

Far Infrared Absorption of CH_2Cl_2 in Isotropic and Cholesteric Solvents

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Received 14th July, 1977

The far infrared broad band absorptions of CH_2Cl_2 , a highly dipolar molecule, have been measured carefully in isotropic and cholesteric solvents in order to bring out, by direct comparison, unusual dynamical effects on solute (probe) molecules dissolved in a mesophase. Whereas the CH_2Cl_2 band maximum (ν_{max}) shifts by some 30 cm^{-1} to lower frequency upon dilution in both CCl_4 and decalin, very little change occurs in cholesteryl linoleate and cholesteryl oleyl carbonate. This is attributed to an unusual persistence of statistical cross-correlation effects which vanish gradually in isotropic solvents. The observed integrated intensity per molecule (A/N) of CH_2Cl_2 is decreased significantly in a cholesteric environment, which may be indicative of an unusually large internal field effect. If this were not so then conservation of $\langle \mu^2 \rangle^{\frac{1}{2}}$, the apparent root mean square dipole, demands the enhancement of another rotational type absorption at frequencies other than those of the far infrared. The reorientation of CH_2Cl_2 in all environments is characterised approximately by itinerant oscillation in two dimensions.

A few papers¹⁻³ have dealt recently with the far infrared absorptions of mesophases (nematogenic and cholesteric). In this submillimetre range ($1\text{--}260\text{ cm}^{-1}$) isotropic liquids exhibit a broad band (Poley) absorption due in the main part to molecular torsional oscillation—the basis for a rotational Brownian diffusion leading to the Debye absorption at frequencies lower than those of the far infrared. There is a little evidence^{1,3} that this broad band is much sharpened and shifted to higher frequencies in the nematogens *p*-methoxybenzylidene *p*'-n-butylaniline, MBBA and *p*-cyano *p*'-n heptylbiphenyl, HCB, but the librational band of interest is usually masked by intramolecular modes due to torsion, or vibrational overtones in these relatively complex molecules.

In the mesophase the immediate molecular environment (nearest neighbour cage) determines through a measurable mean square torque the average rate at which a central molecule reorients about its long or short axis. In HCB, for example,³ where short axis reorientation only is observable, two absorption bands appear about six decades of frequency apart: a rapid torsional process underlies a 140 cm^{-1} peak and the rotational diffusion this sets up is the cause of a low frequency Debye absorption⁴ at $\approx 2\text{ MHz}$. In statistical terms⁵ these two bands, when Fourier transformed together yield an almost exponential orientational correlation function [$C_u(t)$] whose time derivatives are highly oscillatory. However, $C_u(t)$ is affected strongly by cross-correlations in the mesophase, where long range cooperative molecular motions are responsible for, and a consequence of, the pseudocrystalline ordering along the director. This renders incomplete any statistical analysis in terms of molecular autocorrelation, although the main features of the double peak absorptions typical of the liquid crystal phase can be reproduced³ by applying Mori three variable formalism,⁶ for example, directly to $C_u(t)$. The itinerant oscillator model proposed

by Hill⁷ and Wyllie⁸ has been developed recently by Coffey *et al.*,^{9,11} whose treatment is formally identical with¹² a three variable Mori approximation to the angular momentum autocorrelation function (a.c.f.) [$C_{\omega}(t)$]. Under certain conditions [when $C_{\omega}(t)$ is highly oscillatory] the itinerant oscillator can also reproduce the double loss peak¹⁰ even though cross-correlations are neglected, along with dipole-dipole interactions in general.

The twin "disadvantages" of cross-correlations and intramolecular absorptions may be offset to a certain extent by using highly dipolar solutes as probes of the liquid crystal environments, *i.e.*, observing the Poley absorption of the solute as opposed to the nematic or cholesteric solvent. In this paper we use a dilute solution of CH₂Cl₂ in cholesteryl oleyl carbonate and cholesteryl linoleate solvents to investigate the cholesteric environment.² The solute absorptions are compared with their counterparts in dilute CCl₄ and decalin solutions, representative of the isotropic liquid. The effects of cross-correlations in pure liquid CH₂Cl₂ are revealed by accurate measurements of the difference between the far infrared peak frequency in the pure liquid and dilute solution.

