Journal of Molecular Liquids, 32 (1986) 149—160
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE POLEY ABSORPTION IN LIQUID CRYSTALS

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(Received 14 February 1986)

ABSTRACT

The far infrared torsional oscillatory absorption of a nematic liquid crystal has been isolated for the first time free of higher frequency proper modes. This has been achieved using a molecule specially synthesised for this purpose with a dipole moment engineered perpendicular to the long axis so that torsional oscillation about this axis modulates this component only. The far infra-red power absorption of the liquid crystal in the isotropic, nematic, solid and supercooled conditions is therefore a Poley absorption, i.e. the torsional oscillation about the rigid long axis of the liquid crystal molecule itself. The effect of phase changes on a macroscopic level is to sharpen and intensify this absorption. This is clear evidence to the effect that phase changes in liquid crystals are cooperative phenomena, the molecular librational dynamics about the long axis are little different from those in a regular molecular liquid.

INTRODUCTION

The first far infra-red power absorption spectrum of a nematic liquid crystal was reported contemporaneously by three groups in the early

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0167-7322/86/$03.50

seventies [1-3]. The nematic liquid crystal p methoxy benzylidene p´n butyl aniline (MBBA) was then available and was investigated by all three groups. The object of these studies was to isolate the far infra-red Poley absorption, which is now well known to be due to molecular torsional oscillation in the diffusing asymmetric top, and has been reproduced theoretically and with computer simulation. The investigation into the dynamics of MBBA did not produce clear results, because the inter-molecular torsional oscillatory broad band power absorption was masked by higher frequency intra-molecular modes of absorption. The interpretation was complicated further by the fact that MBBA has a dipole moment which is roughly at 45^{o} to the long axis, and this angle fluctuated with time because of the inherent molecular flexibility. On top of this MBBA is a Schiff base and decomposes in the presence of moisture.

Subsequent investigations [4-8] with nematics such as p n heptyl p' cyano biphenyl (7CB) whose dipole moment is accurately parallel to the molecular long axis have resulted in the isolation of the Poley absorption, as expected at relatively high frequencies in the far infra red [5,8], and this has been interpreted using the model of the itinerant oscillator self consistently with dielectric [4] and Kerr effect data. However the far infra-red power absorption in this case is again complicated by intra-molecular proper modes, and special measures had to be taken [8] to identify the inter-molecular absorption of interest, such as supercooling in glassy decalin.

This paper aims to complement the work on 7CB by looking at the torsional oscillation about the long axis of a molecule specially synthezised for this purpose at Krakow. This requires a permanent dipole moment accurately perpendicular to the long axis, as illustrated in fig. (I). In order to remove as far as possible the intra-molecular modes of absorption [1,5,8] of the far and mid infra-red the molecular framework was designed to be rigid with the minimum of alkyl chain flexibility compatible with the ability to exist in a nematic phase near room temperature. The

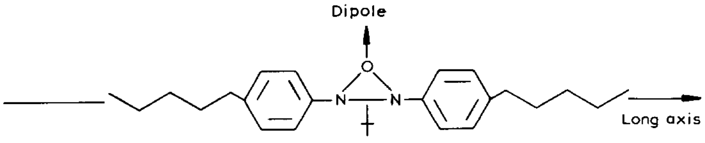


Fig. 1. ■ Sketch of the liquid crystal molecule, showing the dipole moment perpendicular to the long axis.

bridging oxygen illustrated in fig. (I) means that the permanent molecular dipole moment is accurately perpendicular to the molecular long axis, if we neglect the small, temporary dipole moments induced by alkyl chain dynamics. With these considerations in mind, therefore, the determination of the far infra-red power absorption of this molecule in the isotropic liquid, nematic, supercooled and low temperature solid is of key importance, because it provides the most detailed information on the molecular torsional oscillatory dynamics and follows these through the various phases.

