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Effect of Pressure on the Absorption Spectra of Oriented and Amorphous Organic Films

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The absorption spectra of oriented and amorphous naphthacene and pentacene film have been measured at high pressure. The Davydov splitting of 0-0 band in oriented films increase with increasing pressure at the rate of 37 cm^{-1}/kbar for naphthacene and 70 cm^{-1}/kbar for pentacene. The 0-2 vibronic bands of both oriented films show the large red shifts compared with the 0-1 vibronic band. For amorphous films the Davydov splitting is not observed at atmospheric pressure. The pressure induced spectral red shifts in the amorphous state are slightly larger than those in the crystalline-state.

INTRODUCTION

The electronic spectra of molecular crystals differ from those of the corresponding free molecules. One of the prominent features of the spectra of crystals is the shift of the absorption band towards long wavelength, and the other is the appearance of Davydov splitting.

The absorption spectra of naphthacene single crystals have been studied already by several authors.[1, 2, 3] The Davydov splitting of the 0-0 band is about 575 cm^{-1}. The splitting is fortunately discernible even for a randomly oriented microcrystalline film with the use of unpolarized light.[1] In a previous paper, we have reported that the Davydov splitting in naphthacene film increases with pressure at the rate of 37 cm^{-1}/kbar and discussed the results on the basis of a theory of the electronic state of the molecular crystal.[4] The change of the electronic states of molecular crystals at high pressures has been discussed in detail by Rice and Jortner.[5]

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Recently, the absorption spectra of amorphous organic films have been studied.[6-7] The characteristic absorption bands of the crystalline-state disappeared in the amorphous-state; the Davydov splitting of the 0-0 bands in naphthacene and pentacene were not observed in their amorphous films.[6-7]

In this report, we will present some results on the absorption spectra of oriented and amorphous naphthacene and pentacene films at high pressures and will discuss the effect of pressure on the electronic states in these evaporated films.

EXPERIMENTAL

Naphthacene and pentacene were purified by fractional sublimation. Thin oriented microcrystalline films were grown on glass plates at room temperature by sublimation in vacuo. Amorphous films were prepared on glass plates cooled near liquid nitrogen temperature by evaporation in a vacuum of $\sim 10^{-4}$ Torr.[7] Although the X-ray diffraction lines corresponding to (00ℓ) plane were measured for the oriented films, no lines could be found in the case of the amorphous films. The measurement of the absorption spectra was carried out at room temperature with a high-pressure optical cell combined with a spectrophotometer. A hydrostatic pressure up to 6 kbar was applied by means of a pressure transmitting medium (kerosene or white gasoline) through a pressure-intensifier.[4]

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of oriented naphthacene film as a function of pressure. This absorption band in the visible region corresponds to the transition $^1A_{1g} \longrightarrow {}^1B_{2u}$ with a transition dipole moment oriented along the short axis of the planar molecule. The average red shift by compression is -110 cm^{-1}/kbar for the 521 nm band, and -75 cm^{-1}/kbar for the 503, 471 and 440 nm bands. Further, these three bands have indicated the different pressure shifts at higher pressure region.[8] The 521 nm band is the (+) Davydov component of the 0-0 band (polarized along b axis) and the 503 nm band is the (−) one (polarized perpendicularly to b axis). The Davydov splitting of the 0-0 band increased with increasing pressure at the rate of 37 cm^{-1}/kbar. This value is roughly four times larger than that predicted from the dipole approximation.[4] The discrepancy between the observed and predicted values may arise from the assumption that the crystal has isotropic elastic constants, that the relative orientation of the molecules in the crystal is not changed even at high pressure, and also from the neglect of the short-range multipole and long range dipole-dipole interactions.

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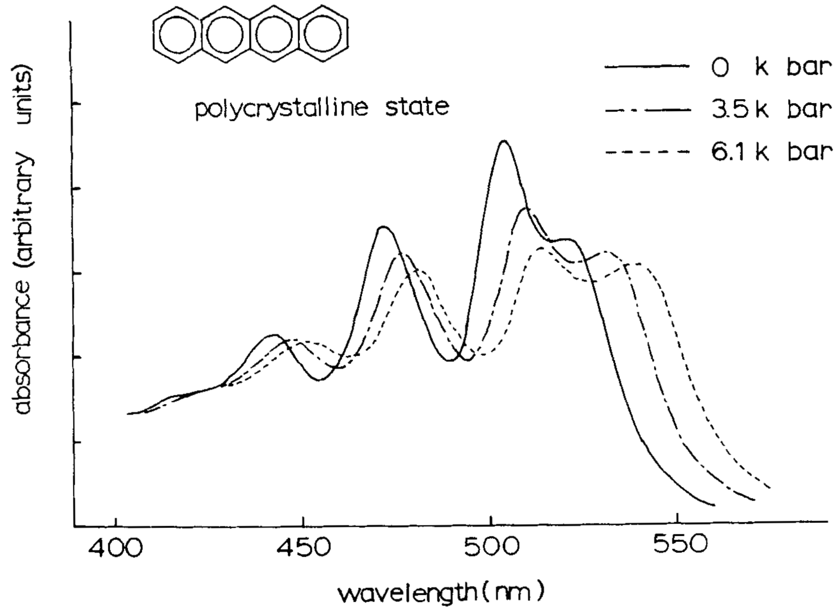

