

CHAPTER 4

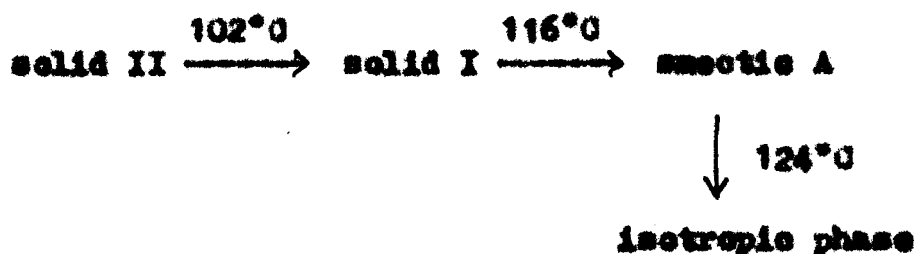
POLYMORPHISM OF THE SPNCTOGEN ETHYL-*p*-AEROXYBENZOATE: FAR-INFRARED AND RAMAN STUDY

4.1 Introduction

Thermotropic mesogens frequently exhibit polymorphic transitions in the solid phase.¹⁻⁵ Owing to the complex structure of mesogenic molecules, such transitions often involve not merely a change of crystal symmetry, but also molecular conformation. Thus, the possible relevance of these transitions to the formation and structure of the mesophase itself has evoked recent interest.⁶ Infrared and Raman techniques, among others, have been used in the past to characterize these transitions in several mesogens⁷⁻¹⁴ However, in many of these cases, the lack of of a detailed knowledge of the crystal structure of the different polymorphs has hampered a clearer understanding of the observed spectral changes. This is especially true of the low frequency spectra in the range below 200 cm^{-1} .

where one often observes the most pronounced differences between the lattice modes of the various polymorphs.

In this chapter, we report the results of a combined far-infrared (FIR) and Raman study of the smectogen ethyl-*p*-oxybenzoate (EPAB). This investigation was motivated by the fact that, unlike the case with most other mesogens, detailed structural data are available¹⁵⁻¹⁷ for this compound in its two crystalline polymorphs as also the smectic phase. EPAB exhibits the following phase transformations upon heating:



Here solid I and solid II denote the polymorphs stable, respectively, above and below 102°C . Amer and Shen¹⁸ have earlier reported the Raman spectra of EPAB in the range $5 - 100 \text{ cm}^{-1}$. In the solid phase, they observed

a single Raman mode at $\sim 22 \text{ cm}^{-1}$, but did not report any differences between the spectra of solids I and II. In contrast, we have noticed marked changes between their FIR spectra in the range $30 - 160 \text{ cm}^{-1}$. In order to further understand these differences, we have studied the FIR absorption of the smectic A and isotropic phases as also the Raman spectra of solids I and II in the region of the internal modes. These results are discussed here in the light of the structural characteristics of the different phases of EPAB.

4.2 Experimental

EPAB obtained from Eastman Kodak Co. was used in the present experiments without further purification. The transition temperatures already mentioned were determined, to within an accuracy of 0.5°C , using a Perkin-Elmer differential scanning calorimeter (Model DSC-2). Polycrystalline samples of solid II and solid I were obtained, respectively, from solvent crystallization and

solidification from the mesophase. Solid I supercools quite easily to room temperature where it exists as a metastable phase for several days¹⁶ before slowly converting to solid II. This made it feasible to investigate the spectra of both polymorphs at room temperature. It is interesting to note that a similar behaviour has been observed in the higher temperature solid phase of CBOOA as well.⁷

The FIR absorption of solid II was studied by dispersing it in the form of fine powder in a polyethylene pellet. The spectra of solid I, smectic A and isotropic phases were obtained with a sample film of $\sim 110 \mu\text{m}$ thickness contained between wedged crystal quartz windows. Other details of the FIR equipment and the experimental procedure have been described in chapter 2 and elsewhere.^{19,20}

Raman spectra were excited by a He-Ne laser with 90 mW of output power at the 632.8 nm wavelength. The

polycrystalline samples were contained in glass capillary tubes and the right angle scattering geometry was used. The scattered radiation was dispersed by a Cary-81 double monochromator equipped with a modified external optics set-up, and detected by a cooled RCA 6852 photomultiplier tube in conjunction with a photon counting system. Whenever required an interference filter peaked at 632.8 nm was inserted in the path of the incident radiation in order to suppress the plasma emission lines from the laser. Further experimental details are given in chapter 2.

