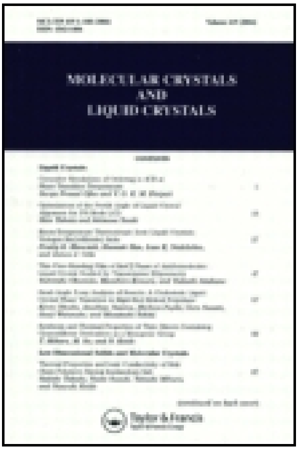

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Anita C. Jones [a] & John O. Williams [a]
[a] Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Wales, U.K.

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Fluorescence Lifetimes and Site-selective Photochemistry of Anthracene Crystals Doped with 2-hydroxyanthracene

ANITA C. JONES and JOHN O. WILLIAMS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Wales, U.K.

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The rise and decay of the prompt fluorescence of 2-hydroxyanthracene (2-OHA) doped anthracene crystals have been investigated at 8 K following excitation with frequency-doubled picosecond pulses from a synchronously pumped dye laser. By studying fresh crystals and crystals irradiated with u-v light at 298 K so as to introduce the photodimer, the roles played by the two different sites (O_8) and (O_9) occupied by the 2-OHA, by the X-traps and by other structural defects in fluorescence and energy transfer have been elucidated. Energy transfer between impurity sites (O_8 and O_9) is slow whereas that between guest associated X-traps and impurity is rapid. For the O_9 site, both before and after photodimerization, a simple time-independent energy transfer occurs from the anthracene host to the 2-OHA guest. The transfer to O_8 sites is associated with the presence of an extended region of disorder associated with the impurity. Such regions are excited directly.

INTRODUCTION

There has been considerable interest recently in the time-dependent prompt fluorescence behavior of both pure and doped anthracene crystals in the 0.5 to 10 nanosecond time range. Galanin and Khan-Magometova[1] and Bale, Bridge and Smith[2] have reported measurements on thin, pure anthracene crystals at low temperatures which indicate that the intrinsic anthracene lifetime at *ca* 1–2 ns is very short in comparison with the values reported earlier by Munro *et al.*[3] It is now recognized that the longer lifetimes reported for anthracene crystals at $T < 77$ K are characteristic of defects and impurities. More recently Galanin, Khan-Magometova and Myasnikov[4] have studied the wavelength dependence of the rise and decay of fluorescence from thin, pure anthracene crystals. Their results are consistent with a model based on the polariton concept of elementary excitations of the crystal discussed earlier by Ferguson,[5] and Brodin *et al.*[6] for anthracene and by Heim and Wiesner[7] for CdS. Bridge and Solomons[8] reported studies of energy transfer in thin anthracene crystals doped with 2-methylanthracene (2MeA) at 5 K by nanosecond spectrofluorimetry and concluded that energy transfer between the host and one of the impurity sites (A) may be described by first order kinetics. Energy transfer between impurity molecules at sites A and B in unstrained crystals occurs by long range resonant exchange.

In this paper we focus attention on the rise and decay of prompt fluorescence from melt-grown anthracene crystals doped with 2-hydroxyanthracene (2OHA). As with 2-MeA, two sites are found for 2-OHA[9-11]—the so called O_8 and O_9 emission series with origins at 24,352 cm^{-1} (O_8) and 24,165 cm^{-1} (O_9). The system has been investigated previously both from the viewpoint of absorption and fluorescence spectroscopy[9-11] and from that of site selective photochemistry[11-13] and for the present study it holds distinct advantages over the system comprising anthracene crystals doped for example with 2-MeA. Amongst these advantages are:

(a) fluorescence from the two sites O_8 (A) and O_9 (B) occupied in the anthracene lattice by 2-OHA is intense with the peaks well separated and relatively free of any background emission.

(b) the impurity emission is well removed from the host anthracene origin so that reabsorption effects with single photon surface excitation can be ignored.

