolving capabilities). The solution of the Schrödinger equation for the pure rotational motion of a symmetric top molecule gives the following equation for $A(\bar{\nu})$ the intensity and frequency of each (unbroadened) $J \rightarrow J+1$ absorption:

$$A(\bar{\nu}) = A(I, J) \sum_{K=-J}^J S(I, K) \frac{(J+1)^2 - K^2}{J+1} \exp[-E(J, K)/kT] \quad (3)$$

where

$$A(I, J) = \frac{8\pi^3 N}{3hcZ_r} \mu^2 \bar{\nu}(J) \{1 - \exp[-hc\bar{\nu}(J)/kT]\};$$

$$S(I, K) = \frac{1}{3}(2I+1)(4I^2+4I+3) \quad \text{for } K=0,$$

$$= \frac{1}{3}(2I+1)(4I^2+4I+3) \quad \text{for } K \neq 0 \text{ or } K = \text{a multiple of } 3,$$

$$= \frac{1}{3}(2I+1)(4I^2+4I) \quad \text{for } K \neq 0 \text{ or } K \neq \text{a multiple of } 3.$$

$$A_0 = h/8\pi^2 I_A c; \quad B = h/8\pi^2 I_B c; \quad \bar{\nu}(J) = 2B(J+1);$$

$$E(J, K) = BJ(J+1) + (A_0 - B)K^2;$$

$$Z_r = \sum_J \sum_{K=-J}^J (2J+1) S(I, K) \exp(-hcE/kT).$$

In this equation μ is the permanent dipole moment, J and K the rotational quantum numbers, I the nuclear spin quantum number of the off-axis nuclei (F), I_A and I_B the moments of inertia about axes parallel and perpendicular, respectively, to the three fold symmetry axis (C—Br), and Z_r the rotational partition function. Thus we have A' of equation (1) as:

$$A' = \sum_J \bar{A}(\bar{\nu})$$

The molecular constants used in evaluating $\bar{A}(\bar{\nu})$ are given in table 2, along with polarisability parameters to be used later.

TABLE 2.—MOLECULAR CONSTANTS OF CBrF₃

temp./K	Z _r	A/cm ⁻¹	B/cm ⁻¹	I	$\bar{\nu}_{\max}/\text{cm}^{-1}$ [eqn (2)]	mean molecular polarisability 10 ²⁴ α ₀ /cm ³	anisotropy of polarisability 10 ²⁴ β/cm ³
295	452 474	0.192 1	0.069 98 ²¹	0.5	9.790	5.3 ± 0.3 ²⁸	0.5
357	602 351	0.192 1	0.069 98	0.5	10.777	5.3 ± 0.3	0.5

The similarity of the position of the calculated $\bar{\nu}_{\max}$ at 295 K of 9.790 cm⁻¹ and the observed of 9.8 cm⁻¹ suggests that a contour drawn through the $J \rightarrow J+1$ delta functions would describe the observed bandshape adequately. For comparison therefore we have used the Heisenberg continuum representation of eqn (3) in the time domain with the experimental "rotational velocity" correlation function $f(t)$ of the introduction section. This function is used because it is essentially¹³ the Fourier transform of $\alpha(\bar{\nu})$. It is the negative of the second derivative of the vectorial correlation function $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ this being essentially the Fourier transform of $\alpha(\bar{\nu})/\bar{\nu}^2$, which requires accurate data in the region (0.001–10) cm⁻¹ for its evaluation.

