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Submillimetre wave spectroscopy of 4-*n*-alkyl-4′-cyano biphenyl liquid crystals

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The absorption coefficient of the 4-*n*-alkyl-4′-cyano biphenyls has been studied in the submillimetre wave range 50–220 cm^{-1}. Molecular processes which give rise to superimposed but distinct absorption bands are reported. These processes have been analysed using a multi-oscillator model for the observed absorption and are assigned to the Poley absorption as well as to intermolecular and intramolecular mechanisms. Spectra at temperatures in the range 20–70°C and of solutions in cyclohexane support the proposed assignments.

1. Introduction

Far infrared (F.I.R.) spectroscopy of liquid crystals is of significant importance because it may be used to probe the liquid-crystalline order. The assignment of the spectral details to the particular aspects of molecular motions offers a challenge to the spectroscopists. Raman spectroscopy has been a convenient technique to observe the molecular motions, which are affected by neighbouring molecules, and these extend in frequency from the microwave to the submillimetre wave region. However, due to the development of fast Fourier transform techniques and digital computers. F.I.R. spectroscopy has also become a versatile complementary technique. F.I.R. spectroscopy allows for the simultaneous observation of different kinds of molecular motions, such as the librational motion of the entire molecule, its intramolecular motions and the intermolecular lattice vibrations. A wealth of information regarding these molecular motions and their interactions can, therefore, be obtained from F.I.R. spectroscopy.

Both smectic and nematic liquid-crystalline phases have been extensively studied by Raman spectroscopy and these investigations are reviewed by Bulkin [1]. The molecular dynamics of mesogenic phases has been discussed and an attempt has been made by Evans [2] to simulate the results. There have been some F.I.R. studies on mesogenic phases [3–10] and in most of these studies the spectra were interpreted from the results on unrelated mesogens and were concerned with the frequency shifts, change in band shape and amplitude of the absorption profile with temperature. In general it is difficult to assign these bands to particular molecular groups or mechanisms. In the absence of any direct evidence several complementary techniques have been used. Venugopalan and Prasad [11] have studied systematically the homologous series of 4,4′-di-*n*-alkoxyazoxy benzenes. Janik *et al.* [12] and Godlewska *et al.* [13] have attempted to correlate F.I.R. studies with neutron scattering experiments on these liquid crystals. Information about molecular motions can also be obtained by comparing the spectrum of the liquid-crystalline phase with that of model molecules with similar dipolar groups to those in liquid crystals. This enables us to determine what similarity, if any, is present between the molecular motions of polar groups in the liquid crystals and in simpler model molecules. For the cyanobiphenyl liquid crystals certain experimental difficulties were experienced in the earlier work and are detailed here.

Liquid crystals of the type 4-*n*-alkyl-4′-cyano biphenyls are of particular interest due to their technological importance. Some dielectric and F.I.R., absorption studies are reported in the literature [14–17]. For these F.I.R. absorption measurements certain experimental difficulties were encountered, for example Reid and Evans [14] observed that the absorption coefficient depends on the thickness of the sample. It was pointed out by Evans [15] that this effect was caused by the triboelectricity produced by the friction on the poly-4-methyl-1-pentene(TPX) windows, which could be eliminated by preheating the windows. Also in his paper [15], a fine structure in the absorption spectrum of 4-*n*-heptyl-4′-cyanobiphenyl (7CB) dissolved in cyclohexane was reported with its origin not yet established. In this paper, we report results on 4-*n*-hexyl-4′-cyano biphenyl(6CB) and 7CB obtained with improved instrumentation and present some aspects of the results, which establish that F.I.R. absorption can be used successfully to probe molecular order in liquid crystals. The order in liquid crystals can be altered by varying the temperature and the alignment of the director through the application of electric or magnetic fields. We attempt to assign the characteristic bands of the nematic phase in unoriented samples in this work.

2. Materials and experimental

6CB and 7CB were supplied by BDH Chemicals Ltd. and were used as such. The transition temperatures quoted by the suppliers and measured by us are given in table 1. We have checked these transition temperatures using a Perkin-Elmer model 4, D.S.C. and they are found to be in agreement with the quoted values to within ± 1°C. F.I.R. absorption spectra were recorded using a phase modulated Grubb–Parsons Michelson cube interferometer. The interferometer is interfaced with a 380Z Research Machines microcomputer [18]. The microcomputer controls a stepper motor, which in turn moves the travelling mirror. The system is designed to collect data for eact step and to transfer it to a Vax 11/730 minicomputer, which is used to Fourier transform the data at the end of each experiment. A thin black polythene sheet is placed in front of the detector to prevent infrared radiation from entering the detector. The small displacement of the mirror for each step and proper filtering of the radiation entering the detector ensures an elimination of the effects due to aliasing, which are inherent in the discrete Fourier transformation [19, 20]. A 6 μm polythene beam divider with a transmission spectrum between 50 and 250 cm^{-1} is used. Z-cut quartz plates each of 1 mm thickness were used as windows for the cell. The combination of the 6 μm beam divider and the Z-cut quartz windows, restrict the available

Table 1. Transition temperatures of 6CB and 7CB.

