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INTENSITY VARIATIONS OF SOME LOW-FREQUENCY RAMAN BANDS IN CRYSTALLINE PHENANTHRENE

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Abstract: The temperature dependence of the frequency and intensity of some torsional modes in the phenanthrene molecule have been investigated by Raman spectroscopy. The aim of these investigations is to check the assumption that the phase transition in phenanthrene may be due to some conformational changes of the molecule in this crystal. It has been observed that there is no appearance of new bands nor the disappearance of existing bands in the spectrum. It has been observed that the intensity of the torsional mode 116 cm^{-1} depends strongly on temperature; however, this behaviour is not directly correlated with the phase transition.

1. Introduction

The existence of the phase transition in phenanthrene at a temperature of about 70°C has been confirmed by several techniques[1-5]. The diffuse character of all phenomena observed indicates that the transition can be of a higher-order type. This was especially confirmed by X-ray measurements performed by Matsumoto[2]. No change of the crystal system nor of the space group was observed, but the spectrum exhibited an anomalous increase of lattice constants occurring in the temperature range from 50°C to 68°C. In spite of the large number of measurements performed, the physical nature of the phase transition remains to be cleared up.

It is well known[6,7] that the molecule in the crystal lattice is slightly distorted due to an overcrowding of the two hydrogen atoms at positions 4 and 5. In this way, the outer rings are displaced in opposite directions and the molecule belongs to the symmetry group C_2. Spielberg et al.[5] assumed from inelastic neutron-scattering measurements that the transition could be associated with intramolecular regrouping. They considered the possibility of a conformational change wich would lead to the displacement of the two hydrogen atoms at positions 4 and 5, in the same direction from the central ring plane. In this case the molecule would be of the symmetry group C_s. The number of Raman-active modes would not change in passing from one group to the other; however, some specific modes could exhibit changes in vibrational frequencies. In this way the problem was reduced to the level of molecular spectroscopy. In particular, the proposed con-

115(B)

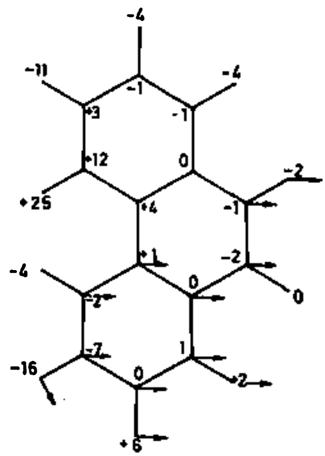

Fig. 1. A calculated torsional mode of the phenanthrene molecule. The positive and negative numbers indicate the displacement vectors in the direction normal to the mean plane of the molecule.

formational change should affect some of the low-frequency torsional modes that were observed and assigned in the spectrum of phenanthrene[8]. Among the different modes corresponding to torsional vibrations, the vibrational mode, which is roughly drawn in Fig. 1 by means of the calculated displacement vectors, should, in our opinion, be very sensitive to conformational changes assumed by Spielberg. This vibrational mode was assigned to the couple of bands 112A and 116 B in the spectrum of crystalline phenanthrene.

2. *Experimental*

The temperature dependence of the Raman bands at 116B and 112A was observed in the temperature range from −195° to + 100°C. The two bands lie in the vicinity of the lattice modes corresponding to the vibrational motion of molecules around their long axis. While mode B remains separated from the vibrational mode by about 16 cm^{-1}, the two modes in the spectrum of species A are separated only by 5 cm^{-1}. The large separation of the two bands in the spectrum of species B in the whole temperature range ensures that the possible »crossing« of the two modes will not occur. Fig. 2 shows the frequencies of some low-frequency modes as functions of temperature. No abrupt change of frequency was observed, although the modes were »softening« along the temperature range from 45° to 72°C. Similar behaviour was observed for other torsional modes. No new bands were observed in the spectrum from about 20 cm^{-1} to 270 cm^{-1}. This indicates that the possibility of a conformational molecular change in the sense proposed by Spielberg may be ruled out.

