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Role of Defects and Reabsorption in the Decay of Fluorescence of Anthracene from 2–350 °K†

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Abstract—Fluorescence spectra and decay times were measured for anthracene crystals grown from the vapour and from the melt, and for anthracene dissolved in polymethylmethacrylate (PMM). The decay times were corrected for reabsorption. The procedure for determining the correction is described. It was facilitated by recording the spectra in digital form on magnetic tape and using a computer to calculate and plot the area accumulated under the fluorescence spectrum as a function of wavelength. Sets of accumulated area curves not only allowed the reabsorption correction to be made but also indicated the relative number of physical defects present in the crystals. They also showed changes in reabsorption with temperature.

The corrected fluorescence decay times of anthracene crystals showed little variation with method of growth or with temperature. They were 5 ± 1 nsec at 2 °K and increased by 1–2 nsec as the temperature was raised to 350 °K. The variation with temperature was much less than the correction for reabsorption, and the interpretation of the change is therefore difficult. In PMM the decay time decreased as the temperature was raised, from about 10 nsec at 2 °K to 5 nsec at 350 °K. The lifetime of defect fluorescence—in the spectral region < 21300 cm^{-1} in crystals with many defects—was approximately double that of defect-free regions.

A maximum intensity at 23512 cm^{-1}, or 260 cm^{-1} from the 0–0 fluorescence band, was found in crystals with many defects. The intensity of this band varied from one crystal to another, and was especially prominent in crystals melt grown under a Xenon atmosphere. Its intensity fell to zero at about 40 °K and it was therefore assigned as a trap.

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1. Introduction

Anthracene has long been a popular material for decay time measurements, because of its efficient fluorescence and its use in scintillation counters. Early measurements of the decay time have been reviewed by Birks(1) and Munro.(2) The values of the decay time ranged from 3.1 nsec to 250 nsec depending on the purity, method of growth, physical form (for example, microcrystals or melt-grown crystals) and so on. The earlier crystals were much less pure than those now available(3–6) and corrections for reabsorption were infrequently or incorrectly applied. Only in a few instances have decay times been reported for temperatures below 77 °K.(7–9) Thus although a good deal of data was available it was inexact and incomplete.

The availability of highly pure crystals has made it possible to distinguish between effects on the luminescence spectra due to chemical impurities or to physical defects. Defects have been shown to give an apparently continuous background to the fluorescence spectrum.(10) The background may however consist of a large number of sharp lines unresolvable by the spectrometers normally used.(11) Physical defects have also been found to influence delayed fluorescence,(12) phosphorescence,(13) electroluminescence(14) and some other properties. To our knowledge, however, there is only one previous investigation of the effect of defects on fluorescence decay times. Fielding and Jarnagin(15) (using polycrystalline material) found two decay times for some (strained, thick) samples but only one for annealed (thick) or thin (sublimation) samples. The decay time also varied in different spectral regions of the fluorescence. Though the present results partly confirm the earlier studies, the present investigation covered a larger temperature range, and used crystals of high purity and controlled geometry which allowed the application of reabsorption corrections.

The experiments described here were undertaken to take advantage of the higher purities now available, in order to provide accurate determinations of decay times over a wide range of temperature, applying the necessary corrections in doing so. At the same time the techniques used for applying the reabsorption correction shed light on the defects present and their role in the decay process.

2. Experimental

SAMPLE PREPARATION

Anthracene (Eastman Kodak Co., X480, H480) was purified by chromatography, sublimation and zone refining before sample preparation.(3) Triplet lifetimes of the product in the final zone refined state were approximately 25 msec. Single crystals were produced (a) by growth from the melt, (b) by slow sublimation,(5) (c) by rapid sublimation in an inert atmosphere, and (d) by evaporation from solution. Solid solutions were produced by thermal polymerisation of PMM containing the required concentration of anthracene. Samples containing concentrations of 10^{-5}–10^{-7} M anthracene were prepared.(15) Precautions were taken to ensure that the plastic samples were uniform in concentration. No luminescence was obtained from a blank plastic sample.