4.3 Results and Discussion

a) Molecular Packing and Conformation

Figure 4.1 shows the four possible rotational conformers of the HPAB molecule. The X-ray data of Krigbaum et al^{15,16} show that the molecules in solid II are all in the high energy cis-cis conformation. On the other hand, in solid I they are found to adopt the cis-trans and trans-cis conformations. There is evidence

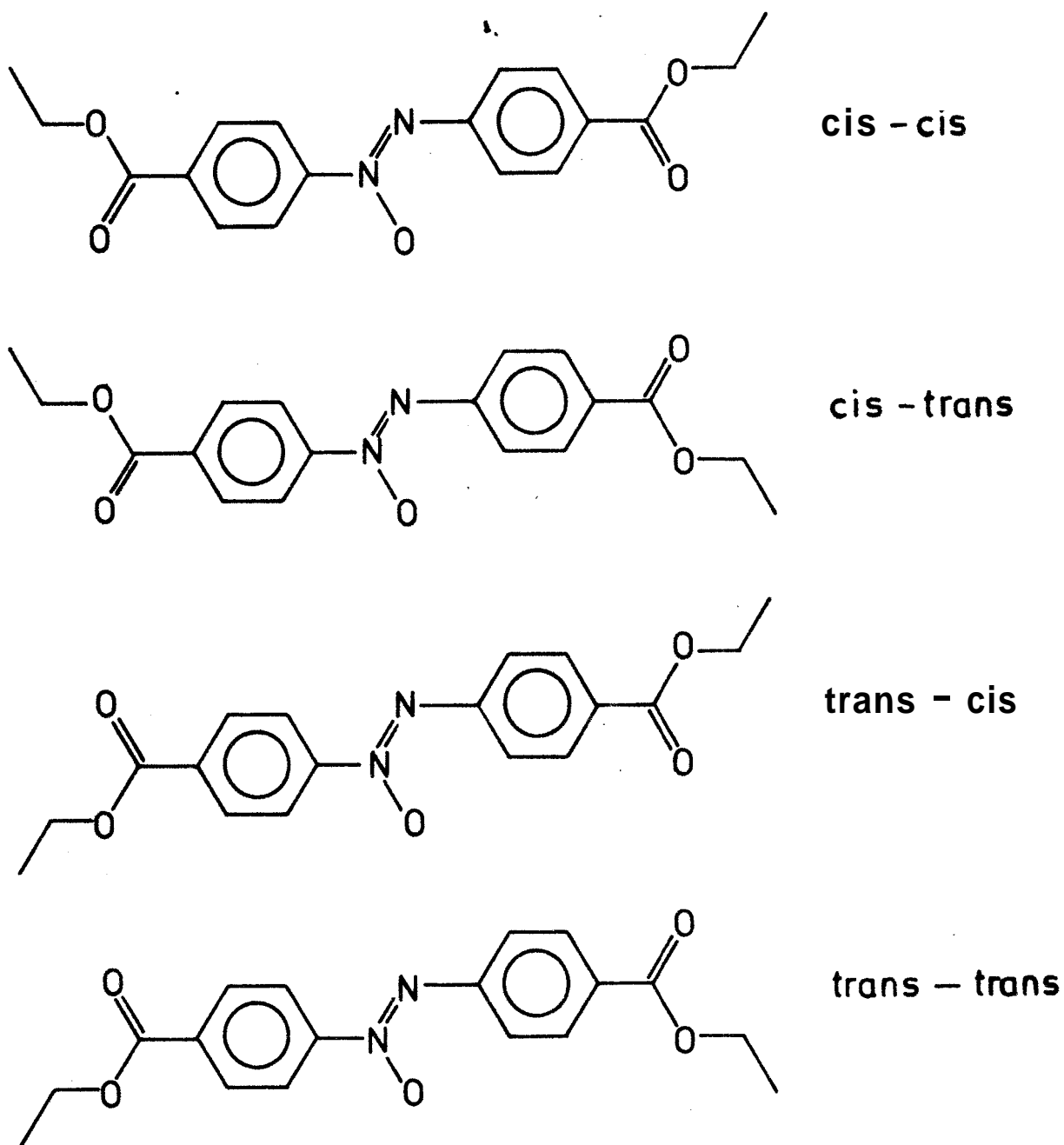


FIGURE 4.1

Four possible rotational conformers of the EPAB molecule- and trans denote the relative orientation of the ester C = O band with respect to the central N - O bond.

of disorder in solid I in the positions of the three atoms of the asoxy group, as they are found to occupy two sets of alternative sites.

