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Effect of Pressure and Temperature on the Intermolecular Mean Square Torque in Liquid CS_2 and CCl_4

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The effects of temperature and externally applied pressure on the intermolecular mean square torque $\langle O(V)^2\rangle$ in liquid CS_2 and CCl_4 are estimated using the induced absorption bands of these liquids at high microwave and far infrared frequencies (2-300 cm^{-1}). For the stick-like CS_2 molecule it is found that $\langle O(V)^2\rangle$ is considerably increased by an external pressure of 11.6 kbar. For this molecule, $\langle O(V)^2\rangle$ increases with T in the range 232-315 K. However, the situation is different for the spherical top CCl_4, where a considerable increase in free volume allows $\langle O(V)^2\rangle$ to decrease slightly from 296 to 343 K, a few degrees below the boiling point at 1 bar.

In order to study the equilibrium, random fluctuations of molecules in liquids, some concepts and techniques have been borrowed fairly recently from the field of statistical mechanics.[1-3] Foremost among these is the correlation function, $C(t)$, which is the covariance divided by the variance of an observable of a stationary, stochastic process.[4] It measures the internal correlation between members of a series of observations in time or space. In general, a necessary and sufficient condition for $C(t)$ to be the correlation function of a continuous, stationary, stochastic, molecular process is that:

$$C(t) = \int_0^\infty \cos \omega t \, dF(\omega) \tag{1}$$

with $F(0) = 0$, $F(\infty) = 1$. $F(\omega)$ is a spectral function and ω is a frequency. For rotational [5, 6] fluctuations of a permanent dipole moment, Gordon[7] has demonstrated that:

$$C(t) = \int_{-\infty}^{\infty} \exp(i\omega t)\left(\frac{3\hbar c}{4\pi^2}\right)\frac{\sigma(\omega)\, d\omega}{\omega[1-\exp(-\hbar\omega/kT)]} \tag{2}$$

where $\sigma(\omega)$ is the absorption cross section per molecule, related to $\alpha(\bar{\nu})/N$ where α is the absorption coefficient per unit absorber length (neper cm^{-1}), and N the number density of molecules (cm^{-3}). Here $\omega = 2\pi\bar{\nu}c$ is the angular frequency with $\bar{\nu}$ the wavenumber in cm^{-1}. Eqn (2) may be regarded as the quantum equivalent of eqn (1), and is derived in terms of a given mechanism. In general, such equations as (1) and (2) are valid for any mechanism in which N similar incoherent absorbers act in unit volume.

In this paper we are concerned with the behaviour of $C(t)$ for non-dipolar liquids,[8] where a temporary dipole moment is imposed on a given molecule because of the fluctuations in the surrounding molecular fields. The motion of the molecule gives rise to a broad absorption in the 0.1-300 cm^{-1} region, which we have assumed can be treated by a modification of the Langevin equation [9] of classical, rotational Brownian motion in a preceding paper,[10] using the correlation function:

$$C(t) = \sum_{i,j} \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_j(t) \rangle,$$

where $\boldsymbol{\mu}_i(0)$ is the dipole induced on molecule i at time $t = 0$. A major assumption of that paper, and of this, is that this function is amenable to manipulation with Brownian theory. Here, we aim to follow the changes of bandshape in liquid CCl_4 and CS_2 with changes of temperature [8] and external pressure.[13] It was shown previously [10, 11] that the problem reduces to that of explaining the corresponding variation in the parameters: $K_0(0)$, $K_1(0)$ and γ of the truncated Mori expansion:

$$\alpha(\omega) = \frac{AK_0(0)K_1(0)\gamma\omega^2}{\gamma^2[K_0(0)-\omega^2]^2+\omega^2\{\omega^2-[K_0(0)+K_1(0)]\}^2}. \tag{3}$$

Here, $K_0(0)$ and $K_1(0)$ are zero-time, equilibrium averages [3] (having the units of s^{-2}), and γ is a frequency (or width) parameter with the units of s^{-1}. The constant A is given by:

$$A = (\varepsilon_0 - \varepsilon_\infty)/n(\bar{\nu})c$$

where $(\varepsilon_0 - \varepsilon_\infty)$ is the dispersion [5] associated with the total absorption [8] from $\sim 0.1\ \mathrm{cm}^{-1}$ to $\sim 300\ \mathrm{cm}^{-1}$. $n(\bar{\nu})$ is the frequency dependent refractive index, which for these weak absorbers is constant to within $\sim \pm 2\ \%$ of the D-line value.

