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FAR-INFRARED SPECTROSCOPY OF LIQUID CRYSTALS

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Abstract—The far-infrared spectra of 7CB in the unaligned and aligned nematic phases are markedly different in overall intensity and absorption band-shape detail. Effects persist into the apparently isotropic solution as typified by CH_2Cl_2 solutions.

INTRODUCTORY REVIEW

The object of this paper is to demonstrate how submillimetre waves, in conjunction with dielectric studies, may be used to aid in the evaluation of the interactions and dynamics associated with the molecules of a mesophase.(1) With such an objective the first far-infrared study of the nematic phase of *p*-methoxybenzylidene *p'n*-butylaniline (MBBA) was carried out independently by Bulkin and Lok(2) and by Evans *et al.*(3) in 1973. The nematic phase (so called from its thread-like appearance under a microscope) is a type of mesophase (or liquid crystal) cloudy in appearance and oily in texture which exists in a temperature range between the solid (crystalline or waxy) and the clear isotropic (i.e. monorefringent) liquid. When a magnetic or electric field is applied the nematic sample becomes birefringent, although still fluid, so that the frequency dependent permittivity and loss has components perpendicular and parallel to the external field vector. In this condition (the aligned mesophase) molecules may be pictured as sharing a common macroscopic orientation along the so-called director axis, whose meandering in space is fixed in the direction of the applied aligning field.

The main feature of the MBBA far-infrared spectrum is a strong and broad absorption band peaking at 130 cm^{-1}. In the pure isotropic phase this shifts slightly to lower frequencies (123 cm^{-1}). The band seems almost to disappear in very dilute solution, and broadens considerably on heating a moderately dilute solution of MBBA in cyclo-octane. At the same time the peak moves to a lower frequency. Thus the absorption is markedly environment-sensitive, the near neighbour interactions involved being strong in the pure nematic phase. It is justifiable to conclude therefore that its origin is torsional oscillation of the MBBA resultant dipole vector μ, occurring at a higher frequency than is usual for isotropic, dipolar liquids such as benzonitrile, neat or in a non-dipolar solvent. In these latter cases it is well known that this so-called Poley absorption is a high frequency continuation of the dielectric loss curve, in the past almost universally and erroneously attributed to rotational diffusion of the inertialess, smooth, hard sphere along one of the diameters of which is positioned a dipole moment. One of the most far-reaching consequences of submillimetre spectroscopy is the realisation that it is essential to regard the whole loss or absorption profile, from static to the high frequency return to transparency of the Poley band as a continuous function of frequency arising from an ensemble dynamic process evolving continuously with time from the initial $t = 0$. On this basis Evans *et al.*(3) carried out some model calculations of the MBBA absorption. The first of these involved a theory of itinerant oscillation due to Hill(4) and Wyllie(5) and of random hopping from discrete libration sites due to Brot.(6) Both were developed by Larkin(3) for use in this type of study. It was found that the potential well experienced by an MBBA molecule in the field of its neighbours needs to be considerably narrower and steeper than that of isotropic dipolar liquids. The well-depth estimated for best fit agreed surprisingly well with a rough calculation using a potential of the form $V = a\exp(-br) - C/r^6$ in which the only intermolecular interactions considered were those between the benzene rings of MBBA packed in an idealized geometry.

A second calculation was later described by Evans and Evans(7) where the development in time of the MBBA dynamics was approximated using a number of basic statistical theorems concerning the canonical ensemble.

Despite this it must be emphasized that any modelling of the rototranslational dynamics in MBBA must of necessity be crude and approximate because of the mathematical need to assume rigid, whole molecule libration, using a very simple representation of the intermolecular potential. Both the Brot/Larkin and Wyllie/Larkin calculations(3) are based on a stochastic theory of the Brownian motion, so that the explicit form (but not the absolute magnitude) of the intermolecular potential is lost in the statistical averaging. The MBBA absorption/loss profile is assuredly environment sensitive, and best described as arising from the librations of a dipole within a flexible framework, the motions of which are determined by and in turn determine the character of the nearest neighbour surroundings.

