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Exciton Diffusion Lengths for Pure and Doped Anthracene Single Crystals from Microscopic Measurements

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An optical microscopic system has been employed to measure the diffusion lengths of singlet excitons in pure and doped anthracene crystals by following the quenching of the anthracene fluorescence by a dye solution. Factors such as the inhomogeniety of dye uptake across the surfaces, the decay of the dye emission with time and correction for reflectivity at the anthracene-solution interface have been accounted for. The diffusion lengths measured—normal to *ab* (001) cleavage sections—are very dependent upon the quality of the crystal surface and the purity of the samples and range from 322 ± 80 Å in acridine doped crystals to 598 ± 51 Å in pure specimens.

INTRODUCTION

The principal method for measuring the diffusion length (L_{eff}) of singlet excitons in anthracene single crystals relies upon the quenching of crystal fluorescence at surfaces covered by an adsorbed layer of a suitable dye such as rhodamine *B*. The number of excitons reaching the surface from the interior of the crystal may then be correlated with the depth of penetration of the light used to excite fluorescence. This technique together with variations involving photo-conductivity measurements have been extensively employed

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by Mulder[1] and recently Cohen, Klein and Ludmer[2] employed a microscopic arrangement in an attempt to differentiate between diffusions in perfect and faulty regions of anthracene crystals. They adequately account for the usually anomalous larger values of the measured diffusion length (L_{eff}) obtained by some authors employing macromeasurements for solution grown crystals in terms of the misalignment of the principal axes of microcrystallites and explain lower values of L_{eff} on the basis of "unevenness of surfaces" frequently associated with emergent dislocations.[3]

However, before definite conclusions may be reached about the effect of dislocations[3] and other structural imperfections[4] on the room temperature diffusion of singlet excitons the often overriding effects of chemical impurities, which may lead to deep trapping of the singlet excitons, must be eliminated. We have, therefore, repeated and extended the earlier micromeasurements of the diffusion length of singlet excitons paying particular attention to the chemical purity of the samples as determined by measurement of the fluorescence spectra at 4K.[5–7] In addition we apply rigorous correction procedures for (a) the decay of the rhodamine emission with time, (b) the inhomogeneous adsorption of the dye on the anthracene surface, (c) the elimination of internal reflection and subsequent scattering of the light during penetration in a rhodamine B quantum counter employed to measure the spectral distribution of the light arriving at the crystal and (d) normalization to equal number of photons absorbed by the crystal by correction for reflectivity at the anthracene-water interface. With such corrections more realistic values of the diffusion length is obtained for pure crystals and the effect of dopants in lowering these values is observed.

EXPERIMENTAL

The experimental arrangement is similar to that described by Cohen, Klein and Ludmer[2] (see Figure 1). Light from a Xenon arc (Oriel Corp: 1 kW) passed through a Hilger and Watts monochromator (D330) and a Nicol prism was focused on an anthracene crystal by means of the objective lens of a Reichert fluorescence microscope. (001) cleavage surfaces of the crystal were covered by a drop of aqueous solutions of 10^{-6} M rhodamine B and 10^{-1} M sodium sulphite spread by a silica disc. The rhodamine emission was collected by the same objective, filtered by a 540 nm cut off filter (to remove most of the anthracene fluorescence) and by an interference filter centred at 600 nm, and detected by a photomultiplier (AVP 150). The photomultiplier response was processed by a photon counter (Brookdeal 5C1) and recorded on to paper tape (ASR 33) for computer treatment of the data.