Gordon²⁹ has shown that the dipole correlation function is given by:

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \int_{-\infty}^{\infty} I(\bar{\nu}) \cos(2\pi\bar{\nu}ct) d\bar{\nu} \quad (4)$$

where

$$I(\bar{\nu}) = 3hn(\bar{\nu})\alpha(\bar{\nu})/16\pi^4\bar{\nu}[1 - \exp(-hc\bar{\nu}/kT)].$$

Here, $n(\bar{\nu})$ is the frequency dependent refractive index, approximately unity in the gas phase, t the time and \mathbf{u} the dipole unit vector. We have:¹³

$$\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle = -\frac{d^2}{dt^2} \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle \quad (5)$$

hence using $J = \bar{\nu}/2B - 1$, we obtain from eqn (3), (4) and (5):

$$\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle_{\text{th}} \propto \int_0^{\infty} \sum_{K=-J}^J \left[S(I, K) \left(\frac{\bar{\nu}^3}{2B} - 2B\bar{\nu}K^2 \right) \exp \left(-\frac{(A-B)K^2 hc}{kT} \right) \right] \times \exp \left[-\frac{Bhc}{kT} \left(\frac{\bar{\nu}}{2B} - 1 \right) \frac{\bar{\nu}}{2B} \right] \cos(2\pi\bar{\nu}ct) d\bar{\nu} \quad (6)$$

as the continuum representation of eqn (3). Thus:

$$f_{\text{th}}(t) = \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle_{\text{th}} / \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle_{\text{th}}$$

This is compared in fig. 2 with the real part of eqn (2), the corresponding experimental representation. Whereas both curves are very similar, $f_{\text{exp}}(t)$ shows very slight collision damping. However the functions in fig. 2 can safely be taken as the norm unaffected by induced dipolar absorption.

THE COMPRESSED GAS AT 28.4 AND 46.2 bar

As can be seen in fig. 3–6, the absorption bands of the compressed gas have developed high frequency shoulders. This is reflected in the time domain (fig. 4 and 6) where $f_{\text{exp}}(t)$ in both cases is considerably damped in comparison with $f_{\text{th}}(t)$ for free rotation [eqn (6)]. The high frequency absorption has been interpreted in terms

of eqn (1), whose constants A' , B' , C and D have recently been predicted by Frost,¹⁰ and are given in table 3 in terms of the rotational constants J and K , the intermolecular separation R , the intermolecular potential energy $U(R)$, and the polarisability factors $\alpha_{\parallel} = 1/3 (\alpha_{\parallel\parallel} + 2\alpha_{\perp\perp})$ and $\delta = (\alpha_{\parallel\parallel} - \alpha_{\perp\perp})$. E , S , Z , etc. are those defined for eqn (3).

TABLE 3.—FROST EQUATIONS

parameter	$\bar{\nu}_n(J)$	
B'	$2B(J+1)$	$\frac{4\pi^3}{3hcZ_r} \int_0^\infty 4\pi R^{-4} \exp[-U(R)/kT] dR \sum_{K=-J}^J \{ (1 - \exp[-hc\bar{\nu}_1(J)/kT]) \times \exp(-Ehc/kT) \bar{\nu}_1(J) [4\alpha_0^2 f_1(J,K) + (40/3)\delta^2 f_1(J,K)K^2/[J(J+2)]] \}$, where $f_1 = (J-K+1)(J+K+1)/(J+1)$.
C	$2B(2J+3)$	$\frac{4\pi^3}{3hcZ_r} \int_0^\infty 4\pi R^{-6} \exp[-U(R)/kT] dR \sum_{K=-J}^J \{ [1 - \exp(-hc\bar{\nu}_2(J)/kT)] \times \exp(-Ehc/kT) \bar{\nu}_2(J) [18\alpha_0^2 f_2(J,K) + (48/5)\delta^2 f_2^2(J,K)] \}$, where $f_2 = (J-K+2)(J-K+1)(J+K+2)(J+K+1)/[(J+1)(J+2)(2J+3)]$.
D	$6B(J+2)$	$\frac{4\pi^3}{3hcZ_r} \int_0^\infty 4\pi R^{-8} \exp[-U(R)/kT] dR \sum_{K=-J}^J \{ (1 - \exp[-hc\bar{\nu}_3(J)/kT]) \times \exp(-Ehc/kT) \bar{\nu}_3(J) [(24x' + 8y)\alpha_0^2 + (176x'/9 + 16y/3)w\delta^2] \}$, with $x' = \frac{5(J+K+3)(J+K+2)(J+K+1)(J-K+3)(J-K+2)(J-K+1)}{(J+2)(J+3)(2J+2)(2J+3)(2J+5)}$, $y = \frac{(J+K+3)(J+K+2)(J+K+1)(J-K+3)(J-K+2)(J-K+1)}{(2J+2)(2J+3)(2J+4)(2J+5)(2J+6)}$, $w = \frac{3(J-K+2)(J-K+1)(J+K+1)(J+K+2)}{(2J+2)(2J+3)(J+2)}$.