	Transition temperatures/°C			
	Quoted		Measured	
Sample	C–N	N–I	C–N	N–I
6CB	14·5	30·0	15·0	29·0
7CB	30·0	42·5	29·5	41·0

spectrum however to the spectral range 50–220 cm^{-1}. The quartz windows do not absorb any solvents and are found not to generate any triboelectricity. With this arrangement we have not observed any dependence of the absorption coefficient of the liquid crystal on the thickness of the sample. The absolute accuracy in the absorption coefficient values in between the various experimental runs is estimated to be 5 per cent however the relative accuracy of the spectral ordinate with respect to wavenumber is found to be in between 1 to 2 per cent. Some 1000 data points with a small step of 0·00025 cm of the moving mirror are collected for every run. This gives a frequency resolution of 2 cm^{-1}. However due to apodization the upper limit in the resolution of the absorption spectrum is 3·6 cm^{-1}. Temperature is varied by passing a variable current through two wire heaters which are connected in series with each other. These heaters are in the form of small strips and are in good thermal contact with the body of a cylinder attached to the cell. The cell and its attachments are of metal and together they form an extended volume which has a large heat capacity. With this arrangement, temperature in the duration of an experiment lasting ca. 30 minutes does not vary by more than 0·5°C. A thermocouple is inserted into the variable cell which is in thermal contact with the sample.

3. Results

Figure 1 shows the spectra of 6CB and 7CB at a temperature of 21°C that is 6CB is in the nematic phase and 7CB in the solid phase. Three distinct features are observed in these spectra; a broad shoulder centred at approximately 100 cm^{-1} and relatively two narrow absorptions at 156 cm^{-1} and 175 cm^{-1} for 6CB and 150 cm^{-1} and 175 cm^{-1} for 7CB. Broadly speaking these observations are rather similar to those of Reid and Evans [14] and Evans [15]. However closer observation of the spectra reveals the presence of at least two additional absorptions on the low frequency side. These observations are being reported for the first time and are of interest because they suggest intermolecular lattice vibrations which are related to the long range

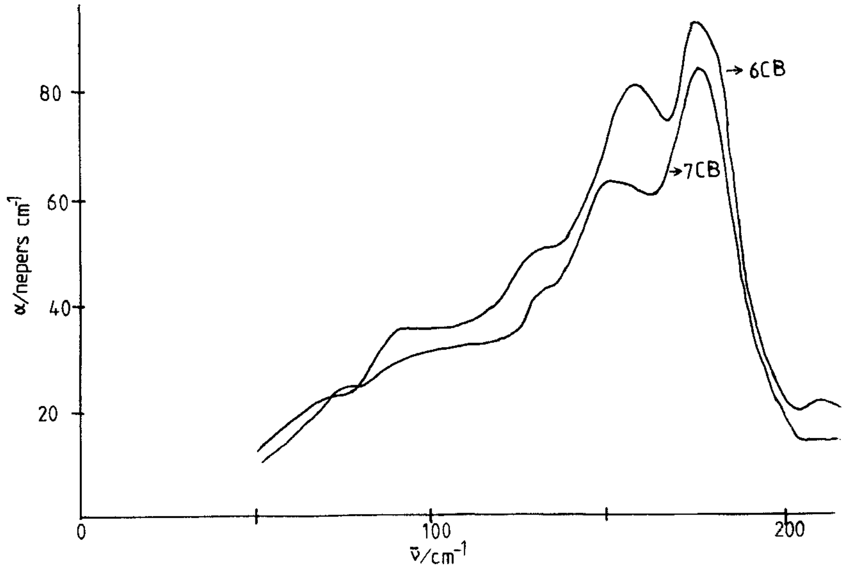


Figure 1. Absorption spectra of 6CB and 7CB at 21°C.

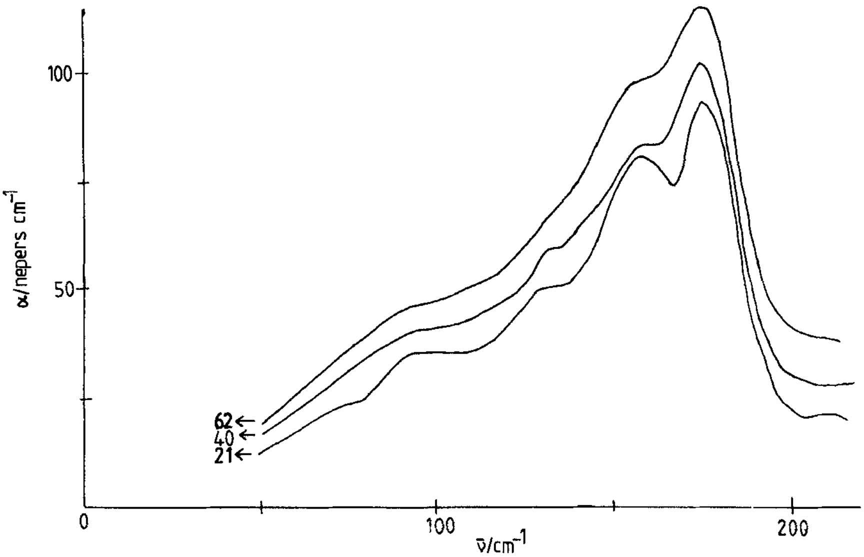


Figure 2. Absorption spectra of 6CB at different temperatures.

orientational order of the liquid crystals in the nematic phase. Figure 2 shows the absorption spectra of 6CB at three temperatures. It is observed that as the temperature is raised some of these absorption bands disappear leaving a broad shoulder on the low frequency side while on the high frequency side a persistent strong absorption at 175 cm^{-1} continues to be observed in the various phases. Similar observations are made for 7CB and are shown in figure 3.