Although the X-ray data can yield only a time-averaged picture, it is reasonable to assume that the conformational disorder in solid I arises because of the reorientational jumps executed by the asoxy group between the two alternative positions. This picture is in accord with recent dielectric relaxation studies on the disordered solid phases²¹⁻²³ of several other liquid crystalline materials, all of which feature an absorption peak in the frequency range below 1 Mc. These peaks have been interpreted as arising from the intramolecular reorientations of specific polar groups in the disordered solid phases.

Table 4.1 summarizes the relevant crystal symmetries and the group theoretical representation of the zone-center external optic modes of solids II and I.

Table 4.1

Crystallographic symmetry and the representation of the zone-center external optic modes in the two solid phases

Solid phase	Space group	No. of molecules in the primitive cell	External optic modes	
			IR active	Raman active
II	$C_1^1(P1)$	2	3 A_u	6 A_g
I	$C_{2h}^6(C2/c)$	4	5 $A_u + 4 B_u$	6 $A_g + 6 B_g$

As both polymorphs possess the inversion symmetry, no coincidences are expected between their infrared and Raman active modes except for any accidental degeneracies. The correlation of the molecular, site and factor group symmetry species is shown in table 4.2. We note that each intramolecular mode of the free molecule would give rise to two Davydov components in solid II. In the case of solid I, the number of Davydov components observable in the infrared and Raman spectra is doubled.

In the smectic phase, the X-ray data¹⁷ are found to be consistent with the existence of centrosymmetric dimers, the centres of the two molecules being displaced along their long axes by $\sim 6.3 \text{ \AA}$. Such a molecular association would also lead to strong dipolar interactions between the ester and the amoxy groups of adjacent molecules.

Table 4.2

Correlation of the molecular, site and factor group symmetry species in the two solid phases.

Mole- cular group	Solid II			Solid I		
	Site group	Factor group	Acti- vity	Site group	Factor group	Acti- vity
C_1	C_1	C_1		C_1	C_{2h}	
A	A	A_u A_g	IR Raman	A	A_u B_u A_g B_g	IR IR Raman Raman

b) FIR Spectra

The FIR spectra of the different phases of EPAB are shown in figures 4.2 and 4.3. Below 160 cm^{-1} , solid II exhibits a strong band centred at 80 cm^{-1} in addition to other weak features at 110, 131 and 145 cm^{-1} . Over the same range solid I exhibits a very broad absorption peak centred at 104 cm^{-1} and a weak shoulder at 150 cm^{-1} . The isotropic phase also shows a broad absorption band although it is less intense and its peak position is lower by $\sim 10\text{ cm}^{-1}$ as compared to solid I. In all these cases, the higher frequency band at $180 \pm 2\text{ cm}^{-1}$ is likely to originate from the intramolecular torsion of the CH_3 end groups.

As the EPAB molecule carries a permanent dipole moment due to the central asoxy group, the Polcy resonance^{24,25} due to its librational motion about the long axis will contribute to the FIR absorption in the fluid phases. Furthermore, even in the isotropic phase, there