FIGURE 1 The absorption spectra of oriented naphthacene film at high pressure: ——— 0 kbar, ——·——3.5 kbar, ------6.1 kbar.

It should be noted that the total absorption intensity is not changed significantly by pressure, but the intensity ratio of the 521 nm band to the 503 nm band increases about 25% at 5.2 kbar. The 503 nm band becomes weak with pressure[8] and disappears under higher compression.[9] Ohigashi suggested that the change of intensity ratio with pressure may be due to the rotation of the intermolecular plane under compression.[10] Further, for determining the absorption intensity, Rice and Jortner indicated that the configuration interaction between electronic states on the basis of crystal field perturbation is of considerable importance.[5]

The absorption spectra in oriented pentacene film at high pressure are exhibited in Fig. 2 for four isobars. A small amount of pentacene dissolved in the pressure medium, white gasoline, so that the total band intensity changed markedly with pressure. It has been already reported that the 630 and 670 nm bands are two Davydov components of the 0-0 band.[7] The Davydov splitting was about 950 cm^{-1} at atmospheric pressure. As is seen from Fig. 3, this splitting increased with increasing pressure at the rate of 70 cm^{-1}/kbar, which is about two times larger than that for napthacene. The larger values of the Davydov splitting, 950 cm^{-1}, and its pressure dependence such as 70 cm^{-1}/kbar in pentacene were very unusual.

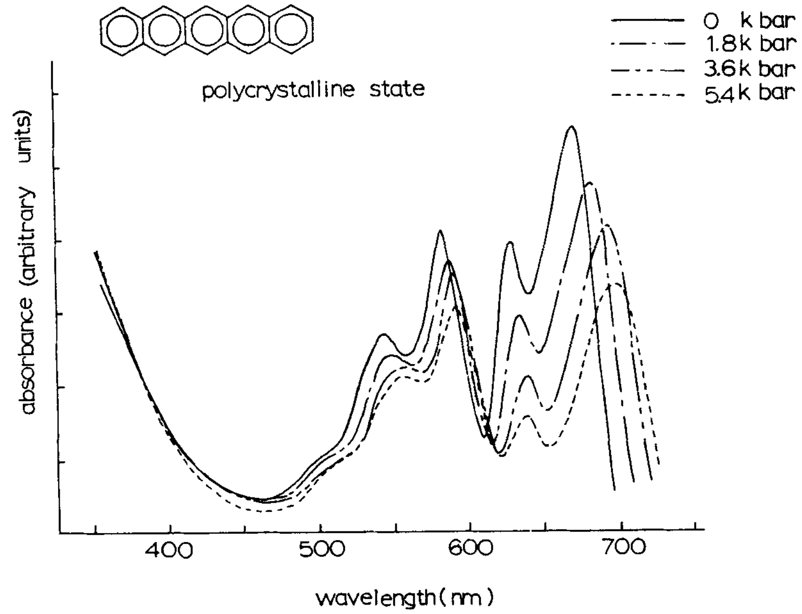

FIGURE 2 The absorption spectra of oriented pentacene film at high pressure: ——— 0 kbar, —— - ——1.8 kbar, —— - - ——3.6 kbar, ----5.4 kbar.

The heats of sublimation of aromatic hydrocarbons with 22 carbon atoms are given in Table 1.[11] The sublimation energy of pentacene is much larger than that of other compounds. The electrical resistance of pentacene decreases rapidly, by a factor of approximately 10^{12}, in the first 200 kbar region at room temperature.[9, 12] The observed factor, 10^{12}, is very large in comparison with other aromatic hydrocarbons. At higher pressure the pseudo-metallic behaviour in pentacene crystals is observed at temperature between 140 and 180 K.[9] These anomalous behaviours suggest that the large pressure dependence of the Davydov splitting is not explained by the usual exciton theory in the weak coupling limit.

