

## Far-infrared absorption spectrum of *p*-azoxyanisole

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**Abstract.** The far-infrared absorption of *p*-azoxyanisole has been studied in the range 20–200  $\text{cm}^{-1}$ , as a function of temperature. The distinct bands in the room temperature spectrum persist even at temperatures very close to the crystal-nematic transition and no marked pre-transition effects are present. A broad absorption band is seen in the spectra of the isotropic, nematic and supercooled nematic phases. The position of this band shifts down by  $\sim 10 \text{ cm}^{-1}$  on going from the nematic to the isotropic phase.

### 1. Introduction

The study of the vibrational spectra of liquid crystals has been of considerable interest in recent years<sup>1</sup>. Infrared absorption and Raman spectra of several liquid crystals have been investigated and have provided useful information regarding the characteristics of the different mesophases. The low frequency modes in these spectra are of particular interest as these are related to the intermolecular forces in liquid crystals. So far, very few studies have been reported on the far-infrared spectra of liquid crystals<sup>2-5</sup>. In this paper, we present some preliminary results of our study of the absorption of *p*-azoxyanisole (PAA) in the region of 20–200  $\text{cm}^{-1}$ . The far-infrared spectrum of PAA in the crystalline, nematic and isotropic phases has been reported earlier by Bulkin *et al.*<sup>3,4</sup>. The present study shows some differences as compared to their work.

### 2. Experimental procedure

The spectra were obtained using the Polytec FIR 30 interferometer\* with an on-line Nova 1200 computer †. The interferograms were Fourier transformed in real time and no apodization was used. To eliminate atmospheric water vapour, the interferometer was kept evacuated during all the measurements. The spectral range of 20–200  $\text{cm}^{-1}$  was covered using two different beam splitters. One had a usable transmission range of 20–160  $\text{cm}^{-1}$  and the other had a range of 50–450  $\text{cm}^{-1}$ . The spectra in the two ranges were obtained with resolutions of 4 and 5  $\text{cm}^{-1}$  respectively. In the region of

\* Polytec GmbH & Co., 7501, Reichenbach, Karlsruhe, West Germany

† Data General Corporation, Southboro, Mass. 01772, USA.

overlap of the two ranges, the observed transmission through the sample agreed to within  $\pm 2\%$  except near the minima in the efficiency of transmission for either beamsplitter. As is known, the noise in the ratioed spectrum can become rather high in such regions.

The PAA samples were contained between two quartz windows of diameter 25 mm and thickness 1.2 mm at the centre. They were cut parallel to the  $c$ -axis and their surfaces polished. The windows were wedged at an angle of  $1^\circ$  to eliminate interference fringes. As a result of the reflection from the beamsplitter, the radiation is partially polarized with the vertical component of the electric vector being more intense.  $\alpha$ -quartz has a doubly degenerate infrared and Raman active zone-centre optical phonon<sup>6</sup> at  $128\text{ cm}^{-1}$ , its polarization lying in the plane normal to the  $c$ -axis. Hence, in order to minimize the absorption of the windows at  $\sim 128\text{ cm}^{-1}$ , the  $c$ -axis was kept vertical.

The windows were pressed together in intimate contact and the reference spectrum was obtained at several temperatures, so as to take into account its temperature dependence. Thus, for a given pair of reference and sample spectra, the difference in temperature between the two was certainly within  $10^\circ\text{C}$ . The reference spectra were quite free from effects of interference fringes arising from either the windows or the extremely small spacing between them. The effective aperture was 15 mm and the sample thickness was usually  $\sim 100\ \mu$ .

PAA supplied by Eastman Kodak Co. was used in this study. The crystal-nematic and nematic-isotropic transition temperatures of the material were  $118$  and  $135^\circ\text{C}$  respectively. Polycrystalline samples were prepared by two different methods. In the first, PAA was finely ground and sieved to eliminate particles larger than  $40\ \mu$ . The sieved powder was then spread into a fairly uniform layer between the quartz windows. Though no effort was made to precisely control the thickness of the layer, it is estimated to be  $\sim 100\ \mu$ . Sieving the powder ensured that the particle size in the sample was smaller than the shortest wavelength in the spectral region of the present measurements. It was experimentally found that this procedure diminished radiation losses due to scattering, especially at the shorter wavelengths.