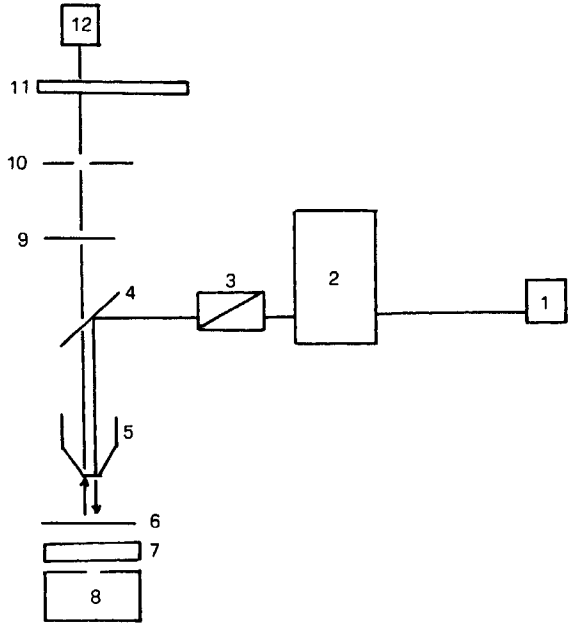

FIGURE 1 A schematic diagram of the experimental arrangement. 1. Xenon arc. 2. Monochromator. 3. Nicol prism. 4. dichroic mirror. 5. objective. 6. crystal covered by rhodamine solution. 7. quantum counter. 8. IP28 photomultiplier (7. and 8. replace crystal for calibration). 9. 540 nm cut-off filter. 10. diaphram to isolate small areas of surface *ca* 5 – 20 um. 11. edge filter. 12. AVP 150 photomultiplier.

PREPARATION OF CRYSTALS

All crystals were grown as boules from the vapour phase by a technique described previously.[8] The starting materials were extensively purified according to methods described elsewhere[9] and crystals were cleaved on (001) planes. The attainment of high purity in the "pure" anthracene crystals is apparent in the low temperature fluorescence spectrum (see Figure 3a) and should be compared with Figure 8 of Lyons and Warren's paper[6] which demonstrates the degree of purity attained by the sublimation of inadequately purified starting materials. In these spectra origins O_3, O_8 (and O_9) may be attributed to methyl- and hydroxy- anthracenes respectively.[7,10]

CONSIDERATION OF CORRECTION PROCEDURES AND TREATMENT OF THE DATA

a) The use of a 540 nm cut-off filter inserted in the optical pathway of the microscope allowed us to clearly distinguish the rhodamine emission (λ_{max} = 605 nm) from the green tail of the anthracene fluorescence. Thus

we observed that even on the clean, freshly cleaved surface of a "pure" crystal the rhodamine B uptake was grossly inhomogeneous. We cannot explain this phenomenon but it resulted in a different response for different directions of polarization. The most simple way to account for this is to plot independently the *a* and *b* polarized data.

b) Careful attention was necessary to avoid a decay in the intensity of rhodamine B emission with time. (In all probability this is due to sensitized photo-oxidation of the anthracene surface). The use of a sulphite solution gives some advantage and in addition it was found that the concentration of rhodamine at 1.0×10^{-6} M is critical. Deviation from this concentration in the worst cases resulted in a disappearance of the rhodamine B emission within *ca* 15 s.

c) In order to obtain the spectral distribution of the excitation light arriving at the crystal ($I_{\text{lamp}}(\lambda)$) a solution of rhodamine B in ethylene glycol, which is an accepted quantum counter may be employed. However, with this solution replacing the crystal and recording the spectrum in reflection led to quite a different "correction curve" than when the experiment was performed in transmission, i.e., with the rhodamine B solution replacing the crystal and the photomultiplier directly below. The "correction curve" in transmission resulted in improved linearity of the final data. It is likely that in reflection internal reflections and scattering vary with depth of penetration of the light thus complicating the response curve.

d) To normalize to equal number of photons absorbed by the crystal at different wavelengths it is necessary to correct the spectra for the reflectivity of the crystal. Values of the reflectivity for anthracene were taken from the paper by Clarke and Philpott.[11] It is also important to take into account the effect on the reflectivity of the thin aqueous rhodamine B layer spread on the crystal. The anthracene reflectivity is therefore

$$R_w = \frac{(\mu - \mu_w)^2 + k^2}{(\mu + \mu_w)^2 + k^2}$$

where μ is the refractive index of anthracene obtained from the reflectivity R

$$R = \frac{(\mu - 1)^2 + k^2}{(\mu + 1)^2 + k^2}$$

and μ_w the refractive index of water, k is the absorption coefficient of anthracene.

