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Triplet Excitation Spectrum of Phenanthrene Crystals†

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The triplet excitation spectrum in molecular crystals is difficult to observe by direct means because of the weak absorption of the triplet state. In particular cases, however, this spectrum can be observed indirectly by looking at the delayed fluorescence which results from triplet-triplet annihilation.[1] This delayed fluorescence is unobservable in phenanthrene for the intensities which are available in a high resolution measurement of the triplet excitation spectrum. Yee and El Sayed[2] have shown that a portion of the excitation spectrum of polycrystalline phenanthrene from 4750Å to 4500Å can be observed at 77 °K by detecting the phosphorescence from a radiative trap. For this purpose a large concentration (2%) of chrysene-d_{12} was used as an impurity. In the present work the excitation spectrum of single crystals of phenanthrene was obtained at room temperature by detecting the phosphorescence from a smaller concentration (0.04%) of 3-bromopyrene. 3-bromopyrene was chosen for this purpose because the (0,0) pyrene triplet level of 16,900 cm^{-1} (in solution) is lower than the corresponding level in phenanthrene (21,600 cm^{-1}), and the addition of the bromine atom enhances the triplet to singlet decay rate.[3]

Phenanthrene with an impurity content of less than 1 ppm was doped with 400 ppm of 3-bromopyrene (K&K20314). Crystals were grown by the Bridgman method and sections of the boule were

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cleaved along the *ab* plane. The samples were 1 cm^2 in the *ab* plane and approximately 2 mm thick along the c′ direction.

The excitation was provided by dispersing the light from a 1000W xenon lamp (Hanovia Model 976C–1) with a quarter meter monochromator (Jarrell–Ash Model 82–410) which was modified to scan cyclically over a fixed region at 4 Å/sec. Second harmonics from the monochromator were eliminated with a long wavelength pass filter combination (Corning CS0–51 and CS3–74). The resulting light was normally incident to the *ab* crystal plane. The crystal luminescence, which has a lifetime of 3 msec, was isolated by a phosphoroscope with a dead time of less than 1 msec and observed by an EMI 9558 photomultiplier which was cooled to $-20\,^{\circ}C$. The signal from the photomultiplier was fed into a photon counting circuit to maximize the signal to noise ratio and the output from this circuit was recorded by a computer of average transients (Northern Scientific NS–550).

Figure 1 shows the room temperature crystal luminescence as a function of excitation wavelength. This result was obtained with 1 mm slits and the spectrum has been corrected for changes in incident intensity. The peaks in the spectrum are found to be at 21,490 cm^{-1}, 21,880 cm^{-1} and 22,900 cm^{-1}. In addition an unresolved peak is seen to be at approximately 23,280 cm^{-1}. The energy spacings of the maxima from the (0,0) transition in order of increasing energy are 390 cm^{-1}, 1410 cm^{-1} and 1790 cm^{-1}. The unresolved peak is roughly at $(1410 + 390)$ cm^{-1}, indicating that the observed portion of the excitation spectrum is composed of vibrational components at 390 cm^{-1} and 1410 cm^{-1}. The shape of the spectrum in Fig. 1 is in good agreement with the molecular spectrum obtained by Marchetti and Kearns.[4] Because of singlet absorption, direct triplet excitation below 4100 Å could not be separated from triplets generated by intersystem crossing.

The excitation spectrum of the (0,0) triplet level was observed for light polarized along the *a* or *b* crystal axis. At room temperature the ratio of luminescence for *a* polarized excitation to that for *b* polarized excitation was found to be 1.3:1. Polarized excitation measurements of the (0,0) transition were also made at 90 °K. At this temperature the enhanced signal allowed 1/2 mm slits to be used. Five runs at 40 scans each were made on each of three crystals at each polarization. No systematic difference in the position of the

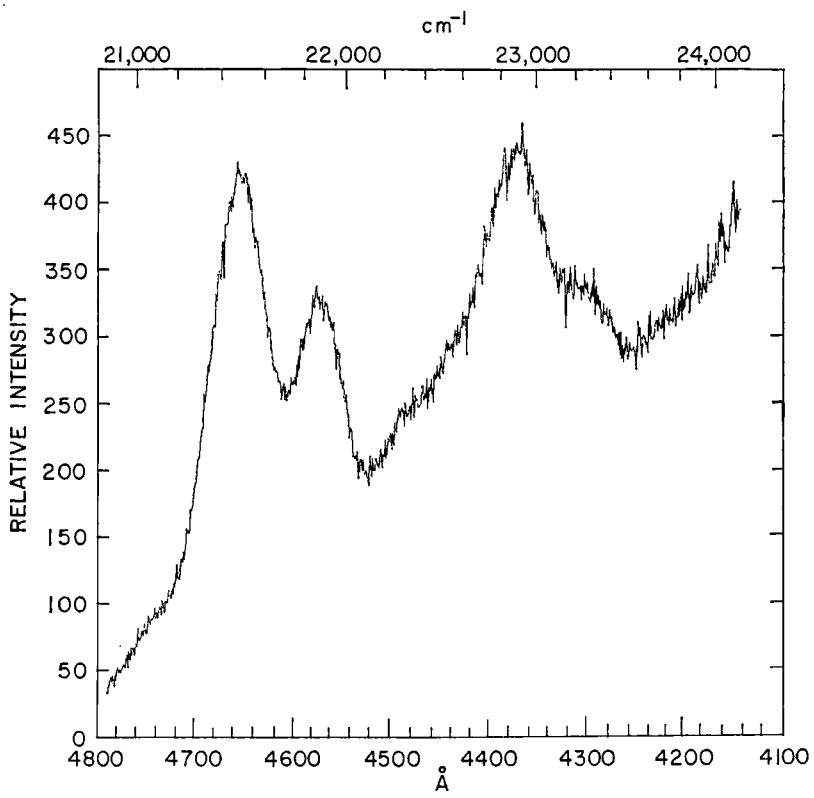

Figure 1. Triplet excitation spectrum of a phenanthrene crystal at room temperature.

(0,0) peak was found between the two polarizations within an uncertainty of 2 cm^{-1}.

Because of spin orbit coupling the factor group components of the triplet state are not necessarily uniquely polarized.[5] To our knowledge the relative absorptions of these two states for either *a* or *b* polarization have not been published for phenanthrene. However, if it is assumed that the factor group components are polarized parallel and perpendicular to the *b* symmetry axis, then the Davydov splitting of the triplet (0,0) level would be less than 2 cm^{-1}.

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