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Delayed Fluorescence and Triplet Lifetime of Crystalline Chrysene

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Abstract—The delayed fluorescence emission spectrum of pure crystalline chrysene at temperatures down to 80 °K has been measured. Careful purification is required in order to remove traces of impurities which trap triplet excitons in chrysene giving rise to impurity fluorescence. The triplet exciton lifetime in crystalline chrysene at room temperature was found to be 30 ± 2 msec.

1. Introduction

Although the properties of chrysene suggest that it may be a suitable compound for the study of molecular crystal behaviour, few data are available for the pure crystalline material. To the best of our knowledge, no measurement of the lifetime of triplet excitons in crystalline chrysene has been reported, although Stevens and Hutton[1] reported observing delayed fluorescence of sublimed films of chrysene. We have therefore investigated the emission spectrum and the decay of delayed fluorescence using purified chrysene.

The transfer of triplet energy in pure molecular crystals such as those of the aromatic hydrocarbons may be described in terms of mobile Frenkel excitons.[2] The decay of these triplet excitons is determined by the following processes: (1) monomolecular decay to the ground state S_0, i.e. phosphorescence and intersystem crossing, characterised by the overall probability β_0; (2) bimolecular triplet triplet annihilation leading to the excitation of the S_1 state, $T_1 + T_1 \rightarrow S_1 + S_0$, characterised by a rate constant γ_{TT}; 3) trapping of triplet excitons at impurity centres or at physical defects, with a probability β_t.

The triplet lifetime, τ_T, in a pure molecular crystal will be determined by the first process alone if the concentration of triplet

excitons is sufficiently low that the condition $\beta_0[T] \gg \gamma_{TT}[T]^2$ is satisfied and the trapping rate β_t is negligible compared with β_0. At room temperature the trapping of triplet excitons by physical defects can mostly be neglected, but the presence of impurities with triplet levels which lie below that of the host crystal can lead to a significant reduction of the triplet lifetime, the magnitude of the trapping probability being a function of the concentration of the impurity and of the energy separation between the host and quest triplet levels.[3]

The decay of triplet excitation can be measured by recording the delayed fluorescence after the interruption of illumination. Population of the triplet state may be achieved either by direct excitation in the region of the $S_0 - T_1$ absorption or by excitation of the S_1 state followed by intersystem crossing to the T_1 state. The decay of the delayed fluorescence is exponential with decay rate $2\beta_0$ when the condition that $\beta_0[T] \gg \gamma_{TT}[T]^2$ is satisfied.[2]

Apart from this homopolar process which leads to the delayed fluorescence of the host substance, two processes can occur which lead to the production of fluorescence originating from the impurity: (1) energy transfer between the singlet states of host and impurity and (2) triplet exciton annihilation between a mobile (host) exciton and a trapped (impurity) exciton. It is therefore often possible to detect small concentrations of impurity by measuring the spectra of prompt and delayed fluorescence, provided that the S_1 states are not so close that the fluorescence of the host and of the impurity overlap completely.[4,5]

2. Experimental

Chrysene (Fluka, purum) was purified as follows. The crude material was first passed in 5 gram batches over a freshly prepared 50 cm column of aluminium oxide (Merck, activity grade 1), using benzene at 50 °C as solvent. This process was carried out in darkness in an atmosphere of nitrogen in order to avoid photo-oxidation. Adsorption chromatography is known to remove polar impurities such as chrysene-quinone, but is ineffective in removing non-polar aromatic hydrocarbon impurities.[6,7]

