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Anomalous Fluorescence of Pure Anthracene Crystal under High Pressure

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The effect of pressure on the fluorescence spectra of a few aromatic hydrocarbons was reported recently.[1] In this report, we present an anomalous fluorescence of anthracene crystals which may be ascribed to a formation of resonance dimers under high pressure.

The emission spectra from anthracene in various states were measured applying pressure up to 52 kbar. The samples used were: (i) an anthracene single crystal, (ii) naphthalene polycrystals containing 5×10^{-3} mole concentration of anthracene, (iii) polystyrene dissolving anthracene of 0·5 wt %, and (iv) anthracene crystals doped with 10^{-3}, 10^{-4} and 10^{-5} mole concentration of tetracene. The high-pressure bomb was similar to the one described by Fitch *et al.*[2]

The shifts of emission bands of anthracene are illustrated in Fig. 1. The wavenumbers of the peaks decreased proportionally to applied pressure; the rates of decrease were 40–45 cm^{-1}/kbar for molecular anthracene dissolved in the hosts and for crystalline anthracene containing tetracene. For an anthracene single crystal, on the other hand, the rate was about 80 cm^{-1}/kbar.

The fluorescence bands of molecular anthracene become broader in some degree but retain vibrational structure even at the maximum pressure. The features resemble those of the spectrum of tetracene in a host anthracene crystal.[3] On the contrary, the fluorescence spectrum of pure anthracene crystal becomes extremely broadened (about 4000 cm^{-1} at 40 kbar) and its vibrational structure disappears. The total intensity of the fluorescence is

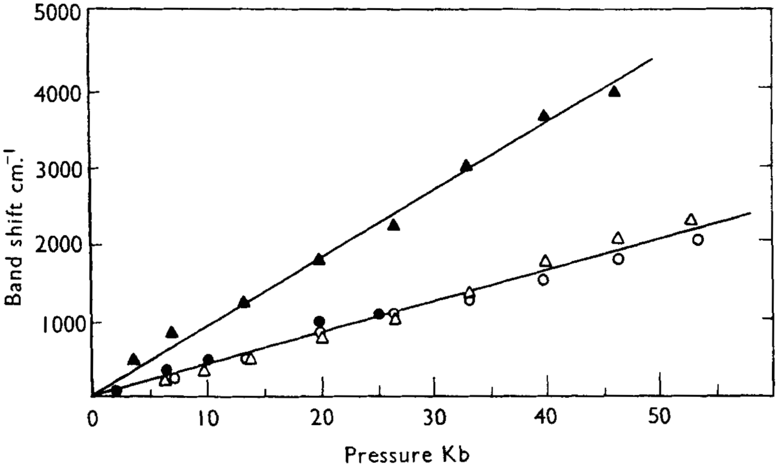

Figure 1. Red shift of band peaks of fluorescence spectra of anthracene; ▲ single crystal, ● crystal containing 10^{-4} mole concentration of tetracene, ○ dissolved in polystyrene, △ dissolved in naphthalene.

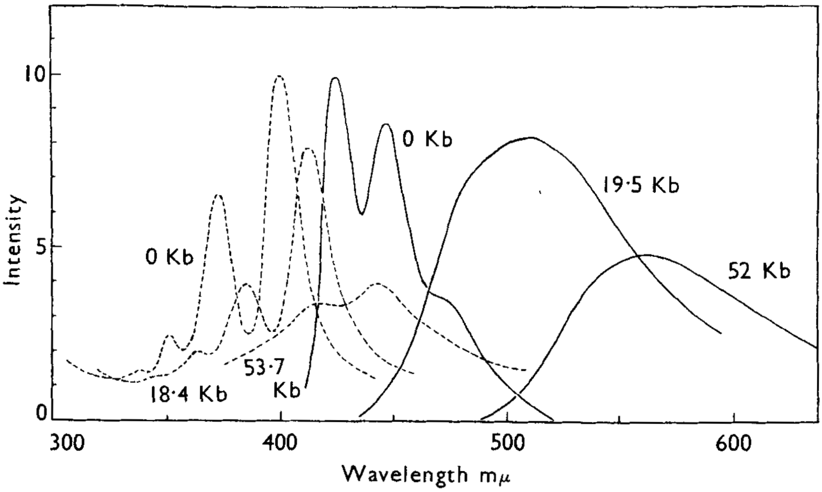

Figure 2. Fluorescence spectra of anthracene single crystal (solid lines) and absorption spectra (dotted lines; Ref. 3).

unchanged up to 30 kbar and decreases slightly above this pressure, which excludes the possibility that the origin of anomalous fluorescence is impurities. Typical examples for pure anthracene crystal are shown in Fig. 2 together with absorption spectra obtained by Wiederhorn and Drickamer.[4] The behaviors of the red shift and the broadening of emission spectra of anthracene solid solution are similar to those of the absorption spectra, i.e., the former have a mirror symmetry with the latter. In the case of the pure anthracene crystal, however, no symmetry can be found as illustrated in Fig. 2.

The characteristics of the anomalous emission spectra of the pure crystal coincide with that of resonance dimer or excited dimer as observed in pyrene and other compounds in the crystalline state.[5,6,7] The decrease of intermolecular distances and the rotation of the molecular planes by compression under high pressure[8] increase the intermolecular interaction between an excited molecule and unexcited adjacent molecules. A strong coupling between the molecules will cause a resonance dimer from which a broad and red-shifted band is emitted. The results coincide with the recent work of Jones and Nicol.[9]

The anthracene–tetracene system involves transfer of excitation energy of the host crystal to a guest molecule.[10] As the pressure is raised, the fluorescence intensity of tetracene increases and that of anthracene decreases.[3] In this case it should be noted that the emission spectrum of the host crystal shifts to the longer wavelength side by the same amount as for molecular anthracene. Furthermore, no dimer emission is observed even at 52 kbar for the crystal containing 10^{-4} mole concentration of tetracene, and the fluorescence intensity of tetracene is not decreased effectively. Since the energy level of the excited dimer is lower than that of tetracene, the energy from the resonance dimers cannot be transfered to tetracene molecules. These facts imply that the formation of the resonance dimer may be prevented by the presence of the energy acceptors.

An excited anthracene molecule in the crystalline state may dissipate its energy through the following competitive processes: (a) $A^* \rightarrow A + h\nu$, (b) $A^* + A \rightarrow A^*A \rightarrow A + A + h\nu'$, and (c) $A^* + T \rightarrow$

$A + T^* \rightarrow A + T + h\nu''$, where A designates an anthracene molecule in the ground state, A* in its excited state, A*A its resonance dimer, and T a tetracene molecule. From our results, it can be predicted that the process (a) occurs at low pressure, and (b) occurs at high pressure but, in the case of energy transfer to an impurity molecule, the process (c) instead of the process (b) becomes predominant.

The probability of the transfer of excitation energy to a tetracene molecule exceeds that of dimer formation.

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