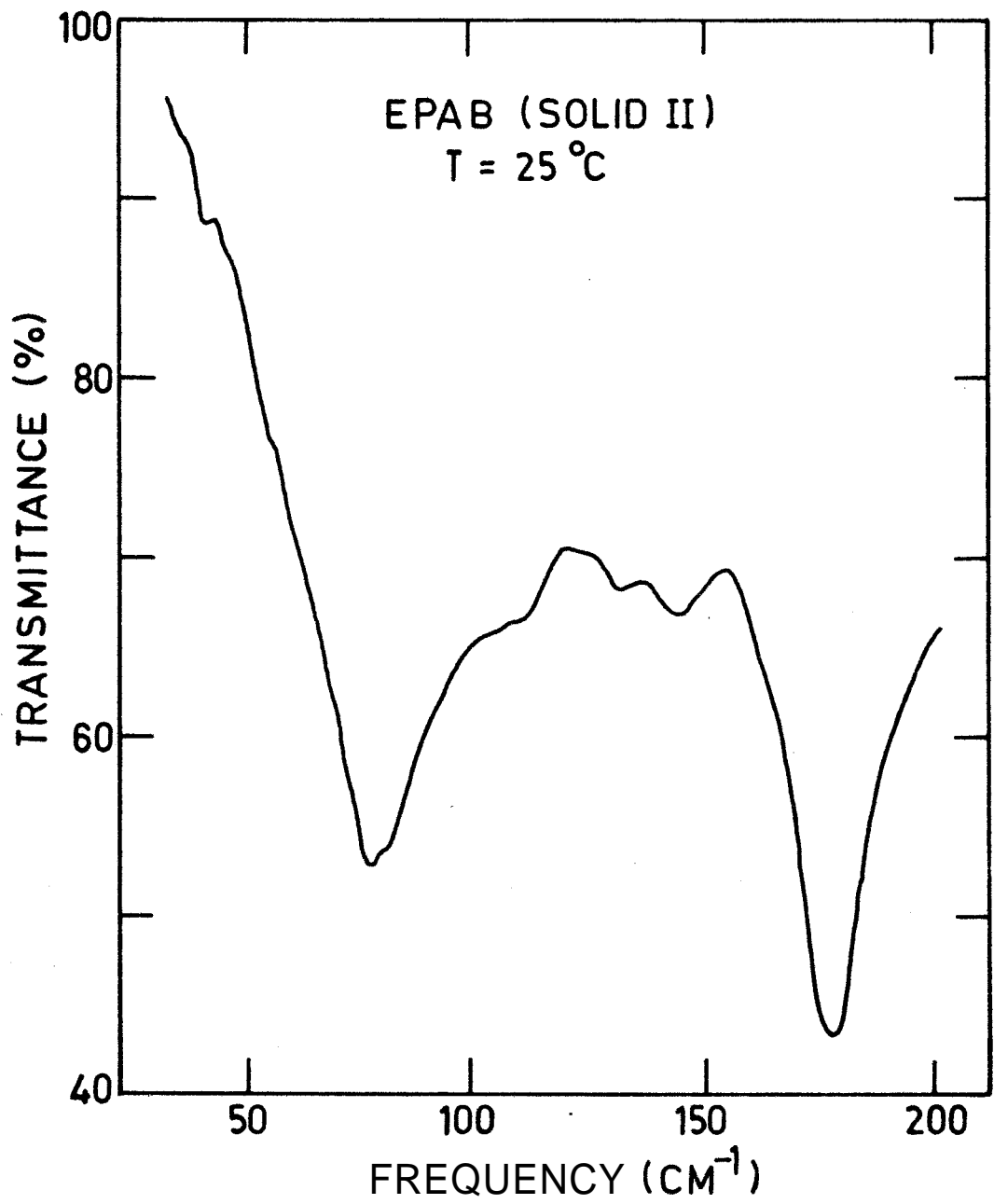
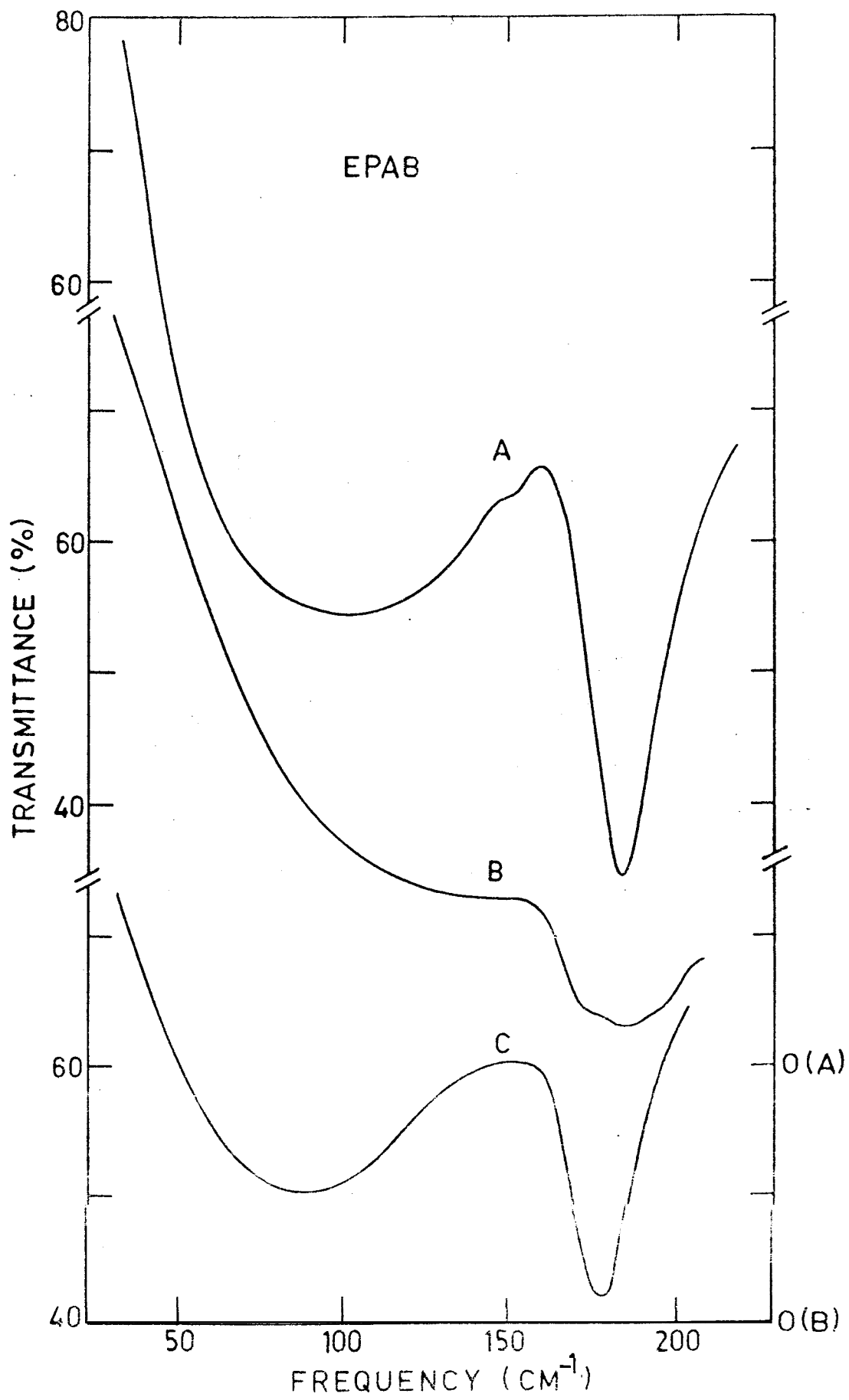