The solution spectra of 6CB and 7CB in cyclohexane at 21°C are also shown in figures 4 and 5, respectively. Sharp absorptions observed in the solution spectra at

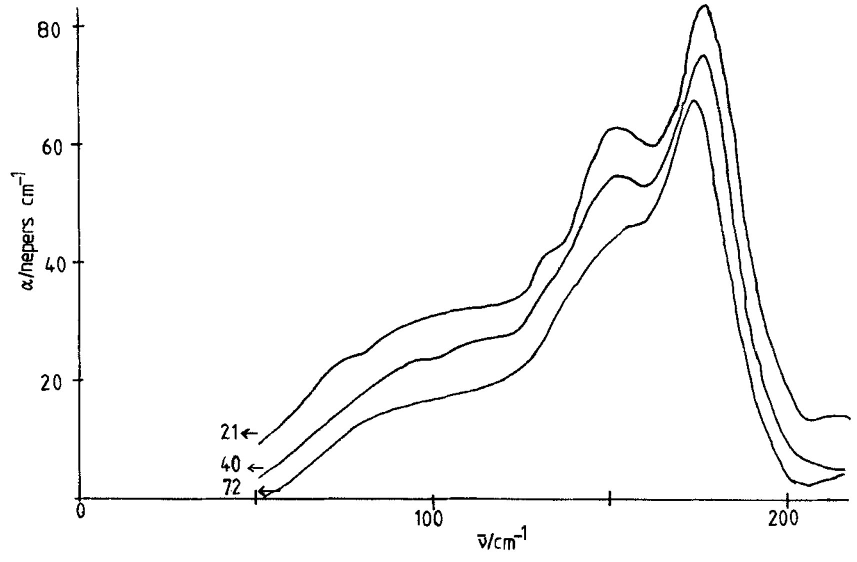


Figure 3. Absorption spectra of 7CB at different temperatures. The ordinate for the 40 and 72°C spectra are shifted downwards by 7 nepers cm^{-1} and 9 nepers cm^{-1} each from their actual positions.

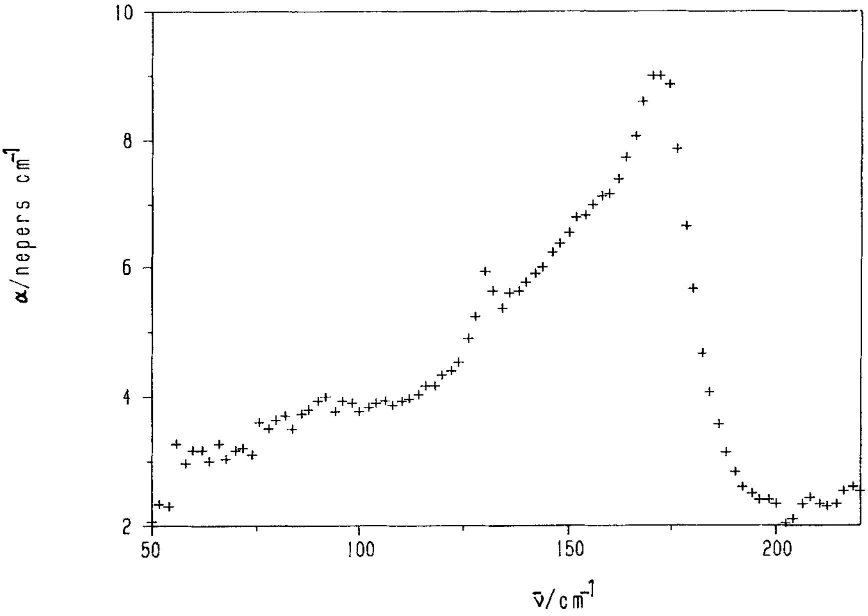


Figure 4. Absorption spectrum of 6 per cent solution of 6CB in cyclohexane.

approximately 128 cm^{-1}, may be ignored as these are due to the cut-off frequency of the Z-cut quartz windows. This is confirmed by recording spectra with TPX windows, where no such lines are observed. These spectra are entirely different from those reported earlier by Evans [15]. In the spectra reported by him, a number of sharp lines

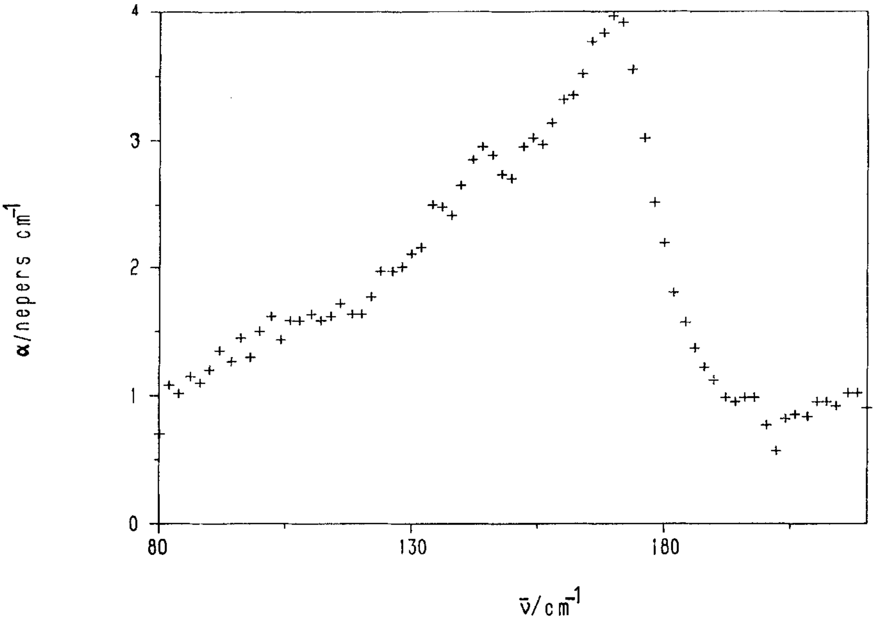


Figure 5. Absorption spectrum of 5 per cent solution of 7CB in cyclohexane.