(c) following irradiation of the crystals at 300 K with UV light ($\lambda \sim 300$–400 nm) site-selective photochemistry occurs whereby heterodimer formation between anthracene and 2-OHA molecules situated at O_9 sites (but not those situated at O_8) takes place.

Because of (a), energy transfer between the two sites may be unequivocally examined and (c) allows us to study the time-dependent fluorescence from crystals before and after the photochemical change. Our main objective, therefore, is to investigate the energy transfer processes and the photochemical reaction in this system by a detailed study of the wavelength dependence of the rise and decay of prompt fluorescence.

EXPERIMENTAL

Materials were purified as described elsewhere[11] and sections of the crystals grown from the vapor phase and containing *ca* 10^{-5} to 10^{-6} M/M 2-OHA have been employed in previous experiments.[11,13] Cleaved (001) plates were employed throughout.

The crystal under investigation was mounted on the cold stage of an Air Products "Displex" cryostat and cooled to 8 K, at which temperature all measurements were conducted. The sample was excited with the externally frequency doubled, cavity dumped output of a Spectra Physics tunable rhodamine 6G dye laser. The dye laser is synchronously pumped by the mode-locked output of a Spectra Physics 171 argon ion laser; the cavity dumped dye laser output consists of pulses of 10's of picoseconds in duration, the repetition rate used here being 4 MHz. Frequency doubling is achieved by a KDP (60° section to C axis) temperature tuned crystal, giving an excitation wavelength of *ca* 290 nm.

The fluorescence was analyzed by a double monochromator, resolution *ca* 5 cm^{-1}, and detected by a cooled RCA 8850 photomultiplier tube. Steady state emission spectra were recorded using an Ortec-Brookdeal photon counter and fluorescence response functions were measured using an Ortec time-correlated, single-photon counting system. In single-photon counting mode the RCA 8850 was operated at 3.3 kV to eliminate the need for amplification of its output, thus considerably improving the timing resolution.[14] The time of arrival of a detected photon is determined by the time to amplitude converter (TAC) operated in "reverse mode" in order to fully utilize the 4 MHz laser repetition rate,[15] the voltage ramp of the TAC being initiated by the arrival of an emitted photon and subsequently halted by the next laser pulse which is detected by a modified IP28 photomultiplier tube. Operation in this mode is possible because of the highly reproducible laser repetition rate. The output pulse from the TAC passes to an Ino-Tech Multichannel analyzer, operating in pulse height analysis mode, where photon counts are accumulated until there are 10,000 counts in the peak channel. The time interval per channel is variable down to 50 ps. An average count rate of <0.002 photons per excitation pulse is used in order to avoid pulse pile-up distortion effects.[16] Data are output from the MCA to a Research Machines 380Z microcomputer and stored on local floppy disk, for subsequent transfer to the main frame Honeywell 6080 computer, via an online link, for analysis.

Fluorescence spectrum and lifetimes were measured, at 8 K, for a fresh crystal; the crystal was then warmed to room temperature, irradiated with a mercury arc (100 W, medium pressure) through a water filter and glass lens, for 75 mins, then cooled again to 8 K. The spectrum and lifetimes were then re-measured.

DATA ANALYSIS

The experimentally observed fluorescence response function consists of a convolution of the true fluorescence response function with the instrument response function. In the present investigation, the host decay times and guest rise times were sufficiently short for the fluorescence functions to be distorted by the instrument function. In such cases correction is achieved by an iterative point for point convolution and non-linear least squares fitting procedure.[17] The theoretical function, with which the instrument function is convoluted, most commonly consists of a sum of exponential terms

$$I(t) = \sum_{i=1}^{n} A_i \exp(-t/\tau_i) \tag{1}$$

In the case of simple time-independent energy transfer, the theoretical response function for the guest emission consists of a difference of exponential terms

$$I_G(t) = B[\exp(-t/\tau_1) - \exp(-t/\tau_2)] \tag{2}$$

where $\tau_1 > \tau_2$, τ_1 determines the decay time and τ_2 determines the rise time. In cases where τ_1 is considerably greater than τ_2, as in the present work, we have found the most satisfactory method of fitting to be as follows. The guest decay time, τ_1, is determined from that part of the response function unaffected by the negative exponential term in τ_2, that is to say the greater part of the decay portion of the response function. The part of the response function dominated by the rise time, τ_2, is then fitted to the above function, holding the known value of τ_1 constant, and τ_2 is thus obtained.