Preliminary fluorescence measurements of chrysene purified in this way showed strong fluorescence peaks which did not agree with those in the spectrum of the prompt fluorescence of chrysene given in the literature.[8,9]. It was suspected that this fluorescence was due to impurities such as 2, 3 benzocarbazole[10] or anthracene. In order to remove anthracene, tetracene and similar aromatic hydrocarbons, which are known to react with dienophilic reagents, the chrysene was refluxed for 8 hours with 5 mole % maleic anhydride, which is unreactive towards chrysene.[11] The addition products and unreacted maleic anhydride were removed by chromatography on aluminium oxide under the conditions given above. Fluorescence measurements showed that small traces of impurity remained after this treatment. Repetition of the last purification step using maleic anhydride followed by chromatography was found to remove these last traces and no evidence could be found for the presence of impurities in the final product. Attempts to purify chrysene by extensive zone-refining alone were unsuccessful and the purification method described is therefore essential prior to zone-refining. Measurements of the prompt and delayed fluorescence spectra were made using crystals grown from the melt by the Bridgman method. Measurements of the triplet lifetime were made using material which had been zone-refined in addition to the previous treatment. In order to avoid interference by oxygen these measurements were carried out with the substance in the zone-refining tube.

Comparison of this purified chrysene was made with a sample obtained from Princeton Organics, Princeton, N.J., whose impurity content was specified as 10^{-2} % (10^{-4} relative) or less. Prompt fluorescence spectra were obtained using the 313 nm line of a 500 Watt HBO Mercury lamp, isolated by a 3 mm UG 5 filter (Schott), a 313 nm interference filter (Schott) and 50 mm aqueous K_2CrO_4 solution for the excitation. The fluorescence emission was observed at 90° to the incident light through a double grating monochromator (Bausch & Lomb, slit 2 nm bandwidth) with a photomultiplier (RCA 7265). No correction was made for the spectral sensitivity of the photomultiplier.

Delayed fluorescence spectra were obtained in two different ways. In the first a phosphoroscope was employed in order to isolate the weak delayed fluorescence excited by a 450 Watt XBO xenon lamp

from the intense prompt fluorescence. Integration of the delayed fluorescence signal using a boxcar integrator (PAR Model 160) led to a significant improvement of the signal/noise ratio. In the second method the delayed fluorescence was excited directly in the region of the $S_0 - T_1$ absorption[12] with the 488 or 514 nm lines of a continuous argon laser (Coherent Radiation Model 50) and the emission detected with the monochromator-photo-multiplier combination described above, the multiplier output passing via a preamplifier to a T-Y recorder.

The decay of the delayed fluorescence was also measured using the above two methods of excitation, in the second case the laser beam being chopped at a suitable frequency. Signal averaging techniques using the boxcar integrator allowed measurements of the decay to be made at intensities sufficiently low that the influence of bimolecular decay could be neglected. Low temperature measurements of the delayed fluorescence excited by the 488 nm line of the argon laser were made with the crystal mounted in a Dewar vessel which could be cooled with cold nitrogen to ca. 80 °K.

3. Results and Discussion

Impure samples of chrysene obtained by chromatography of the crude material showed a prompt fluorescence spectrum similar to that reported by Perkampus and Pohl[13] for evaporated films of chrysene, with peaks at 398 and 419 nm. The spectrum of the delayed fluorescence of this impure material was essentially identical with that of the prompt fluorescence. These spectra are not in agreement with those reported by Birks and Cameron[8] and by Wegner, Koes and Kulshreshtha.[9]

Repeated purification of the chrysene with maleic anhydride led to a significant change in the fluorescence spectra. The peaks at 398 and 419 nm were replaced by peaks at 389 and 408 nm and at the same time the total fluorescence intensity was reduced. The prompt fluorescence spectrum of the purified chrysene agrees closely with those reported in Refs. 8 and 9. Figure 1 shows the spectrum of prompt and delayed fluorescence of chrysene purified in the way described. With the exception of the peak at 370 nm (0–0 transition), which is absent in the delayed fluorescence, it can be seen that the