As illustrated in Fig. 3, the rates of peak shifts of 0-0(+), 0-0(−), 0-1 and 0-2 band were approximately −130, −50, −60 and −93 cm^{-1}/kbar. According to the exciton theory in weak coupling limit, Rice and Jortner predicted[5] that the red shifts of 0-n vibronic bands for the anthracene p band reduce with increasing quantum number, n. The 0-2 vibronic band of pentacene shows the large shift compared with the 0-1 vibronic band. In the case of naphthacene, similar result has been found at higher pressure.[8] These results indicate that the crystal field effect in naphthacene or pentacene crystals is stronger than that in ordinary aromatic hydrocarbons such as anthracene.

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TABLE 1
The heats of sublimation of five aromatic hydrocarbons with 22 carbon atoms.

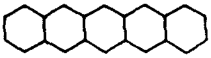
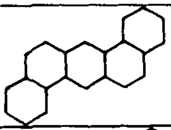
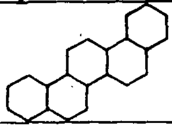
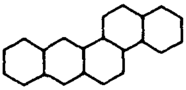
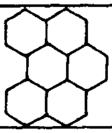
Molecule	Structure	ΔH kcal/mol
Pentacene $C_{22}H_{14}$		37.7
1,2,5,6-Dibenzanthracene $C_{22}H_{14}$		33.9
Picene $C_{22}H_{14}$		33.5
3,4-Benztetraphen $C_{22}H_{14}$		32.6
1,12-Benzperylene $C_{22}H_{11}$		30.0

Figure 4a and 4b exhibit the effect of pressure on the absorption spectra of amorphous naphthacene and pentacene films at room temperature. The absorption bands in these films were similar to those of the corresponding free molecules in solution. The Davydov splitting of the 0-0 bands found in oriented films disappeared in the amorphous films. Since the shapes of the absorption spectra were essentially unchanged at high pressure, amorphous naphthacene and pentacene did not crystallize by compression up to 5.4 kbar. The spectral red shifts with pressure are shown in Fig. 5a and 5b. The rates of peak shifts of the 0-0, 0-1 and 0-2 bands were approximately −130, −65 and −80 cm^{-1}/kbar for naphthacene, −140, −93 and −110 cm^{-1}/kbar for pentacene, respectively.

Rice and Jortner proposed[5] that the spectral shift of nth vibronic band to fth excited electronic state of molecular crystals, Δ_f^n can be displayed in the form:

$$\Delta_f^n = D_f + W_f + C_f^n(k) \tag{1}$$

where D_f is the uniform shift of the manifold of energy level which appear in the

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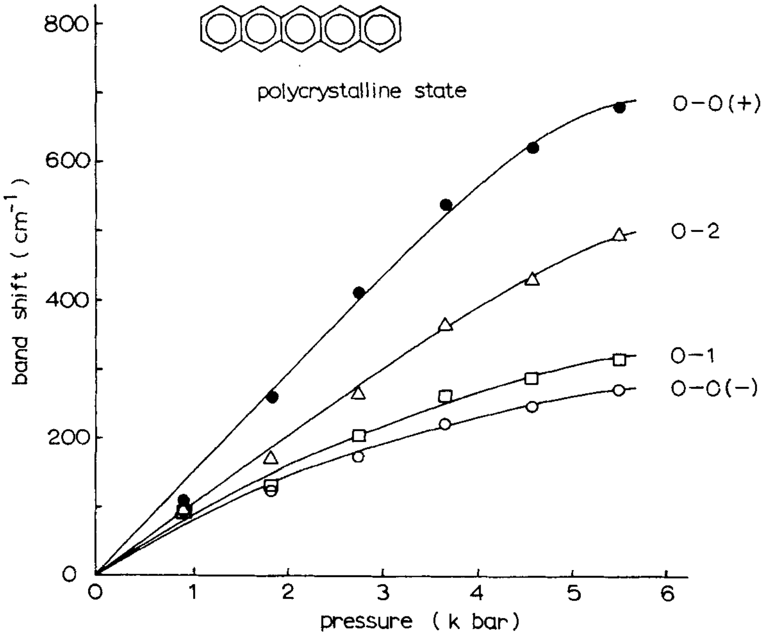

FIGURE 3 Pressure shifts of the 0-1 and 0-2 vibronic bands and the two components of the 0-0 band in pentacene microcrystal.