e) Recent improvements in the technique of reflectance spectroscopy allow us to obtain reliable absorption spectra for thick crystals and also of non-basal surfaces. Values of the absorption coefficient were therefore also taken from the work of Clarke and Philpott.[11]

f) From the exciton diffusion model the photosensitized fluorescence and absorption spectra are related by the expression[1]

$$\phi_\lambda = a[(1 + D/sL)(1 + 1/k_\lambda L)]^{-1}$$

where ϕ_λ is the relative intensity of photosensitized emission, s is the fraction of excitons arriving at the surface which are annihilated, a is the fraction of excitons annihilated at the surface that leads to dye emission, D is the exciton diffusion coefficient and L is the diffusion length. Thus in a plot of $1/\phi_\lambda$ against $1/k_\lambda$ the ratio of intercept to slope gives L. We have plotted the reciprocal of the intensity of rhodamine emission relative to the intensity of the 392 nm peak (I^{392}/I) against the reciprocal of absorption coefficient expressed in Angstrom units. The ratio of the intercept to the slope gives directly the value of L uncorrected for any reabsorption of emission that occurs, i.e., L_{eff}. The inhomogeniety of the rhodamine uptake is apparent leading to different slopes for a and b polarization but the same value of L_{eff}.

g) Exciton energy in molecular crystals such as anthracene is transported not only by excitons but also by emission and reabsorption of fluorescence light. Corrections for this reabsorption may be made according to the procedure outlined by Mulder[1] (using Figure 3.4 of Mulder's paper) and assuming 80% reflection of the fluorescent light at the illuminated anthracene-water surface. Such corrections reduce the measured diffusion lengths L_{eff} as follows: 600 Å to 400 Å, 500 Å to 320 Å, 400 Å to 260 Å and 300 Å to 190 Å. Due to uncertainties in such correction factors L_{eff} values are quoted in the present paper.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of I^{392}/I against $1/k$ for (a) "pure" vapour grown anthracene crystal (b) vapour grown crystals containing 10^{-4} M/M carbazole and (c) a vapour grown crystal containing 4.5×10^{-5} M/M acridine. The diffusion lengths obtained normal to (001) planes are shown in Table I (which also contains typical values obtained by other authors). The fluorescence spectra of these three crystals at 4K are shown in Figure 3. Carbazole and acridine have their first excited singlet levels (S_1) above and within the exciton band of anthracene respectively and as such are responsible for the generation of X traps[5] (as distinct from chemical traps[6]) in the host anthracene structure.[8] Carbazole introduces shallow traps *ca* 300 cm^{-1} deep whilst the traps due to acridine are deeper *ca* 1400 cm^{-1}. Consequently it would be expected that at room temperature the X-traps introduced by acridine would be more efficient in trapping singlet excitons than those formed by approximately the same concentration of carbazole. The values of the