were observed. However an absence of these lines from the present spectra demonstrates that these sharp lines could possibly have arisen from the aliasing phenomenon of discrete Fourier transformation. Aliasing in Fourier spectroscopy can be eliminated only by proper band limiting of the signal. These lines are not observed now because the desired signal is being properly filtered, as already described in the experimental section. It may be observed that these solution spectra also have only three distinct features which correspond to those observed at higher temperatures in the isotropic phase. This indicates that as expected certain bands which are present in the spectra of neat form in ordered phases at 21°C are absent from the disordered solution spectra. From figures 4 and 5 we note that some modes of absorption present in the pure liquid at 21°C disappear in solutions of cyclohexane.

On the application of a d.c. electric field (8 kV/cm), we find that the overall intensities of the absorption at 158 cm^{-1} and 175 cm^{-1}, for 6CB in its nematic phase see (figure 6.) are reduced considerably and these are only barely distinguishable from each other. However a broader peak centred at 100 cm^{-1} does emerge in the spectrum eventually, and this grows to a significant amplitude as the d.c. field is increased. We observed therefore that an external d.c. electric field enhances the Poley absorption in liquid crystals.

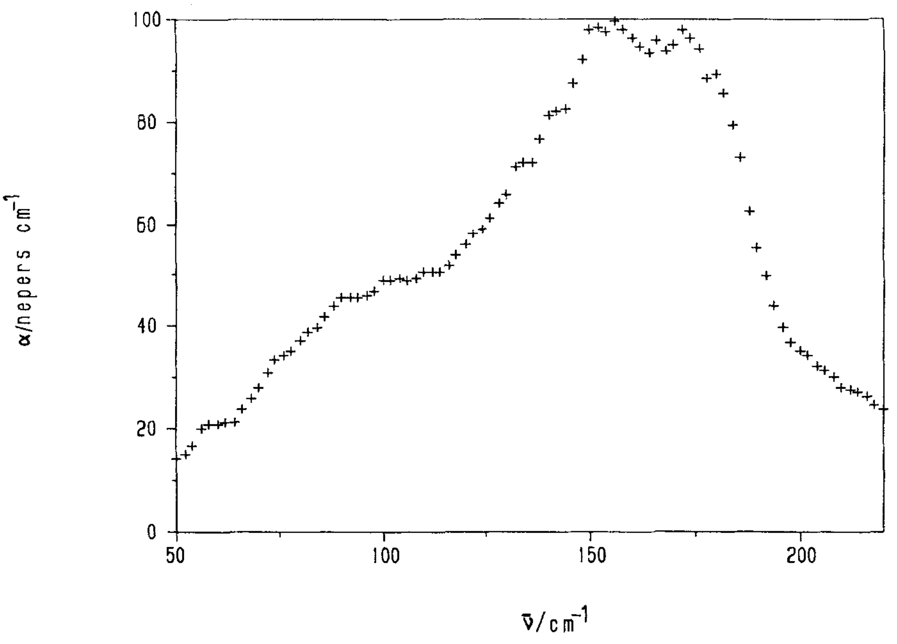


Figure 6. Absorption spectrum of 6CB in the presence of an 8 kV d.c. field.

4. Theory and discussion

A system composed of different molecular motions, presumably uncoupled, may be described by a linear combination of a number of damped harmonic oscillators. Each oscillator of the system may be represented in the absence of the electric field by the equation,

$$I\ddot{\phi} + \zeta\dot{\phi} + V_0\phi = 0, \tag{1}$$

where ϕ is the angle that the electric dipole moment makes with the reference direction. The reference direction is that of the electric field which is assumed to be *on* for $t = -\infty$ prior to its being switched off at $t = 0$. I is the moment of inertia of the reference molecule which is represented by the oscillator. $\zeta\dot{\phi}$ is the frictional couple acting on the molecule. The potential energy of the harmonic oscillator is

$$V(\phi) = 1/2V_0\phi^2, \tag{2}$$

where V_0 is a constant. Let $\beta = \zeta/I$; β being the friction coefficient. Using the linear response theorem [21],

$$\varepsilon^* = \varepsilon(\omega) - j\varepsilon(\omega),$$

at an angular frequency ω, becomes

$$\varepsilon^*(\omega) = \frac{S'}{(\omega^2 - \omega_0^2) + j\beta\omega}, \tag{3}$$

Here $\omega_0^2 = V_0/I$, is the resonant frequency of the harmonic oscillator, S' is a constant dependent on the dipole moment and moment of inertia of a molecule.