EXPERIMENTAL

The spectra were obtained with a Mark III Grubb-Parsons/N.P.L. Fourier transform spectrometer using phase modulation of the radiation reaching a transistorised Golay detector. With a signal to noise ratio of $> 10^3$, reproducibility between successive interferograms was excellent ($\pm 0.5\%$), while systematic uncertainties due to convergence in the beam, window material absorption, channelling, beam divider characteristics, *etc.*, were minimised by repeating the measurements under different sets of such conditions. The uncertainty in the final spectrum is unlikely to exceed $\pm 1\%$ except where the window material exhibits a sharp peak which may not be eliminated wholly by thick/thin ratios of sample pathlength. This is at 128 cm^{-1} for quartz and 72 cm^{-1} for polythene.

The variable path cell used was a standard VC-01 type accurate to $\pm 5\text{ }\mu\text{m}$, so that uncertainties in the pathlength are small. Reproducibility between runs using TPX, high density polyethylene and quartz windows was acceptably good ($\pm < 1\%$). With path lengths of $\approx 0.1\text{-}0.5\text{ mm}$ convergence effects are minimised.

The purity of the cholesteric solvents was checked by observing transition points under a polarising microscope. Probes were AnalaR grade, redistilled from type 3-A zeolite.

RESULTS

The far infrared absorption spectra, corrected for solvent absorption, are shown in fig. 1 and 3, and the integrated absorption intensity $A/\text{neper cm}^{-1}$ is plotted against the molecular number density $N/\text{molecule cm}^{-3}$ in fig. 2 for solutions in CCl₄ and decalin. It is estimated that A is accurate to within about $\pm 3\%$ of its given value. It is seen that A/N is a constant within the experimental uncertainty over the whole range of dilution in both CCl₄ and decalin. It has been the common practice to compare this factor with an equation due to Gordon¹³ for the integrated intensity of sharp (near infrared) rotovibrational peaks, but Hill¹⁴ has recently demonstrated its inapplicability to broad bands. The accuracy of far infrared data now demands a more reasoned approach (such as that of Hill) to this problem of intensity. This development is not attempted here. Similarly the much used Polo/Wilson correction¹⁵ for internal field effects on A is not applicable to accurate broad band data, being too roughly approximate. However, it is clear that no enhancement or otherwise of the apparent root mean square dipole $\langle \mu^2 \rangle^{\frac{1}{2}}$ is discernible between dilute isotropic solution and solute. This does not accord with the recent speculations made by Gerschel¹⁶ on the basis of temperature variations in the far infrared bands

of the highly dipolar CH_3F , CF_3H and CH_3Cl in the pure liquid state. [However, A/N varies in a cholesteric environment (fig. 2)]. There is a shift on dilution with both CCl_4 and decalin to lower frequency in $\bar{\nu}_{\text{max}}$, the band peak frequency (cm^{-1}). In all probability this would not be discernible were the uncertainty in $\alpha(\bar{\nu})$, the power absorption coefficient (neper cm^{-1}), to rise much above about $\pm 5\%$, simply because the peak position $\bar{\nu}_{\text{max}}$ would not be defined clearly enough. This shift in $\bar{\nu}_{\text{max}}$ ought to be matched by one to higher frequency in f_{max} the microwave loss peak frequency.

