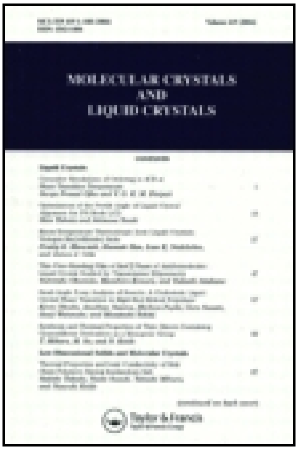

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Influence of Reabsorption and Defects on Anthracene Crystal Fluorescence

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To cite this article: J. B. Birks (1974): The Influence of Reabsorption and Defects on Anthracene Crystal Fluorescence, Molecular Crystals and Liquid Crystals, 28:1-2, 117-129

To link to this article: http://dx.doi.org/10.1080/15421407408083156

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 117-129
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Printed in Dordrecht, Holland

The Influence of Reabsorption and Defects on Anthracene Crystal Fluorescence

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(*Received November 29, 1973*)

Expressions are derived for the influence of host crystal and defect reabsorption, exciton trapping and thermal detrapping, and defect and impurity fluorescence on the fluorescence properties of a "pure" organic molecular crystal. The reabsorption spectra of crystal anthracene and its defects are discussed, and data on the thickness and temperature dependence of its fluorescence lifetime are analysed. The exciton transfer rate in "pure" anthracene crystals is time-independent at $t > 0.1$ ns.

INTRODUCTION

The fluorescence properties of an organic molecular crystal are influenced by

a) reabsorption of the fluorescence photons, and
b) trapping of the singlet excitons by defects and impurities.

Reabsorption, due to the overlap of the absorption and fluorescence spectra, occurs even in a perfect pure crystal, and defects and impurities introduce additional reabsorption in a real crystal. Exciton trapping by defects and impurities is absent in a perfect crystal, but it occurs in all real crystals. This paper discusses the influence of reabsorption, defects and impurities on the fluorescence of organic molecular crystals, with particular reference to crystal anthracene.

PERFECT CRYSTALS

In a perfect pure fluorescent crystal in which reabsorption of the fluorescence occurs with probability a_{MM}, the observed (technical) fluorescence lifetime τ^t_M, quantum yield Φ^t_{FM}, spectrum $F^t_M(\bar{\nu})$ and spectral area A^t_M (= $F^t_M(\nu)\,d\nu$) are related to the corresponding molecular (exciton) parameters Φ_{FM}, $F_M(\nu)$ and A_M by the following Equations [1, 2]

$$\tau^t_M = \frac{\tau_M}{1 - a_{MM}\,\Phi_{FM}} \tag{1}$$

$$\Phi^t_{FM} = \frac{(1 - a_{MM})\,\Phi_{FM}}{1 - a_{MM}\,\Phi_{FM}} \tag{2}$$

$$A^t_M = (1 - a_{MM})\,A_M \tag{3}$$

$F^t_M(\bar{\nu})$ and $F^t_M(\nu)$ are normalised in the low wavenumber ($\bar{\nu}$) region, where the spectral profile is not affected by reabsorption. Relations (1)-(3) do not involve "the major assumption . . . that reabsorption is uniform in all directions", as stated by Munro *et al.* [3]. Otherwise they would only be applicable to volume excitation of the crystal, e.g. by X-rays. (see Appendix).

They do, however, assume that only one fluorescent and absorbing species is present, and that the molecular fluorescence parameters τ_M, Φ_{FM} and $F_M(\bar{\nu})$ and the absorption spectrum $\kappa_M(\bar{\nu})$ are constant throughout the system. The absorption probability a_{MM} is the weighted sum of a series of partial absorption probabilities a_p, where a_p is the absorption probability of the p^{th} generation of fluorescence photons. With external optical excitation of a unitary fluorescent system the absorption probability a_1 for the primary fluorescence photons, generated by the incident light, differs from the absorption probabilities a_2, $a_3 \ldots a_p$ for the secondary, tertiary and p^{th} generations of fluorescence photons produced by reabsorption, because of the different spatial distributions of the emitting molecules. The values of a_p and a_{MM} depend on the conditions of excitation and observation of the fluorescence. The values of a_{MM} in relations (1) – (3) are identical only if τ^t_M, Φ^t_{FM} and $F^t_M(\bar{\nu})$ are determined under *identical excitation and observation conditions.* (see Appendix).

REAL CRYSTALS

A real fluorescent organic molecular crystal contains defects and impurities, commonly fluorescent, which provide traps for the singlet ($^1M^*$) excitons of the host crystal. A real crystal is a multi-component fluorescent system consisting of the host species ^1M (molecular parameters τ_M, Φ_{FM}, $F_M(\bar{\nu})$ and $\kappa_M(\bar{\nu})$) and n guest species ^1X_n (molecular parameters τ_n, Φ_{Fn}, $F_n(\bar{\nu})$ and $\kappa_n(\bar{\nu})$, with $n = 1$, 2, 3 . . .). The exciton trap depth of ^1X_n is $\Delta E_n = \bar{\nu}_{oM} - \bar{\nu}_{on}$, where $\bar{\nu}_{oM}$ and $\bar{\nu}_{on}$ are the zero-point energies of the singlet-excited species $^1M^*$ and $^1X_n{}^*$, respectively. The mole fraction of ^1X_n is $[^1X_n]$.