The goodness of fit of the theoretical function to the experimental curve is assessed by the reduced chi-square statistic,[18]

$$\chi_\nu^2 = \frac{1}{\nu}\sum_{i=1}^{n} \frac{(I_i - Y_i)^2}{I_i} \tag{3}$$

where I_i and Y_i are the experimentally observed and theoretically calculated number of counts in the ith channel, n = the number of data points and $\nu = n - m - 1$, the number of degrees of freedom remaining after fitting n data points with m parameters. A chi-square value of 1.0 indicates a perfect fit.

Since, however, the range of acceptable values for chi-square is difficult to define, an additional criterion is used, namely the randomness of the temporal distribution of weighted residuals, r_i, as quantified by a plot of the autocorrelation function, C_i, versus i[19]

$$r_i = \frac{I_i - Y_i}{\sqrt{Y_i}} \tag{4}$$

$$C_i = \frac{1}{l}\,\frac{\sum_{j=1}^{l} r_j \cdot r_{j+i}}{\frac{1}{n}\sum_{j=1}^{n} r_j^2} \tag{5}$$

where $l = n/2$.

These criteria are considered adequate if the following condition can be met[20]

$$\delta t.\ I_{\max}.\ \mathrm{Var}(E_{\max})/[\tau \cdot E_{\max}\ \mathrm{Var}(I_{\max})] < 1$$

where δt = the sampling interval, $I_{\max}$ = number of counts in the maximum of the measured fluorescence function, $\mathrm{Var}(I_{\max})$ = the variance in $I_{\max}$, $E_{\max}$ = the number of counts in the maximum of the measured instrument function.

RESULTS

Fresh crystal

The uncorrected fluorescence spectrum for the fresh crystal is shown in Figure 1. There is a low level of the broad background emission characteristic of melt-grown anthracene crystals and assignable to local centres of exciton trapping with a continuous energy spectrum, probably formed as a result of a statistical distribution of local areas of lattice compression in regions of dislocation ensembles.[21]

The defect band centered at 402.7 nm (24,834 cm^{-1}) has been shown by Craig and Rajikan[22] to be resolvable into three X-trap emissions, X_i, X_2 and X_3, X_2 being the "deformation band" reported by several workers. The wavelengths at which fluorescence response functions were measured are indicated on the spectrum. Emission from unperturbed anthracene molecules and the defect band emission will be referred to collectively as host emission. Emission from both the O_8 and O_9 sites of 2-OHA at 410.6 nm (24,352 cm^{-1}) and 413.8 nm (24,165 cm^{-1}) respectively will be referred to as guest emission.

The host fluorescence response functions (see e.g. Figure 2) could be fitted by simple mono-exponential or, in the case of 402.7 (24,834 cm^{-1}) and 404.8 nm (24,703 cm^{-1}), bi-exponential functions. The second component in the latter is due to a contribution from the broad background emission with lifetime *ca* 2 ns. The anthracene lifetime obtained was 1.1 ± 0.06 ns, and this was common to the defect emission, which showed no detectable rise. The guest fluorescence response functions consisted of a rise and decay (Figure 3) and could be satsfactorily fitted with a difference of two exponential terms as detailed earlier. The O_8 site exhibits a decay time of 7.5 ± 0.4 ns and a rise time of 0.6 ± 0.1 ns. The O_9 site has a decay time of 8.7 ± 0.4 ns and a rise time of 1.0 ± 0.1 ns.