The position of the permanent molecular dipole moment means that the torsional oscillation responsible for its modulation as a function of angular coordinate will be that about the molecular long axis. Therefore, if our piece of molecular engineering described above be successful, and if all irrelevant intra-molecular modes have indeed been eliminated, the far infra-red spectrum will provide an ideal method for looking in detail at the effect of phase changes on local molecular dynamics in a liquid crystal [9]. Furthermore, long axis libration of this kind takes place relatively freely, so that the Poley absorption maximum shows up in the fifty to one hundred wavenumber region, as in regular molecular liquids [10]. It is possible therefore to study the liquid crystal dynamics relatively straightforwardly and this provides a much greater insight than with MBBA or 7CB.

EXPERIMENTAL METHODS

Great care was taken to produce far infra-red power absorption coefficients accurate both on the ordinate and the abscissa, respectively the power absorption coefficient, $\alpha(\bar{\nu})$, in neper cm^{-1} and the wavenumber, $\bar{\nu}$, in cm^{-1}. This was achieved with an N.P.L./Grubb-Parsons "Cube" interferometer, Mark III, interfaced with a Research Machines 380Z Microprocessor and Honeywell 6080 local mainframe. For each spectrum, several interferograms were obtained and Fourier transformed on this system by placing the sample cell outside the interferometer and evacuating as much as possible of the optical configuration up to the Golay detector.

The sample was accurately thermostated and the sample path length [10] determined to within 0.01 mm. The limiting uncertainty in the power absorption coefficient is related to the inverse of the uncertainty in the path length used to attentuate the incident radiative power I_o. The sample cell was specially designed to take accurately machined quartz optical flats, aliasing effects were eliminated with suitable combinations of filters, and all mirrors were kept free of oil vapour and moisture with a combination of pumping and drying agents such as silica gel.

The power absorption coefficient was measured repeatedly until all signs of spurious features in the transmissivity of the instrument were eliminated. The results illustrated in this paper are samples taken under especially favourable conditions.

RESULTS AND DISCUSSION

Fig. (2) illustrates the far infra red power absorption of the liquid crystal of fig. (I) in the isotropic liquid phase at 357 K, in the nematic

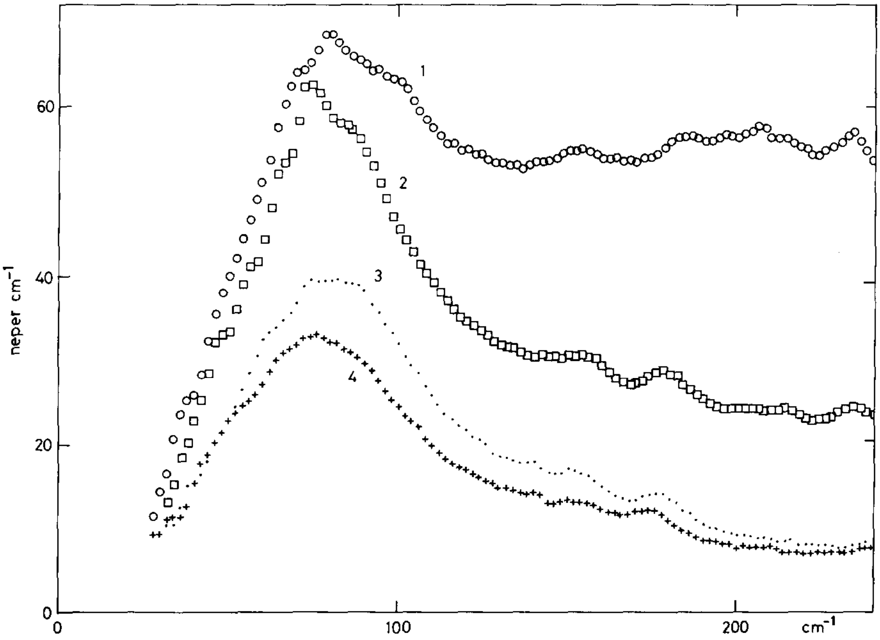


Fig. 2. Far infra-red power absorption of the molecule of fig. (1) in three or possibly four phases.

1) Crystalline (?) solid at 233 K.

2) Supercooled glassy solid at 295 K.

3) Nematic at 311 K.

4) Isotropic liquid at 357 K.

<u>Ordinate</u>: Power absorption coefficient (neper cm^{-1}).