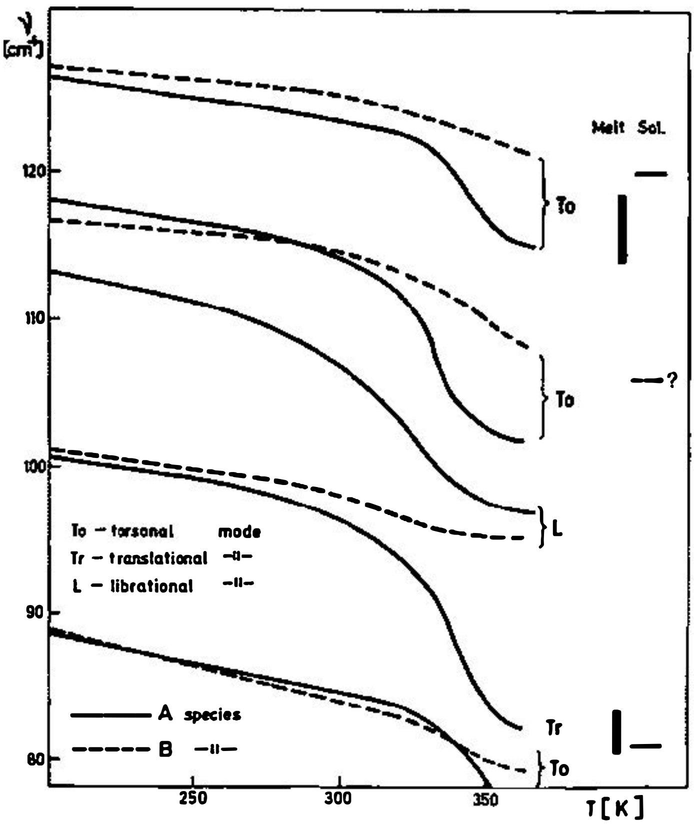

Fig. 2. Temperature dependence of frequencies of some low-frequency modes in the Raman spectrum of the phenanthrene crystal.

The present measurements, however, give evidence on another feature of the phenanthrene spectrum. The mode 116B exhibits an anomalous change in intensity with increasing temperature. Fig. 3 shows some of the recorded spectra at different temperatures. The torsional mode 116 cm^{-1} is the dominant band in the spectrum at —195°C; its intensity, however, decreases with increasing temperature and becomes negligible in comparison with the band 99 cm^{-1} (vibrational mode) at temperatures corresponding to the phase transition. It must be emphasized

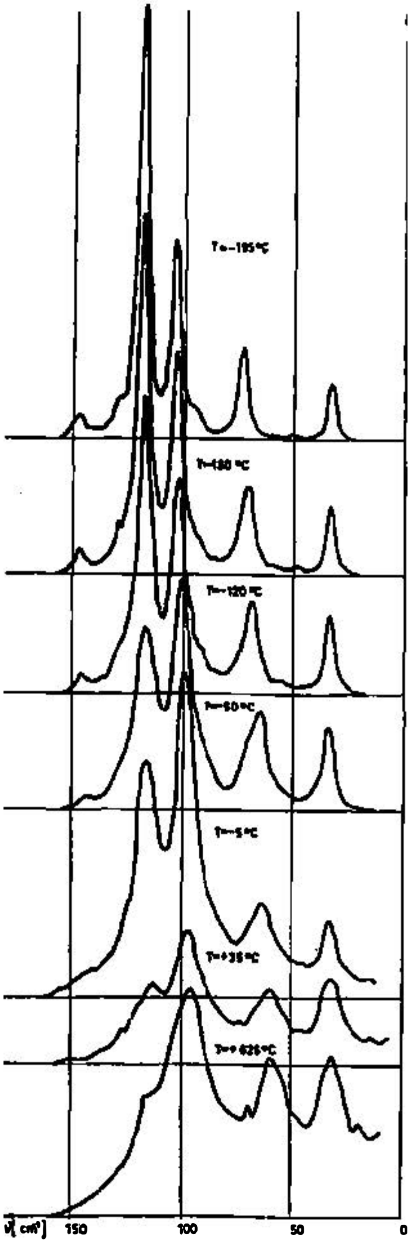

Fig. 3. Polarized Y(ZY)X Raman spectra of the phenanthrene single crystal at different temperatures.

that the band 116 cm^{-1} does not disappear and its frequency can be measured up to the melting point. The possibility of an increase in intensity of the band 99 cm^{-1} may be discussed. In order to remove both the possible variation in intensity of the band 99 cm^{-1} and the temperature effect, we compared the intensity ratio of the bands 116 cm^{-1} and 99 cm^{-1} relative to the band 63 cm^{-1}. This band exhibits stability in intensity and is sufficiently distant from the doublet considered. The integral intensity had to be considered due to the considerable broadening of the bands with increasing temperature. In determining the intensity of the bands 116 cm^{-1} and 99 cm^{-1} we assumed a triangular band shape. At low temperatures, it was easy to determine the intensity of these bands. However, at

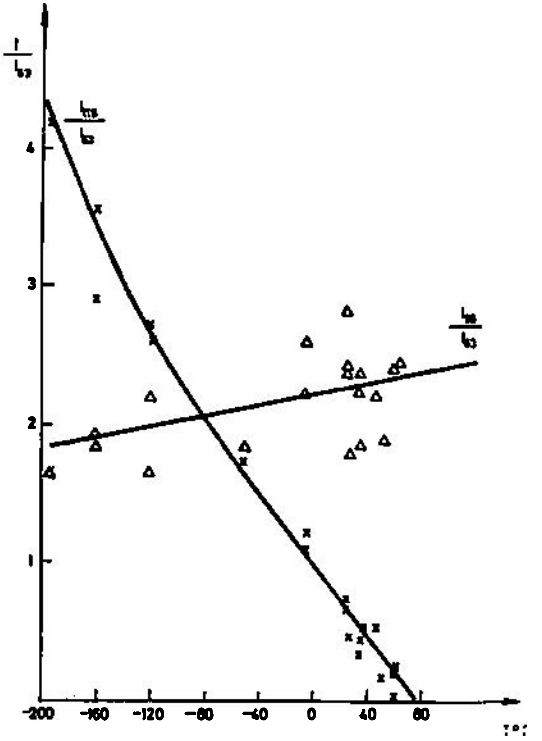

Fig. 4. Temperature dependence of intensities for the Raman bands 116 cm^{-1} and 99 cm^{-1}.