If the system is assumed to consist of N such uncoupled harmonic oscillators with different characteristic frequencies, then the complex permittivity of the entire system may be given by a linear superposition of the equations of the type [22] (3).

$$\varepsilon^*(\omega) = \sum_{k=1}^{N} \frac{S_k'}{(\omega_{0k}^2 - \omega^2) + j\beta_k\omega}, \tag{4}$$

The subscript k corresponds to the kth oscillator. In this expression, S_k' can be interpreted as the relative magnitude of the dielectric loss corresponding to the kth oscillator. Separating out the imaginary part of equation (4) in which we are interested, we obtain,

$$\varepsilon''(\omega) = \sum_{k=1}^{N} \frac{S_k'\beta_k\omega}{(\omega^2 - \omega_{0k}^2)^2 + \beta_k^2\omega^2}. \tag{5}$$

The power absorption coefficient, $\alpha(\omega)$, is related to dielectric loss via the Maxwell relationship

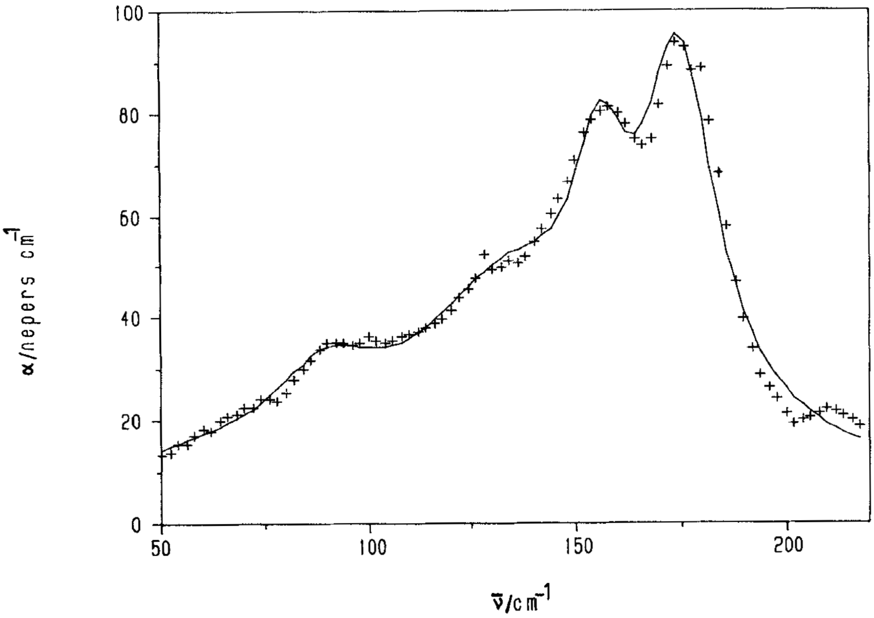
$$\alpha(\omega) = \frac{\omega\varepsilon''(\omega)}{n(\omega)c}, \tag{6}$$

where $n(\omega)$ is the real part of the refractive index of the system under investigation at the angular frequency ω. The power absorption coefficient in wavenumbers ($\bar{\nu} = \omega/(2\pi c)$) can be expressed using equations (5) and (6) as

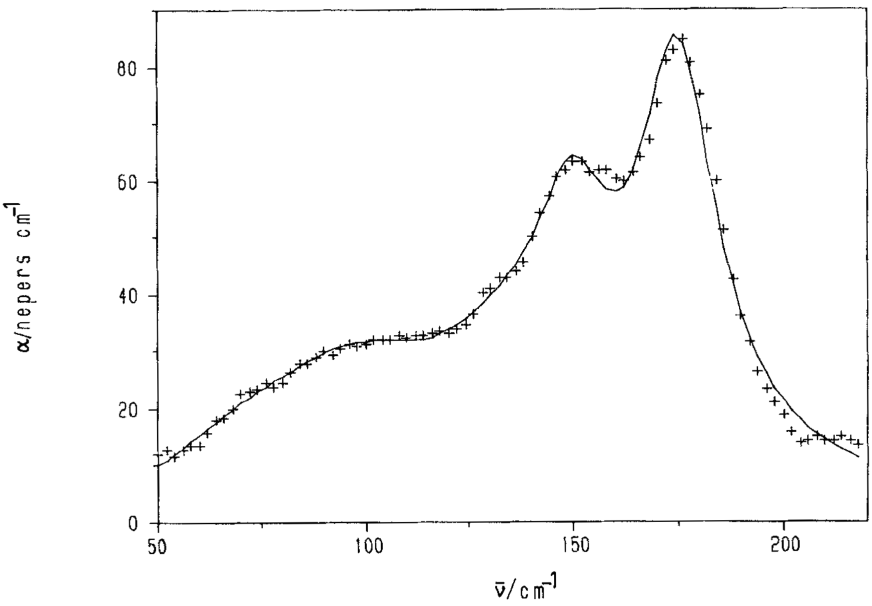
$$\alpha(\nu) = \frac{2\pi}{n(\bar{\nu})} \sum_{k=1}^{N} \frac{S_k\bar{\nu}^2\beta_k}{(\bar{\nu}_{0k}^2 - \bar{\nu}^2)^2 + \bar{\nu}^2\beta_k^2}. \tag{7}$$

Now the strength of each oscillator is given by the ratio S_k/β_k and the friction of each oscillator by β_k. In the absence of measurements for $n(\bar{\nu})$, we assume it to be approximately a constant over the frequency range of the present work. This can be justified partially on the basis of known results of the refractive index for some dipolar liquids [23], which indicate that $n(\bar{\nu})$ varies by not more than 12 per cent in the spectral range 50–220 cm^{-1}. This percentage variation is unlikely to affect the general fitting of the $\alpha(\bar{\nu})$ data. To our knowledge no experimental results on $n(\bar{\nu})$ for these liquid crystals are available.