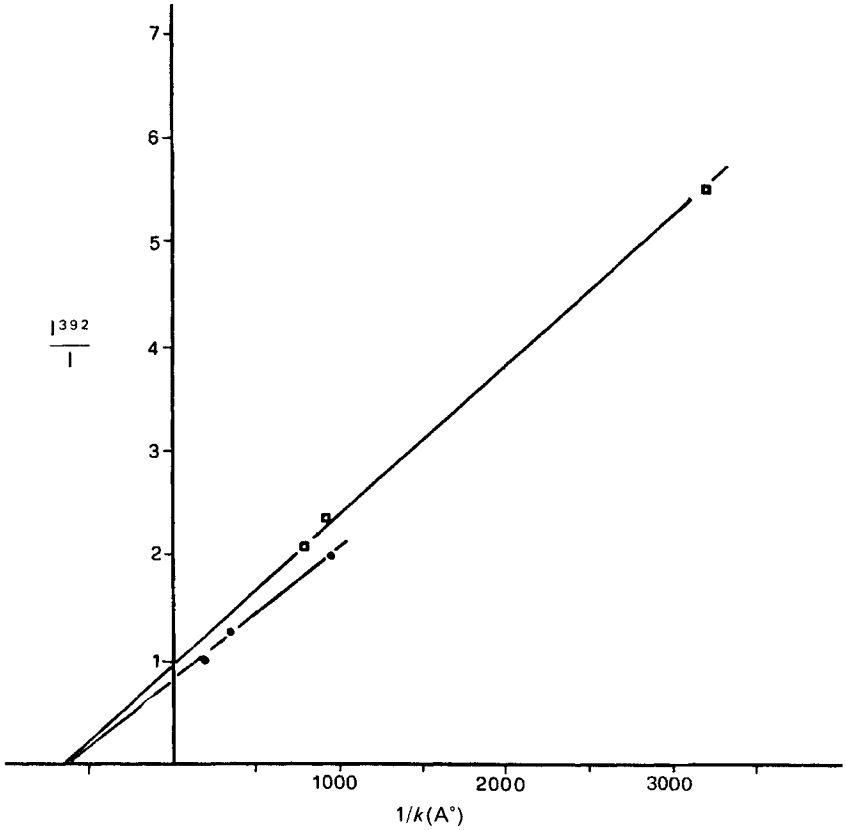

FIGURE 2 Dependence of the reciprocal of the rhodamine emission intensity (I) relative to the rhodamine emission intensity for excitation wavelength 392 (I^{392}), versus the reciprocal of the absorption coefficient (k) of the anthracene at the turning points of the absorption spectrum. (a) "pure" vapour grown anthracene crystal.

diffusion length L_{eff} quoted above, being highest for the pure anthracene crystals and appreciably lowered when acridine is present, is consistent with such a picture. The lowering of the value of L_{eff} for the carbazole doped sample probably has nothing to do with the presence of shallow X-traps but may be caused by an unknown impurity present at a concentration of $< 1 \times 10^{-6}$ M/M and not readily detected in the low temperature fluorescence spectra.

An alternative explanation for the reduction in the exciton diffusion length for carbazole doped crystals (and one preferred by us) may be put forward on the basis of increased intensity in the phonon peaks evident in the low temperature fluorescence spectra at 25,100 cm^{-1} to 24,900 cm^{-1}. Indeed