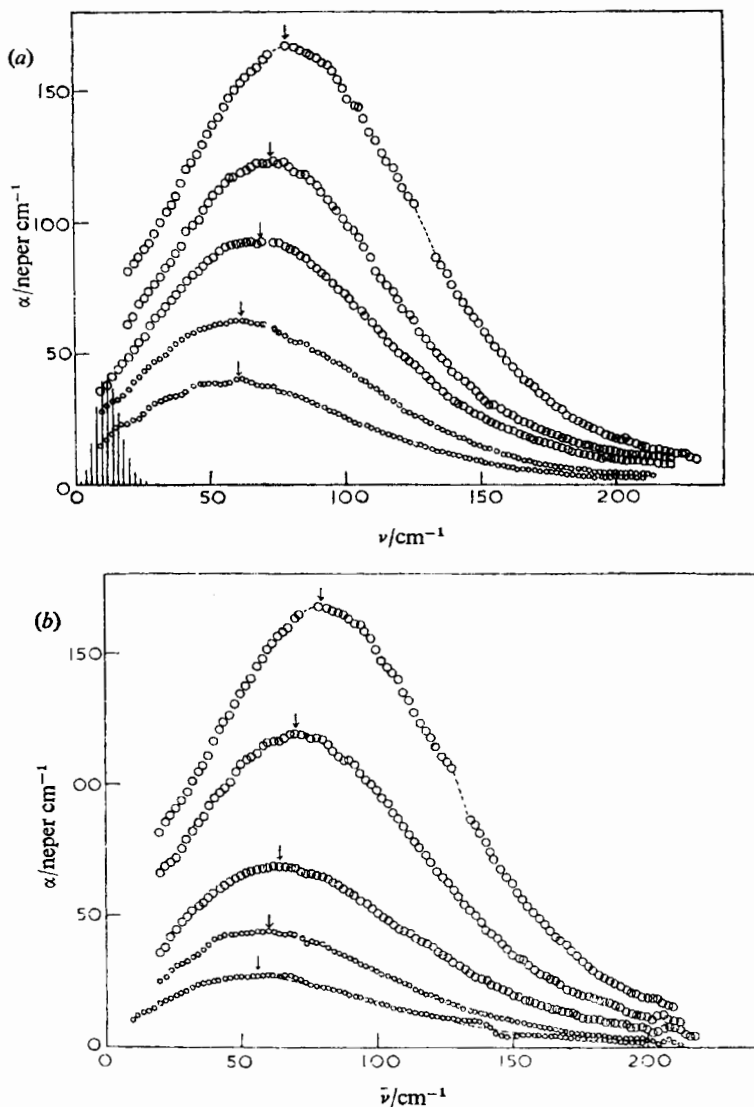


FIG. 1.—(a) Absorption of dichloromethane in CCl_4 at 298 K, corrected for solvent absorption. From top to bottom: pure CH_2Cl_2 ($N = 9.4 \times 10^{21}$ molecule cm^{-3}); $N = 7.22 \times 10^{21}$ molecule $\text{CH}_2\text{Cl}_2 \text{ cm}^{-3}$; $N = 4.93 \times 10^{21}$ molecule $\text{CH}_2\text{Cl}_2 \text{ cm}^{-3}$; $N = 3.25 \times 10^{21}$ molecule $\text{CH}_2\text{Cl}_2 \text{ cm}^{-3}$; $N = 1.97 \times 10^{21}$ molecule $\text{CH}_2\text{Cl}_2 \text{ cm}^{-3}$. (b) The same in decalin [for N of fig. 2(a)].

The stick spectrum represents some $J \rightarrow J+1$ ($\Delta K = 0$) lines for quantised free rotation of CH_2Cl_2 (arbitrary intensity).

In statistical terms the difference is due to the gradual disappearance of cross-correlations between the dipole vectors of different solute molecules until at infinite dilution only autocorrelations are non-zero. The $J \rightarrow J+1$ ($\Delta K = 0$) absorption lines for quantised free rotation in the inertial symmetric top CH₂Cl₂ (fig. 1) peak ≈ 40 cm⁻¹ away from $\bar{\nu}_{\max}$ in the most dilute solution.

In the cholesteric solvents there is, in contrast, no significant shift in $\bar{\nu}_{\max}$ with dilution but, after correcting for solvent absorption, A/N tends to fall below the value