(i) *Decay Time Measurements*

The fluorescence decay times were measured by means of a pulse-sampling technique.(2) A high pressure hydrogen discharge lamp was used as the excitation source. Optical filters were used to select the desired excitation wavelength, 3300 A–3800 A. Fluorescence from the specimen was detected by a 56 UVP photomultiplier and sampled on a Tektronix 531 A oscilloscope equipped with a 1S1 plug-in. The result was recorded on an X–Y recorder. Care was taken to ensure the stability of reproducibility of the shape and intensity of the excitation pulse, in view of the short decay time of anthracene. The excitation pulse characteristics were: decay time ~ 1.5 nsec, half width ~ 2 nsec, and repetition rate ~ 2000 $\sec^{-1}$. The corrected decay curve of the specimen was obtained by convoluting the experimental decay curve with that of the excitation lamp, and assuming an exponential decay.(2) This technique was satisfactory for most fluorescence decay curves, which were exponential at least to $I_{\max}/10$. The decay curves for crystals with many defects were in some cases slightly non-exponential over this intensity range and gave slightly longer decay times. The results for the defect crystals were however given the same corrections.

(ii) *Steady State Fluorescence Spectra Measurements*

A digital spectrometer system described elsewhere was used.(16) A monochromator or varioilluminator was used to select the same excitation region as used for decay time measurements, 3300–3800 Å, and a Spex double monochromator with a 6256B cooled photomultiplier tube was used to analyse the fluorescence emission. The photomultiplier output was digitised and recorded on magnetic tape. This facilitated the application of wavelength and intensity corrections and further analytical treatment of the data.

The liquid helium cryostat (Andonian Associates Inc., Waltham, Massachusetts) was equipped with three windows, which enabled several experiments to be carried out without altering the geometry of the optical apparatus. The decay time excitation lamp was normally mounted on one window and the decay time photomultiplier on a window at right angles. When the decay time had been measured the decay time photomultiplier was removed and the spectrum was excited through that window and observed through the third window. This required accurate rotation of the crystal through 90° but preserved the excitation and viewing geometry which was necessary for the spectra to be useable for reabsorption corrections. Alternatively, both decay time and fluorescence excitation could be made through the third window for measurements in " transmission ". These arrangements were especially useful for determining the reabsorption corrections.

3. Reabsorption Effects

In a material such as anthracene in which the absorption and emission spectra overlap, both the observed emission spectra and decay times depend upon the measuring geometry and/or crystal size. The theory for the effect of reabsorption on decay times has been reviewed by Birks and Munro,(2) the corrected life decay time being given (for anthracene) by

$$\tau = \tau_{\text{obs}}(1 - aQ) \tag{1}$$

where Q is the quantum efficiency and a is the ratio of the area of the observed to non-reabsorbed spectra. The major assumption used in this calculation is that reabsorption is uniform in all directions, though in practice this is seldom valid. Thus we have attempted to determine experimentally the value of *a* and its variation with temperature using the following techniques:

(a) From the fluorescence band shapes, assuming these to be Lorentzian, and observing the changes in shape and size with temperature.

(b) From observations on the effects of crystal thickness on the emission spectra and decay rate. This technique was unsatisfactory since the excited portion of the crystal was not the same at all temperatures, and the crystals were not perfectly uniform.

(c) From normalised spectral areas. In the present experiments the spectral region affected by reabsorption extended from the 0–0 band to 4370 Å. The fraction of the total emission spectra observed at wavelengths shorter than 4370 Å, compared to the fraction observed at longer wavelengths, will decrease as the reabsorption increases (Fig. 1). The magnitude of this ratio for a spectrum