FIGURE 4.2

Far-infrared absorption spectrum of solid II at 25°C.

FIGURE 4.3

Far-infrared absorption spectra of solid I and the fluid phases. (A) solid I at 25°C, (B) smectic phase at 116°C, (C) Isotropic phase at 125°C. The respective ordinate scale marks corresponding to spectra A and B are indicated along the right vertical axis.



would be a characteristic barrier which hinders exchange between the different possible conformers of molecule. At longer times, this conformational exchange will contribute to the overall dielectric relaxation process in the microwave region. As general theoretical considerations^{26,27} and experimental observations in cases show,^{28,29} the short-time behaviour of such a low frequency dipolar relaxation process should be manifested as a torsional band in the FIR region. We therefore attribute the broad band centred at 94 cm^{-1} in the isotropic phase to the superposition of such a torsional band and the Poley absorption. In chapter 3 we have seen that the FIR absorption spectra of the p-azoxyanisole (PAA) series of liquid crystals can also be understood on this basis.²⁰

Compared to both solid I and the isotropic phase, the spectrum of the smectic A phase appears highly broadened. The extent of this broadening seems far too

large to be accounted for by any experimental artifact, such as the effects arising from the scattering of radiation by the polydomain liquid crystal sample. From the reproducible nature of this spectrum we conclude that the broadening arises due to the specific intermolecular interactions obtaining in the smectic phase, i.e., the formation of dimers and the resultant dipolar interactions between the terminal and central polar groups of the two adjacent molecules. The resultant changes in the shape of the potential barrier which hinders the librational and low frequency torsional modes may then cause the increased broadening of these bands. The absence of such a broadening in the isotropic phase is explained by the fact that the concentration of such dimers would be negligible in this phase. It is also seen that the molecular packing in solids II and I is such that the ester and asoxy groups of adjacent molecules are further removed from each other than in the smectic phase.