<u>Abscissa</u>: cm^{-1}

phase at 311 K in the solid at 295 K and at 233 K. It is clear from all four results that the broad, featureless absorption characteristic [10] of the torsional oscillatory dynamics of regular liquids is well resolved in the isotropic and nematic phase, and in the solid at 295 K. In the solid at 233 K there is visible at higher frequencies the onset of proper mode absorption, in the shape of what appears to be a number of unresolved lattice modes of relatively high intensity. This means that the complete Poley absorption is not as well resolved at 233 K, but its peak at below 100 cm^{-1} is still clearly visible. A qualitative interpretation of these spectra can therefore be given in the following terms.

i) The most important observation of relevance to the torsional oscillatory dynamics of the molecule of fig. (1) is that the peak of the far infra red absorption remains roughly in the same place at all four temperatures. There is a slight shift to higher frequency between the isotropic and nematic phases which is no more than could be expected in a regular liquid such as dichloromethane on the grounds of temperature difference alone [11]. In other words from fig. (2) alone there would be no reason to suspect that a phase change had occurred. Similar reasoning is applicable to the other two spectra in this figure. There is very little difference between the bandshapes in the nematic phase for instance, and that in the solid at 295 K. This remarkable result could be interpreted to mean that the torsional oscillatory dynamics in the isotropic liquid are already highly cooperative and in consequence that the isotropic liquid is, in dynamical terms, anticipating the change to nematic status. This liquid crystalline condition is well known to be intermediate between that of the isotropic molecular liquid and the crystalline solid, and indeed there is not much of a bandshape difference between the nematic Poley absorption and that of the solid at 295 K, which is probably a supercooled glass. It seems that further cooling of this glass induces crystallisation producing the spectrum shown in fig. (2) at 233 K. No corroborative evidence for this supposition is available yet from X ray diffraction and related sources.

ii) The integrated absorption intensity (sometimes known [10] as the "cross section"), i.e. the area of the curves in fig. (2), increases as the temperature is decreased, and this is due to the increasing density - the number of dipoles per unit volume. There is a disproportionately large increase from the nematic to the higher temperature solid, probably indicating that there is a jump, i.e. a discontinuity, in the density at the isotropic to nematic phase transition temperature [9]. In contrast the cross section increases much less rapidly as the temperature of the solid is lowered to 233 K. This means that if there is a phase change as the solid is cooled it cannot be accompanied by much of a density change. Alternatively the cooling in the solid could be accompanied by an increase in packing symmetry, and this may have an effect on the internal field [12,13]. Additionally there are always present in far infra red spectra such as these interaction induced absorptions [14], and these are always superimposed on the "pure" Poley absorption of the librating molecule itself.

The main qualitative conclusion is that the torsional oscillatory dynamics of the long axis of the molecule in fig. (1) are remarkably similar in the three or possibly four phases illustrated in fig. (2). One would expect much more pronounced differences when a regular liquid such as dichloromethane freezes [11], and observations are available [10] in several rotator molecules of more pronounced spectral differences between liquid, rotator phase and crystalline solid. This pronounced similarity in long axis dynamics in this type of nematogen is surely a key point in explaining the existence of the intermediate state of matter between liquid and crystalline solid.

It will be interesting to consider in future dielectric loss and permittivity work [4] on this molecular liquid and nematogen, to see whether the results of fig. (2) are paralleled at lower frequencies. The power absorption curves of fig. (2) can be converted straightforwardly [10] into dielectric loss, and the wavenumber range of that figure corresponds to frequencies in the terahertz. The complete range of dielectric loss vs. frequency is well known [10,12] to stretch downwards to the megahertz and beyond to lower frequencies. Naturally any quantitative attempt at explaining these spectra in terms of molecular dynamics must be capable of reproducing the dielectric loss and the power absorption from the same equations of motion. Only then will a clear view of the dynamics begin to emerge.