In the second method, a bubble-free film of the isotropic liquid was formed between the windows and the thickness of the film was kept at  $\sim 100\ \mu$  using a teflon spacer. The isotropic liquid was then slowly cooled. This again resulted in a polycrystalline sample in which the crystallite size was much larger than the average wavelength in the spectral region of interest. Thus, this method of sample preparation was also effective in diminishing the loss of radiation due to scattering.

The measurements in the nematic and isotropic phases were carried out on films of thickness  $\sim 100\ \mu$ . It was possible to maintain the liquid sample between the windows, without any leakage into the surrounding

vacuum. No attempt was made to orient the nematic sample. Though the cell windows were wedged, the parallelism of the liquid film can, in principle, create interference fringes that can distort the ratioed spectrum. However, from the available data on the refractive indices of  $\alpha$ -quartz<sup>7</sup> in the far-infrared region and on the dielectric constants of liquid crystalline PAA in the microwave region<sup>8</sup>, it is to be expected that such fringes will be of a very small amplitude. Indeed, experimentally no observable effects were seen.

The windows together with the sample were held in a copper block which was heated with a variable temperature cell\*. Measurement and control of temperature were accomplished using a cu-constantan thermocouple in conjunction with a TC/30 temperature controller†. Temperature measurements were accurate to  $\pm 1^\circ\text{C}$  and fluctuations were within  $0.5^\circ\text{C}$ . After the controller indicated the desired temperature, about 15 min. were allowed for the sample to reach thermal equilibrium before carrying out any measurements.

### 3. Experimental results and discussion

#### 3.1. Crystalline phase

Figure 1 shows the absorption spectrum of polycrystalline PAA at room temperature. Trace A shows the spectrum obtained using sieved powder. It is seen that clear absorption bands are present at 45, 68, 94, 140 and  $156\text{ cm}^{-1}$ . The shoulder at  $\sim 86\text{ cm}^{-1}$  is noteworthy as it was repeatedly observed in different measurements. Weak absorption features have also been observed at 31, 39 and  $56\text{ cm}^{-1}$ . The mode at  $31\text{ cm}^{-1}$  is in a region of poor signal-to-noise ratio and the other two appear as shoulders riding a slope. For these reasons it was not always easy to discern these features. However, the other features shown here were always clearly observable. Trace B shows a typical spectrum obtained when the sample was prepared by slow cooling from the isotropic phase. Comparison with trace A shows that the main features are common to both. The mode which appears as a shoulder at  $\sim 86\text{ cm}^{-1}$  in Trace A, is now more clearly seen. On the basis of this and other similar spectra obtained by us, it appears that there are actually two modes here, situated at  $\sim 86$  and  $94\text{ cm}^{-1}$ . The two modes could not be resolved more distinctly even with a spectral resolution of  $2\text{ cm}^{-1}$ ; presumably this is due to the close proximity of the modes and the fact that the line-width of each at room temperature is greater than  $4\text{ cm}^{-1}$ . The weak absorption line observed at  $124 \pm 1\text{ cm}^{-1}$  is also manifested as a perceptible shoulder in trace A, as is shown in the inset. However, it was not readily reproducible each time a new sample was prepared. Also, as  $\alpha$ -quartz exhibits a strong

\* Spectroscopic Accessory Co., 241, Main Road, Sidcup, Kent DA 146 QS, UK.

† Polytec GmbH & Co.