From table 4.1 we note that three nondegenerate external optic modes of A_g symmetry are expected in the FIR spectrum of solid II. The observed spectrum contains at least four distinct features below 160 cm^{-1} , indicating that certain other low frequency, intramolecular deformations or combination modes also occur in this region. The broad absorption band in solid I resembles that of the isotropic phase. The Polcy absorption is an improbable cause of this broad feature as there is no evidence to suggest that the molecules in solid I are free to reorient about their long axes. However, as in the isotropic phase, the conformational disorder due to the hindered reorientations of the polar asoxy group should once again lead to a torsional band in this case in the FIR region. In addition, there must be present the nine external optic modes of representation $5 A_g + 4 B_g$. The superposition of so many features within a relatively narrow spectral region appears to be the most likely explanation for the composite, unresolved absorption profile observed in solid I.

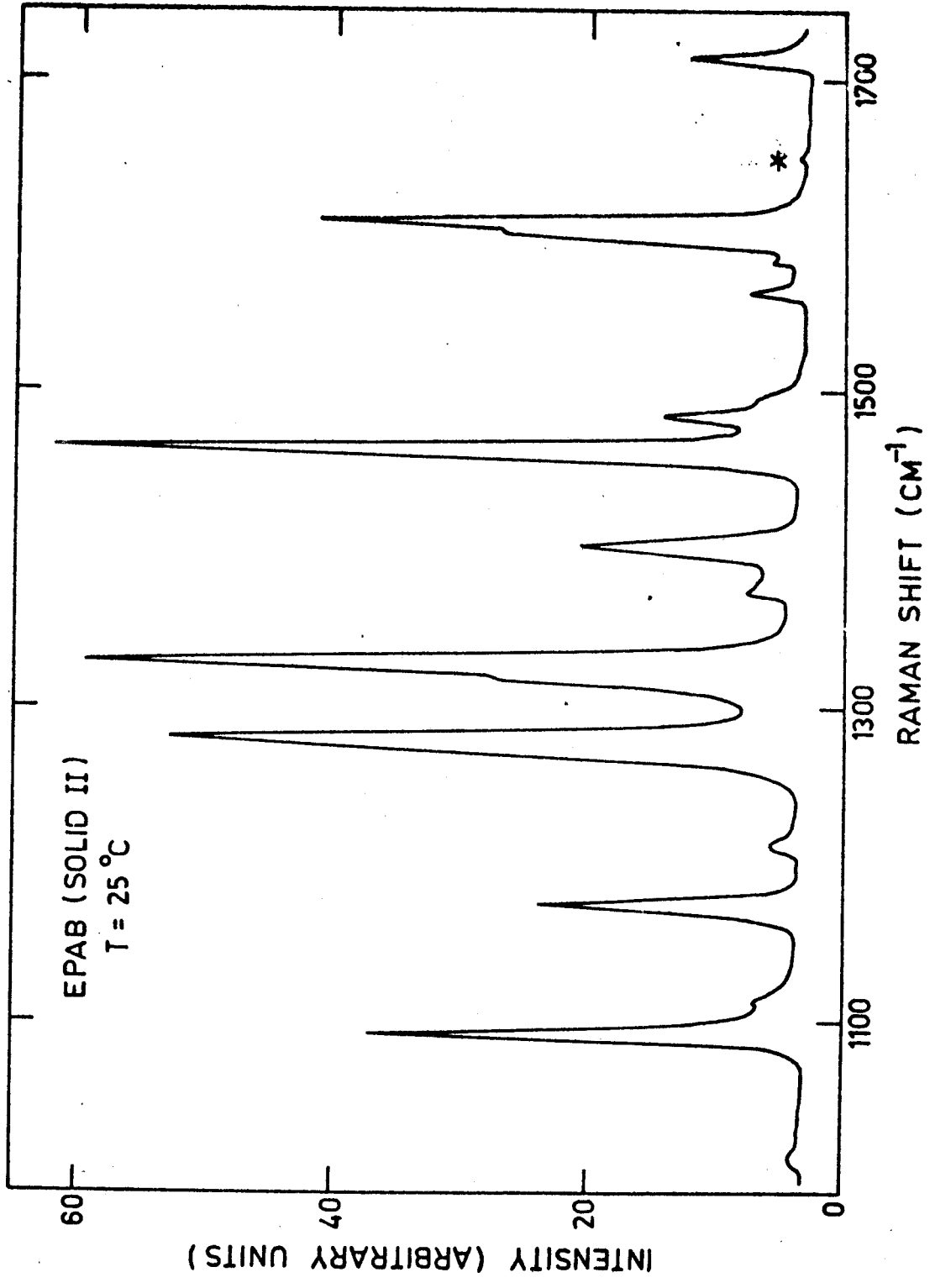
b) Raman Spectra

The detailed Raman spectra of KPAB in the region of the internal modes have not been published so far.¹⁸ The most intense Raman lines of both polymorphs occur in the region $1000 - 1750 \text{ cm}^{-1}$. Figure 4.4 shows the spectrum of solid II in this interval. As is seen from table 4.2, all these Raman lines must be of A_g symmetry. The number of Raman active Davydov components should, in principle, be doubled in solid I as new modes of both A_g and B_g symmetry must be present. However, no new lines were present in solid I over this spectral range although there were clear changes in the