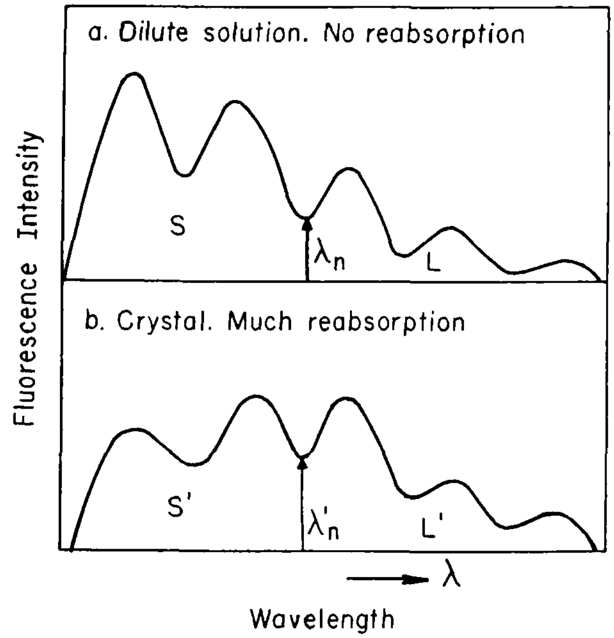

Figure 1. *Diagram illustrating the use of spectral areas for calculating the reabsorption factor* a. Reabsorption occurs for $\lambda < \lambda_n$ and it is assumed that $\lambda_N = \lambda_{N'}$. After normalisation, $L + S = 1 = L' + S'$, and $a = 1 - L/L'$.

unaffected by reabsorption was determined from a series of experiments. This included measurements upon the following:

(1) dilute anthracene–hexane solutions
(2) dilute anthracene–plastic specimens
(3) very thin microcrystals prepared by rapid sublimation in an inert atmosphere
(4) thin microcrystals grown from hexane solutions; front and back surface excitation
(5) thin sublimation flakes (100 μ); front or back surface excitation, extrapolated to zero thickness.

The results from all specimens were comparable and gave $S/L = 0.15 \pm 0.01$. A similar value was calculated from methods (a) and (b). From this ratio and the area ratio for the measured spectra which included reabsorption, corrections for reabsorption to the measured lifetimes were easily computed, giving τ.

As a final check thick (~ 0.5 cm) crystals were studied using front and back surface excitation, and though the τ_{obs} differed at room temperature by $\sim 250\%$, after correction for the different a's, the decay rate was found to be the same within $\pm 15\%$.

Several other experimental characteristics which could have altered the crystal characteristics were also studied. These included crystal annealing, temperature cycling, and angle of incidence of the exciting light. No effects were observed on the spectra, decay times or reabsorption corrections.

4. Results

(A) ANTHRACENE IN PMM

The lifetime of anthracene in PMM was measured for thick and thin samples cut from plastic ingots with anthracene concentrations of 10^{-5}–10^{-7} M. Figure 2 gives a typical result, showing an increase in τ_{obs} as temperature decreases. Included in Fig. 2 are the radiative lifetimes corrected for reabsorption, and the total spectral area recorded.

(B) ANTHRACENE CRYSTALS

Figure 3 shows the front surface fluorescence spectrum obtained for a sublimation flake at 295 °K and 2 °K and the spectrum of a

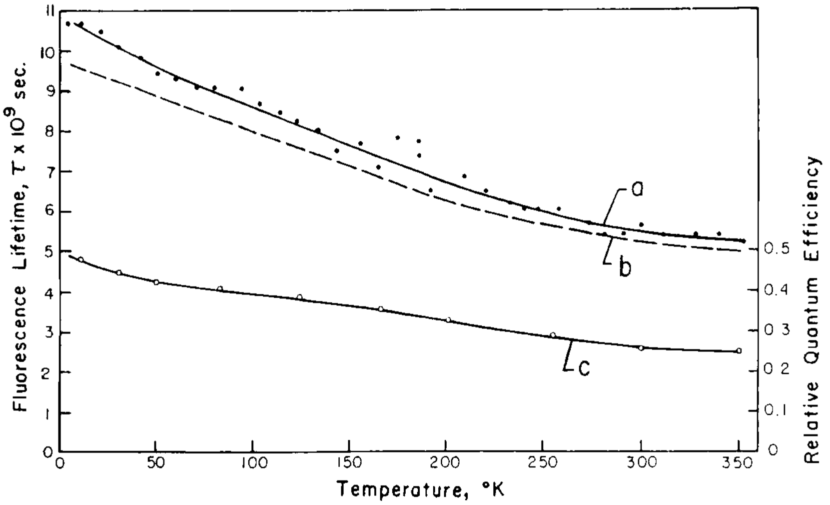

Figure 2. Fluorescence lifetime and quantum efficiency of anthracene in PMM as a function of temperature. (a) Observed lifetime; (b) Lifetime corrected for reabsorption; (c) Relative quantum efficiency.

melt grown crystal at 2 °K. A broad background emission occurred at low temperatures for melt grown crystals. If the low temperature sharp line spectrum (sublimation flake) is subtracted from the low temperature spectrum of melt grown crystals, then a defect spectrum very similar to that observed in electroluminescence⁽¹⁴⁾ remains. The defect emission is associated with physical defects rather than chemical impurities. Similar spectra were obtained for all crystals investigated, though each crystal showed a different degree of defect emission depending upon the method of preparation. Defect emission increased from thin sublimation flakes to solution grown crystals to melt grown crystals. Melt grown crystals prepared under xenon showed most defects.