Photodimerised crystal

The fluorescence spectrum after photodimerisation is shown in Figure 1. In addition to the decrease in relative intensity of O_9 emission, associated with the

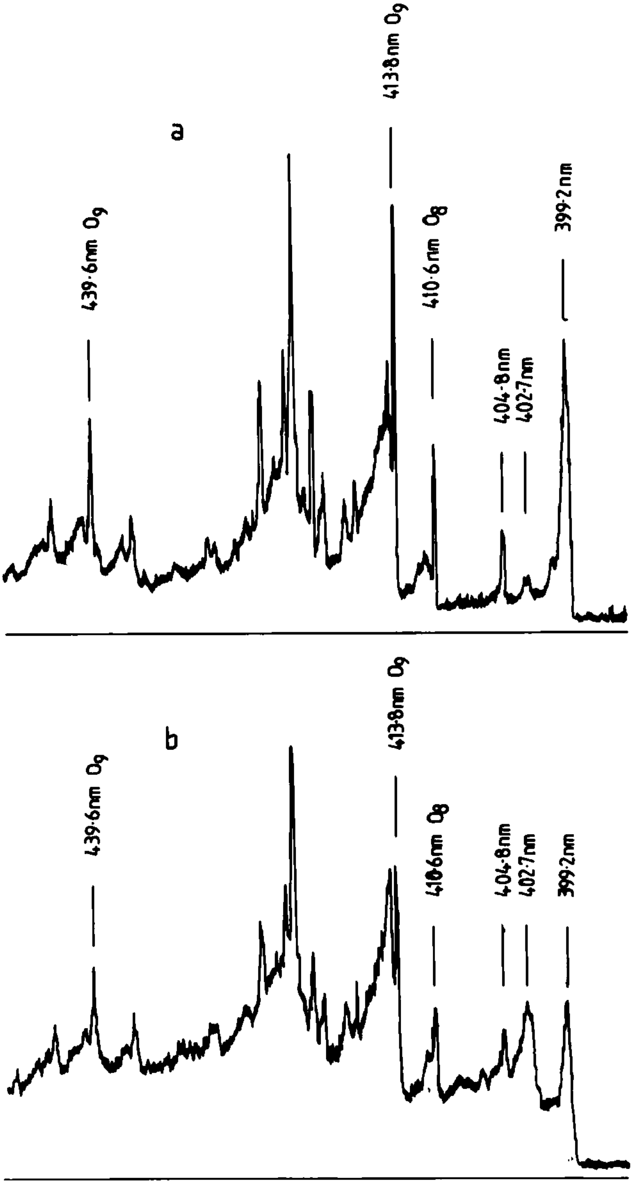

FIGURE 1 Fluorescence spectrum of 2-OHA doped anthracene single crystal at 8 K before (a), and after (b) irradiation at 298 K. The wavelengths at which fluorescence response functions were measured are indicated on the spectrum.