The spectra for 6CB and 7CB at different temperatures show multiple absorption bands. These spectra have been fitted to the model to obtain the parameters for each



(a)



(b)

Figure 7. (*a*) Numerical curve fitting of the spectrum for 6CB at 21°C. +, Experimental; −, numerical. (*b*) Numerical curve fitting of the spectrum for 7CB at 21°C. +, Experimental; −, numerical.

mode of molecular motion. A Harwell subroutine library is used to obtain the fit, the subroutine employed is VA05A which can handle upto twentyfive unknown variables to minimize the object function. The method used in this subroutine is a compromise among three different algorithms for minimising a sum of squares, namely Newton–Raphson, steepest descent and Marquardt. Using the ideas of Broyden, in each iteration it improves an approximation to the first derivative matrix. A particular difficulty is experienced in obtaining a fast convergence, especially when we used all three characterizing parameters namely $S_k(\bar{\nu})_k$ and β_k for each oscillator and a total of fifteen parameters ($k = 1, \ldots, 5$), as variables. Hence we first fix the positions of the frequency maxima $(\bar{\nu})_k$, which are known accurately from the spectra, this is then followed by varying S_k and β_k ($k = 1, \ldots, 5$). This procedure gave a fast convergence and the same end results at the minimum of the least squares function, for different starting values for amplitude and friction coefficient variables. Having obtained the least squares minimum we perturbed slightly the frequency positions of maximum absorption and thus obtained improved fits for the experimental data to the model. The fitting procedure is repeated with different starting values for the variables; the final test squares minimum is found to be nearly the same in all cases. A χ^2 test is performed after having allowed for a 5 per cent error in the ordinate accuracy. We have found that χ^2 calculated from the numerical fitting is always lower than that obtained from statistical tables. This implies that in all cases the fitting is optimal at the 95 per cent confidence level. It should be stressed here that closeness of the experimental data to the model needs to be interpreted with caution since as many as ten variables are involved in the computation n.b. frequency positions being known almost exactly from the spectra. What the fit does indicate however is that to a first approximation the system comprises a number of damped harmonic oscillator type motions. Amplitude, frequency and friction coefficient of these motions can be established and these can form a starting point for a discussion of the true nature of these absorptions.

The quality of the fits for 21°C spectra is shown in figures 7 (*a*) and (*b*). The fits for the higher temperature spectra are also found to be good and the best fit parameters for 6CB and 7CB are listed in tables 2 and 3, respectively. At higher temperatures

Table 2. Numerical curve fitting results for 6CB at different temperatures.

Temperature/°C	Phase	Oscillator type	S_k/cm^{-2}	β_k/cm^{-1}	$\bar{\nu}_k$/cm^{-1}	(S_K/β_k)†/cm^{-1}
21	Nematic	Poley	30·9	166·0	75·0	0·19
		Intermolecular	5·0	32·2	90·0	0·16
		Intermolecular	13·1	53·7	135·0	0·24
		Intramolecular	3·7	16·0	156·0	0·23
		Intramolecular	8·1	20·6	175·0	0·39
32	Iostropic	Poley	30·6	118·6	96·0	0·26
		Intermolecular	6·5	62·6	140·0	0·10
		Intramolecular	6·8	38·2	160·0	0·18
		Intramolecular	5·1	17·6	175·0	0·29
40	Isotropic	Poley	42·0	115·5	95·0	0·36
		Intermolecular	2·6	35·1	132·0	0·07
		Intramolecular	14·6	48·5	158·0	0·30
		Intramolecular	5·5	18·1	175·0	0·31
62	Isotropic	Poley	47·7	116·5	95·0	0·41
		Intramolecular	25·9	59·8	159·0	0·43
		Intramolecular	4·0	15·4	175·0	0·26

† (S_K/β_k) represents the strength of the oscillator.

Table 3. Numerical curve fitting results for 7CB at different temperatures.

Temperature/°C	Phase	Oscillator type	S_k/cm^{-2}	β_k/cm^{-1}	$\bar{\nu}_k$/cm^{-1}	(S_K/β_k)†/cm^{-1}
21	Nematic	Poley	13·3	69·4	76·0	0·19
		Intermolecular	8·2	52·9	100·0	0·16
		Intermolecular	5·8	44·9	136·0	0·13
		Intramolecular	4·8	22·1	150·0	0·22
		Intramolecular	8·9	22·7	175·0	0·39
30	Nematic	Poley	9·7	55·7	70·0	0·17
		Intermolecular	5·3	48·6	95·0	0·11
		Intermolecualr	6·9	51·6	114·0	0·13
		Intramolecular	11·1	36·7	151·0	0·30
		Intramolecular	6·6	18·3	176·0	0·36
40	Nematic	Poley	22·5	97·9	83·0	0·23
		Intermolecular	6·2	54·0	114·0	0·11
		Intramolecular	8·8	34·6	150·0	0·25
		Intramolecular	6·5	19·9	175·0	0·33
72	Isotropic	Poley	40·0	144·0	106·0	0·28
		Intramolecular	6·5	33·9	152·0	0·19
		Intramolecular	4·5	16·6	174·0	0·27 .