QUANTITATIVE INTERPRETATION

Standard methods of quantitative interpretation of power absorption in the far infra-red range and lower frequencies are well established and available in the literature [10,15,16]. The first stage is to Fourier transform the power absorption coefficient into a rotational velocity correlation function [10]. Neglecting cross correlations [12] and collision induced effects [14] the Fourier transforms obtained in this way are, to a first approximation, the auto-correlation function:

$$\langle \dot{\underset{\sim}{\mu}}(t)\cdot\dot{\underset{\sim}{\mu}}(o)\rangle \ \langle \dot{\mu}^2\rangle$$

i.e. of the time derivative of the dipole moment $\underset{\sim}{\mu}$. This establishes contact between the far infra red spectrum and the ensemble molecular dynamics, because this type of time correlation function can be built up from stochastic differential equations of motion like the Kramers equation or the Langevin equation and developments [16], and also by molecular dynamics computer simulation [17].

Fig. (3) shows the results of three direct Fourier transforms of the data in fig. (2) in the isotropic, nematic and supercooled solid condition. The rotational velocity correlation functions are oscillatory on a picosecond time scale, and are similar in nature to their well documented equivalents [10] in regular isotropic liquids such as dichloromethane which are not

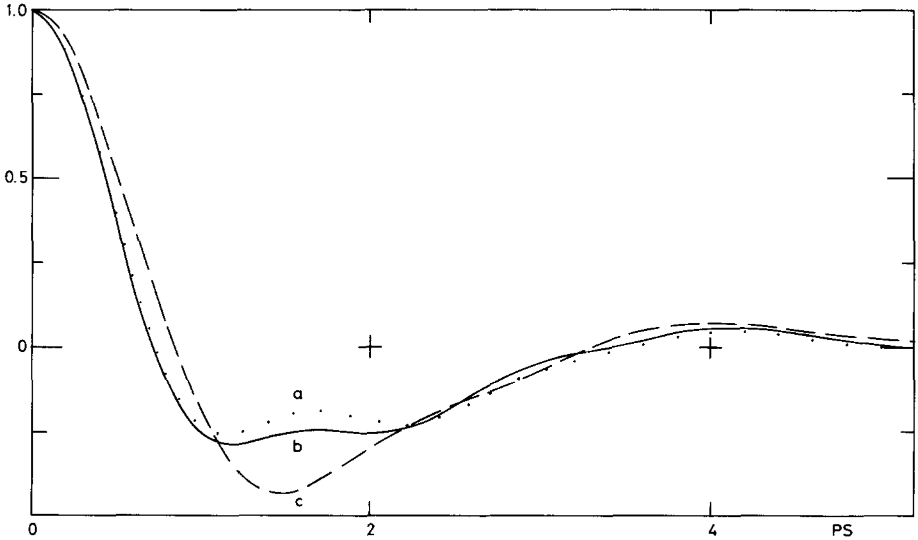


Fig. 3. Direct Fourier transforms of curves (2) to (4) of fig. 2.

a) Normalised Fourier transform in the isotropic liquid.

b) In the nematic.

c) In the supercooled glassy solid.

<u>Ordinate</u>: Normalised Fourier transform

<u>Abscissa</u>: time in ps.

known to support liquid crystalline phases before the normal freezing point. At longer times (from about 3 to 5 ps) the three curves of fig. (3) are almost identical. This echoes the similarity at low frequency in the equivalent power absorption spectra at low frequency in fig. (2). The evolution at intermediate times of up to about 2 ps is distinguishable in fig. (3), that of the two liquids being more oscillatory, in the sense that there are two observable minima in comparison with one deep inimum in the solid. The three Fourier transforms in fig. (3) are all normalised to unity at the time origin so that any difference in time dependence reflects the equivalent difference in normalised frequency dependence in the power spectra. Fig. (3) shows that in terms of molecular dynamics the difference in time dependence is slight, and especially so between the nematic and isotropic phases. As with the frequency domain spectra, it would be impossible to discern from the correlation functions that any phase changes were taking place. In fact more pronounced ones are observable simply by changing the temperature of a regular isotropic molecular liquid, e.g. dichloromethane [11].