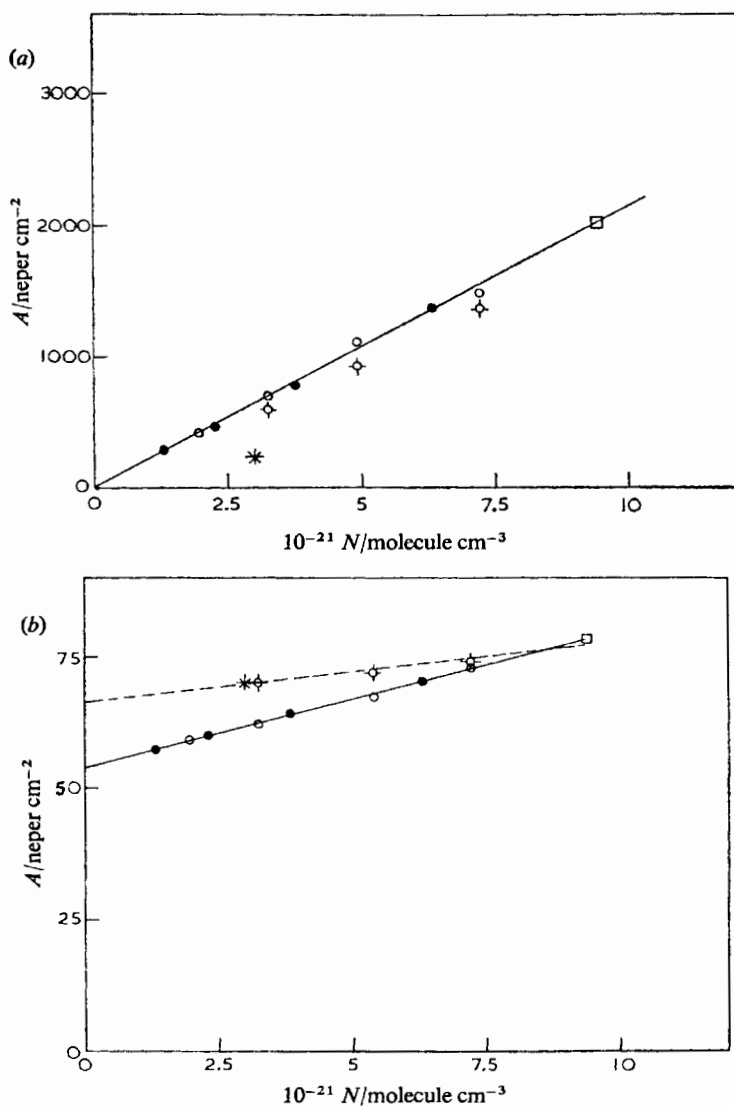


FIG. 2.—(a) Plot of A against N for CH₂Cl₂ in all environments, at 298 K. \circ , In CCl₄; \square , pure CH₂Cl₂(l); \bullet , in decalin; \diamond , in cholesteryl oleyl carbonate (c.c.o.); $*$, in cholesteryl lineoleate (C.L.). —, Best straight line through the CCl₄ and decalin data.

(b) Plot of $\bar{\nu}_{\max}$ against number density in CCl₄ and decalin. —, Best straight line through the CCl₄ and decalin data. - - -, Best straight line through the cholesteric data. \square , Pure CH₂Cl₂; \circ , CCl₄ solution; \bullet , decalin solution; \diamond , in C.C.O.; $*$, in C.L.

in the pure CH_2Cl_2 . The absence of solvent shift can be interpreted as a continued effect of unusual cross-correlation between the probe and solvent molecules persisting after the solution has become visibly transparent. It is clear from very recent Kerr-effect studies¹⁷ that mesomeric behaviour is observable well beyond clarification.

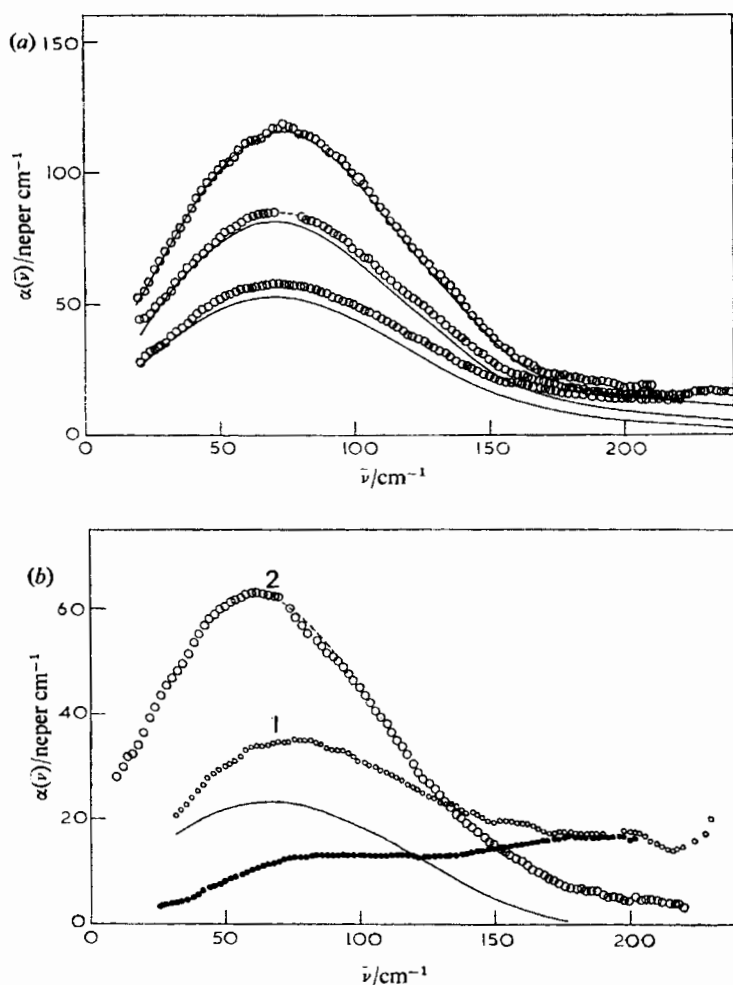


FIG. 3.—(a) \circ , CH_2Cl_2 in cholesteryl oleyl carbonate, at 298 K. —, Corrected for solvent absorption.