† (S_K/β_k) represents the strength of the oscillator.

a smaller number of oscillators are required to reproduce the experimental data. This shows that certain processes disappear at higher temperatures. Having resolved the spectra into different, individual processes we attempt to assign each process at the molecular level and these are grouped as intramolecular absorptions, Poley absorption and intermolecular lattice vibrations.

5. Intramolecular absorptions

Careful observation of the figures and the tables suggest that the processes on the high frequency side, in the range 150–175 cm^{-1} do not change on their frequencies

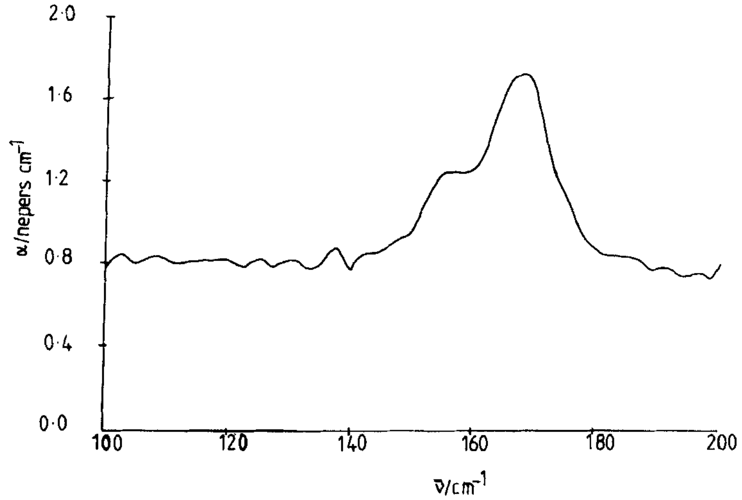


Figure 8. Absorption spectrum of 1 per cent molar benzonitrile solution in cyclohexane.

of maximum absorption appreciably on forming isotropic phase either thermally or on dilution in cyclohexane. This immediately suggests that these peaks originate from intramolecular modes. Of these two the higher frequency mode seems more fundamental as its position is not altered at all, whereas the lower frequency mode appears to depend to some extent on the liquid-crystalline order and on the end chain length; this mode has slightly different frequencies for 6CB and 7CB. The nitrile group can execute torsions about the molecular axis on its own or in conjunction with the benzene ring to which it is attached. Hence there are two possible modes which exhibit absorptions in the range 150–175 cm^{-1}. For benzonitrile we observe a single peak at 170 cm^{-1} (see figure 8) and for cyanobiphenyl Evans [15] observed two peaks at 160 and 180 cm^{-1}. These observations suggest that the lower frequency mode, at 156 cm^{-1} for 6CB and 150 cm^{-1} for 7CB, is due to the rotation of cyanophenyl whereas the higher frequency mode, 175 cm^{-1} for both 6CB and 7CB, is due to the CN group torsions alone.

6. Poley absorption

Poley absorption is a high frequency adjunct of the Debye rotational diffusional process. For dipolar liquids, Poley absorption is associated with the moment of inertia of the reference molecule and the potential energy of interaction with its surroundings. Poley absorption is that part of the total absorption which is due to librations of the dipolar molecule alone; these librations are superimposed on the rotational diffusional process. This part of the absorption is resonant in character.

For a two particle non-linear itinerant oscillator) model, the two particles are assumed to be of equal moment of inertia and are coupled with a cosine potential

$$V = -2V_0 \cos\theta,$$

where θ is the angle the reference dipole makes with the neighbouring dipole, which represents the surroundings. The resonant angular frequency of the absorption (Ω_{FIR}) is approximated by [24–26]

$$\Omega^2_{\mathrm{FIR}} = 4V_0/I(1 - kT/4V_0).$$

V_0 is the magnitude of potential energy of interaction and is given by [26]

$$V_0 = \frac{2(\varepsilon_r - l)}{2\varepsilon_r + l}\frac{1}{l_c^3}\mu^2,$$

where ε_r is the relative permittivity of the medium, l_c is the correlation length i.e., the length over which the neighbouring dipoles are correlated and μ is the dipole moment of a molecule. Now if we assume that these particles are coupled to each other through a harmonic potential (linear itinerant oscillator model) then the angular frequency of maximum power absorption [25] is simply

$$\hat{\Omega}^2_{\mathrm{FIR}} = 4V_0/I.$$

The effect of non-linearity is, therefore, simply to introduce a subtractive term of $kT/4V_0$ from unity. In general $kT/4V_0 \ll 1$, and so the effect of non-linearity is small except at higher temperatures. The effect of an increase of temperature is to decrease V_0 through an increase in l_c. Hence both the linear and non-linear itinerant oscillator models predict a decrease in the frequency of maximum absorption with an increase in temperature. This is in accord with experiment for most dipolar liquids and for alkoxyazoxybenzene liquid crystals [13]. In liquid crystals however, the form of the potential energy of interaction between the neighbouring molecules is likely to be more complicated than for isotropic liquids. Furthermore certain other intermolecular modes of motion may fall into the same range of frequencies as the Poley absorption. We find (see figures 3 and 4) that for the cyanobiphenyls, the Poley absorption is rather a broad peak with little structure and furthermore the width of the peak increases with increase in temperature. It would appear therefore that in the cyanobiphenyls, there is a distribution in the librational frequencies. This may result from the different moments of inertia of the molecule or its parts associated with the motion which also involves a change in the direction of dipole moment. This distribution in the librational frequencies may also come from a distribution in the magnitude and the width of the potential energy of interaction. For this reason we do not observe (see table 3) a systematic trend in the lower frequency part of the F.I.R. absorption with temperature.