The classical correlation function [1-3] is an even, equilibrium, function of time, by Onsager's reversibility principle, and $K_0(0)$, $K_1(0)$ are related [3, 9, 11] to the coefficients of its series expansion in time. In the simplest case [6] of the induction of a dipole moment through the collision of two molecules, the corresponding [12] $C(t)$ has time coefficients which are all dependent on the mean intermolecular potential energy U. In general, the mean square torque, $\langle O(V)^2 \rangle$, the derivative of U, will be approximately the product of a mean square force and a shape factor of dimension L^2 which is not at all easy to estimate.

Carbon disulphide can be frozen at room temperature with a pressure of 12-13 kbar and Bradley *et al.*[13] made an early study, with prototype apparatus, of the far infrared band of the liquid up to 11.6 kbar. They found that the absorption peak shifts by about 35 cm^{-1} to higher frequency through the pressure induced phase change at 293 K. We show below that this is equivalent to a large increase in both $K_0(0)$ and $K_1(0)$, *i.e.* an increase in the torque $\langle O(V)^2 \rangle$ and thus in the slope of U. The dispersion $(\varepsilon_0 - \varepsilon_\infty)$ decreases slightly, reflecting perhaps an enhanced degree [14] of intermolecular symmetry, since the induced absorption would disappear if each molecule occupied permanently a site of inversion symmetry.

Such pressure data are difficult to come by, and we have taken the easier, less informative course of making accurate measurements over the frequency range 2-200 cm^{-1} of liquid CCl_4 from 298-343 K, a few degrees below the boiling point. The change in $K_0(0)$ and $K_1(0)$ is less pronounced, but real.

EXPERIMENTAL

The absorption spectra were obtained using a Grubb–Parsons/NPL cube interferometer [8] adapted for phase modulation of wide-band radiation reaching one of two detectors. The first was a Rollin InSb, liquid–helium cooled detector [6] carrying a 4 mm black-polyethylene filter. This covered the range 2-31 cm^{-1}; a Golay SP 16 pneumatic detector was used from 20 to 200 cm^{-1}. At room temperature, the specimen was held in front of the detectors in a dry-box containing a VC–01, RIIC variable-path-length liquid cell. The cell was inserted in a thermostatically controlled collar which could be attached to the output port of the interferometer. The temperature could be varied between 293 and 373 K within an estimated error of ±2 K. The geometrical optics were carefully designed in order to minimise the uncertainties [15] inherent in precise measurements of the submillimetre spectra of low-loss dielectrics such as liquid CCl_4.

The low temperature measurements were made with a fixed path-length cell, RIIC type FH–01, used in conjunction with the variable temperature unit, RIIC type VLT–2, which provides the range 99 to 500 K. The temperature was stable to within ±2 K. The whole of the apparatus was kept at $\sim 10^{-2}$ Torr to reduce absorption by water vapour.

The absorption coefficients $\alpha(\omega)$ were calculated using standard [8, 15] techniques of Fourier transformation, and are significant to within about ±(1-1.5) %. The liquid CCl_4 was prepared using techniques designed to reduce its water content.[5, 8, 15, 16]

RESULTS AND DISCUSSION

The results are summarised in table 1 and in fig. 1 and 2. They were obtained by fitting eqn (3) to the experimental data using the least squares algorithm NAG EO4FAA of the Univ. of Oxford 1906A computer. The change in the shape and position of the absorption band is most pronounced between those of CS_2(l) at 1 bar and 11.6 kbar [fig. 1(*a*)], the latter pressure being almost enough to cause solidification [13] at 293 K. In order to interpret this shift, three factors have to be kept in mind:

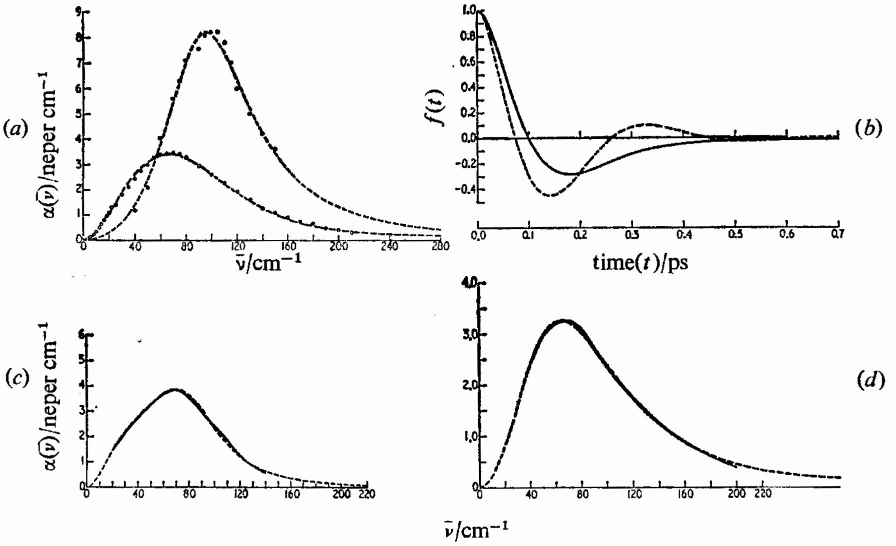

FIG. 1(*a*).—◆ Some experimental observations [13] of the far i.r. absorption of liquid CS_2 at 11.6 kbar, 293 K; - - - eqn (3) with the parameters $K_0(0)$, $K_1(0)$, γ and $(\varepsilon_0-\varepsilon_\infty)$ shown in table 1; ○ the absorption [8] of CS_2(l) at 296 K, 1 bar; - - - eqn (3). (*b*) The function $-\ddot{C}(t)$ normalised to unity at $t = 0$; curve (1) (solid line): CS_2(l) at 296 K, 1 bar, curve (2) (dotted line): CS_2(l) at 293 K, 11.6 kbar. (*c*) — Experimental [8] absorption of CS_2(l) at 232 K; - - - eqn (3). (*d*) — Experimental [8] absorption of CS_2(l) at 315 K; - - - eqn (3).

(*a*) by eqn (1), the function $\alpha(\omega)$ is a probability distribution function [3] of frequencies (ω); (*b*) we are looking at the effect of a dipole induced in a given molecule by the resultant effect of all the other molecular fields in the system. This dipole is also modulated by the motion of the molecule which carries it. We suppose that the band shape reflects primarily the effect of this latter modulation. We can justify this only *a posteriori*, *i.e.*, the data do nothing to contradict it and (*c*) the absorption band is shifted (by ~35 cm^{-1}) to higher frequencies and considerably sharpened by the 11.6 kbar of external pressure.

Therefore, at the higher pressure there is a greater probability that the motion of the induced dipole moment is associated with the central frequency (ω_0) of ~100 cm^{-1} (0.33 ps). If ω_0 is of a librational origin, as is often assumed,[5, 6, 9] then the barrier to the torsional oscillation of the stick-like CS$_2$ molecule will become greater, and the energy wells [17] within which the molecules librate will become more evenly distributed in shape and depth. In the limit of infinitely high barriers separating molecules librating at the single frequency ω_0, the band would collapse to a line (a Dirac delta function at ω_0), provided that each molecule in the (crystalline) lattice did not occupy a site of inversion symmetry, when it would disappear completely,[14] there being no resultant field on any given molecule, and no induced dipole.