In terms of molecular dynamics, specifically torsional oscillation about the long axis of fig. (1), the conclusions to be drawn from fig. (3) are as follows.

i) In the isotropic liquid at 357 K the torsional oscillatory dynamics are almost identical to those of the nematic at 311 K. This means that the factors responsible for the isotropic nematic phase change are to be defined on the multi-molecule level. The minute difference between the torsional oscillatory dynamics on the single molecule level must be amplified by six or seven orders of magnitude by a million or more molecules acting cooperatively to produce macroscopically observable phenomena. A well known example of this is the ability of a weak electric field to cause alignment of the nematic director resulting in observable macroscopic birefingence. This is manifest in the dielectric loss and permittivity [9,10], which are therefore phenomena involving the cooperative motion of millions of molecules.

ii) It is probable therefore that the time dependence of inter-molecular dynamical cross-correlations in the far infra-red region is very similar or identical to that of auto-correlations such as that of $\dot{\underset{\sim}{\mu}}$. In other words, the dynamics of the far infra-red, i.e. picosecond and sub-picosecond dynamics, evolve primarily from a consideration of the torsional oscillatory behaviour of individual molecules, such as the one illustrated in fig. (1). It is therefore possible to attempt to describe the far infra-red power absorption with Langevin equations [16-20].

DESCRIPTION USING A SIMPLE LANGEVIN EQUATION

One of the simplest relevant class of Langevin equation [16, 18-20] is:

$$I\ddot{\theta}(t) \quad + \quad I\beta\dot{\theta}(t) \quad + \quad V'(\underline{0}) \quad = \quad \dot{W}(t) \quad - \tag{1}$$

$$V \quad = \quad -V_o \cos 2\theta(t)$$

The equivalent Kramers equations is:

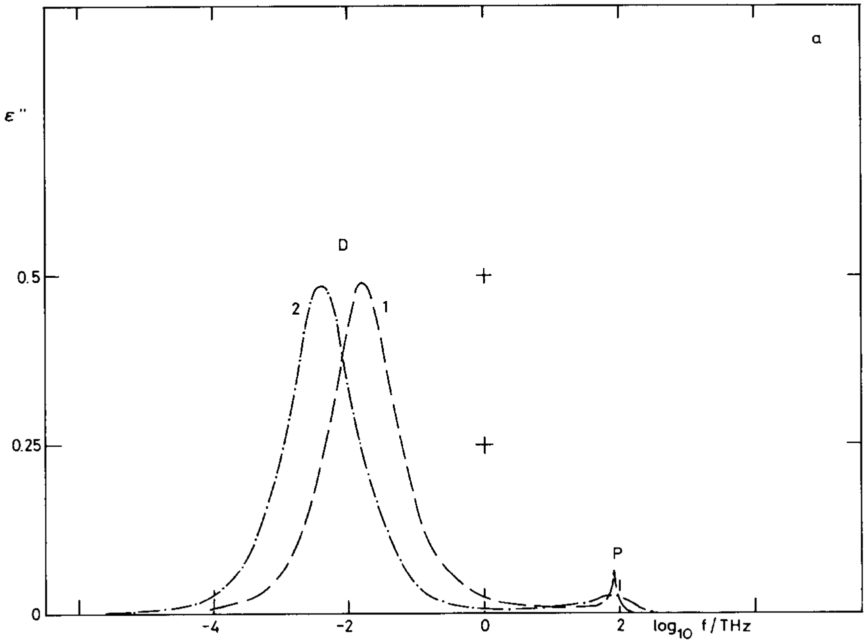
$$\frac{\partial\rho}{\partial t} + \dot{\theta}\frac{\partial\rho}{\partial\theta} - \frac{V'}{I}\frac{\partial\rho}{\partial\dot{\theta}} = \beta\frac{\partial}{\partial\dot{\theta}}\left[\dot{\theta}\rho + \frac{kT}{I}\frac{\partial\rho}{\partial\dot{\theta}}\right] \tag{2}$$

for the conditional probability density. Here I is the effective moment of inertia associated with the two dimensional librational motion described by the Langevin equation (1). θ is the angular displacement in two dimensions, β the rotational friction coefficient and W a Wiener process [10,20]. The potential energy V is a "minimal" representation of the true mean intermolecular potential energy. The Kramers equation can be solved by standard differential differencing [18,20] and the spectrum in fig. (2) can be matched approximately as first described by Reid [18]. The parameters involved in this comparison are the α,β and γ parameters of Raid [18], defined by :

$$\alpha \; = \; \left(\frac{kT}{I}\right)^{\frac{1}{2}} \quad ; \quad \gamma \; = \; \frac{V_o}{2(IkT)^{\frac{1}{2}}} \quad ;$$