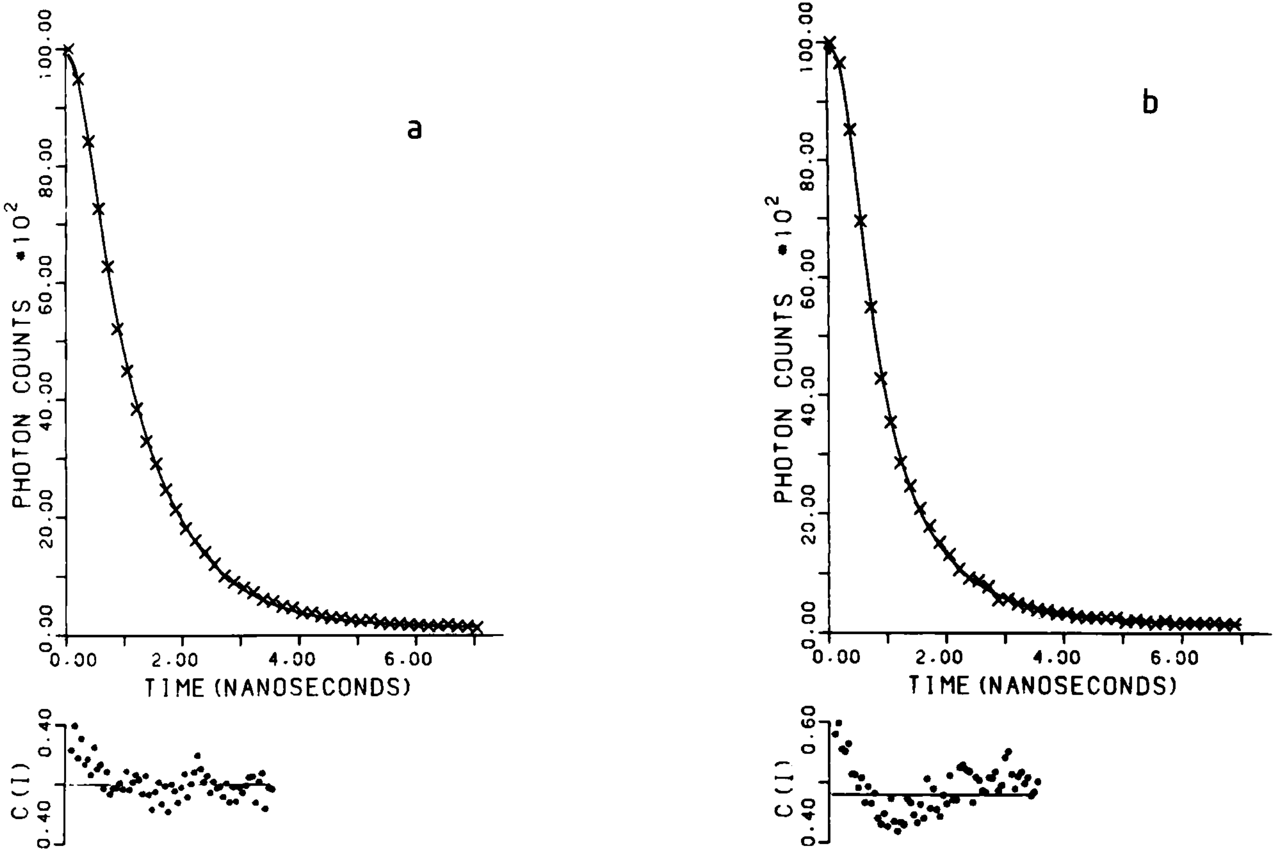

FIGURE 2 Fluorescence response functions at 8 K of anthracene at 399.2 nm, (a) before, and (b) after irradiation of the crystal at 298 K. Crosses refer to experimental points; the lines to the theoretical function. χ_ν^2 values are (a) 1.1 and (b) 1.1.