This process is reflected in the behaviour of the correlation function associated with these bands [fig. 1(*b*)]. In this figure are illustrated the Fourier transforms [6] of eqn (3) proportional to $-\ddot{C}(t)$, normalised to unity at $t = 0$. By stationarity [1, 3, 4] a correlation function $C(t)$ which links the vector $\boldsymbol{y}(0)$ to $\boldsymbol{z}(t)$ has the property that:

$$\begin{aligned}\ddot{C}(t) &= \frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle \boldsymbol{y}(0)\,.\,\boldsymbol{z}(t)\rangle \\ &= -\langle \dot{\boldsymbol{y}}(0)\,.\,\dot{\boldsymbol{z}}(t)\rangle \end{aligned} \tag{4}$$

where the angular brackets [1, 3, 9] denote averaging over phase space. It has been shown previously [18] that $C(t)$ in the case of induced absorption is defined as:

$$\begin{aligned} C(t) = {} & \left\langle \boldsymbol{U}_1\left(0, \sum_i \sum_2^\infty (a_{i,n}\boldsymbol{R}_i^{-n})\right) \cdot \boldsymbol{U}_1\left(t, \sum_i \sum_2^\infty a_{i,n}\boldsymbol{R}_i^{-n}\right)\right\rangle + \\ & \left\langle \boldsymbol{U}_1\left(0, \sum_i \sum_2^\infty (a_{i,n}\boldsymbol{R}_i^{-n})\right) \cdot \sum_{j=2}^{i} \boldsymbol{U}_j\left(t, \sum_i \sum_2^\infty a_{i,n}\boldsymbol{R}_i^{-n}\right)\right\rangle \end{aligned} \tag{5}$$

where there are $(1+i)$ molecules in the system. In eqn (5) $\boldsymbol{U}_1$ is a unit vector in the direction of the resultant induced dipole on a given molecule (due to i other molecules) at the instant t. This dipole arises from the field term:

$$\sum_i \sum_2^\infty a_{i,n}\boldsymbol{R}_i^{-n}$$

where expansion in terms of point multipole terms [6] $a_{i,n}$ has been used. (In principle, a much better technique of representing the resultant electrostatic field would be to sum up the local charges [6, 8] on individual atoms of each molecule in the system). $\boldsymbol{R}_i$ is the vector linking the molecule 1 to the molecule i. $C(t)$ consists of an autocorrelation and a cross-correlation term, the latter ~~linking~~ the value of $\boldsymbol{U}_1$ to $\boldsymbol{U}_j$ of other molecules j. In the simpler case of permanent dipolar absorption, St. Pierre and Steele [19] have realised the full significance of $-\ddot{C}(t)$ as a combined angular momentum/orientation correlation function, which reduces [20] to that of the perpendicular component of the angular momentum only when this decays much faster than the orientational correlation, *i.e.*, in the limit of frequent collisions. In our case, the situation is more complicated, but our $-\ddot{C}(t)$ is in general a combinatorial angular momentum/orientation correlation function of the resultant vector $\boldsymbol{U}_1(t)$ of a given molecule. This is dependent, simultaneously, on all the other molecular fields in the system. Gas phase theories of induced abosrption [21, 6] reduce this number of molecules to one (bimolecular interaction), or at most two. In liquids it could probably be approximated by the coordination number.

The less-damped behaviour of $-\ddot{C}(t)$ at 11.6 kbar [fig. 1(*b*)] is an indication that the " colliding " molecules are rebounding more in a way that results in preferential reversals of the orientation of the angular momentum vector, *i.e.*, orientational correlation is rebuilt as the molecule starts to return to its original orientation. The angular forces resulting from mechanical anisotropy seem to be enhanced at the greater pressure, an effect which can be seen reflected in the very large increase in the torque dependent [10] parameters $K_0(0)$ and $K_1(0)$ (table). The equivalent function,[1-3] $-\ddot{C}_R(t)$ of depolarised Rayleigh scattering has recently been observed with applied pressure by Dill *et al.*,[22] van Konynenberg *et al.*,[23] and Perrot *et al.*[24] The oscillations in $-\ddot{C}_R(t)$ are strongest in anisotropic molecules at high pressure, indicating that angular forces resulting from mechanical anisotropy lead to a tendency towards molecular librations. These and our results for $-\ddot{C}_R(t)$ and $-\ddot{C}(t)$ respectively, indicate that complete randomisation of the molecular angular momentum after collision is not a valid assumption.