The accumulated area curves gave a very clear indication of reabsorption. This is clear from inspection of Figs. 4–6. Thus the curves for Fig. 4, in which reabsorption was negligible due to the low concentration of anthracene, showed almost no change with temperature. The curves in Fig. 5, for a nearly defect-free crystal, showed different slopes as the temperature was altered. Some of the curves cross, showing the presence of some defect emission at low temperatures. The curves for a crystal with many defects (Fig. 6) show yet another form. The curves again cross, and the large

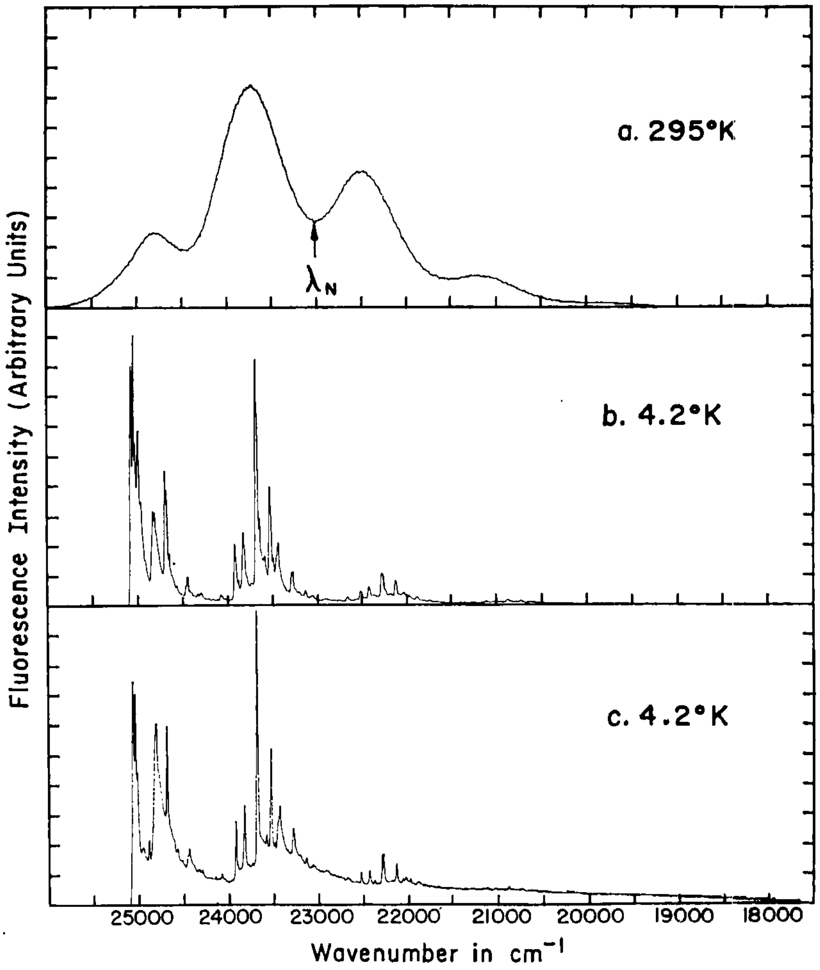

Figure 3. Fluorescence spectra of anthracene crystals, with front surface excitation. (a) and (b) are for a sublimation flake free of defects, while (c) is for a melt grown crystal containing many defects.