(b) \circ , (1) 3.00×10^{21} molecule CH_2Cl_2 cm^{-3} in cholesteryl lineolate, at 298 K. —, corrected for solvent absorption (\bullet). \circ , (2) for comparison, absorption of 3.25×10^{21} molecule CH_2Cl_2 cm^{-3} in CCl_4 .

There is a large decrease in A/N in CH_2Cl_2 /cholesteryl linoleate ($N = 3 \times 10^{21}$ molecule cm^{-3} fig. 3); this result implies that the "isotropic" value of $\langle \mu^2 \rangle^{\frac{1}{2}}$ would be conserved only by the enhancement of another rotational type absorption at some other frequency, were the decrease not attributable solely to a greatly enhanced internal field effect.

DISCUSSION

The solution spectra were analysed for molecular dynamical properties by statistical methods in the time domain. The $\alpha(\bar{\nu})$ data were Fourier transformed to give the "rotational velocity" correlation function defined¹⁸ by:

$$C(t) = -\ddot{C}_u(t) = \left\langle \sum_i \mathbf{u}_i(t) \cdot \mathbf{u}_i(0) \right\rangle \propto \int_0^\infty \frac{\bar{\nu} \alpha(\bar{\nu}) \cos(2\pi \bar{\nu} ct)}{1 - \exp(-hc\bar{\nu}/kT)} d\bar{\nu}. \quad (1)$$

These are plotted for CH₂Cl₂/CCl₄ in fig. 5, where it can be seen that there is a significant difference between $C(t)$ for the most dilute solution and that for the neat liquid. All curves are normalised at $t = 0$. The form of $C(t)$ for the solution in cholesteryl oleyl carbonate and cholesteryl linoleate are very similar to that for pure CH₂Cl₂. It is possible to fit this function for dilute solutions (no dipole-dipole coupling) using the Coffey/Calderwood version⁹⁻¹² of the itinerant oscillator model. For details of this planar mechanism see ref. (9) to (12). Here we state that the librations of a molecule within a cage of its neighbours are represented by the angular motion of a disc harmonically bound within an annulus which is itself undergoing rotational Brownian motion. The equations of motion governing this system lead to an angular velocity a.c.f. $C_\theta(t)$ of the form:

$$\begin{aligned} C_\theta(t) &= \langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)^2 \rangle; \quad (t > 0) \\ &= \frac{1}{1+\Gamma} \left[\left(\cos \omega_1 t + \frac{(\sigma_1 + \Gamma \sigma_2)}{\omega_1} \sin \omega_1 t \right) e^{-\sigma_1 t} + \Gamma e^{-\sigma_2 t} \right] \end{aligned} \quad (2)$$

where θ is a coordinate which specifies the angular position of a dipole μ lying along the axis of the disc at any time $t > 0$. Further $\sigma_1 + i\omega_1$; $\sigma_1 - i\omega_1$; and σ_2 are then roots of the equation

$$s^3 + \beta s^2 + (\omega_0^2 + \Omega_0^2)s + \beta \omega_0^2 = 0.$$

The factor Γ is given by:

$$\Gamma = \frac{-2\sigma_1(\sigma_1^2 + \omega_1^2)}{\sigma_2(3\sigma_1^2 - \sigma_2^2 - \omega_1^2)}.$$