TABLE 1.—PARAMETERS* OF EQN (3) FOR CS_2(l) AND CCl_4(l)

liquid	T/K	P/bar	$10^{40}I$/ g cm^2	$xK_0(0)$	$xK_1(0)$	$x^{\frac{1}{2}}\gamma$	$(\varepsilon_0-\varepsilon_\infty)$
CS_2	296	1	258.6	26.2	170.2	20.3	0.026
	293	11 600	258.6	79.9	247.6	32.7	0.018
	232	1	258.6	21.9	114.3	12.0	0.034
	315	1	258.6	29.9	212.0	27.0	0.020
CCl_4	296	1	242	10.9	80.6	14.2	0.019
	313	1	242	10.2	65.1	12.2	0.017
	328	1	242	9.1	51.2	10.1	0.016
	343	1	242	10.3	77.7	14.6	0.016

* $x = I/2kT$

The effect of temperature [fig. 1(*c*) and 1(*d*)] on $K_0(0)$ and $K_1(0)$ is not as pronounced as that of pressure, but for CS_2(l) both increase with T. This dependence of $\langle O(V)^2\rangle$ is predicted by both harmonic well dynamics, where $\langle O(V)^2\rangle \propto kT \propto \theta$, the angular displacement; and in hard-core collisions, where $\langle O(V)^2\rangle \propto N'kT/\phi$, with N' a force coefficient and ϕ a mean angle of free rotation. Therefore, no discernible " loosening up " of internal structure can be observed in CS_2(l) over the range 232-315 K, the intermolecular torque being determined by the thermal energy available to each molecule (kT).

The situation is different for the spherical top CCl_4 (fig. 2) over the range 296-343 K, the latter being a few degrees below the boiling point at 1 bar. Both $K_0(0)$ and $K_1(0)$ decrease in this range as T increases, although the values at 343 K are slightly anomalous (see table). Therefore, there must be a considerable increase in free volume, and thereby translational freedom, as the boiling point is approached, in order to overcome the thermal effect ($\langle O(V)^2\rangle \propto kT$). An important indication of the table is that $\langle O(V)^2\rangle$ is always much smaller for CCl_4 than for CS_2, implying that molecular geometry plays an important part in determining the extent of rotational freedom in these liquids.

It is relevant to note that the nuclear magnetic resonance spin-rotation relaxation time [25] T_1 of liquids is observed to decrease as temperature is raised, following an

Arrhenius law. T_1 is inversely proportional [3] to τ_J, the angular momentum correlation time, which thus increases with temperature. τ_J is a measure of the mean time during which a molecule seems to retain its angular momentum, and in spherical top molecules [25-27] in the liquid [26, 27] state it is known that spin-rotation interaction is the dominant relaxational mechanism, τ_J becoming long even at temperatures well below the critical point. In contrast, for asymmetric tops [28] and stick-like [29] molecules, spin-rotation interaction becomes appreciable only at high temperatures, the ratio between dielectric and n.m.r. relaxation times being close to the Hubbard [30] ratio of 3. In stick-like molecules, the motion about different symmetry axes is often observed [29] to be highly anisotropic, *e.g.*, in liquid $CH_3C{\equiv}CH$ near the critical point, the rotation about the C_{3v} axis is eight times faster than that about the perpendicular,[29] the contribution of spin-rotation relaxation being about equal to that of the spin-spin magnetic dipolar correlation time, and not dominant, as in spherical tops. Even about the C_{3v} axis, free rotation is not implied, since the observations can be explained with a model of rotational diffusion.