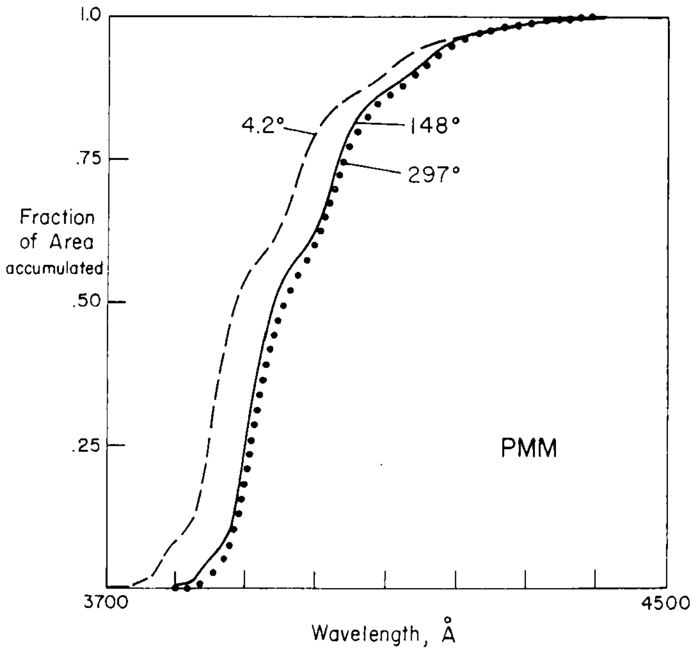

Figure 4. Several " accumulated area " curves for a specimen of anthracene in PMM. Many such curves (calculated and plotted by computer) were plotted for each specimen. Note that there is little change in the curves with temperature. Reabsorption in the plastic specimens was negligible.

proportion of defect emission causes the inflections of Figs. 4 and 5 nearly to disappear. The accumulated area curves were used to calculate *a*.

The effect of temperature on the fluorescence decay time of two anthracene crystals is shown in Fig. 7. One of the crystals (Fig. 7(a)) was a thick melt grown while the other (Fig. 7(b)) was a sublimation flake. The lifetimes corrected for reabsorption could both be represented by a single curve (Fig. 7(c)). The corrected lifetimes are therefore independent of the method of crystal preparation.

5. Discussion

(A) ANTHRACENE IN PMM

For the dilute solutions used here there was a monotonic increase in the lifetime with decreasing temperature. This is correlated with

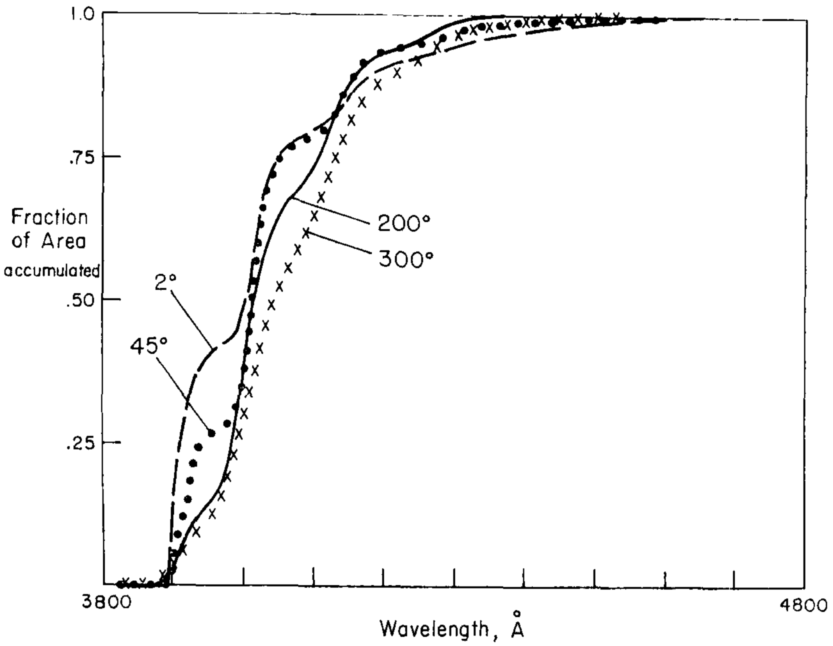

Figure 5. Several " accumulated area " curves for a sublimation flake containing few defects. Note the abrupt changes in slope as maxima are approached or passed, and that the curves for 2 and 45 °K cross the other curves. The crossing is thought to be due to the presence of some defect fluorescence at low temperatures.