high temperatures, the separation of the bands encountered difficulties and, therefore, a larger number of measurements was needed. Fig. 4 shows the variation of intensity ratios with temperature for the two modes. While the behaviour of the band 99 cm^{-1} exhibits a slow increase in intensity ratio, the ratio for the band 116 cm^{-1} exhibits a constant fall. It is worthwhile to mention that the corresponding A component of the torsional mode, the band 112 cm^{-1}, exhibits the same behaviour. However, the measurements of this band encounter much more difficulties, since the vibrational band is several times stronger even at very low temperatures and rapidly takes dominance over the whole spectrum. At high temperature, similarly to the band B. the band 112 cm^{-1} does not disappear but appears as a very weak shoulder on the neighbouring band.

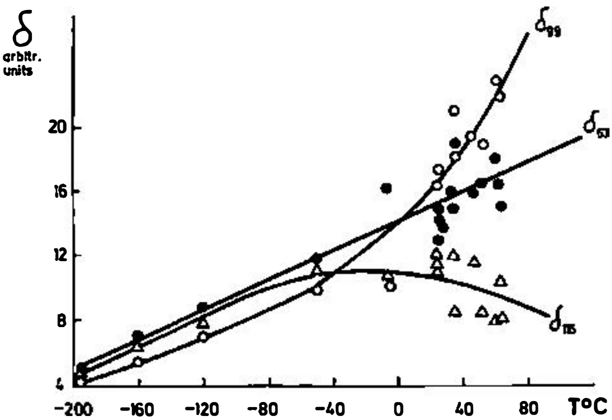

Fig. 5. Temperature dependence of Raman bandwidths.

Fig. 5 shows the measured bandwidths as functions of temperature. Although the accuracy of these measurements is rather poor, they clearly indicate the different temperature dependence of the three bands. The linear dependence of the internal mode 63 cm^{-1} and the exponential dependence of the vibrational mode 99 cm^{-1} are characteristic of the spectra of molecular crystals[9]. The bandwidth 116 exhibits a deviation relative to the bands 63 cm^{-1} and 99 cm^{-1}. Thus far we have found no explanation for such behaviour, and additional, more accurate measurements are needed to account for this departure.

3. *Discussion*

The results of the present measurements indicate that a torsional molecular mode exhibits a decrease in intensity with increasing temperature. The essential information extracted is the fact that the decrease starts from very low temperature, far from the temperature of the phase transition. The conclusion may be drawn that this mode is not directly associated with the phase transition in crystalline phenanthrene.

In a study of the structure of phenanthrene by X-ray and neutron scattering, Kay et al.[10] discussed the distorsion of the molecule in the crystal due to the overcrowding of the two hydrogen atoms. They concluded that the distorsion in phenanthrene is larger than in other crystals that exhibit molecular overcrowding. They observed that crystal forces could play an important role in molecular configuration. This could be of some importance in the interpretation of the observed intensity dependence on temperature. The intensity of the Raman bands studied might be associated with the degree of distorsion of the molecule. As suggested by Kay et al[10], this presumption could be tested by measuring molecular distorsion at low temperature by X-ray and neutron diffraction.

4. Conclusion

The results obtained in this work can be summarized as follows:

No conformational change in the molecule of crystalline phenanthrene has been observed by Raman spectroscopy.

Internal modes show no tendency towards disappearance nor towards abrupt changes in frequency, at the temperature of the phase transition.

The only change observed is the variation in intensity of the band assigned to the torsional mode. This variation seems not to be associated with the phase transition. It may be assumed that the variation in intensity is associated with the degree of distorsion of the molecule in the crystal lattice. However, to draw more reliable conclusions, further X-ray and neutron-scattering measurements are desirable. It is hoped that such measurement could contribute to the general attempt to explain the intensity of Raman bands.

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PROMJENE INTENZITETA KOD NEKIH NISKOFREKVENTNIH RAMAN VRPCI U KRISTALINIČNOM FENANTRENU

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Sadržaj

Zavisnost frekvencije i intenziteta nekih torzionih modova o temperaturi u molekuli fenantrena istraživana je pomoću Raman spektroskopije. Istraživanja su vršena za provjeru pretpostavke da fazni prijelaz u fenantrenu može biti prouzročen konformacionim promjenama molekula tog kristala. Nove vrpce nisu opažene. Interni modovi u spektru ne pokazuju tendenciju k nestajanju.

Opaženo je, da intenzitet torzionog moda 116 cm^{-1} znatno zavisi o temperaturi; međutim, to ponašanje nije u direktnoj korelaciji s faznim prijelazom.