

to the volume, such as the breathing vibration of the lattice, while the optical process may involve other coordinates.

In view of all these differences the relationship between the thermal and optical processes would seem to be tenuous. However, an analysis has been performed<sup>1,5</sup> which relates the energies involved in optical and thermal processes. It has been quite successful in predicting electronic transitions from the location and half-width of the optical absorption peak as a function of pressure. It gives:

$$E_{th} = h\nu - 3.6(E_{1/2})^2 R \quad (1)$$

Here  $E_{th}$  is the energy for thermal transfer,  $h\nu$  is the peak location,  $E_{1/2}$  the peak half-width and  $R$  the ratio of force constants of ground and excited states; all energies are in electronvolts. (We shall generally give energies in eV in this paper:  $1 \text{ eV/atom} \cong 23 \text{ kcal/g atom} = 9.6 \times 10^4 \text{ J/g atom}$ . Upon occasion it will be convenient to speak of peak shifts in  $\text{cm}^{-1}$ :  $1 \text{ eV} \cong 8000 \text{ cm}^{-1}$ ). Pressures are given in kilobars ( $1 \text{ kbar} = 987 \text{ atm} = 10^8 \text{ Pa}$ ). At the end of this paper we shall show that this analysis also forms the basis of an informative description of a wide variety of electronic excitations based on optical absorption and emission measurements as a function of pressure.

## HYDROCARBONS

We consider first the electronic properties of polyacenes under pressure. We compare and contrast the behaviour of anthracene and pentacene. Both crystallize in similar 'herringbone' structures. The ground state has  $A_{1g}$  symmetry, is non-polar and is not very reactive, in the solid state at least. The lowest energy excited state wave functions have nodes between the carbons ( ${}^1L_a$  symmetry) and a significant dipole moment so that its interactions with neighbouring molecules must be considerably stronger than that of the ground state. Both molecules have some tendency for 'self-complexing', i.e. electron transfer between neighbours; this is greater in the excited state than in the ground state.

The major difference is that in anthracene the  ${}^1L_a$  state lies over 3 eV above the ground state, while in pentacene it lies about 2 eV above the ground state. There is also a somewhat greater tendency for self-complexing for the larger molecule.

As can be seen in *Figure 2*, there is a very large decrease in optical excitation energy with increasing pressure. (A  $V/V_0$  of 0.7 corresponds roughly to 100 kbar.) The absolute shift is about the same for both molecules,  $\sim 0.65 \text{ eV}$  in 100 kbar, but this constitutes a much larger fraction of the original excitation energy for pentacene than for anthracene. The peaks also broaden significantly with increasing pressure<sup>1,5,6</sup>. At 1 atm  $E_{th}$  for anthracene  $\sim 3.3 \text{ eV}$  and for pentacene  $\sim 2.0 \text{ eV}$ . By 200 kbar  $E_{th}$  for anthracene is  $\sim 1.5 \text{ eV}$ . The rate of decrease slows rapidly with increasing pressure. The electrical resistance decreases with increasing pressure, but it always remains high and there is always a significant activation energy for carrier production, so it remains a semiconductor. All processes are reversible.

In pentacene, by 200 kbar  $E_{th}$  is  $\sim 0$ . At sufficiently low temperature

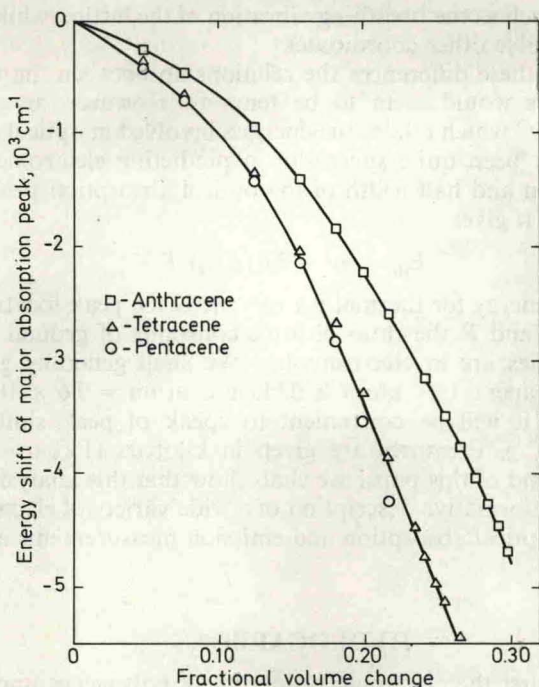


Figure 2. Shift of absorption peaks against  $\rho/\rho_0$ : three polyacenes

(below  $\sim 200$  K) one finds that the resistance increases with increasing temperature so that one has a kind of metal—probably a semimetal like bismuth with an estimated resistivity of  $10^{-2}$ – $10^{-4}$  ohm-cm. At room temperature above 200 kbar the resistance starts to drift upwards with time. After 24 h at 300 kbar the increase may be several orders of magnitude. This

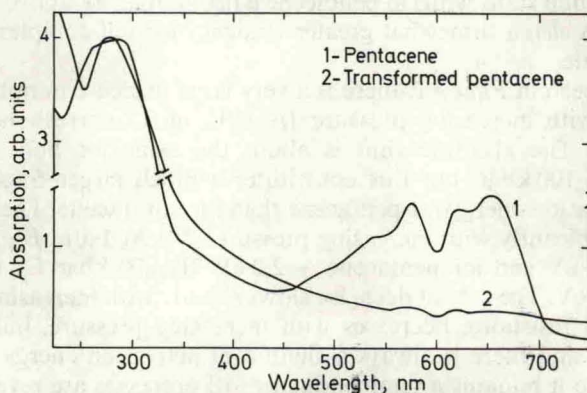


Figure 3. Electronic spectra of pentacene and reacted pentacene