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RAMAN STUDY OF PARA-AZOXYDIANISOLE AT THE PHASE TRANSITIONS*

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ABSTRACT

Raman scattering was used to probe the phase transitions of the nematic liquid crystalline material, p-azoxydianisole. The intensities of several Raman modes were shown to change abruptly at the phase transitions, but no detectable frequency shift of any mode was observed. Our results suggest that the Raman spectrum of p-azoxydianisole is only affected by short-range ordering. Qualitative interpretation of the results is given.

Using Raman scattering technique, we have investigated the phase transitions of the nematic liquid-crystalline substance p-azoxydianisole (PAA). Although Raman spectra of this substance have previously been obtained,[1,2] no systematic investigation of the temperature dependence of the Raman modes has been reported. Furthermore, to our knowledge, no investigation of the low-frequency Raman modes has ever been made. In this note, we would like to report the results of our measurements of the temperature dependence of the Raman modes in two spectral regions: 30-100 cm^{-1} and 1225-1300 cm^{-1}. The intensities of these modes change significantly during the phase transitions. Our results indicate that the Raman spectrum of PAA is affected mainly by short-range interaction between neighboring molecules, and that Raman scattering, in general, can be used to probe the change of short-range ordering during the phase transitions.

The experimental setup was the same as that described by Landon and Porto,[3] with a 40 mw He-Ne laser as the exciting source. The PAA sample was recrystallized three times for purity. For better temperature control, the sample cell was inserted in a copper block and then immersed in an oil bath. The sample temperature was monitored constantly, and temperature fluctuations were less than 0.035°C.

A spectral range of ± 1900 cm^{-1} about the laser line was investigated. There are around 30 strong Raman lines (of the same order as the 992 cm^{-1} line of pure benzene) in that range. As the substance changes phases from solid to nematic and into isotropic liquid, some of the lines disappear, but most of them decrease in intensity and become broader.

Three of the lines, however, show little change (< 10%) in their integrated intensities. In particular, the line at 1095 cm^{-1} also shows essentially no change in its linewidth. It was, therefore, chosen as the internal calibration line in our intensity measurements. Generally speaking, the spectra of the nematic phase resemble those of the isotropic liquid more than those of the solid. None of the observed Raman lines show any detectable frequency shift in the phase transformation. For the high-frequency Raman modes, our spectra have general resemblence to those obtained by others,[1,2] but the detailed structure is quite different, especially for nematic and liquid phases. The difference may be attributed to the better quality of our spectra.[4]

Two spectral regions show more significant changes under phase transformation (see Fig. 1). The first region from 1225 to 1300 cm^{-1} was first investigated by Freymann and Servant.[1] They reported observing two lines at 1247 and 1276 cm^{-1} in the solid and nematic phases and that the line at 1247 cm^{-1} disappeared in the liquid phase. Our spectrum for solid PAA in Fig. 1a, however, indicates that the composite spectrum of this region can be decomposed into four symmetric lines at 1246 (± 2), 1252, 1261, and 1276 cm^{-1} with the respective intensity ratio of 3.7:1:4.2:6.3. The strongest line is roughly 1/2 as strong as the 992 cm^{-1} line of benzene. As the temperature increases through the solid-nematic transition, the three lines at lower frequencies decrease sharply in intensity and merge into a single broad peak. However, assuming that the lines are always symmetric, we can still decompose the spectrum into four lines at approximately the same frequencies as before. In Fig. 2a, we have plotted the normalized integrated intensity of the 1246 cm^{-1} line (calibrated against the intensity of the 1095 cm^{-1} line) as a function of temperature.[5] It is seen that the curve has the characteristic quasi discontinuity at the solid-nematic phase transition. However, no such discontinuity occurs at the nematic-isotorpic transition. The integrated intensity of the 1276 cm^{-1} line remains unchanged through the phase transitions, but the linewidth changes as shown in Fig. 2b. Again, the variation of the linewidth with temperature has a quasi discontinuity at the solid-nematic transition.

