Fluorescence Spectrum of Pyrene Vapor: Emission from the Second Excited Singlet State[*1]

Akira NAKAJIMA and Hiroaki BABA

Division of Chemistry, Research Institute of Applied Electricity, Hokkaido University, Sapporo

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It is generally believed that in isolated polyatomic organic molecules, with the exception of azulene, internal conversion occurs at such a high efficiency that fluorescence cannot be observed from excited singlet states other than the first.[1–5] We have recently measured the fluorescence spectrum of pyrene vapor and detected an emission which can be assigned to fluorescence from the second excited singlet.

Fluorescence and excitation spectra were measured with a Hitachi fluorescence spectrophotometer of type MPF-2A, to which an electric furnace was attached. All the spectra were corrected for instrumental factors. Pyrene was highly purified by chemical treatment, chromatography, vacuum sublimation and zone melting.

Figure 1 shows fluorescence spectra of pyrene vapor. In the near ultraviolet region, pyrene has four electronic absorption bands denoted by I, II, III and IV. In Fig. 1, the wavelengths of the exciting light, 323, 268 and 236 mμ correspond to the 0–0 transitions for II, III and IV, respectively. It is seen that excitation into the third or fourth excited singlet gives rise to an additional emission between 320 and 360 mμ, *i. e.*, in the region adjacent to the absorption band II. The fluorescence excitation spectrum obtained by monitoring the emission in the above region was different from that obtained by monitoring at a wavelength longer than 360 mμ (Fig. 2). The excitation spectrum monitored at 370 mμ is normal and is in agreement with the absorption spectrum. On the contrary, the excitation spectrum monitored at 340 or 330 mμ differs markedly from the absorption spectrum in intensity distribution, although both spectra have essentially the same vibrational structure. Thus, the quantum yield of the emission between 320 and 360 mμ increases rapidly with excitation into successively higher singlet states. These experimental results can be explained by attributing the emission in the 320—360 mμ region to the fluorescence which originates from the second excited singlet of the pyrene molecule.

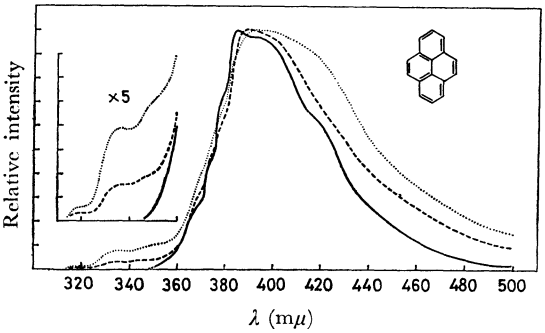

Fig. 1. Fluorescence spectra of pyrene vapor at 200°C and ∼3 mmHg obtained by excitation at different wavelengths: solid line, 323 mμ; dashed line, 268 mμ; dotted line, 236 mμ.

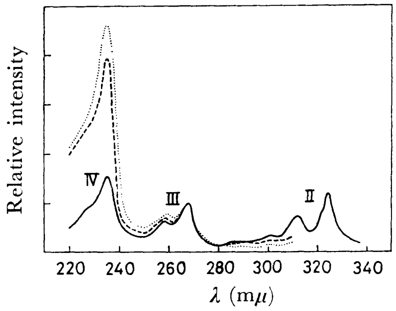

Fig. 2. Excitation spectra of pyrene vapor at 205°C and ∼3 mmHg obtained by monitoring at different wavelengths: solid line, 370 mμ; dashed line, 340 mμ; dotted line, 330 mμ.

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