a comparable increase in relative fluorescence efficiency, as shown in Fig. 2. The chief process competing with radiative decay is intersystem crossing to the triplet manifold.(17) Hence the change of fluorescence with temperature probably results from changes in the vibrational content of the S_1 state. The most accessible triplet state, T_2, lies 600 cm^{-1} below S_1.(18) The importance of the vibrational overlap integral between the initial and final states in radiationless transitions is well recognized. In fact, the variation of this vibrational overlap integral accounts for the observed range of radiationless transition rates in aromatic molecules (often within an order of magnitude). However the theory does not provide a quantitative description of the energy levels used to establish the precise matching required in the transitions.(19,20) In general the overlap for the zero point level of the initial state to particular vibrational levels of the final state is calculated, and the finer details of energy

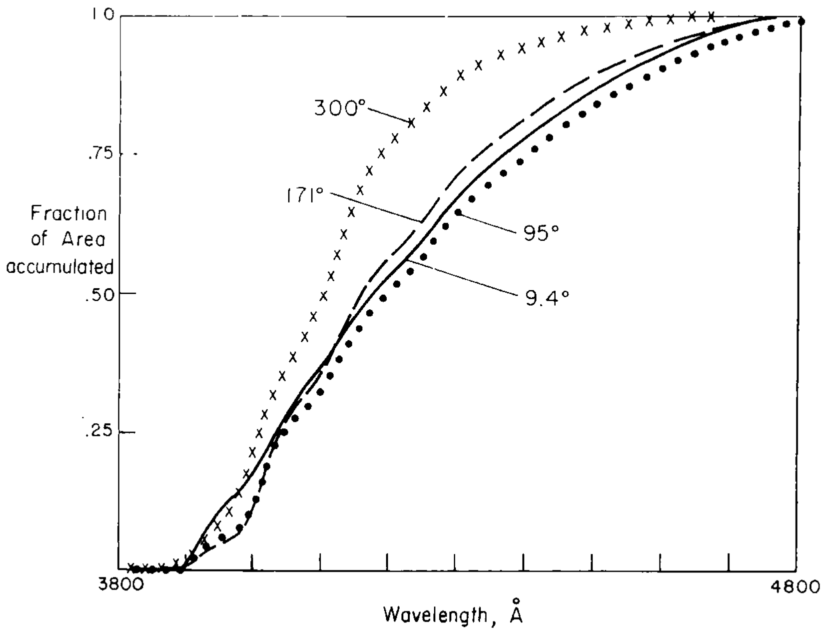

Figure 6. Several " accumulated area " curves for a melt grown crystal containing many defects. Note that the changes in slope have been smoothed, in comparison with Fig. 5, by the presence of strong defect emission. Note also that some of the curves again cross as the temperature is raised and redistribution of the fluorescence spectrum occurs.

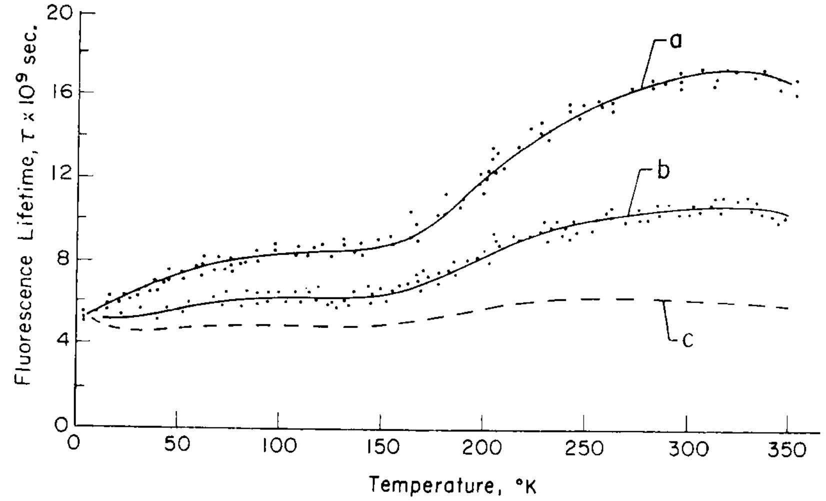

Figure 7. Fluorescence decay times of two anthracene crystals as a function of temperature. (a) Observed lifetime for a melt grown crystal; (b) Observed lifetime for a sublimation flake; (c) Corrected results for both crystals combined on one curve.