The low-frequency region from 30-100 cm^{-1} is also of interest. The spectrum of solid PAA shows three Raman modes at 40 (±2), 52, and 72 cm^{-1} located on the tail of the central scattering component, as shown in Fig. 1. The intensity ratio is 1:1.4:2.4 respectively, the 72 cm^{-1} mode being 1/4 as intense as the 1276 cm^{-1} mode. In transition from solid to the nematic phase, the 72 cm^{-1} mode vanishes completely, and the intensities of the modes at 40 and 52 cm^{-1} drop sharply with their intensity ratio becoming 4:1. The latter two modes also disappear suddenly at the nematic-to-liquid transition. While the intensities vary, the frequencies and the linewidths of the three modes remain unchanged. Figure 3 shows the variation of the normalized integrated intensities of the three modes with temperature. Here again, the curves exhibit the characteristic discontinuities at the phase transitions.

To explain our results qualitatively, we can use the simple model suggested for PAA.[6,7] In the solid phase, the molecules $CH_3O-(C_6H_4)-N_2O-(C_6H_4)-CH_3O$ are all aligned and fixed in regular positions. Two neighboring molecules are half-overlapped, with the benzene rings facing each other and the CH_3O groups in close contact with the N_2O groups.[6] In the nematic phase, the long axes of the molecules are still essentially aligned, but the molecules are no longer rigidly fixed in position and they can rotate more or less freely about their own long axes.[7] The rotation of the benzene-ring groups is presumably less hindered because no permanent dipole moment is attached to the benzene ring. Finally, in the liquid phase, disordering in the molecular alignment sets in.

As suggested by Freymann and Servant,[1] the Raman lines around 1260 cm^{-1} should arise from the vibrational modes of the $CH_3O-(C_6H_4)-N_2O$ group. These modes are likely to be strongly affected by intermolecular interaction when neighboring molecules are overlapping in a manner described above for the solid phase. In the nematic phase, since the molecules can move and can rotate about their long axes, the probability of finding two neighboring molecules with this particular relative position and orientation is smaller than that of the solid phase. Consequently, the intensities of these modes drop sharply. That the mode frequencies remain unchanged suggests that here only the optical excited states are modified by the intermolecular interaction. The sudden increase in the linewidth of the Raman modes at the phase transition indicates the onset of rotational freedom the molecules acquire in going to the nematic phase.

The same model can be used to explain the observation of the low-frequency modes. Unlike the soft lattice modes in ferroelectrics,[8] these modes do not change in frequency during the phase transition. They are most likely the intermolecular modes arising from interaction between the $CH_3O-(C_6H_4)-N_2O$ groups of two neighboring molecules and should be affected primarily by short-range ordering. The 72 cm^{-1} mode may depend strongly, and the other two less strongly, on the relative position and orientation of the neighboring molecules. As a result, the 40 and 52 cm^{-1} modes persist in the nematic phase although their intensities decrease. It is interesting to note from Fig. 3 that the modes with higher frequencies show more drastic changes at the solid-nematic transition. This seems to suggest that the modes with higher frequencies have deeper but narrower intermolecular potential wells. These intermolecular modes do not have sidebands due to rotation or libration of individual molecules. Consequently, little change in their linewidths should be expected at the phase transition.

In an attempt to study the influence of magnetic field on ordering in PAA, we applied a field of 4.0 kOe on the sample and varied the temperature. This field is strong enough to induce macroscopic alignment and, hence, saturation of the dielectric constant in PAA.[9] We have, however, seen no effect of the field on the phase-transition temperatures of PAA. The Raman spectrum, after calibrated against the 1095 cm^{-1} line, also showed no field dependence at any temperature. The field is apparently not strong enough to modify the short-range interaction between molecules. This is an agreement with the conclusion drawn by others that in nematic substances, a magnetic field has effect only on a macroscopic scale but not on local individual molecules.[10]

We also observed in our experiment abrupt broadening of the central Rayleigh-wing component at both solid-to-nematic and nematic-to-liquid phase transitions. This is clearly due to the onset of rotation and libration of the molecules at the phase transitions. However, systematic investigation on this Rayleigh-wing scattering is yet to be performed.