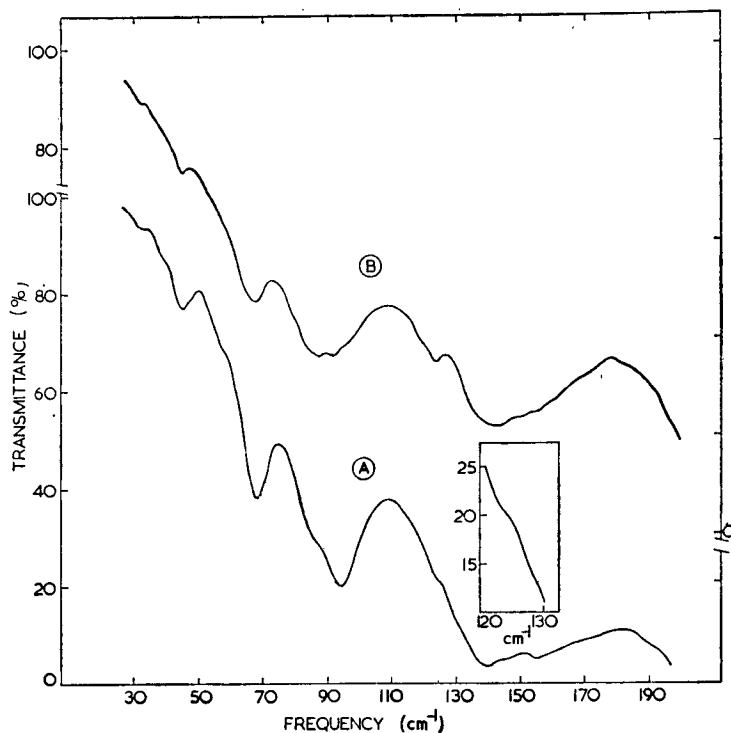


Figure 1 Far-infrared absorption spectrum of polycrystalline PAA at 25°C. (A) Sample prepared with sieved powder. The region 120–130  $\text{cm}^{-1}$  is shown enlarged in the inset. (B) Sample prepared by slow cooling from the isotropic phase.

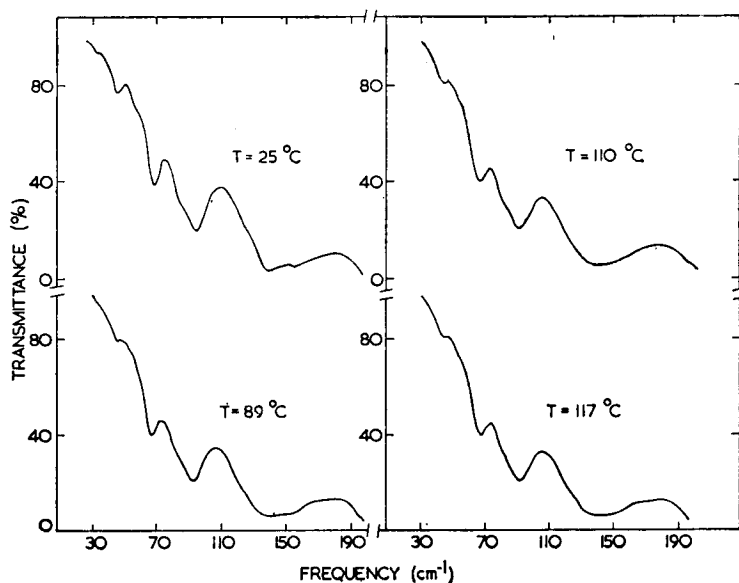
absorption around 128  $\text{cm}^{-1}$ , slight distortions may occur in the ratioed spectrum in the vicinity of this line. For these reasons, the identification of this line as an absorption mode of PAA must be regarded as tentative at present. Further experiments to ascertain this are in progress.

With either method of sample preparation, we have not observed the modes at 115  $\text{cm}^{-1}$  and 180  $\text{cm}^{-1}$ , reported earlier<sup>3</sup>. Table I lists the absorption frequencies observed in polycrystalline PAA at 25°C in the range 30–200  $\text{cm}^{-1}$ . The accuracy of the line positions is  $\pm 1 \text{ cm}^{-1}$ , except for the weaker features denoted by an asterisk. In these cases as well as for the broader lines, the frequencies are accurate to  $\pm 2 \text{ cm}^{-1}$ . The frequencies reported earlier<sup>3</sup> are also listed for comparison.