matches are said to result either from other levels of the molecule or the environment. Only when the density of vibrational states is low are these details likely to be significant. For anthracene, where the $S_1 - T_2$ energy gap is only ~ 600 cm^{-1}, the low density of states may become important at 4 °K. Moreover in solution the decaying state S_1 is almost degenerate with the first harmonic of the 590 cm^{-1} vibration of the T_2 vibrational states. This degeneracy may provide the principle channel for intersystem crossing, though the difficulties in determining the mechanism of spin-orbit coupling remain obscure.(16,20) At higher temperatures, the population of the vibrational levels of the S_1 state will provide additional pathways for the intersystem crossing process. However the temperature dependence of the lifetime shows no activation energy, which indicates that within the range of experimentally accessible vibrational levels, no single level is especially important.

(B) ANTHRACENE CRYSTALS

The interpretation of spectral and decay time measurements on anthracene is complicated by three factors: (1) reabsorption, (2) the temperature dependence of the quantum efficiency, and (3) defect emission. These will be considered in turn.

The correction formulae developed for reabsorption are based on the assumption that the probability of photon reabsorption at any point in the crystal is constant, and that this is correct is shown in the fluorescence spectrum. In most physical situations neither of these assumptions is strictly valid. Thus since the exciting light is absorbed close to the surface, the changes in geometry of the measuring system with respect to the excited surface will lead to different reabsorption effects. Therefore the use of front surface spectra gives a lower limit to the reabsorption. The desired parameter for reabsorption corrections is the average probability of photon reabsorption, or the probability integrated over all directions. However, the experimental technique used in two cases, where the normalized spectral areas were compared, gave *comparable* values for the " true " decay time even though the reabsorption corrections, for front and back surface measurements, were different. Furthermore, all crystals, independent of preparation and dimensions, gave corrected lifetimes ~ 6 ns ± 1 ns. More careful consideration of this correction is necessary however before the remaining temperature dependence (Fig. 7) is explained, in view of the large correction factor at high temperatures. It is also possible that at low temperatures a change in observed decay rate may be caused by the changing population of levels within the exciton band which themselves have different lifetimes. Indeed considering the $k = 0$ levels only, the results of Matsui(21) for the intensity and splitting of the Davydov components of the anthracene S_1 band predict a lifetime change similar to that shown in Fig. 7. A similar suggestion has been made by Powell.(9) The quantum yield of crystalline anthracene is nearly unity at room temperature(18) and, on the basis of current theories of radiationless transitions, there is little reason to suppose this quantum yield would show appreciable variation with temperature. However this does not necessarily apply to crystals where the emission can originate from different k levels in the exciton band,(22) or from different Davydov components.(23) This is important when considering naphthalene fluorescence decay rates, but is an unknown factor in the case of anthracene.

The quantum efficiency has been assumed unity throughout this work. This has been shown valid within ±10% for the present temperature range, the experimental error being due in principle to large variations in reabsorption and to sample geometry changes on cooling. The slight variation in quantum efficiency is even found for crystals which showed much defect emission. In general " defect " emission increased as the crystal preparation technique was changed from sublimation and solution flakes to thick sublimation flakes (2 mm) to melt grown (helium atmosphere) to melt grown (Xenon atmosphere). The defect emission probably originated from excitons trapped at physical defect sites. In cases in which defect emission dominates, it is difficult to assess the degree of fluorescence reabsorption, though it is certainly much less than in defect free crystals. The results indicate that the defect emission decay is non-exponential and somewhat longer than that of the free excitons.

6. Conclusions

The temperature variation of the anthracene singlet exciton lifetime in PMM may be understood in terms of radiationless transition processes. The lifetime was found to increase from 5 to 10 ns as the temperature decreased from 350° to 4 °K. This behaviour contrasts with that observed for crystalline anthracene, whose lifetime of 5 nsec is almost independent of temperature after correcting for reabsorption. Comparison of accumulated spectral areas gave reabsorption corrections leading to consistent (5 ± 1 ns) corrected lifetimes even though the correction was sometimes as large as 20 nsec. The present results are in agreement with recent predictions concerning $S_1 \rightarrow T_1$ and $S_1' \rightarrow T_2$ processes in anthracene solid solutions and in anthracene crystals. Analysis of deuterated anthracene will be needed⁽¹⁷⁾ before the mechanism of the radiationless processes can be completely described.

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