We have shown here that Raman scattering can be used to probe phase transitions and short-range ordering in liquid crystalline materials. Combination of Raman studies with other methods of investigation, such as NMR, etc., may yield a better picture of intermolecular interaction in these materials. We are extending our study to the other members of the homologous series of the 4,4'-bis (alkoxy) azoxybenzenes. Preliminary results indicate that, in general, the temperature dependence of both the low-frequency and the high-frequency Raman modes conform with the results obtained from PAA. A full report of the investigation will be published elsewhere.

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FIGURE CAPTIONS

Fig. 1. Raman spectra of PAA from 30 to 100 cm^{-1} and from 1225 to 1300 cm^{-1} in the three phases.

(a) Solid phase at T=113.9°C

(b) Nematic phase at T=116.8°C

(c) Liquid phase at T=134.8°C

The slit width is 2 cm^{-1}.

Fig. 2(a). Normalized integrated intensity of the 1246 cm^{-1} line as a function of temperature.

(b). Variation of the linewidth of the 1276 cm^{-1} Raman mode with temperature.

Fig. 3. Normalized integrated intensity of the low-frequency Raman modes as a function of temperature.

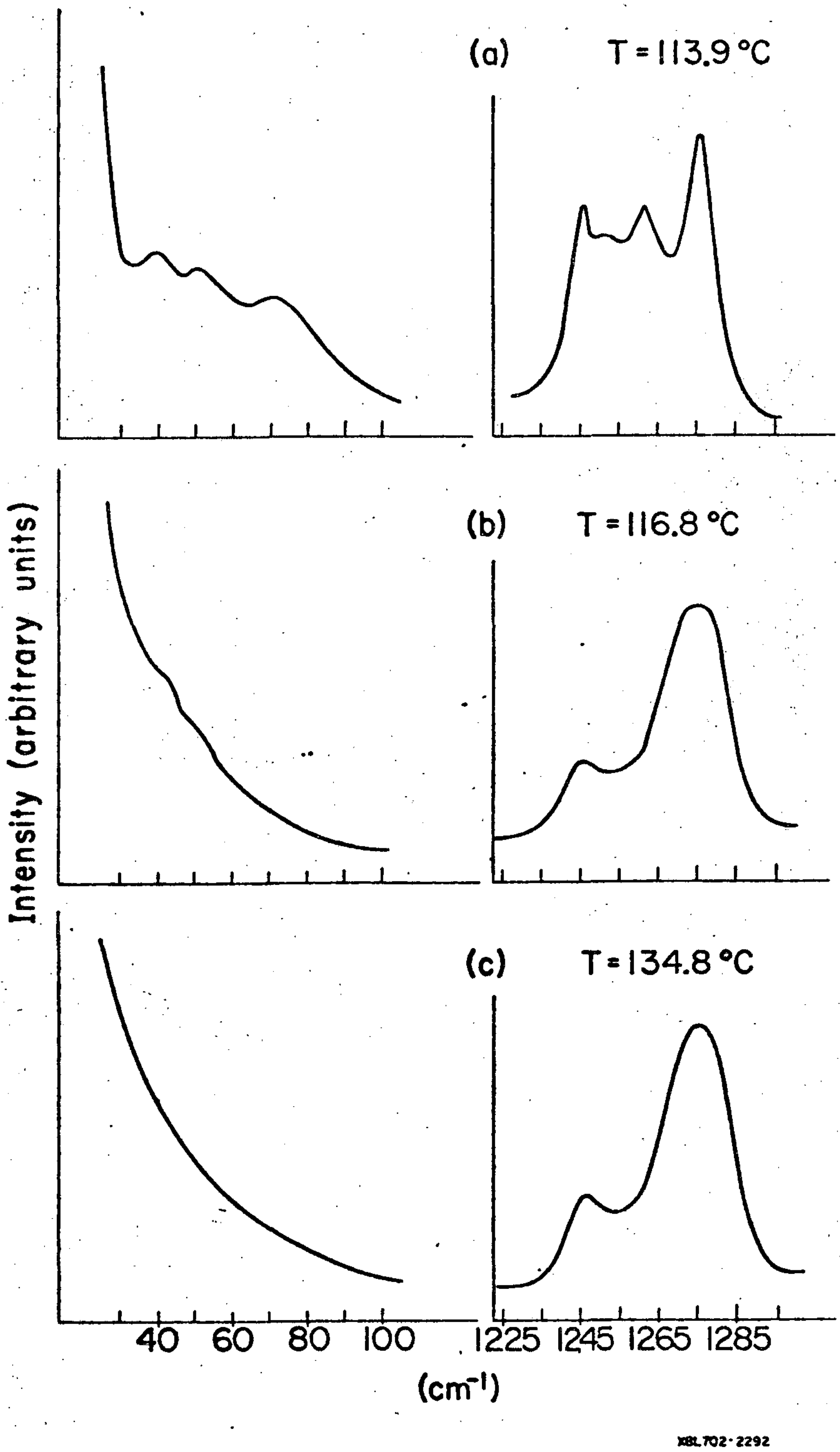
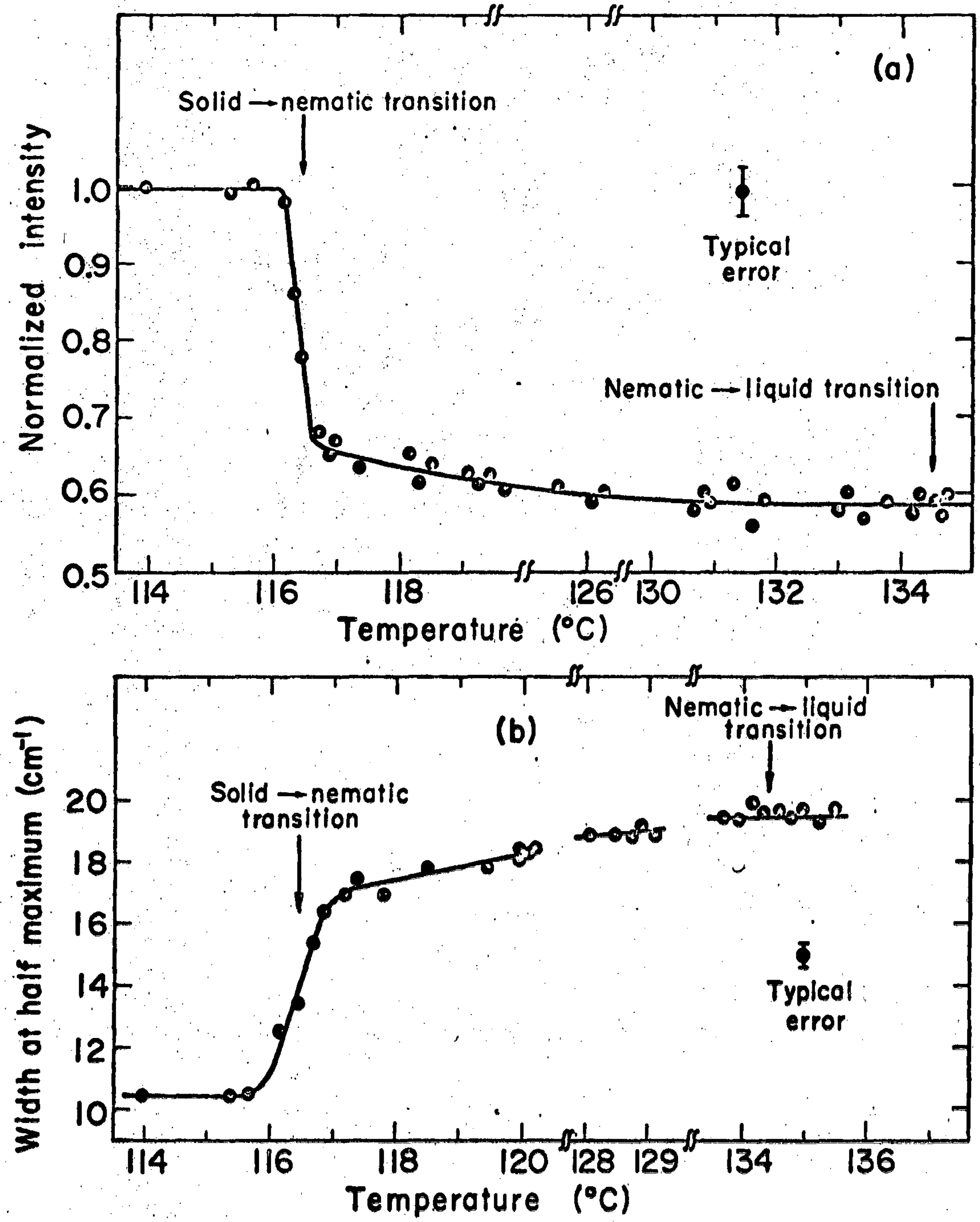

