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Far Infrared Spectrum of the γ-Phase of *p*-Dichlorobenzene

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We have studied the far IR spectrum of the γ-phase of *p*-dichlorobenzene by use of an NPL Grubb Parsons modular interferometer with digital transformation of the observed interferograms. Polycrystalline sample was mounted in a metal holder attached to a liquid nitrogen cooled, cold finger. Several thicknesses of beam splitter were used together with TPX windows to contain the sample.

This γ-phase, first observed by Dean and Lindstrand(1) has recently been identified and studied by Raman spectroscopy(2) and it has been shown that the stability ranges of the three solid phases of *p*-dichlorobenzene can be described as follows:

T K		279		304		326
Phase	γ	$\gamma \leftrightarrows \alpha$	α	$\alpha \rightleftarrows \beta$	β	$\beta \rightleftarrows$ liquid
			monoclinic(6) 2 molecules per unit cell Space group C^5_{2h} Site group C_i		triclinic(5) 1 molecule per unit cell Space group C_i Site group C_i	

However, the α phase is easily frozen to low temperature if no precautions are taken.

Hadni(3) has recently studied the far IR spectrum of single crystal of the α phase, using polarized light and he has been able to assign the observed frequencies. Others(4) had previously studied what was supposed to be the α-phase but they observed spectra which were utterly different.

Following the method previously described(2) to obtain this γ-phase, the β-phase has been rapidly cooled down to 123 K. The spectrum recorded at this temperature shows only a broad line at 127 cm^{-1} which corresponds to the well known internal vibration $B_{3u}$$^{(7)}$ (out-of-plane chloride vibration). This proves that the spectrum corresponds to the quenched β-phase because, according to the group theory, no pure liberation mode can be active in far infrared for this crystalline structure and the three translation modes are acoustical ones.

By slowly warming the sample to 260 K we have observed a spectrum which shows three lines which lie at 44.5, 86 and 119.5 cm^{-1}. By cooling again to 123 K, the recorded spectrum shows two narrow lines at 50 cm^{-1} and 95 cm^{-1} and two close lines around 120–130 cm^{-1}.

So, we can conclude that the two lines which lie at 44.5 cm^{-1} and 86 cm^{-1} at 260 K and which shift respectively to 50 cm^{-1} and 95 cm^{-1} at 123 K represent two intermolecular vibration modes.

Furthermore we can say that a third lattice mode certainly lies around 130 cm^{-1}, near the internal B_{3u} mode because at 123 K we

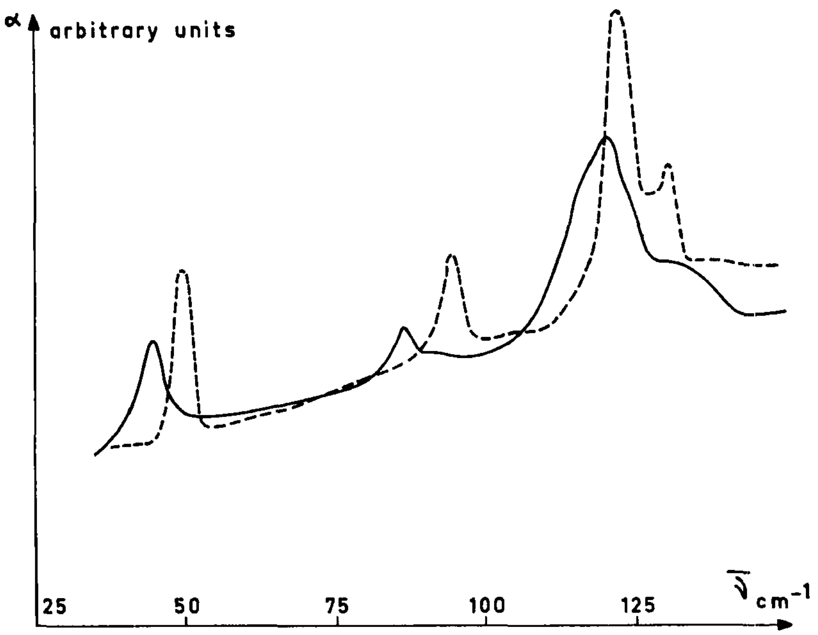

Figure 1. Far infrared spectra of the γ phase of p. dichlorobenzene: --- = 123 K; — = 260 K.

could observe a splitting of this latter line. This line could not be a combination mode between an internal B_{2u} mode (227 cm^{-1}) and the intermolecular vibration mode which lies at 95 cm^{-1} because such a line would lie around 140 cm^{-1} at 260 K.

We can see that the spectra we observed are different from those observed by Hadni in the α-phase; and as we have followed the thermal procedure previously described to obtain the γ-phase, we can conclude that the spectra of Fig. 1 correspond to the γ-phase of *p*-dichlorobenzene.

As from 123 K to 260 K the temperature-shifts of the Raman and far IR lines which lie around 50 cm^{-1} are very close (some 5 to 6 cm^{-1}), we cannot say whether these lines correspond to the same modes or different ones. The situation is the same for the lines observed in the vicinity of 130 cm^{-1}, consequently we cannot conclude as to the existence of a symmetry center in the corresponding space group. We can only say that if the three lines which we observe in far IR and the six lines recorded in Raman are the only ones which are allowed we have certainly two molecules per unit cell.

In order to assign the observed lines further studies are in process.

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