relative intensities of several lines. This indicates that the coupling between the four molecules in the primitive cell is rather weak. Consequently, the magnitude of the factor group splitting between the A_g and B_g modes is too small to be observed for all these intramolecular modes, unless one takes recourse to polarization studies on oriented single crystals of solid I.

The modes at 1350 and 1460 cm^{-1} can be assigned, respectively, to the $N - O$ and $N = N$ bond stretching

FIGURE 4.4

Raman spectrum of solid II in the 1000-1750 cm^{-1} range; $T = 25^\circ\text{C}$. The asterisk denotes a possible plasma emission line from the laser.




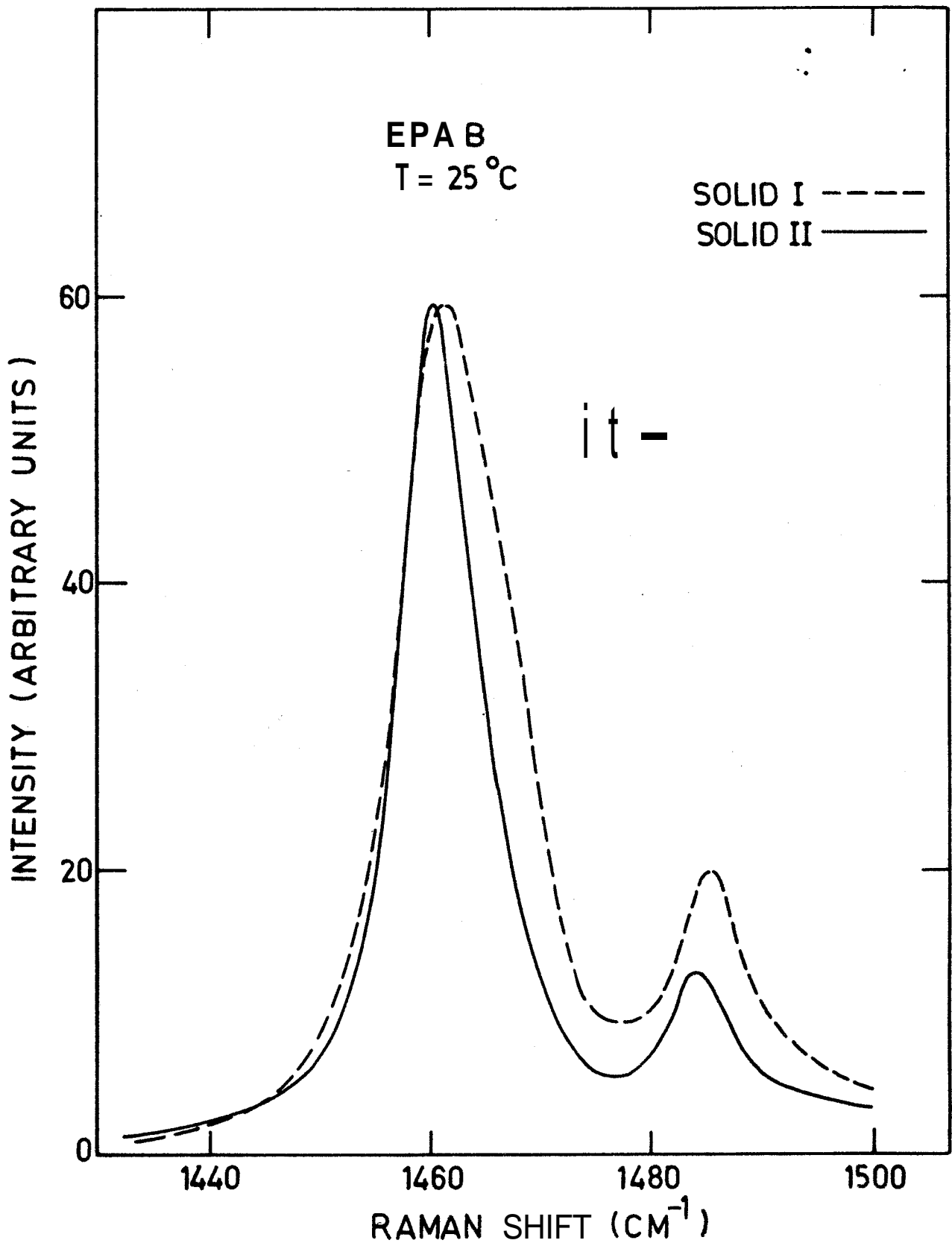
vibrations.³⁰ In view of the observed disorder in the positions of the atoms of the asoxy group¹⁶ in solid I, W have compared the respective lineshapes of these two modes in both solid phases. These measurements were performed using a spectral resolution of 1.2 cm^{-1} , which is 7 - 10 times smaller than the FWHM (full width at half maximum intensity) of the lines in question. Hence the effects of instrumental broadening on the observed line shapes should be negligible. No measurable broadening was seen in solid I for the mode at 1330 cm^{-1} , although it should be noted that the shoulder at 1320 cm^{-1} interferes with the task of estimating the intrinsic width of the N-O stretching mode in both solid phases. The FWHM of the N-N stretching mode increases by $\sim 4 \text{ cm}^{-1}$ on going from solid II to solid I, as is shown in figure 4.5. The relative intensity of the band at 1485 cm^{-1} also increases in solid I as compared to solid II. If the broadening of the line at 1460 cm^{-1}  to originate from the reorientations