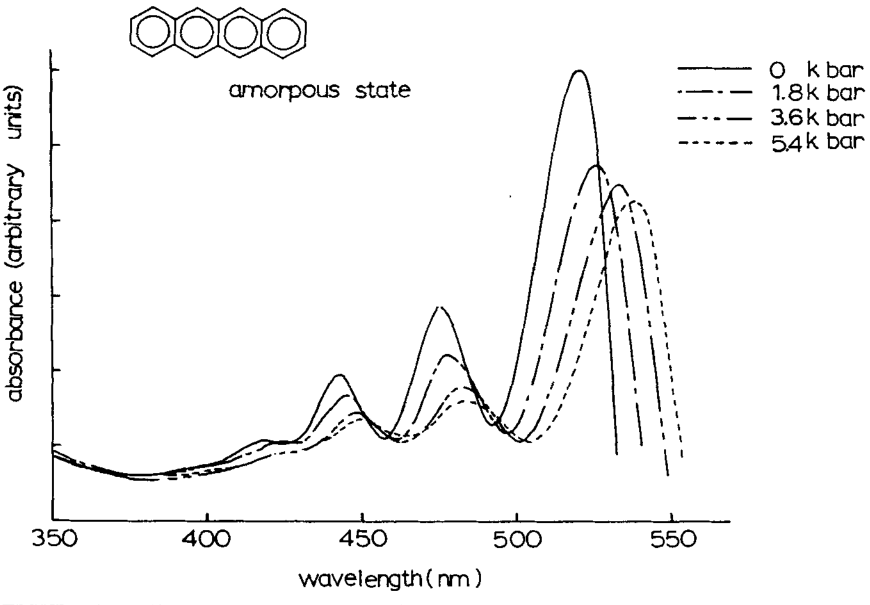

FIGURE 4a The absorption spectra of amorphous naphthacene film at high pressure: ———— 0 kbar, —— - ——1.8 kbar, —— – ——3.6 kbar, — 5.4 kbar.

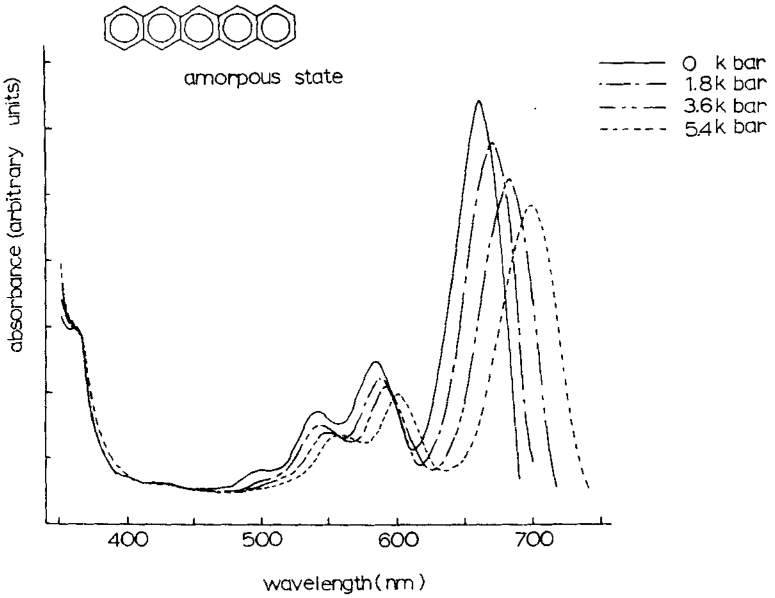

FIGURE 4b The absorption spectra of amorphous pentacene film at high pressure: ——— 0 kbar, —— - —— 1.8 kbar, —— -- —— 3.6 kbar, --- 5.4 kbar.