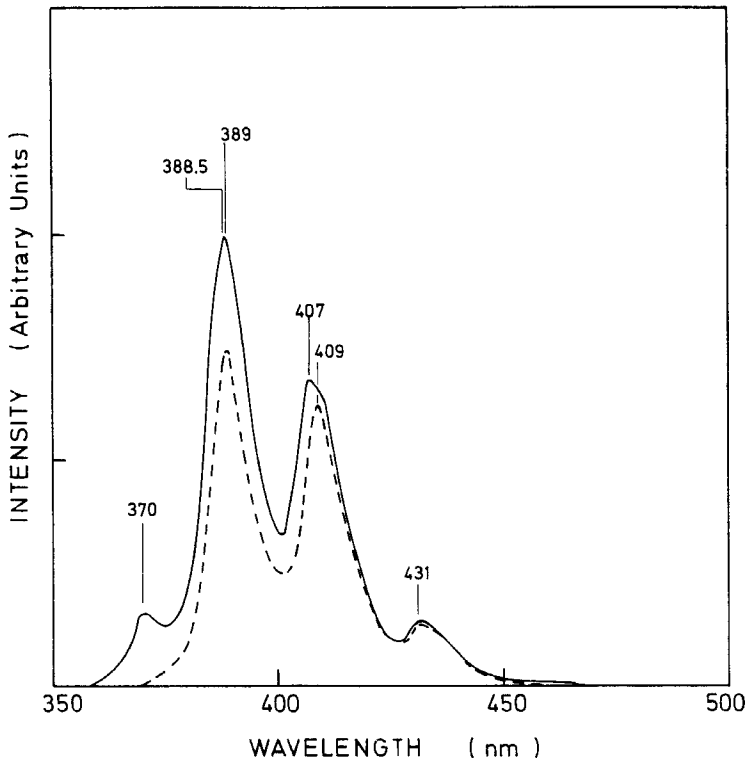

Figure 1. Emission spectra of prompt (———) and delayed (– – – –) fluorescence of purified chrysene crystal (295 °K).

agreement between the two spectra is good. The absence of the peak at 370 nm in the delayed fluorescence emission may be attributed to surface quenching of triplet excitons as well as to the reabsorption of fluorescent light of this wavelength. For comparison Fig. 2 shows the prompt and delayed fluorescence of the chrysene sample provided by Princeton Organics. In this case the spectrum of delayed fluorescence is not identical with that of the prompt fluorescence and peaks which may be attributed to impurities occur in both spectra.

Although identification of the impurity on the basis of the spectroscopic data is not possible we believe that possibly 2, 3 benzocarbazole or anthracene are present in the less pure samples of chrysene, leading to changes in both the prompt and delayed fluorescence. The