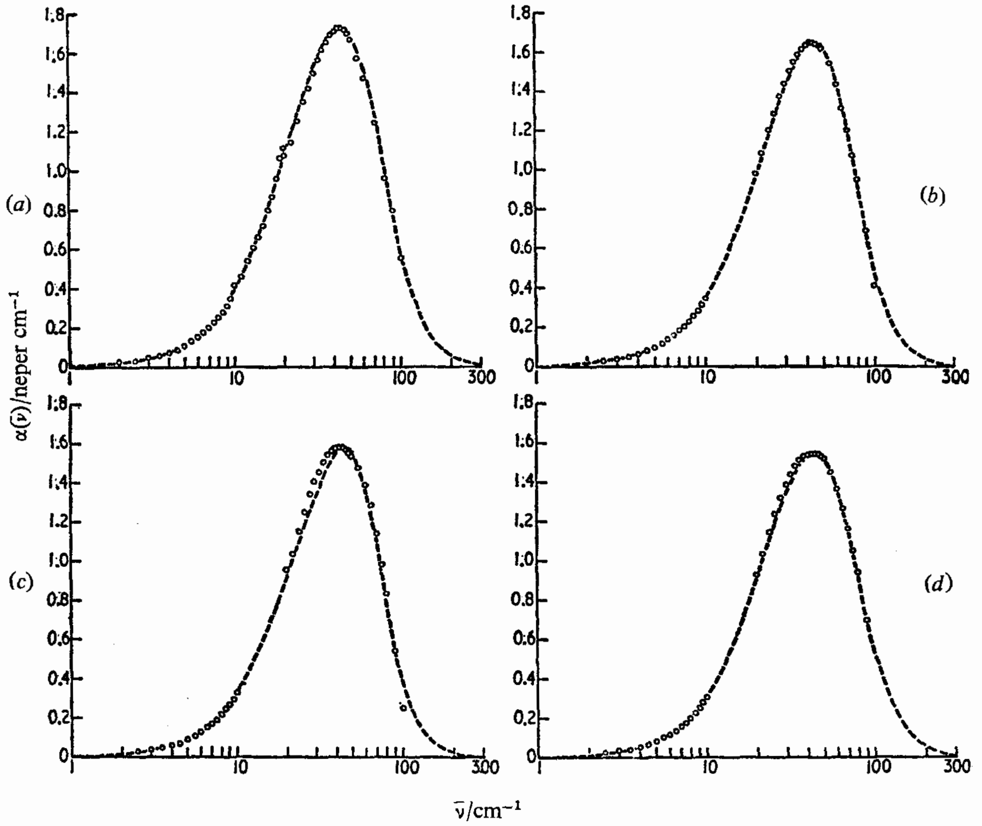

FIG. 2.—Far infrared absorptions of CCl_4(l) at four temperatures, ○, exptl.; ---, eqn (3). (*a*) 296 K; (*b*) 313 K; (*c*) 328 K; (*d*) 343 K.

As mentioned in the introduction, the dispersion $(\varepsilon_0 - \varepsilon_\infty)$ is lower at 11.6 kbar than at 1 bar on CS_2(l), and also decreases with temperature for both liquids. There remains a considerable amount of theoretical work to do, probably with the aid of computer simulations, before this observable can be interpreted in terms of molecular constants (initially in terms of point multipole moments of the field). In liquids, it is, naturally, a multimolecular property, but in the limit of quadrupole [6] induced absorption in bimolecular collisions, it is given [8] by:

$$\varepsilon_0-\varepsilon_\infty = \frac{1}{4\pi(\varepsilon_0^{-3})}\frac{1}{kT}N^2\alpha_pQ^2\int_0^\infty\frac{1}{R^6}\exp\left(-\frac{U(R)}{kT}\right)\mathrm{d}R$$

for a radial intermolecular potential $U(R)$. Here N is the number of molecules per unit volume, which decreases as the temperature, T, is raised. Q is the molecular point quadrupole moment [31] and α_p the molecular mean polarisability.

Thus $(\varepsilon_0-\varepsilon_\infty)$ decreases as T is increased in the simple two-molecular model. The table indicates that this is so for $CS_2(l)$ and $CCl_4(l)$ in the temperature ranges considered. The limits of this model in describing molecular dynamics in the liquid state are reached when the variation of the dispersion with pressure [5, 6, 14] (effectively N) is considered. This equation has $(\varepsilon_0-\varepsilon_\infty)\propto N^2$, which is opposite to that observed for $CS_2(l)$ at 1 bar and 11.6 kbar. The same trend was demonstrated for compressed gaseous and liquid CO_2 by Ho *et al.*,[14] and explained in terms of cancellation of inducing fields by the increasingly symmetric disposition of the molecules around a central one.

Accurate temperature and pressure data in the far i.r./microwave frequency range are needed for more molecules of widely disparate geometries before the trends found in this work can be verified or otherwise. Measurements at varied temperature but constant density, and vice versa will be especially fruitful, but difficult to obtain.

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