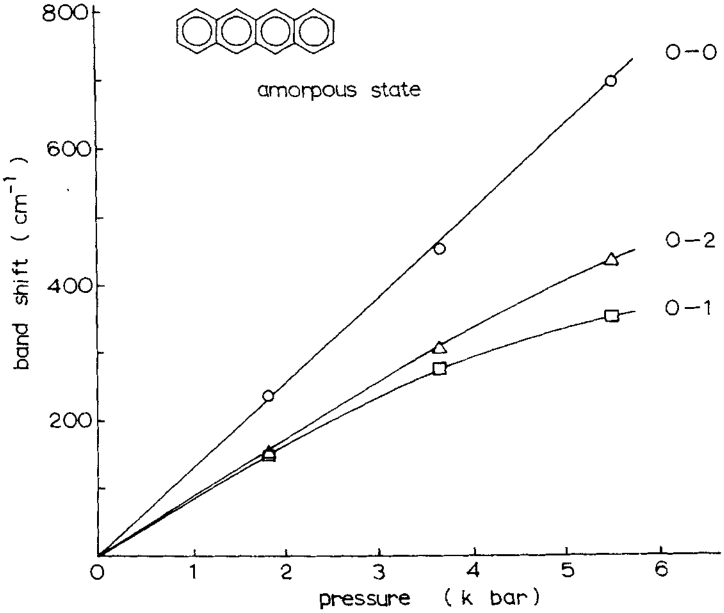

FIGURE 5a Pressure shifts of the 0-0, 0-1 and 0-2 vibronic bands in amorphous naphthacene.

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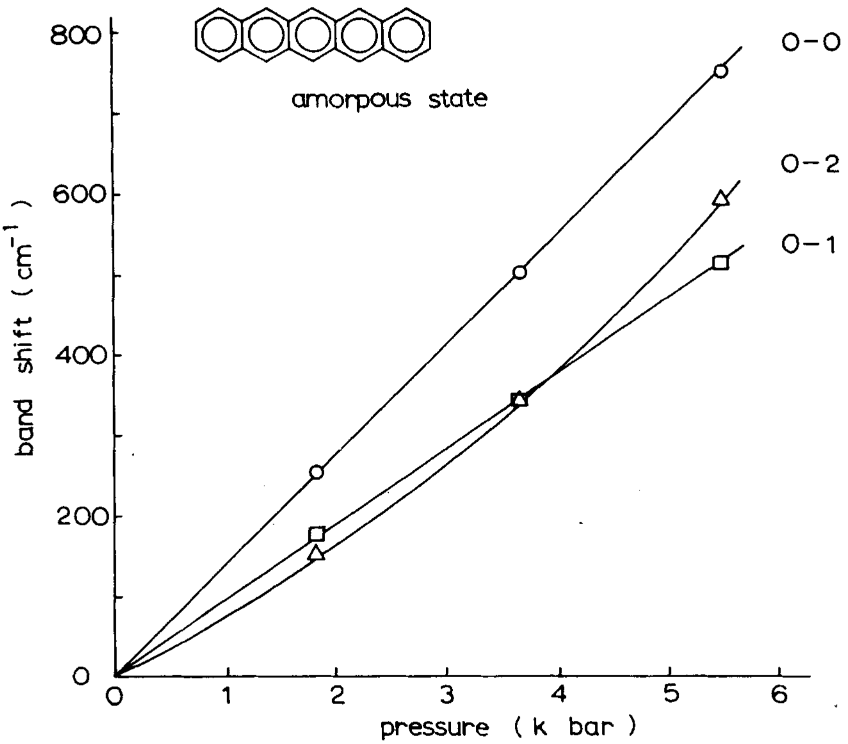

FIGURE 5b Pressure shifts of the 0-0, 0-1 and 0-2 vibronic bands in amorphous pentacene.

usual exciton theory. $C_f^n(k)$ is a shift based on the intermolecular interactions between translationally equivalent molecules. The solvent shift, W_f in Eq. (1), arises from the dispersion force. An order of magnitude estimate for this shift is given by

$$W_f \approx \sum_i R_i^{-6} \alpha (\mu^2 + \tfrac{1}{9} \alpha E_f) \tag{2}$$

where R_i is the intermolecular separation, α the polarizability, E_f the excitation energy and μ the transition dipole moment.

In the amorphous state, D_f and C_f^n (k) do not contribute to the pressure shift, which is then due only to the solvent shift, W_f. The spectral red shifts in amorphous state spectra are slightly larger than those in crystalline-state spectra. These findings suggest that the exciton shift $C_f^n(k)$ in the crystal is very small.

The vibronic bands of naphthacene in polystyrene matrix show identical shifts within experimental error.[8] On the contrary, the rates of shifts of vibronic bands in amorphous films are very different. The red shifts of the 0-0 band were very large. As observed in crystalline-state spectra, the shift of the 0-2 band is larger than that of the 0-1 band. It should be noted that the relative intensities of the vibronic components in amorphous state spectra are different from those in solution spectra.[7] As shown in Eq. (2), the solvent shift W_f is related to the magnitude of the transition dipole moment. The anomalous shift of the 0-0 band arises from the large intensity of this band.

On the basis of these results and discussion we conclude that the intermolecular interactions in the amorphous state are never weak in comparison with those in the crystalline-state.

Acknowledgement

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