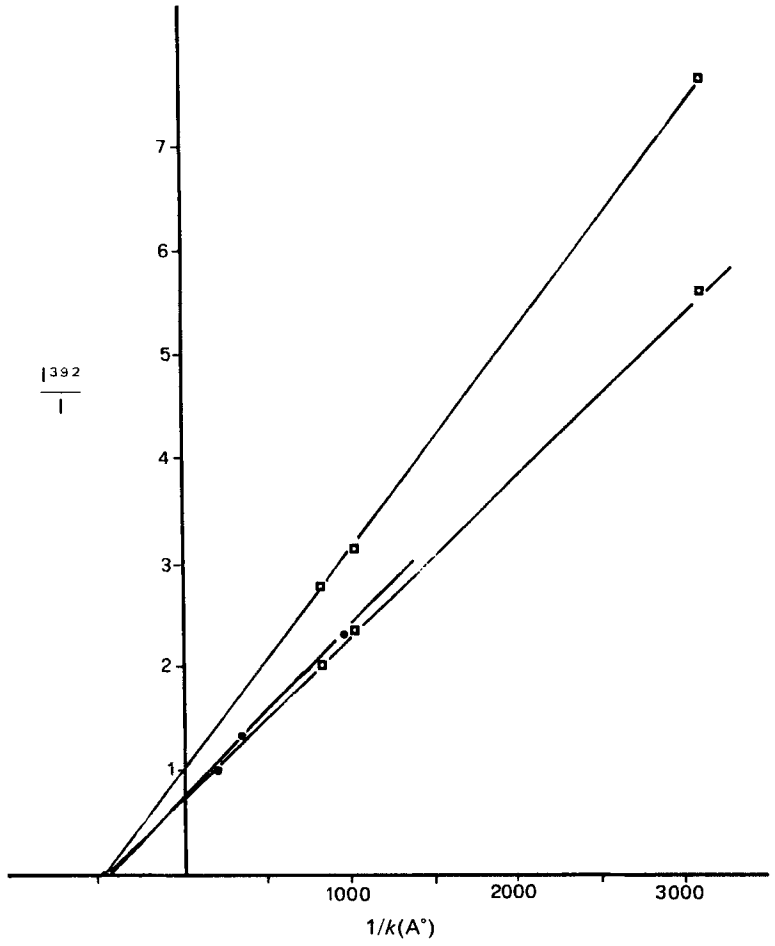

FIGURE 2 Dependence of the reciprocal of the rhodamine emission intensity (I) relative to the rhodamine emission intensity for excitation wavelength 392 (I^{392}), versus the reciprocal of the absorption coefficient (k) of the anthracene at the turning points of the absorption spectrum. (b) vapour grown crystal + 10^{-4} M/M carbazole.

Bridge and Vincent[7] rationalize this increased intensity in the phonon bands in terms of localized phonons at perturbation sites of the lattice. It is also accepted that large exciton-phonon coupling constants mean short mean free paths and consequently a reduced diffusion length may be due to phonon assisted decay of excitons at defect sites in the crystal. A consequence of such a mechanism would be a reduction in the fluorescence lifetime of anthracene/carbazole crystals equivalent to the reduction in the diffusion length, i.e., 20–30%.

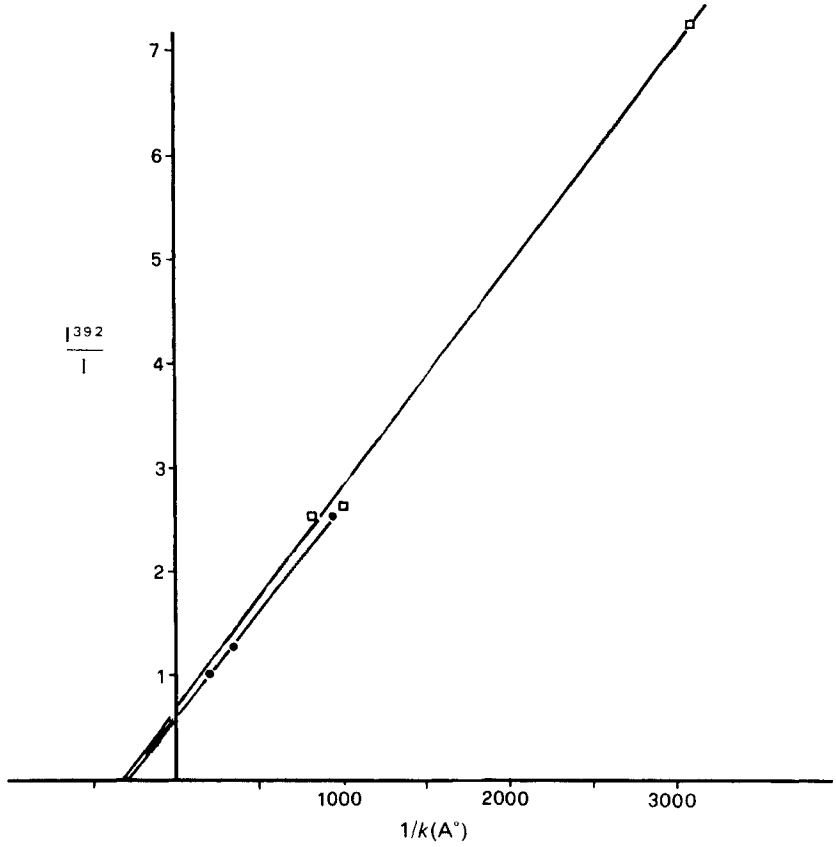

FIGURE 2 Dependence of the reciprocal of the rhodamine emission intensity (I) relative to the rhodamine emission intensity for excitation wavelength 392 (I^{392}), versus the reciprocal of the absorption coefficient (k) of the anthracene at the turning points of the absorption spectrum. (c) vapour grown crystal + 5×10^{-5} M/M acridine.

It is also apparent that previous determinations of L_{eff} for both pure and doped samples yield appreciably lower values indicating the probable "impure" nature of the parent anthracene employed.