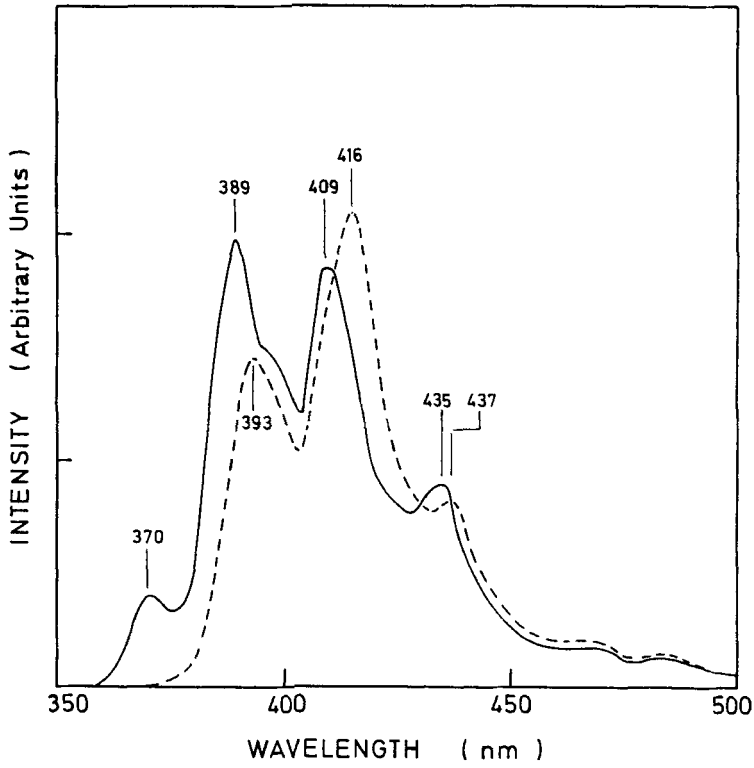

Figure 2. Emission spectra of prompt (———) and delayed (– – – –) fluorescence of chrysene supplied by Princeton Organics, Princeton, New Jersey. (PAR grade, impurity concentration $<10^{-2}$ mole %) (295 °K).

delayed fluorescence is particularly sensitive to the presence of guest molecules in the crystal which trap triplet excitons.[5] This is evident in Fig. 2, where the shoulders due to impurity emission in the prompt fluorescence are replaced by peaks in the delayed fluorescence, i.e. the delayed fluorescence of chrysene due to free-free triplet-triplet annihilation is completely quenched. Thus, it is not feasible to make meaningful measurements of the triplet exciton lifetime under these conditions, since the observed delayed fluorescence comes almost entirely from the impurity due to free-trapped triplet-triplet annihilation. It is clear that it is virtually impossible to separate the emission due to impurity from that originating from chrysene itself.

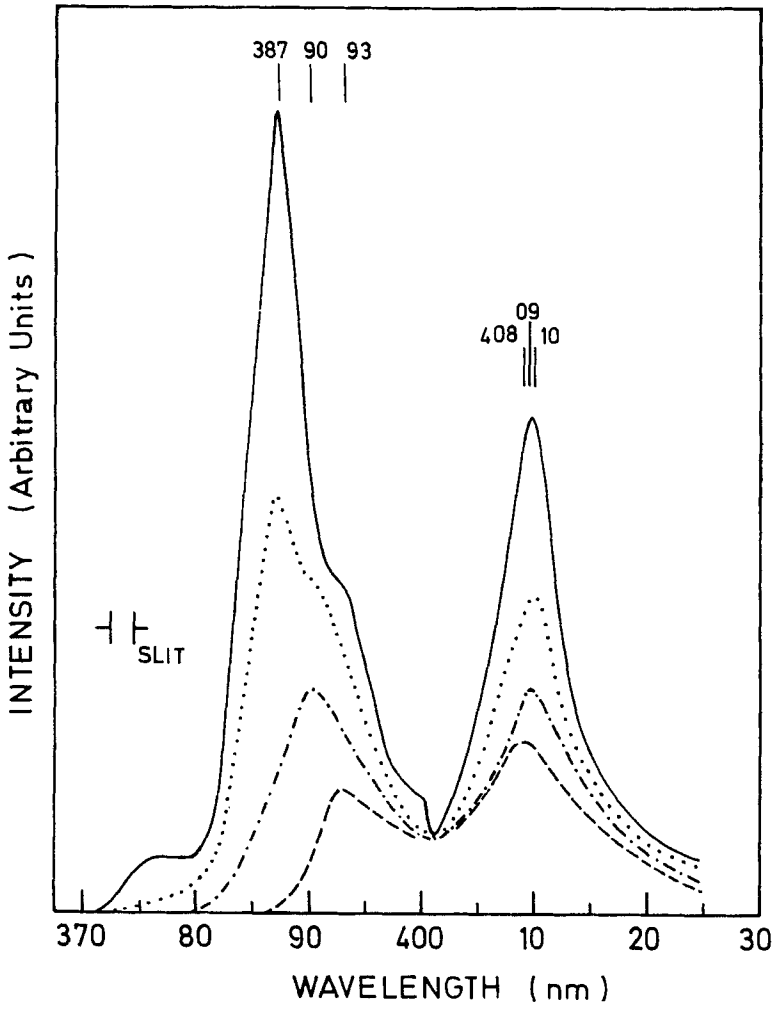

Figure 3. Temperature dependence of delayed fluorescence emission spectrum of chrysene (λ excitation 488 nm). ——— 80 °K; ···· 180 °K; -·-· 240 °K; - - - - 295 °K.