FIGURE 4.5

Raman line shapes of the band at 1460 cm^{-1} in solid II and I, $T = 25^\circ\text{C}$. The observed spectrum of solid I has been numerically scaled up by a factor of 1.5 so as to normalize the peak intensity of this band in both phases. The spectral slit width is also indicated.



of the azoxy group in solid I, they would have to occur on a rather fast time scale, with a correlation time in the range of 2-3 psec. This however seems unlikely as no such broadening was seen for the N-O stretching mode. Also, as noted earlier, the typical reorientation rates of intramolecular polar groups in the disordered solid phases of other mesogens are found to be well below 1 MHz. One therefore expects that the reorientations of the azoxy groups in solid I should also occur on a similar, slow time scale. If so, this motion would appear frozen so far as the infrared and Raman spectra of solid I are concerned. We are thus led to attribute the broadening of the band at 1460 cm^{-1} to an unresolved Davydov component of the N-N stretching mode in solid I. This is also supported by the fact that the line shape is quite symmetric in solid II, but exhibits an asymmetry on the higher frequency side in the case of solid I.

4.4 Conclusions

The present study shows that the spectral changes which accompany the phase transitions in liquid crystalline substances are better understood when they can be correlated with the structural characteristics of the different phases. As expected, the signatures of the two solid modifications of MPAB are found to be distinctly different in the FIR region. Although the spectrum of solid I has a superficial resemblance to that of the isotropic phase, evidently the factors contributing to the broad band absorption cannot be entirely identical in the two cases. The FIR spectrum of the isotropic phase would be dominated by the Peley absorption and the torsional band associated with the cis-trans isomerism of the molecules. The latter feature should be present in solid I also in view of the conformational disorder obtaining in this phase. In addition, the infrared-active external optic modes must contribute to the FIR absorption of solid I.

The Raman line corresponding to the N-O bond stretching mode shows no significant broadening between solids II and I. Based on this and the evidence from the dielectric dispersion studies of other am—
—, we conclude ** the reorientations & the acy groups in solid I should be far too slow to influence the line shapes of the N-O and N-N bond stretching modes. Hence the broadening of the latter mode in solid I is attributed to the presence of an unresolved Davydov component on the higher frequency side of the main peak.

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