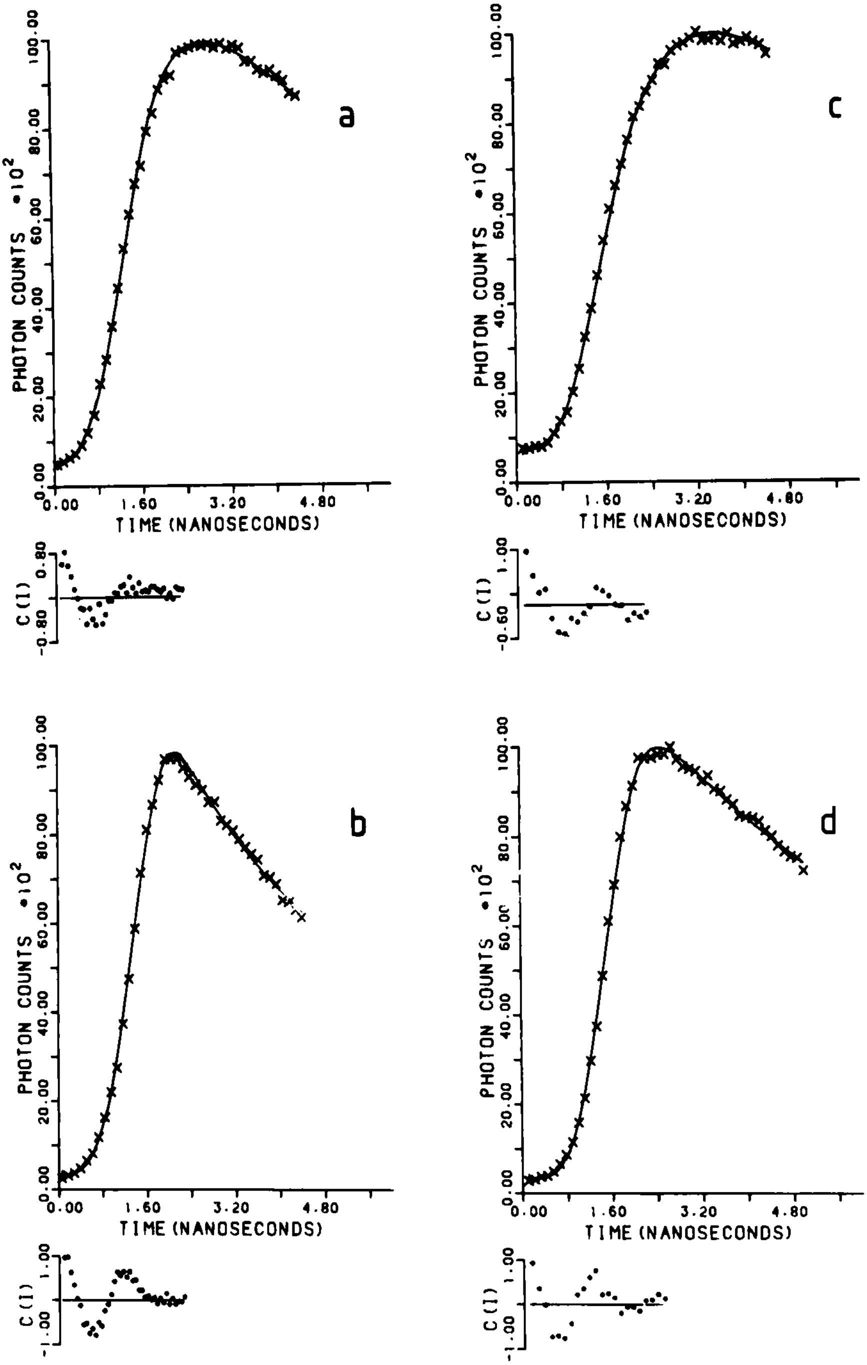

FIGURE 3 Fluorescence response functions at 8 K of O_8 (a and b) and O_9 (c and d) before and after irradiation of the crystal at 298 K. Crosses refer to experimental points; lines to the theoretical function χ_ν^2 values are (a) 1.4; (b) 2.5; (c) 1.5; (d) 2.0.

site-selectivity of dimerisation,[12,13] we note the considerable increase in intensity of the broad background emission together with that of the defect band. The host fluorescence response functions could be satisfactorily fitted with a bi-exponential function; the second component being due, as in the fresh crystal, to the background emission with lifetime in the region of 1–2 ns, but now in greater proportion. A lifetime for anthracene of 0.4 ± 0.2 ns was obtained, and this again appeared to be common to the defect emission. The estimated inaccuracy of this lifetime is due to its shortness compared with the instrument function together with the significant contribution to the decay from the background emission. At this point we simply note the fact that photodimerisation results in a considerable decrease in the host fluorescence lifetime. The guest fluorescence response functions also contained a contribution from the background emission. The decay time of the O_8 site was found to be 7.6 ± 0.4 ns, and that of the O_9 site 8.7 ± 0.4 ns.

