Fluorescence Spectra of High-purity Coronene Thin Film

Takashi Kajiwara, Koichi Ohno, Satoshi Iwashima and Hiroo Inokuchi

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Tokyo

(Received June 13, 1969)

Commercial and synthesized crude coronene contains perylene as an impurity, and its fluoresence spectra depend much on the degree of purification.[1]

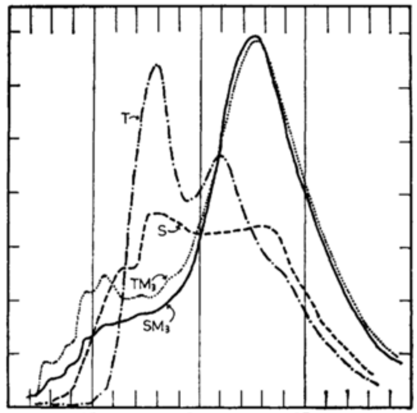

Fig. 1. The fluorescence spectra of the sublimed thin films of coronene of various degrees of purity at room temperature.
T: Commercial coronene, (crude).
S: Synthesized coronene, (crude).
TM_3: Commercial coronene purified by treatment with maleic anhydride for 3 hr (see text).
SM_3: Synthesized coronene purifide by treatment with maleic anhydride for 3 hr (see text).

Figure 1 shows the fluorescence spectra of sublimed thin films of coronene at room temperature. High-purity coronene (TM_3 and SM_3 in Fig. 1) shows a broad excimer-type fluorescence around 525 mμ, as do pyrene, α-type perylene, and benzo[*g,h,i*]perylene. The maxima around 480 mμ and 510 mμ of the fluorescence of crude coronene (T and S in Fig. 1) are due to those of perylene, because these maxima are enhanced as the concentration of perylene in the coronene matrix is increased.[2] The sample denoted as T in Fig. 1 contains about a 10^{-3} mol/mol concentration of perylene. Though benzo[*g,h,i*]perylene is also included in crude coronene, its influence on the fluorescence spectra of solid coronene is not obvious.

Figure 2 shows the temperature dependence of the fluorescence spectra of a sublimed thin film of high-purity coronene (SM_3). As the temperature decreases, the fluorescence bands around 446 mμ and 474 mμ gradually increase and the broad band around 525 mμ decreases. When the sample specimen is cooled to 4.2°K, the broad band disappears and the spectra with distinct vibrational structures appear; these spectra are similar to the fluorescence spectra in its *n*-heptane solution.[3] It is remarkable that the vibrational structures show a fairly good correspondence with the faint structures observed in the short-wavelength region (430 mμ—480 mμ) of the fluorescence spectra at room temperature. It is also interesting that the fluorescence spectra at 77°K are very different from those at 4.2°K. The measurement of the fluorescence spectra in the temperature region from 77°K to 4.2°K will now be undertaken.

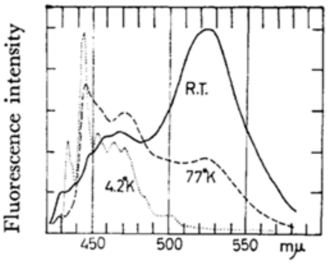

Fig. 2. Temperature dependence of the fluorescence spectra of a sublimed thin film of high purity coronene (SM^3). The relative fluorescence intensity is not corrected.
Fluorescence maxima: at 4.2°K, 434, 436, 443, 453, 464, 469, 484, and 502 mμ.

The method of purification is as follows.[4] A crude (commercial or synthesized) coronene is treated for more than 3 hr with maleic anhydride, upon which perylene and benzo[*g,h,i*]perylene change to carboxylic acid anhydride. These anhydrides are then eliminated by precipitation, making use of the fact that their solubilities in the solvent, xylene, are much less than that of coronene. Further, the coronene is purified by repeated recrystallizations and sublimations. The perylene concentration in the matrix can be decreased to less than 10^{-5} mol/mol by these procedures.

---

[1] The same phenomena are observed in benzo[*g,h,i*]perylene. T. Kajiwara, I. Shirotani, H. Inokuchi and S. Iwashima, *J. Mol. Spectry.*, **29**, 454 (1969).

[2] B. Stevens, *Spectrochim. Acta*, **18**, 436 (1962).

[3] D. E. Heine and H. W. Offen, *Mol. Cryst.*, **5**, 217 (1969).

[4] The details of the purification procedure are given in: S. Iwashima, K. Ohno, T. Kajiwara and J. Aoki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **90**, 884 (1969).