Due to the reduction in thermal release of excitons from shallow traps, trapping will become more effective if the temperature of the crystal is reduced. Experimentally it was found that chrysene which had been purified only once with maleic anhydride showed evidence of trapping by impurities. Thus, although at room temperature the delayed fluorescence spectrum showed only small shoulders due to impurity fluorescence, cooling the sample led to a progressive increase in the height of the impurity peaks at the expense of the chrysene fluorescence. At 220 °K the quenching of the chrysene fluorescence was essentially complete and the delayed fluorescence spectrum resembled that of less pure samples at room temperature (e.g. as shown in Fig. 2).

The behaviour of pure chrysene obtained by reacting the material twice with maleic anhydride was completely different. Even at the lowest temperatures attained no evidence of emission from impurity centres could be found. Figure 3 shows the delayed fluorescence spectrum of pure chrysene as a function of the crystal temperature. The changes in relative intensity of the two peaks are probably related to changes in the absorption coefficient with temperature which tend to reduce the effects of reabsorption of the delayed fluorescence emission. Thus at the lowest temperature at which measurement was made the 0–0 emission peak becomes visible.

Since oxygen is known to reduce the triplet exciton lifetime in aromatic hydrocarbon crystals,[14,15] measurements were carried out with material in the zone-refining tube. We believe that the purified chrysene samples contain sufficiently low concentrations of impurity that the measured lifetime is not greatly affected by trapping at room temperature. The lifetime found using substance in the upper end of the zone-refining tube was 30 ± 2 msec. This value does not necessarily represent an upper limit for the lifetime of triplet excitons in chrysene since the polycrystalline nature of the sample may be sufficient to significantly shorten the lifetime by surface quenching effects. However, measurements with single crystals prepared by the Bridgman technique gave values of the triplet lifetime which were similar to that observed in the zone-refining tube.

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REFERENCES

1. Stevens, B. and Hutton, E., *Proc. Phys. Soc.* (*London*) **81,** 893 (1963).
2. Avakian, P. and Merrifield, R. E., *Mol. Cryst.* **5,** 37 (1968).
3. Baessler, H., Vaubel, G. and Kallmann, H., *J. Chem. Phys.* **53,** 370 (1970).
4. Benz, K. W., and Wolf, H. C., *Z. Naturforschg.* **19a,** 177 (1964).
5. Benz, K. W., Häcker, W. and Wolf, H. C., *Z. Naturforschg.* **25a,** 657 (1970).
6. Meier, R. and Fletschinger, J., *Angew. Chem.* **68,** 373 (1956).
7. Reucroft, P. J., McGhie, A. R., Hillman, E. E. and Damiano, V. V., *J. Cryst. Growth* **11,** 355 (1971).
8. Birks, J. B. and Cameron, A. J. W., *Proc. Roy. Soc.* (*London*) **A249.** 297 (1959).
9. Wegner, U. E., Kroes, R. L. and Kulshreshtha, A. P., *J. Luminesc.* **4,** 134 (1971).
10. Gerkin, R. E. and Winer, A. R., *J. Chem. Phys.* **56,** 1359 (1972).
11. Clar, E. and Lombardi, L., *Berichte* **65,** 1413 (1932).
12. Sponer, H., Luminescence of Organic and Inorganic Materials, Internat. Conf. in New York 1961, p. 143, (John Wiley, N. Y. 1962).
13. Perkampus, H. H. and Pohl, L., *Z. Phys. Chem.* (*N.F.*) **40,** 162 (1964).
14. Benz, K. W., Port, H. and Wolf, H. C., *Z. Naturforschq.* **26a,** 787 (1971).
15. Johnson, R. C., Ern, V., Wiley, D. W. and Merrifield, R. E., *Chem. Phys. Lett.* **11,** 188 (1971).