Thus in using eqn (1) we again suffer an aesthetic difficulty in that it yields sets of discrete line spectra (fig. 3 and 5) whereas the experimental absorption is obviously a broad continuum at our resolution and sample pressure. There are also weaknesses inherent in the Frost theory because cross-relaxation between overlapping lines³⁰ of $J \rightarrow J+n$ transitions is not considered; also there is the fact that an eigenstate of the interacting pair is taken as the product of the eigenstate of the isolated molecule. This is adequately correct only for a purely central intermolecular potential $U(R)$, which can be approximated by a Lennard-Jones form. Moreover, each $J \rightarrow J+n$ line will be broadened in practice, so much so that $J \rightarrow J+2$ lines have rarely³¹ been individually resolved. There remain the vexed questions of translational⁶ and overlap⁵ absorption which have been adequately treated only for small linear molecules such as hydrogen. In the case of the relatively heavy CBrF₃ molecule pure translational absorption ($\Delta J = 0$) should occur at very low frequencies and thus not affect A/N or the bandshape very much, although this effect is responsible for the width of the induced infra-red lines (deviating, of course, from Frost's delta functions). Van Kranendonk and Kiss⁵ found the total A/N due to overlap induction and the interference effect between the quadrupolar and overlap moments in hydrogen to be about 8% of the total. Ho, Birnbaum and Rosenberg³ found that neglect of overlap absorption would lead to a value of the quadrupole moment in CO₂ only about 1% too large. Therefore we feel justified in avoiding an explicit treatment of the overlap absorption in CBrF₃ in this work.

The limiting uncertainty in the evaluation of eqn (1) is, in fact, linked to the choice of the Lennard-Jones parameters used with the (assumed) radial distribution function. We have taken values of $\epsilon/k = 423$ K, $\sigma = 4.4$ Å corrected to the same extent as those for CClF₃ as was found necessary by Barnes and Sutton³² to account for their second dielectric virial coefficient data.

Since we have two unknowns in eqn (1) ($|Q|$ and $|\Omega|$), if octopole-induced absorption is considered important, an analysis of the variation of A with N is not alone sufficient to determine both $|Q|$ and $|\Omega|$. To do this a comparison of bandshape is necessary, using iterative techniques until the optimum matching between experimental results and eqn (1) is obtained. This procedure is conveniently and sensitively^{1,2} carried out in the time domain by comparing $F_{\text{exp}}(t)$ with the Fourier transform of eqn (1). In a way analogous to that used in deriving eqn (6) from eqn (3), it can be shown that:

$$\begin{aligned}
F_{\text{th}}(t) &\propto \left\{ \int_{-\infty}^{\infty} \frac{\bar{v}\alpha(\bar{v}) \cos(2\pi\bar{v}ct) d\bar{v}}{[1 - \exp(-hc\bar{v}/kT)]} \right\}_{\text{eqn (1)}} \\
&= \Xi \left\{ 2N\mu^2 \left(I_4 \int_0^{\infty} \sum_{K=-J}^J \left[S(I, K) \left(\frac{\bar{v}^3}{2B} - 2B\bar{v}K^2 \right) \Gamma_K \right] \times \right. \right. \\
&\quad \exp \left[-\zeta \left(\frac{\bar{v}}{2B} - 1 \right) \frac{\bar{v}}{2B} \right] \cos(2\pi\bar{v}ct) d\bar{v} + \\
&\quad NI_4 \int_0^{\infty} \sum_{K=-J}^J \left\{ S(I, K) \Gamma_K \exp \left[-\zeta \left(\frac{\bar{v}-2B}{2B} \right) \frac{\bar{v}}{2B} \right] \times \right. \\
&\quad \left. \left[4\bar{v}(\bar{v}-2BK)(\bar{v}+2BK)\alpha_0^2/2B + \frac{4}{3}\delta^2 \frac{(\bar{v}-2BK)^2(\bar{v}+2BK)^2K^2}{(\bar{v}-2B)(\bar{v}+2B)} \right] \cos(2\pi\bar{v}ct) d\bar{v} \right\} + \\
&\quad N^2Q^2I_6 \int_0^{\infty} \sum_{K=-J}^J \left\{ S(I, K) \Gamma_K \exp \left[-\zeta \left(\frac{\bar{v}}{4B} - \frac{3}{2} \right) \left(\frac{\bar{v}}{4B} - \frac{1}{2} \right) \right] \times \right. \\
&\quad \left. \left[18\alpha_0^2 f(\bar{v}, K) + \frac{48}{5}\delta^2 f^2(\bar{v}, K)/\bar{v} \right] \right\} \cos(2\pi\bar{v}ct) d\bar{v} + \\
&\quad N^2\Omega^2I_8 \int_0^{\infty} \sum_{K=-J}^J \left\{ S(I, K) \Gamma_K \exp \left[-\zeta \left(\frac{\bar{v}}{6B} - 2 \right) \left(\frac{\bar{v}}{6B} - 1 \right) \right] \times \right. \\
&\quad \left. \left[(24x'' + 8y')\alpha_0^2 + \left(\frac{176x''}{9} + \frac{16y'}{3} \right) w'\delta^2 \right] \right\} \cos(2\pi\bar{v}ct) d\bar{v} \right\}. \quad (7)
\end{aligned}$$

Here,

$$\begin{aligned}
\Xi &= \pi cn/Z_r, \quad I_n = \int_0^{\infty} 4\pi R^{-n} \exp[-U(R)/kT] dR, \\
\Gamma_K &= \exp[-(A_0 - B)K^2 hc/kT], \quad \zeta = Bhc/kT, \\
f(\bar{v}, K) &= \frac{\bar{v}[\bar{v}-2B(2K-1)][\bar{v}-2B(2K+1)][\bar{v}+2B(2K+1)][\bar{v}+2B(2K-1)]}{8B(\bar{v}-2B)(\bar{v}+2B)} \\
x'' &= \frac{5[\bar{v}+6B(K+1)](\bar{v}+6BK)[\bar{v}+6B(K-1)] \times}{[\bar{v}-6B(K-1)](\bar{v}-6BK)[\bar{v}-6B(K+1)]\bar{v}} \\
&\quad \frac{6B(\bar{v}+6B)(2\bar{v}-12B)(2\bar{v}-6B)(2\bar{v}+6B)}{6B(\bar{v}+6B)(2\bar{v}-12B)(2\bar{v}-6B)(2\bar{v}+6B)} \\
y' &= \frac{\bar{v}[\bar{v}+6B(K+1)](\bar{v}+6BK)[\bar{v}+6B(K-1)] \times}{[\bar{v}-6B(K-1)](\bar{v}-6BK)[\bar{v}-6B(K+1)]} \\
&\quad \frac{12B(2\bar{v}-12B)(2\bar{v}-6B)(2\bar{v}+6B)(2\bar{v}+12B)}{12B(2\bar{v}-12B)(2\bar{v}-6B)(2\bar{v}+6B)(2\bar{v}+12B)} \\
w' &= \frac{3(\bar{v}-6BK)[\bar{v}-6B(K+1)][\bar{v}+6B(K-1)](\bar{v}+6BK)}{6B(2\bar{v}-12B)(2\bar{v}-6B)\bar{v}}
\end{aligned}$$