Dipole–dipole interaction is of some limited importance in the nematic phase and contributes to the far-infrared/dielectric absorption, but has been ignored in our model calculations. It has been observed that in solid MBBA and 130 cm^{-1} band splits into at least four partially resolved peaks,(3) so that there is a possibility, as pointed out by Sciesinska *et al.*(8) that the torsional vibrations and other low frequency *internal* modes of the MBBA molecule account for all the absorption below 170 cm^{-1}. They cite as evidence changes in the spectra which they associate with different phases of MBBA solid and in the persistence of the absorption in solution. However, as mentioned above, the experiments of Bulkin and Lok and of Evans *et al.* indicate that this is not the case, i.e. the 130 cm^{-1} band shape and position is dilution sensitive. Furthermore, it is a fundamental theorem(9) that all dipolar fluids in which multibody interactions predominate must have a Poley absorption somewhere in the far-infrared frequency region.

The low frequency loss curve in MBBA, i.e. the extrapolation of the 130 cm^{-1} band to MHz frequencies, appears to cover in this representation little more than 1.3 decades at half peak height. It would seem possible, therefore, to describe this curve by the classical Debye theory of rotational diffusion. However, this approach fails badly at frequencies greater than 5 cm^{-1}, where a low intensity plateau appears theoretically at $\alpha(\bar{\nu}) \doteqdot 2$ neper cm^{-1}. (Here $\alpha(\bar{\nu})$ is the optical absorption coefficient related to dielectric loss, ϵ'', by $\alpha(\bar{\nu}) = 2\pi\epsilon''\bar{\nu}/n(\bar{\nu})$, where $n(\bar{\nu})$ is the refractive index.)

Studies are reported in this paper of the cholesteric phases of cholesteryl linoleate and cholesteryl oleyl carbonate, and of the nematic and aligned nematic states of 4*n* heptyl 4′cyanobiphenyl (7CB) using submillimetre absorptions. In this molecule the resultant dipole moment lies along an axis such that a very high activation energy libration process only is infrared active. Small amounts of rigid, intensely dipolar molecules such as CH_2Cl_2 have been introduced into these phases so that the effect of a liquid crystalline environment on the intensity, position and bandshape of the far-infrared *probe* absorption may be monitored.

The following advantages accrue.

(1) Cross-correlation terms between guest molecules (dynamic and electrostatic), not amenable to ready mathematical analysis, are minimised in dilute solution in the nematic or aligned nematic solvent.
(2) The probe can be chosen to be particularly suitable for model simulation of its absorption profile (i.e. to be rigid and intensely absorbing).
(3) The influence of a liquid crystalline environment on molecular motion may be measured directly against the equivalent spectra in an isotropic solvent such as CCl_4.

We monitor below with far-infrared absorption peaks the alignment of 7CB with both a.c. and d.c. electric fields of up to 7 kV cm^{-1}.

The 7CB spectra are rich in detail and thus in intermolecular dynamical information, but consequently difficult to model satisfactorily. However, an attempt has been made with the method of Evans and Evans mentioned above. Probing techniques simplify the mathematical tasks bringing it into the realm of the tractable.

EXPERIMENTAL

The spectra were obtained with a Grubb–Parsons/N.P.L. Mark III cube interferometer using phase modulation of the signal reaching the detector (IR 50 Golay). Signal-to-noise ratios are estimated to be high enough for an uncertainty of *ca.* ± 2% or less in the optical absorption coefficient $\alpha(\bar{\nu})$. Special care was taken in the dilution studies to eliminate uncertainties in concentration by making each solution up by weight to 0.1 mg.

A cell for field applications was constructed entirely from poly 4 methyl pent-l-ene polymer (TPX) except for the copper electrodes, whose spacing was accurately defined. The fields were applied parallel to the TPX windows, so that alignment of the molecules perpendicular to the submillimetre radiation was maintained. For 7CB a threshold d.c. voltage of about 2 kV was required before intensity effects and splittings became discernible. Preliminary runs on the nematic phase of 8CB (the *n*-octyl analogue of 7CB) show that a considerable time (up to 1 or 2 hr) elapses before the absorption intensity has diminished to equilibrium.