The temperature dependence of the absorption spectrum in the crystalline phase is shown in figure 2. As PAA is heated, there is a gradual reduction in the intensity of all the absorption bands. The modes observed at 140  $\text{cm}^{-1}$  and 156  $\text{cm}^{-1}$  at room temperature become broadened and less distinct. No marked frequency shifts are seen except for the mode at 94  $\text{cm}^{-1}$  which shifts down by  $\sim 2.5 \text{ cm}^{-1}$  at 117°C as compared

**Table 1** Far-infrared absorption frequencies of polycrystalline PAA (in  $\text{cm}^{-1}$ ) at  $25^\circ\text{C}$ , in the range  $30\text{--}200\text{ cm}^{-1}$ . The weaker lines are denoted by an asterisk.

Present work	31*	39*	45	56*	68	86	94	—	124*	140	156
Reference 3	—	—	50	—	70	84	—	115	—	135	150

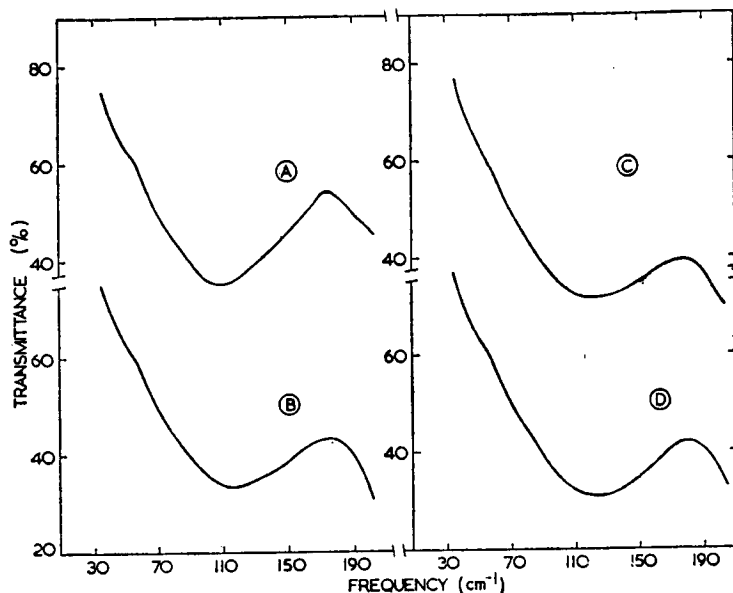


**Figure 2** Absorption spectrum of polycrystalline PAA at different temperatures.

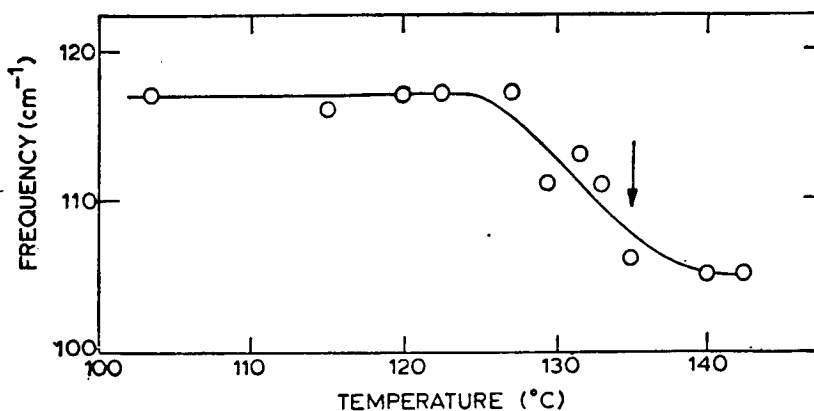
to  $25^\circ\text{C}$ . It can be seen that the distinct absorption lines seen at room temperature persist even at temperatures close to the crystal-nematic transition and that no marked pretransition effects are manifested. In this respect as also regarding the features observed in the spectra as a function of temperature, the present results differ from those reported earlier<sup>3</sup>.