A further possibility in the cyanobiphenyls is that librational motion can occur about three mutually perpendicular axes, one of them being the long molecular axis and the other two being perpendicular to this axis. In the nematic phase due to nematic ordering potential the librational motion about the short axes is highly hindered, whereas the librational motion about the long axis is relatively free. In the isotropic phase, the librations about both the long and short molecular axes are possible. In the cyanobiphenyls it appears that the frequencies of these two librational motions are very close and hence they broaden the Poley absorption (see figures 1 and 2) at higher temperatures. The effective moment of inertia of the molecules in the liquid crystal phases seems to be a sensitive function of temperature and this is possibly one of the main reasons for the unsystematic variation of the lower frequency F.I.R. absorption with temperature.

7. Intermolecular vibrations

As previously noted, some absorption frequencies which are present at 21°C are found to be absent from the higher temperature spectra. On heating the samples, a phase change from crystalline to nematic and then to isotropic in the case of 7CB and from nematic to isotropic in the case of 6CB is brought about. This accompanies a removal of the long range molecular order which is present at temperatures below the nematic to isotropic transition. From tables 2 and 3, it may be noted that five oscillating frequencies are required to fit the data below the N–I transition, four in the vicinity and only three well above this transition. This suggests that one of the modes disappears at the N–I transition and the second survives slightly above this transition. We may postulate therefore that at temperatures below the N–I transition two different regimes of molecular long range order coexist. In each of these regimes, the molecules are arranged in a particular manner. The observed modes are proposed to result from the dynamics of the molecules in each of these regimes in a liquid-crystalline system. A possible mechanism of dynamics is the collective motion of the molecules within a regime; termed as pseudo-lattice vibrations of the molecules. As the temperature is raised, one of these regimes disappears followed by the other one at temperatures well above the N–I transition.

These regimes can not exist in dilute solutions of these liquid crystals in non-polar solvents, whose F.I.R. absorption is negligible as the solution is isotropic. The dilute solution spectra of the cyanobiphenyls in cyclohexane (see figures 4 and 5) have not shown these absorption bands and thus support the proposed molecular mechanisms. These absorption bands have been observed for the first time and need to be confirmed by complementary techniques such as Raman spectroscopy and neutron scattering.

8. Effect of temperature on absorption intensity

The overall absorption intensity for most bands of 6CB increase with an increase in temperature. For some bands the increment is higher than for others for the reasons already given. This suggests that the number density of the dipoles involved in the librational and torsional processes increases with an increase in temperature. Of the three curves reported in figure 2, the one with the least absorption intensity corresponds to 6CB in its nematic phase, whereas the remaining two are for its isotropic phase. Since the rotational motion of the molecules is severely hindered in the nematic phase, it is reasonable to expect that the number density of the molecules involved in such motions increases with an increase in temperature. The dependence of the nematic potential on temperature overrides the normal density effect in 6CB. The absorption intensity for 7CB like that of 6CB also increases with temperature from 50–100 cm^{-1}, although the increment is much smaller than for 6CB. On the contrary, the absorption intensity decreases slightly with an increase in temperature for 7CB in the 100–220 cm^{-1} region, except for a marked decrease for the 150 cm^{-1} band. The most likely reason for this odd behaviour could come from the change in density from the crystalline to the nematic phase. One of the three spectra shown in figure 3 (i.e. at 21°C) corresponds to 7CB in its crystalline phase whereas the spectrum at 40°C is that of 7CB in its nematic phase and that at 72°C is in its isotropic phase. Note that the spectra of 7CB at 40°C and 72°C are shown scaled downwards in figure 3. It would seem that the effect of the density change from crystalline to nematic phase competes much more effectively with that arising from the hinderance to librations and torsions in the crystalline and nematic phases. Since figure 3 shows the spectra of three phases of 7CB as opposed to two of 6CB in figure 2, the effect of the density on the spectra is much more apparent in 7CB than in 6CB. Another small possibility may arise from an experimental limitation; the formation of voids in the material on its solidification cannot be avoided completely. Though during the experiment, the sample was cooled slowly to prevent the formation of voids, nevertheless their presence cannot be ruled out. This will introduce an additional complication in the interpretation of the change in the absorption intensity with temperature.

9. Conclusions

The absorption spectrum results from different molecular mechanisms which appear to be uncoupled (or only loosely coupled). These molecular mechanisms are grouped into three categories of molecular motions namely intramolecular motions, molecular libration and pseudo-lattice vibrations. From tables 2 and 3 it may be noted that β_k, which represents the friction of the kth oscillator, is the least for intramolecular motions and is the highest for the Poley absorption. This suggests conclusively that the intramolecular motion is due to the smaller molecular groups; in the present case the nitrile and cyanophenyl groups. Poley absorption is due to the molecular librational mechanism. The friction experienced by the intermolecular motions lies in between these two types of motion. In the nematic phase, the molecules tend to be aligned with respect to the director, with long range order. It seems quite likely that the molecules vibrate either with respect to each other or in unison over a long range, i.e. the so-called director modes. These frequency bands are influenced by the extent of the order and are being observed in the F.I.R.

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