If $\psi(t)$ is the angle which a point on the rim of the annulus makes with the reference direction at time t and if I_1 is the moment of inertia of the annulus, then $I_1 \beta \dot{\psi}$ is the frictional couple acting on the annulus due to the surroundings. ω_0 is the angular frequency of oscillation of the disc when the annulus is held in a fixed position and $\Omega_0^2 = (I_2/I_1)\omega_0^2$. From general statistical considerations it can be proved that

$$\begin{aligned} \omega_0^2 &= \langle \ddot{\theta}(0)^2 \rangle / \langle \dot{\theta}(0)^2 \rangle \\ \Omega_0^2 &= \frac{\langle \dot{\theta}(0)^2 \rangle}{\langle \ddot{\theta}(0)^2 \rangle} - \frac{\langle \ddot{\theta}(0)^2 \rangle}{\langle \dot{\theta}(0)^2 \rangle} \end{aligned} \quad (3)$$

where we may designate by "mean square torque derivative" the average $I_2 \langle \ddot{\theta}(0)^2 \rangle$ and by "mean square torque" the average $I_2 \langle \dot{\theta}(0)^2 \rangle$. Eqn (3) follow from the remarkable fact¹² that eqn (2) is formally identical with the result of Mori three-variable formalism applied to $C_\theta(t)$. From eqn (2) it is possible to calculate the function:

$$-\ddot{C}_{\cos\theta}(t) = \left\langle \frac{d}{dt} (\cos \theta(t)) \left[\frac{d}{dt} (\cos \theta(t)) \right]_{t=0} \right\rangle$$

the two-dimensional equivalent of $-\ddot{C}_u(t)$. The assumption involved in equating these two autocorrelation functions is that the CH_2Cl_2 dipole vector moves in a plane. The extension of any realistic model of Brownian motion such as the itinerant oscillator to libration in space is a formidably difficult task mathematically,¹⁹⁻²² even for simple geometries such as the sphere with an embedded dipole.

In the initial equation of motion⁹ no account is taken of dipole-dipole coupling²³ and thus the most dilute solution data of CH_2Cl_2 in CCl_4 have been used for obtaining the optimum fit of $-\ddot{C}_{\cos \theta}(t)$ to $-\ddot{C}_u(t)$ (fig. 4). This was obtained by a non-linear least mean-squares algorithm²⁴ using ω_0^2 , Ω_0^2 and β as variables. For best fit

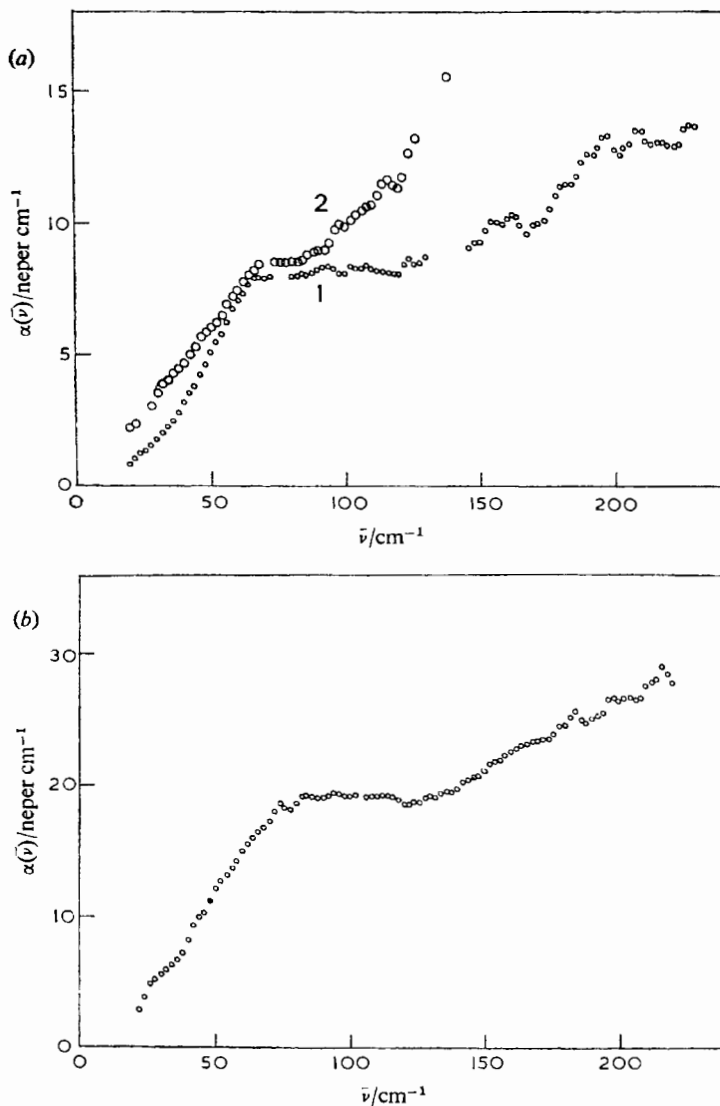


FIG. 4.—(a) (1) Absorption of cholesteryl oleyl carbonate supercooled in a mesophase at 296 K. (2) Absorption of cholesteryl oleyl carbonate solid at 296 K. (b) Absorption of supercooled cholesteryl linoleate in a mesophase at 296 K.