It is believed that the microscopic method for measuring the exciton diffusion length in various crystals is superior to those that average information over a large surface area. As pointed out by Cohen, Klein and Ludmer[2] this technique eliminates the possibility of variation in domain orientation within a large sample. However, because of the inhomogeneity of rhodomine B uptake on apparently clean, smooth surfaces the exact role of surface heterogeneity often associated with gross crystalline defects is difficult to define. Furthermore, only defects providing fairly deep traps are likely to be

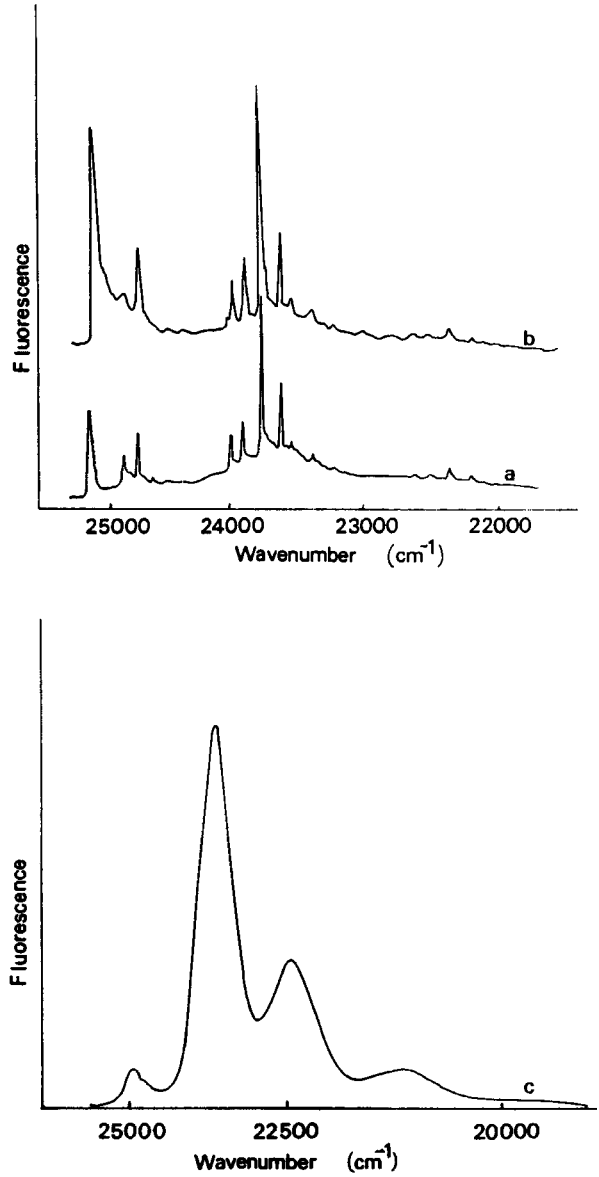

FIGURE 3 Fluorescence spectra at 4K of (a) "pure" vapour grown anthracene crystal (b) vapour grown crystal + 10^{-4} M/M carbazole (c) vapour grown crystal + 5×10^{-5} M/M acridine.

TABLE I

Nature of crystals	$L_{eff}(A^c)$	Authors and reference
"Pure" Anthracene—cleaved thick vapour grown (ca 1 mm)	598 ± 51	Present work
+ 10^{-4} M/M carbazole	450 ± 45	Present work
+ 4×10^{-5} M/M acridine	322 ± 80	Present work
Anthracene (scintillation grade)—thin vapour grown (50 – 200 um)	490 ± 10	Cohen, Klein and Ludmer[2]
Anthracene (scintillation grade)—thin solution grown (50 – 200 um)	470 ± 10	Cohen, Klein and Ludmer[2]
Anthracene (chromatographed) —solution grown (50 – 200 um)	400	Mulder[1]
—vapour grown (50 – 200 um)	400	Mulder[1]
—solution grown		
+ 10^{-4} M/M tetracene	80	Mulder[1]
+ 10^{-2} M/M acridine	ca 100	Mulder[1]

effective in room temperature measurements. A possible correlation between the sites of dye uptake and regions on the surface comprising a new recently discovered[12] crystallographic modification of anthracene providing deep structural traps for the singlet exciton deserves examination.

Acknowledgements

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