RESULTS AND DISCUSSION

The effect of applying an increasing d.c. electric field to the nematic phase of 7CB is to decrease the overall intensity across the whole of the far-infrared range and the spectrum is split into peaks hitherto unresolved in the unaligned condition. An intensity decrease on application of an external field has been observed in the Raman by Schwartz and Wang.(10) An explanation was given in terms of the collective stabilization due to the large ensemble of molecules aligned by the field. However, the appearance of so many extra peaks in the far-infrared is entirely novel. The signal-to-noise ratio of a typical spectrum is high.

If these peaks are intermolecular in origin then one possible explanation of their appearance is that the increased alignment under the effect of a field accentuates the underlying lattice modes, i.e. brings out single-crystal type behaviour but with the residual translational freedom (N.M.R. studies)(11) associated with the liquid crystal phase still being retained. This kind of dynamical effect is indicated also by the fact that the overall intensity drops due to polarization of the radiation reaching the detector, i.e. the aligned nematic phase is acting as a polarizer. The question of what happens to the torsional oscillating Poley absorption in these circumstances is an interesting one. In an attempt to describe quantitatively this process and its low frequency counterpart, the loss peak observed by Moutran(12) in 7CB at 6 MHz, a model for the dynamics in the nematic phase has been developed(7) which produces a single Poley type absorption at about 127 cm^{-1}. However, that this is one of many possible intermolecular mode may be deduced from the field effect described earlier. In reality there are probably many such sharp Poley modes each contributing to the slower diffusional process which appears as a MHz loss peak.

In order to avoid for the moment the difficulties of quantitative interpretation associated with the far-infrared spectra of pure liquid crystals we use in this paper a technique commonplace in NMR studies(11) of probing the cholesteric or nematic environment with small, rigid, dipolar molecules, and observing the effect of the environment on the rotational motions of the probe. We chose CH_2Cl_2 because its far-infrared Poley absorption is intense and well-defined. The far-infrared broad band absorptions in CH_2Cl_2 have been measured carefully in isotropic solutions in CCl_4, decalin and in cholesteryl linoleate, cholesteryl oleyl carbonate and 7CB in order to bring out by direct comparison unusual dynamical effects on the CH_2Cl_2 molecules themselves. Whereas the CH_2Cl_2 band maximum ($\bar{\nu}_{max}$) shifts by about 30 cm^{-1} to lower frequency on dilution in both CCl_4 and decalin, there is a smaller corresponding change when CH_2Cl_2 is dissolved in cholesteryl linoleate and cholesteryl oleyl carbonate. This may be attributed to a persistence of statistical cross-correlations (time dependent Kirkwood factor) which vanish gradually in isotropic solvents. The observed integrated intensity per molecule (A/N) of CH_2Cl_2 is decreased significantly compared with that in CCl_4 or decalin. This reflects an unusual constraint on angular movement (polarisation) which persists when the concentrations of CH_2Cl_2 are such that no liquid crystalline properties are apparent on a macroscopic scale, e.g. when birefringence has disappeared from the 7CB solutions. This substantiates recent Kerr effect studies(13) where it was shown that the beginnings of liquid crystal behaviour can be discerned in the 'isotropic' phase long before the transition temperature into the mesophase. In the mesophase itself, this type of partial ordering was first observed by Saupe(14) using NMR methods of studying benzene in a nematic phase. Additional dynamical information is found in the far-infrared because the bandshape of the Poley absorption contains dynamical information at short times in the orientational autocorrelation function, while NMR studies yield areas beneath a correlation function, and not the details of its analytical dependence.

By reproducing the autocorrelation function appropriate to the far-infrared by a suitable model (in this case itinerant oscillation), the following related functions can be calculated:

(i) the orientational a.c.f., or dielectric decay function $\langle \cos \theta(t) \cos \theta(0) \rangle$, where θ is the angle between the dipole and the measuring field;
(ii) the torque a.c.f. which mirrors the molecular librations by oscillating about the time axis;
(iii) the angular velocity a.c.f., the area beneath which is the NMR spin-rotation relaxation time.

CONCLUSIONS

(1) The far-infrared spectra of 7CB in the unaligned and aligned nematic phases are markedly different in overall intensity and in details of the absorption. This difference could conceivably be useful in the analysis of the aligned liquid-crystals used in display devices.
(2) The integrated intensity per molecule of the CH_2Cl_2 Poley band is anomalously low when dissolved in three different solvents which have liquid crystal phases. This persists into the apparently isotropic solution.

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