The radial distribution integrals (I_p) in (7) were evaluated with the tables of Buckingham and Peple³² and $F_{\text{th}}(t)$, normalised as usual to unity at $t = 0$, was computed on a CDC 7600. The best matches between $F_{\text{th}}(t)$ and $f_{\text{exp}}(t)$ obtained are displayed in fig. 4 and 6, which were those obtained with $|Q| = 4.6 \times 10^{-26}$ e.s.u., $|\Omega| = 10 \times 10^{-34}$ and $|Q| = 4.8 \times 10^{-26}$ e.s.u., $|\Omega| = 11 \times 10^{-34}$ e.s.u. respectively. The matches show the neglect of broadening in each $J \rightarrow J+n$ line, and neglect of cross-relaxation between overlapping lines in the considerable underdamping of $F_{\text{th}}(t)$ as compared with $f_{\text{exp}}(t)$. This, together with the uncertainty in the (Lennard-Jones) parameters of an uncertain angle-independent representation of the intermolecular potential render the mean values of $|Q| = (4.4 \pm 0.4) \times 10^{-26}$ e.s.u. and $|\Omega| = (11-12) \times 10^{-34}$ e.s.u. preliminary and tentative. Nevertheless, by symmetry, CBrF_3 is not expected to have a large $|Q|$ and our values do not contradict this.

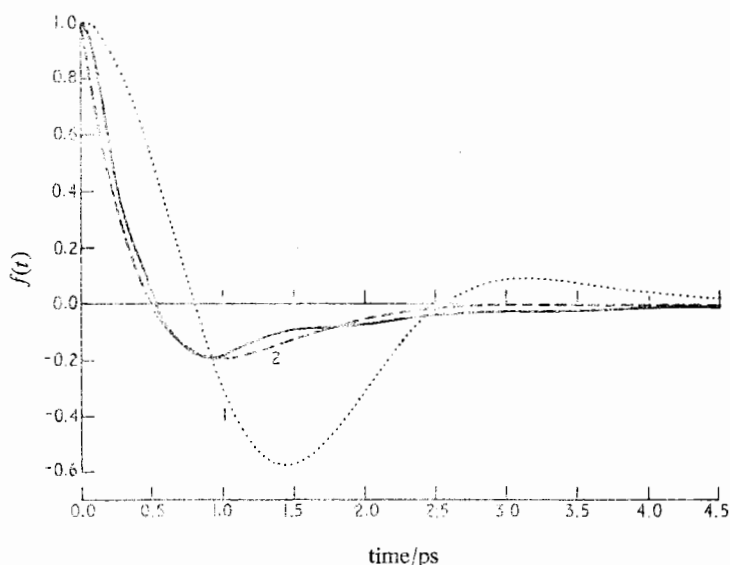


FIG. 8.—Plot of $f_{\text{exp}}(t)$ from the data of fig. 7 (—): free rotor [$f_{\text{th}}(t)$] at 295 K [--- (1)]; $F''(t)$ with $\tau_r = 7$ ps, $\tau = 0.65$ ps, $\tau_a = 0.8$ ps [---(2)].

THE LIQUID AT 295 K

Qualitatively, in the frequency domain (fig. 7), $\bar{\nu}_{\text{max}}$ has moved only slightly, from the 9.8 cm^{-1} of the gas at 1.2 bar to 11.0 cm^{-1} in the liquid at the same temperature.

This observation, together with the fact that the high frequency tail of the absorption is less pronounced than in the compressed gas might lead one to the conclusion that the liquid phase absorption is merely a much broadened version of that of the free rotor. That free rotation is not occurring in the liquid can be seen from fig. 8, where $f_{\text{exp}}(t)$ is highly damped in comparison with the free rotor $f_{\text{th}}(t)$. The function $f_{\text{exp}}(t)$ also shows slight superimposed oscillations on the main curve, a phenomenon which has been observed^{13, 34} in dense dipolar liquids, where the oscillations are much more pronounced.