Obtaining a fit to the rises of the O_8 and O_9 emissions was inhibited by the presence of the background component and the shortness of the rise time. We were able, however, to obtain sufficiently good fits to estimate the rise time of O_9 to lie in the same range as the host decay time, i.e. 0.4 ± 0.2 ns, and the O_8 rise time to be very short and certainly less than 0.1 ns. We note that the decay times of both the 2-OHA sites remain unchanged, within experimental error, upon photodimerisation, but that their rise times are considerably shortened.

DISCUSSION

Guest to Guest Energy Transfer

The O_8 site of 2-OHA is of higher energy than the O_9 site and less abundant, consistent with a more crowded orientation of molecules at the O_8 site.[10] The O_8 site has a shorter fluorescence lifetime than O_9 and it is reasonable to consider an explanation in terms of an additional decay channel provided by energy transfer from O_8 to O_9. However, our results show no evidence of guest to guest energy transfer. For the fresh crystal the O_9 fluorescence response function is satisfactorily fitted by a simple difference of exponential terms, the rise time showing good agreement with the anthracene host decay time. If guest to guest energy transfer constituted a significant non-radiative decay channel, the decay time of O_8 would be expected to depend on the concentration of O_9 sites. On photodimerisation the concentration of O_9 sites decreases; however we observe no accompanying change in the O_8 decay time, and the O_9 rise time remains consistent with the anthracene decay. We, therefore, conclude that guest to guest energy transfer is slow compared with host to guest energy transfer and does not significantly contribute to the decay of O_8. This is in agreement with the spectroscopic observations of Brillante *et al.*[10] and contrary to the observations of Bridge and Solomons[8] for 2-methylanthracene doped anthracene.

Guest Associated X-traps and their Role in Energy Transfer

The 2-OHA sites constitute point defects in the anthracene host lattice and thus would be expected to have X-traps associated with them; in principle there should be two X-trap types, one for each site. Brillante *et al.*[10] have observed only one X-trap of depth 108 cm^{-1}, associated with the 2-OHA guest in anthracene. They have shown this trap to be induced at the O_8 site rather than at O_9, and from the relative strengths of trap and O_8 absorption and emission have inferred that, as expected for an X-trap in close association with an impurity molecule, there is rapid energy transfer from trap to impurity.

Both Craig and Rajikan[12] and Burland and Thomas[13] have observed that photodimerisation is accompanied by the decrease in intensity of an emission line at 22 cm^{-1} from the origin of the anthracene luminescence spectrum at 4 K. This line is a feature of the emission spectra of pure as well as doped anthracene crystals and Craig and Rajikan assign it to a pure crystal X-trap with which the O_9 site is associated, an impurity molecule and a trap being removed at each photochemical event. Rapid energy transfer would be expected between the 22 cm^{-1} trap and the O_9 site as between the 108 cm^{-1} trap and the O_8 site. However, the 22 cm^{-1} emission is relatively intense in fresh anthracene—2-OHA crystals[12,13] which is inconsistent with rapid energy transfer between trap and impurity. Burland and Thomas[13] observed a pronounced minimum in the excitation spectrum of both O_8 and O_9 sites corresponding with the absorption wavelength of the 22 cm^{-1} X-trap, indicating that excitation of the X-trap impeded energy transfer to both O_8 and O_9 sites. This evidence certainly contradicts the assumption of rapid energy transfer between the X-trap and O_9, and suggests an equivalent relationship between the trap and both sites. The explanation given is that an intermediate is formed between the X-trap and 2-OHA at both sites, to the exclusion of emission from O_8 and O_9. However, on direct excitation of O_8 and O_9, emission maxima are observed, implying that the intermediate is formed only upon excitation of the X-trap. Furthermore, it would seem reasonable to expect that energy transfer from the anthracene host should occur via the X-traps which presumably surround the impurity, so, if excitation of the X-trap impedes emission from O_8 and O_9, no guest emission should be observed from the mixed crystal.

