The Effect of Pressure on the Fluorescence Spectra of Anthracene, Chrysene and Pyrene

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Recently the fluorescence spectra of aromatic molecular crystals have been found to be intimately connected with the crystal structure; the anomalous, long wavelength emission has been explained in terms of the formation of the excited dimer state.[1-3] In this note we will present a study of the effect of static high pressure on the fluorescence spectra of anthracene, chrysene and pyrene.

A Drickamer-type optical cell[4] available for measurement under high pressure up to 52 kb. was used. A small amount of pure crystal was put in the optical cell and excited by a 365 mμ mercury light. The measurement of the fluorescence spectra was made with a Bausch and Lomb 250 mm. monochromator and by a sensitive-photomultiplier detecting system.

The emission peaks of these crystals were found to shift remarkably to lower frequencies almost linearly with an increase in the pressure, the shift being 80 cm^{-1}/kb. for anthracene and 40 cm^{-1}/kb. for chrysene and pyrene (cf. Fig. 1). The vibrational structures in the fluorescence spectra were blurred under high pressure. The red shifts could be reversed for pyrene and chrysene by applying and releasing the pressure, but the shift was irreversible for anthracene. The fluorescence

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1) J. Ferguson, *J. Chem. Phys.*, **28**, 765 (1958).

2) B. Stevens, *Spectrochim. Acta*, **18**, 439 (1962).

3) J. Tanaka, This Bulletin, **36**, 1237 (1963).

4) R. A. Fitch, T. E. Slykhouse and H. G. Drickamer, *J. Opt. Soc. Am.*, **47**, 1015 (1957).

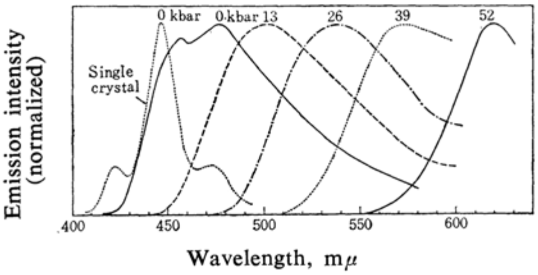

Fig. 1. Shifts of fluorescence bands.
The values for anthracene were determined from the reduced zero pressure value (475 mμ).

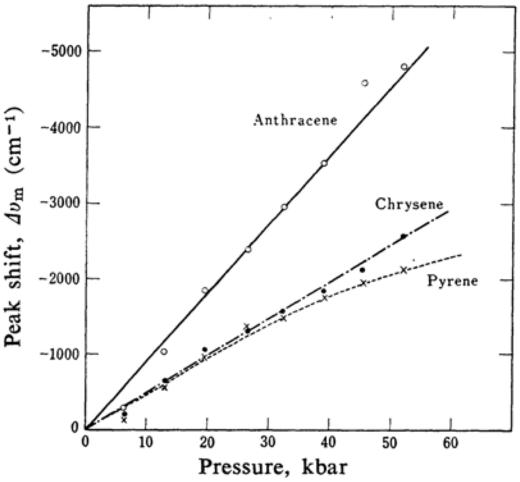

Fig. 2. Change in the fluorescence spectrum of anthracene with an increase in the pressure at room temperature.

of anthracene did not recover completely to the original spectrum once it had been pressed under high pressure, and it showed a strong broad emission in the 475 mμ region (cf. Fig. 2). The red shift of the crystal might be explained by assuming a potential energy diagram in which the curve for the ground state is steeper than that of the excited state and in which the minimum of the excited state is located at a smaller configurational coordinate than the ground state.[5]

The larger red shift of the anthracene crystal needs some comment. According to Wiederhorn and Drickamer,[6] the absorption spectrum of the anthracene crystal shifts to frequencies lower by 45 cm^{-1}/kb. with an increase in the pressure. The red shift of 80 cm^{-1}/kb. of the fluorescence will be partly due to the shift of the ^1L_a excited level. The second point to be considered is that the 475 mμ emission occurs even after the pressure is released. This might be explained by assuming the formation of an emission center of the dimer type produced under the high pressure. As a result of the hysteresis effect of the pressure, the emission center will remain in the crystal and the 475 mμ band will occur from this emission site, even if the pressure is released. This idea is supported by the observation that the 475 mμ band disappears when the pressed crystal is warmed up in vacuo.

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[5] P. D. Johnson and F. E. Williams, *Phys. Rev.*, **95**, 69 (1954).

[6] S. Wiederhorn and H. G. Drickamer, *J. Phys. Chem. Solids*, **9**, 330 (1959).