Neglecting thus the hypothesis of free molecular rotation in the liquid, we assume that the potential experienced by a given molecule due to its nearest neighbours does not have spherical symmetry. One therefore has a certain number of potential wells separated by barriers.³⁵ Using Kauzmann's treatment of this situation one obtains,

neglecting the inertia of the molecule, an expression identical to the well known solution of Debye.³⁷ Brot³⁸ has recently revised Kauzmann's treatment using multiple wells and including the inertial term. The consequences of Brot's model are: (i) while they are resident in one of the wells, the molecules undergo torsional scillation (libration); (ii) the time of jump (τ_j) from one well to the next or another is not negligible.

With a mean time between adiabatic collisions of τ and a mean of residence in the well of τ_r the autocorrelation function of a unit dipole vector undergoing such motion is given³⁹ by:

$$F(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\text{Brot}} \\ = (1 - 2\beta^2) \left[\exp(-t/\tau_r) + \int_0^t \exp(-t_j/\tau_r) \frac{H(t-t_j)}{\tau_r} dt_j \right] \\ + 2\beta^2 \left[\exp(-t/\tau_r) V(t) + \int_0^t \frac{\exp(-t_j/\tau_r)}{\tau_r} V(t_j) H(t-t_j) dt_j \right] \quad (8)$$

where

$$V(t) = \exp(-t/\tau) \left[\cos at + \frac{\sin at}{a\tau} \right] \quad \text{for } \omega_0 > 1/\tau \\ = \exp(-t/\tau) (1 + t/\tau) \quad \text{for } \omega_0 = 1/\tau \\ = \exp(-t/\tau) \left[\cosh bt + \frac{\sinh bt}{b\tau} \right] \quad \text{for } \omega_0 < 1/\tau$$

with

$$a = [\omega_0^2 - 1/\tau^2]^{\frac{1}{2}}, \quad b = [1/\tau^2 - \omega_0^2]^{\frac{1}{2}}$$

where $\omega_0 = 2\pi\bar{\nu}_0 c$ is the proper frequency of libration and where $H(t-t_j) = \exp[-(t+t_j)/\tau_a] [1 + (t-t_j)/\tau_a]$. The second derivative [$F''(t)$] of $F(t)$, whose negative gives $\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle_{\text{Brot}}$, has been evaluated³⁴ for $\tau_r = 7.0$ ps, $\tau = 0.65$ ps, $\tau_a = 0.8$ ps and is displayed in fig. 8 with the experimental function $f_{\text{exp}}(t)$. Superficially, the agreement is good although $F''(t)$ contains three arbitrary parameters (τ , τ_a and τ_r) which reduces its significance somewhat. Nevertheless, $\tau_r = 7$ ps ought to be roughly comparable with the Debye relaxation time τ_D (microwave data is needed to confirm this).

It is instructive to compare $F(t)$ (with an apparent mean time between "collisions" of $\tau = 0.65$ ps) with the equivalent autocorrelation function derived from a model which allows of free rotation between the assumed instantaneous collisions. Such is McClung's J -diffusion model for symmetric top molecules,⁴⁰ and several of these functions for CBrF_3 are given in fig. 9 for various mean times between collisions (τ). The Brot function $F(t)$ is plotted on the same scale on the same figure, and loses correlation much less rapidly than the McClung function with the same τ of 0.65 ps. Unfortunately, since accurate data down to about 0.001 cm^{-1} are unavailable, the equivalent experimental function is unknown, but judging from the close similarity between the derivatives $f_{\text{exp}}(t)$ and $F''(t)$, it will probably resemble Brot's function rather than McClung's.