so that with an approximate knowledge of the effective moment of inertia I the complete spectrum can be expressed in terms of only two free parameters, the friction coefficient β and the barrier height V_o. By "complete" spectrum we mean the zero frequency to terahertz frequency dielectric loss and power absorption [21]. At present only the results of fig. (2) on the power absorption are available, but future measurements of the dielectric loss will be available in due course. In the meantime the power absorption spectra equivalent to the rotational velocity correlation functions of fig. (3) can be matched from eqn. (2) as shown in fig. (4) with the parameters shown in the figure. In this figure are also shown the theoretical predictions of the frequency of maximum dielectric loss, and it will be interesting in future work to compare these predictions with experimental data.

A more detailed theoretical study of the complete far infra-red and dielectric data will be available in future work with the theory of long rod dynamics developed by Moscicki [9]. At present, this theory is designed for nematogens and lyotropic liquid crystals with dipole moments roughly


a
ε''
0.5
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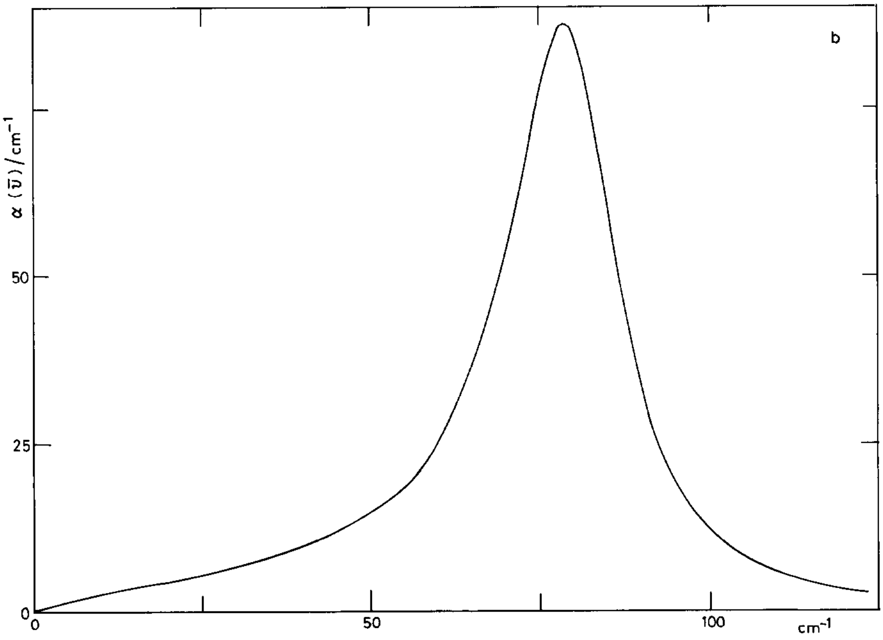
0
D
2
1
P
-4
-2
0
2
log10 f/THz


b
α (ν̄)/cm-1
50
25
0
0
50
100
cm-1

parallel to the long axis, but could be adapted for the type of molecule described in this paper, i.e. with the dipole accurately perpendicular to the long axis.

ACKNOWLEDGEMENTS

The Nuffield Foundation and Leverhulme Trust are thanked respectively for a "Small Grant" and a Fellowship to MWE. The University of Wales is thanked for the award to MWE of the Pilcher Senior Fellowship and the S.E.R.C. for the award of an Advanced Fellowship to GJE. The visit of Dr. Moscicki was funded by the award from the Nuffield Foundation.

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Fig. 4.

a) Dielectric loss curves from the Langevin equation.

1) $I = 100 \times 10^{-40}$ gm cm^2; β = 10 THz; γ = 70 THz.

2) β = 30 THz.

D = peak of the dielectric loss curve at GHz frequencies.

P = peak of the far infra-red Poley absorption at THz frequencies.

b) Power absorption with the parameters of fig (4a, curve 1).

Ordinate: a) Dielectric loss

b) Power absorption coefficient in neper cm^{-1}.

Abscissa: a) log (f/THz)

b) $\bar{\nu}$/cm^{-1}.

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