### 3.2. Liquid crystalline and isotropic phases

Figure 3 shows the spectra in the isotropic and liquid crystalline phases. Trace A shows the spectrum of the isotropic phase at  $140^\circ\text{C}$ , while traces B, C and D show the spectra in the nematic phase at  $131.5$ ,  $120$  and  $103.5^\circ\text{C}$ , respectively. It should be noted that at  $103.5^\circ\text{C}$ , the nematic phase is supercooled. All four traces are characterized by one broad absorption band and a shoulder at  $\sim 50\text{ cm}^{-1}$ . It is of interest to note here that in case of *p*-azoxyphenetole also, a broad absorption band was



**Figure 3** Absorption spectrum of PAA in the isotropic and nematic phases. (A) Isotropic phase at 140°C. (B) Nematic phase at 131.5°C. (C) Nematic phase at 120°C. (D) Supercooled Nematic phase at 103.5°C.



**Figure 4** The frequency at maximum absorption for the band shown in figure 3, as a function of temperature. The solid line is a smooth curve drawn through the experimental points. The arrow denotes the nematic-isotropic transition point.

observed and it was attributed to the orientational vibrations of the molecule about its long axis<sup>2</sup>. The position of the band in figure 3 was seen to exhibit a temperature dependence which is shown in figure 4. The data points correspond to the frequency at maximum absorption for each temperature and the solid line is a smooth curve drawn through the

experimental points. In the isotropic phase, owing to the more symmetric shape of the band, the position of maximum absorption could be estimated with better accuracy and was found to be  $105 \pm 2 \text{ cm}^{-1}$ . However, in the nematic phase the band is shallower and less symmetric, rendering the estimation somewhat more difficult. Hence, the frequencies indicated in figure 4 for the nematic phase are accurate to within  $\pm 5 \text{ cm}^{-1}$ . Nonetheless, the trend of the temperature dependence shown here was reproducible with different samples. Thus, it is of interest to consider the origin of this absorption band<sup>2,9</sup> and inquire if the higher frequency of the band in the nematic phase is related to the orientational order obtaining in that phase.

In this context, it is desirable to extend the study of the liquid crystalline phase with aligned samples and polarized radiation. It is also of interest to determine the symmetries of the modes observed in the crystalline phase, through polarization studies on single crystals. Such information should prove useful in understanding the external modes and intermolecular forces in PAA. We plan to pursue further studies related to these aspects in the near future.

### Acknowledgements

The author expresses his thanks to Professor S. Chandrasekhar for many valuable discussions and for his keen interest and encouragement during this work.

### References

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### DISCUSSION

**Khetrupal:** You pointed out that Bukin *et al.* have carried out a theoretical calculation of frequencies that predicts a band near  $119 \text{ cm}^{-1}$  and this is identified with the mode they observe at  $115 \text{ cm}^{-1}$ . However, this mode is absent in your spectrum. Does this imply that you disagree with their calculation also?

**Venugopalan:** It should be noted that other prominent bands of the room temperature spectrum observed previously\*, agree fairly well with the present study. In view of this and the observed strength of absorption for the mode at  $115\text{ cm}^{-1}$  in the earlier work, we would have expected to observe that band also. In order to eliminate possible effects arising from the technique of sample preparation, we have used sieved powder, powder pressed into a thin disc as well as samples obtained by slow cooling from the isotropic phase. In all the cases, we have failed to observe the band at  $115\text{ cm}^{-1}$ . Regarding the empirical calculation of the frequencies by Bulkin *et al.* †, I am not familiar with the complete details of that work at present.

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\* Bulkin B J and Lok W B J. *Phys. Chem.* 77 326 (1973).

† Bulkin B J, Grunbaum D, Kennelly T and Lok W B Paper presented at this Conference.