The bandshape and $f_{\text{exp}}(t)$ are both influenced by induced absorption, mainly at higher frequencies, and which may be responsible for the short time oscillations in the time function. Gordon¹⁸ predicts the total integrated intensity per molecule due to all rotational type motions (in the microwave and far infrared) as:

$$\left(\frac{A}{N} \right)_{\text{Gordon}} = \frac{2\pi\mu^2}{3c^2 I_A} \\ = 2.55 \times 10^{-20} \text{ cm}$$

whereas the observed value is (table 1) 6.2×10^{-20} cm. This is reduced to 4.5×10^{-20} cm after a correction for the (assumed) static¹⁵ internal field.^{14, 17} [Such a correction does not affect the bandshape and thus not $f_{\text{exp}}(t)$]. This still leaves almost 50% of the absorption unaccounted for by permanent dipolar absorption, mostly at higher frequencies.

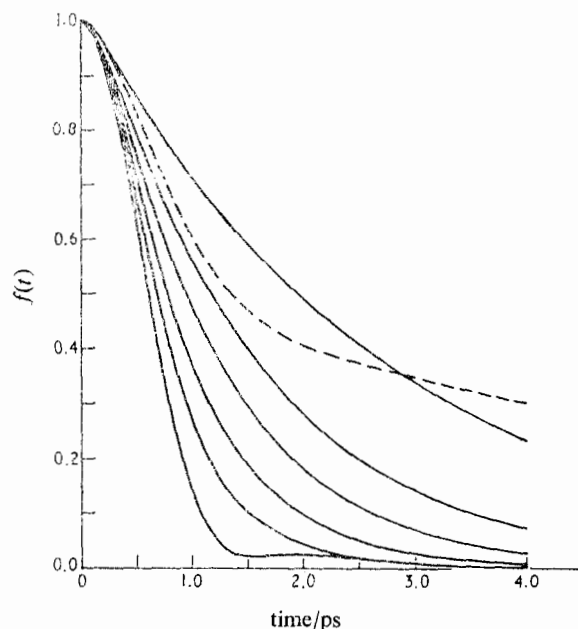


FIG. 9.—Vectorial autocorrelation functions calculated from the extended diffusion model of McClung⁴⁰ (—). From top to bottom, the curves are for values of the mean time between collisions (τ) of 0.1, 0.2, 0.3, 0.5, 1.0 ps and the free rotor ($\tau \rightarrow \infty$). $F(t)$ from eqn (8) with $\tau_r = 7$ ps, $\tau = 0.65$ ps and $\tau_a = 0.8$ ps (---).

DISCUSSION

Although there is no great change in \bar{v}_{max} from the fairly dilute gas to the liquid, the bandwidth and bandshape change considerably. This indicates that the molecular interaction and motion also vary considerably with progressive compression and liquefaction. The basically simple Frost representation suffers from predicting a series of delta functions at discrete frequencies corresponding to various $J \rightarrow J+n$ transitions and consequently the equivalent Heisenberg representation [eqn (7)] does not resemble the observed broad continuum absorption [$f_{\text{exp}}(t)$] satisfactorily. However, the values of $|\mathcal{Q}|$ and $|\Omega|$ obtained agree fairly well for different N , indicating that three body interactions, leading to terms in N^3 in eqn (1), are not significant at these molecular number densities. Obvious improvements in the theoretical description would be an account of translational absorptions ($\Delta J = 0$) and especially translational broadening of each $J \rightarrow J+n$ line, together with cross-relaxation between overlapping lines. Working in the time domain seems to be a sensitive and convenient method of comparing predicted and experimental absorptions.

In the liquid, the problem of separating the contribution of induced dipoles remains unsolved, but the model of permanent dipolar libration within potential wells generated by neighbouring molecules seems to give a fairly satisfactory repre-

sentation of the absorption (fig. 8). The comparison of fig. 9 suggests that extended diffusion models such as that of McClung are less realistic in the liquid phase.

Experimentally, microwave data on compressed gas-liquid systems are needed to evaluate the autocorrelation function $\langle \mu(0) \cdot \mu(t) \rangle$ which will be considerably less affected by induced absorption (being insensitive to data above 10 cm^{-1}), and frequency dependent refractive index data in the whole region ($0.001\text{--}100 \text{ cm}^{-1}$) is needed in order to evaluate the effect of the dynamic internal field in the liquid.

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