$\omega_0^2 = 16.4 (kT/I_B) \text{ s}^{-1}$; $\Omega_0^2 = 80.7 \times (kT/I_B) \text{ s}^{-2}$; $\beta = 6.2 \times (kT/I_B)^{\frac{1}{2}} \text{ s}^{-1}$ (where I_B refers to CH₂Cl₂ as a symmetric top). From this fitting it is possible to calculate the following autocorrelation functions and power spectra, functions which illuminate several aspects of the rotational dynamics of CH₂Cl₂ in solution.

- (i) The orientational a.c.f. $\langle \cos \theta(t) \cos \theta(0) \rangle$, the dielectric decay function.
- (ii) The torque a.c.f. $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)^2 \rangle$. This is not defined for a Debye rotational diffusion, or Gordon m -diffusion.²⁵
- (iii) $\tilde{C}_\theta(\omega) / \tilde{C}_\theta(0)$, the normalised power spectrum of θ , [the Fourier transform of $C_\theta(t)$].
- (iv) $\tilde{C}_\theta(\omega) / \tilde{C}_\theta(0)$, the power spectrum of $\dot{\theta}$.

These functions are shown in fig. 5. It is clear that the variation in $-\ddot{C}_u(t)$ due to decreasing cross-correlations is of the order of the residual difference between

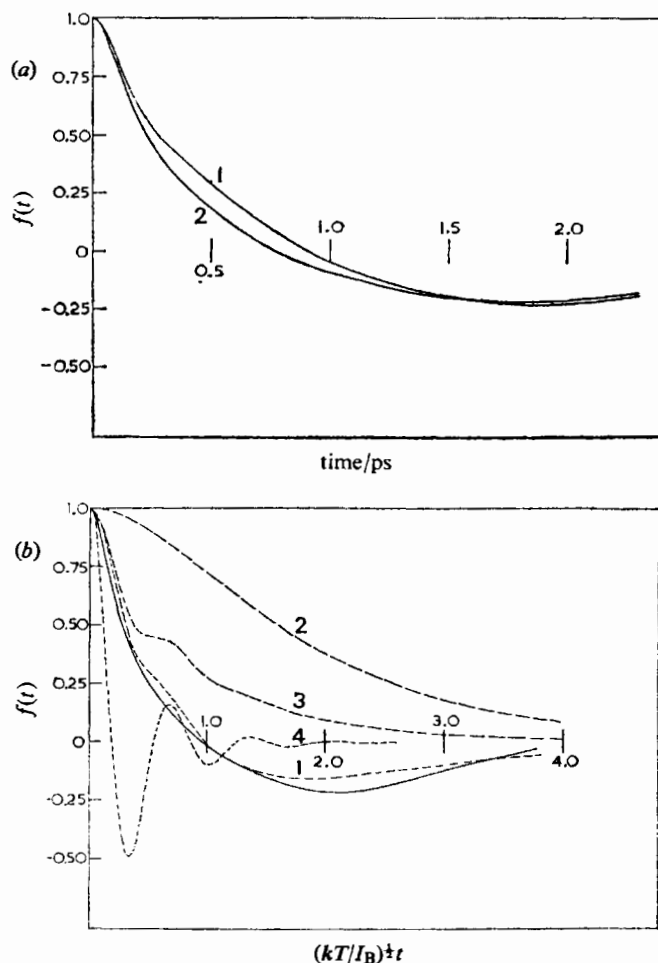


FIG. 5.—(a) (1) $-\ddot{C}_u(t)$ for pure CH₂Cl₂ liquid at 296 K. (2) $-\ddot{C}_u(t)$ for 1.97×10^{21} molecules CH₂Cl₂ cm⁻³ in CCl₄.

(b) —, Curve 5 (a), 2.