(a) T = 113.9 °C
(b) T = 116.8 °C
(c) T = 134.8 °C
Intensity (arbitrary units)
40 60 80 100
1225 1245 1265 1285
(cm⁻¹)
XBL 702-2292

Fig. 1



XBL702-2297

Fig. 2

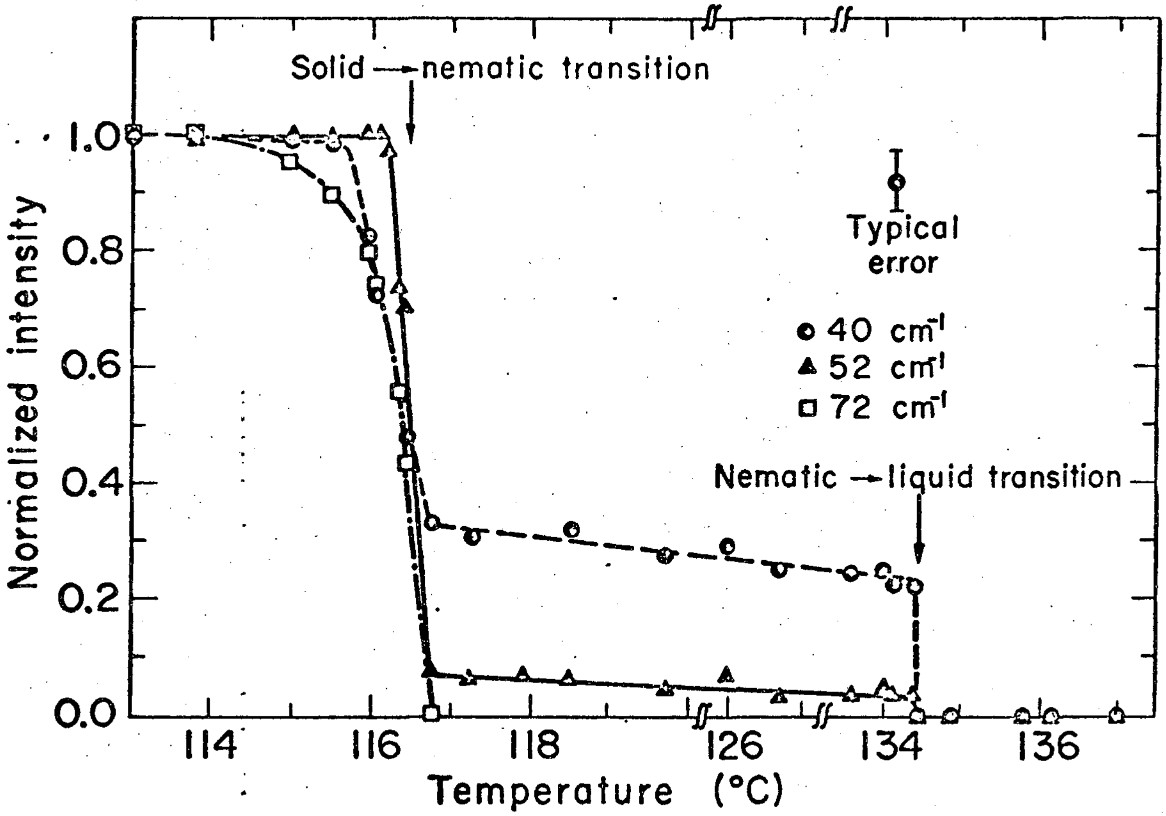


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Fig. 3

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