We suggest that the 22 cm^{-1} trap is not closely associated with either the O_8 or O_9 site, but is simply an X-trap isolated within the host lattice. The effect observed in the excitation spectra, recorded at 2 K, may be merely due to the trapping of the excitation by the X-trap which is isolated from O_8 and O_9 by anthracene molecules of the host lattice which are higher in excitation energy. The intensity of the 22 cm^{-1} line in pure anthracene crystals has been noted to be sensitive to the physical state of the crystal;[22] the change in intensity on heterodimer formation may be as a result of the accompanying disruption of the lattice and the depopulation of the 22 cm^{-1} trap in favor of the increased number of deeper traps, such as those responsible for the observed increased intensity of the defect band. It would seem likely that the O_9 site should be associated with an X-trap, and, since there is no evidence for the induction of an X-trap by the presence of O_9, this site may be associated with another of the X-traps known to be present in pure anthracene crystals.

If the transfer of energy to a guest molecule from an X-trap is rapid, then the participation of the trap in host to guest energy transfer will not be apparent from observation of the guest fluorescence response function, the rise time of which will reflect a slower decay process preceding population of the trap.

Host to Guest Energy Transfer

For the O_9 site, both before and after photodimerisation, our results are consistent with simple time-independent energy transfer from the anthracene host to the 2-OHA guest, and, if an X-trap is associated with the O_9 site, rapid trap to guest energy transfer.

In the case of the O_8 site, the result obtained, namely that the rise time of emission, both before and after photodimerisation, is considerably shorter than the rise time of O_9 and the decay time of anthracene, is rather difficult to rationalize. If one assumes that the only absorbing species is the unperturbed anthracene of the host lattice, and that all other species are populated by the decay of the latter, this result appears inexplicable since all species of shorter lifetime than anthracene, which are pumped by decay of anthracene, should show the anthracene decay time. But the species whose decay is populating O_8 has a decay time shorter than anthracene and so is apparently being excited by some means other than energy transfer from anthracene. We attempt here to provide a plausible explanation of this result. It has been shown that the two substituent orientations of 2-OHA in anthracene interact differently with the host lattice in that an X-trap of depth 108 cm^{-1} is induced at the O_8 site, whereas the O_9 site apparently induces no trap but is, rather, associated with some existing pure crystal X-trap. We postulate that in addition to the localized and quasi-discrete perturbation at the core of the defect caused by the O_8 substituent, there is an associated macroscopically strained region extending a considerable distance into the rest of the crystal, in accordance with the model described by Schipper and Walmsley;[23] furthermore, this region of lattice distortion is so extensive that it competes with the anthracene molecules of the host lattice for absorption of incident photons and thus receives excitation directly, rather than indirectly by energy transfer. We suggest that the observed rise time of O_8 emission corresponds to the decay time of some species present in this disordered region, possibly the longest lived in a series of traps participating in the energy transfer process. Emission from a disordered region of this type could be a contributory part of the broad background observed in the fluorescence spectrum, and a structureless absorption could easily be concealed in the absorption spectrum by the broadness produced by overlapping progressions of phonon bands.

Effects on Photodimerisation

The increased intensity of the defect band and broad background emission indicates that photodimerisation causes considerable disruption of the crystal lattice, the strain apparently being largely accommodated by the propagation of existing defects. A similar increase in the defect band emission has been observed by Craig and Rajikan[22] on photodimerisation of pure anthracene crystals, when the fresh crystal shows this emission. Their spectra showed that the intensity distribution between the three lines comprising this emission changed, X_2 gaining intensity at the expense of X_1 and X_3. Although unresolved in our spectra, a similar redistribution can be seen in the spectra of Burland and Thomas[13] on heterodimer formation.

The marked decrease in the host decay times and guest rise times may be accounted for by the efficient non-radiative decay channels provided by the increased number of traps resulting from the induced disorder. The O_9 rise time remains in good agreement with the anthracene decay time and the O_8 rise time remains considerably shorter than that of O_9, becoming almost undetectably short. The guest decay times are unchanged by photodimerisation indicating that the 2-OHA substituents behave as discrete molecules, unaffected by the state of the surrounding host lattice, decaying by radiative rather than non-radiative processes.

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