---, (1) $-C_{\cos \theta}(t)$, l.m.s. best fit to curve 5(a).2. } Normalised to unity at $t = 0$
 (2) $C_{\cos \theta}(t)$, calculated from the fitting.
 (3) $C_\theta(t)$; (4) $C_{\dot{\theta}}(t)$

$-\ddot{C}_0(t)$ and the optimised $-\ddot{C}_{\cos\theta}(t)$. Therefore, one can conclude only that the itinerant oscillator model of reorientation in a plane represents to within about $\pm(5-10)\%$ the absorption spectrum of CH_2Cl_2 in all environments. In other words the formalism is not yet sensitive enough to describe the small, extra cross-correlation which undoubtedly persists in the mesophase + probe mixtures studied here.

However, it is clear that the torque a.c.f. is highly oscillatory and the power spectrum of torques correspondingly sharp (fig. 6). In contrast the spectrum of angular velocities ($\dot{\theta}$) falls off rapidly to zero. The a.c.f. $C_{\dot{\theta}}(t)$ is non-negative but obviously not exponential. Considering²⁶ the rotational velocity a.c.f. of typical liquids in the far infrared, it is highly unlikely that a *simple* Langevin equation of motion will be able to give an adequate representation of the molecular dynamics. In the itinerant oscillator, the far infrared peak frequency is equivalent to ω_0 , so that we have:

$$\omega_0^2 = (2\pi\bar{v}_{\max}c)^2 = \langle T_q^2 \rangle / 2I_2kT.$$

where $\langle T_q^2 \rangle = \langle \dot{\theta}(0)^2 \rangle I_2$ and $I \equiv I_2$. Accordingly in both this and Mori formalism the mean square torque experienced by the probe molecule becomes significantly smaller upon dilution in an isotropic solvent, but this is not so in the cholesteric environment. Since the torque is the derivative of intermolecular potential with respect to orientation, it follows that the r.m.s. barrier to rotation of the small probe molecule remains as high in the mesophase as in the pure liquid CH_2Cl_2 .

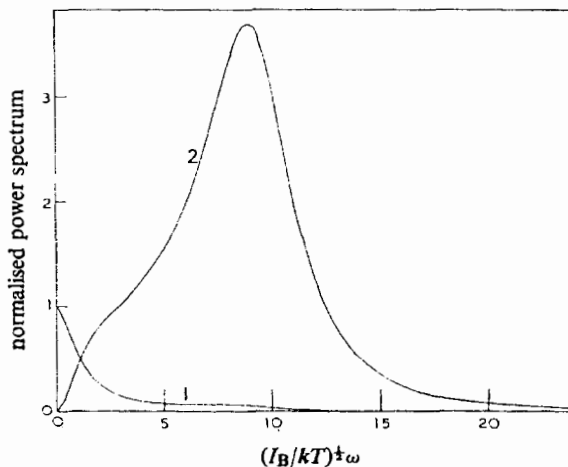


FIG. 6.—Fourier transforms of: (1) $C_{\dot{\theta}}(t)$ and (2) $C_{\ddot{\theta}}(t)$, the former normalised to unity at $\omega = 0$.

It would be beneficial if these far infrared data were to be supplemented by those from microwave and lower frequency dielectric spectroscopy in the first instance, especially in view of the fact that the probe absorption in cholesteryl linoleate is anomalously low. Kerr effect relaxation¹⁷ seems to be an especially sensitive method of discerning the onset of liquid crystalline properties in the apparently isotropic fluid, and could be used to supplement the far infrared results reported here. There has been an extensive effort with probe + mesophase mixtures with n.m.r. relaxation,²⁷ but correlation functions, as opposed to correlation times, are rarely forthcoming from such studies.

The significant departure from linearity of the (A/N) against N plot ought to be investigated further with slightly dipolar solvents, thus allowing near neighbour dipolar

effects to be distinguished from the longer range internal field effects additionally present in the cholesteric solvents used. We are indebted to a referee for this valuable suggestion. Incoherent, inelastic neutron scattering could conceivably be used to investigate the apparent finding that CH₂Cl₂ is behaving in C.C.O. and C.L. as in the pure liquid. The solvents would have to be of such a nature that the solute scattering cross-section predominated.

Further far infrared work would benefit from the maximum experimental variation of mean square torque, since this determines the peak frequency of the Poley absorption along with molecular inertia and temperature; it would be revealing to probe supercooled mesophases.

The S.R.C. is thanked for an equipment grant and studentships for C. R. and G. J. E., the Ramsey Memorial Trust for a fellowship to M. W. E.

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