The fluorescence behaviour of a multi-component system can be analysed in terms of its fluorescence response functions [4]. k_{FM} and k_{Fn} are the radiative decay rates of $^1M^*$ and $^1X_n{}^*$, respectively; k_M $(= 1/\tau_M)$ and k_n $(= 1/\tau_n)$ are the total decay rates of $^1M^*$ and $^1X_n{}^*$; k_{nM} $[^1X_n]$ is the *net* rate of $^1M^*$ exciton transfer to ^1X_n; and a_{MM} and a_{nM} $[^1X_n]$ are the probabilities of reabsorption of $^1M^*$ fluorescence by ^1M and ^1X_n, respectively.

The rate equations for the mole fractions of excited host $[^1M^*]$ and excited guest $[^1X_n{}^*]$ molecules, following δ-function excitation of $[^1M^*]_0$ at time t=0, are as follows,

$$-\frac{d[^1M^*]}{dt} = (k_M - a_{MM}\,k_{FM} + \sum_n k_{nM}\,[^1X_n])\,[^1M^*] \tag{4}$$

$$-\frac{d[^1X_n{}^*]}{dt} = k_n\,[^1X_n{}^*] - (a_{nM}\,k_{FM} + k_{nM})\,[^1X_n]\,[^1M^*] \tag{5.n}$$

The $^1M^*$ fluorescence response function is

$$i_M^t(t) = (1 - a_{MM} - \sum_n a_{nM}\,[^1X_n])\,k_{FM}\exp(-k_M^t\,t) \tag{6}$$

where

$$k_M^t = k_M - a_{MM}\,k_{FM} + \sum_n k_{nM}\,[^1X_n] \tag{7}$$

The technical $^1M^*$ fluorescence parameters are

$$\tau_M^t = 1/k_M^t = \frac{\tau_M}{1 - a_{MM}\,\Phi_{FM} + \sum_n \sigma_{nM}\,[^1X_n]} \tag{8}$$

$$\Phi_{FM}^t = \frac{(1 - a_{MM} - \sum_n a_{nM}\,[^1X_n])\,\Phi_{FM}}{1 - a_{MM}\,\Phi_{FM} + \sum_n \sigma_{nM}\,[^1X_n]} \tag{9}$$

$$A_M^t = (1 - a_{MM} - \sum_n a_{nM}\,[^1X_n])\,A_M \tag{10}$$

where

$$\sigma_{nM} = k_{nM}/k_M \tag{11.n}$$

Comparison with relations (1)-(3) for a unitary fluorescent system shows that in a multi-component system τ_M^t and Φ_{FM}^t are reduced by $^1M^*$ exciton transfer to $\Sigma\,[^1X_n]$, and that Φ_{FM}^t and A_M^t are reduced by $^1M^*$ fluorescence reabsorption by $\Sigma\,[^1X_n]$. Relations (1)-(3) are not valid for a multi-component system.

From (4) and (5.n) the $^1X_n{}^*$ fluorescence response function is

$$i_n^t(t) = \frac{(a_{nM}\, k_{FM} + k_{nM})[^1X_n]\, k_{Fn}}{(k_M^t - k_n)} \{\exp(-k_n t) - \exp(-k_M^t t)\} \quad (12.n)$$

The technical $^1X_n{}^*$ fluorescence parameters are $\tau_n^t = \tau_n$, $A_n^t = A_n$, and

$$\Phi_{Fn}^t = \frac{(a_{nM}\, \Phi_{FM} + \sigma_{nM})[^1X_n]\, \Phi_{Fn}}{1 - a_{MM}\, \Phi_{FM} + \sum_n \sigma_{nM}\, [^1X_n]} \quad (13.n)$$

The parameters k_{nM} and σ_{nM} decrease with increase in temperature T. At low temperatures $k_{nM} = k_{nM}^0$ and $\sigma_{nM} = \sigma_{nM}^0$. At higher temperatures the net rate k_{nM} $[^1X_n]$ of $^1M^*$ transfer to ^1X_n is less than k_{nM}^0 $[^1X_n]$ because of the thermally-activated reverse transfer from $^1X_n{}^*$ to ^1M at a rate

$$k_{Mn} = k'_{Mn} \exp(-\Delta E_n/kT) \quad (14.n)$$

Hence

$$k_{nM} = \frac{k_n\, k_{nM}^0}{k_n + k_{Mn}} = \frac{k_{nM}^0}{1 + \sigma_{Mn}} = \frac{k_{nm}^0}{1 + \sigma'_{Mn} \exp(-\Delta E_n/kT)} \quad (15.n)$$

where $\sigma_{Mn} = k_{Mn}/k_n$ and $\sigma'_{Mn} = k'_{Mn}/k_n$. Equation (8) thus becomes

$$\tau_M^t = \frac{\tau_M}{1 - a_{MM}\, \Phi_{FM} + \sum_n \left\{ \dfrac{\sigma_{nM}^0\, [^1X_n]}{1 + \sigma'_{Mn} \exp(-\Delta E_n/kT)} \right\}} \quad (16)$$

where $\sigma_{nM}^0 = k_{nM}^0/k_M$. This relation describes the influence of reabsorption and exciton trapping on the fluorescence lifetime of the host crystal.

ANTHRACENE CRYSTALS

Guest species The principal impurity and defect species which have been identified in "pure" crystal anthracene are designated as follows.

($^1X_1$). 2-Methylanthracene (2-MA) is present in all anthracene crystals, and its fluorescence bands (the 0_n bands) are observed in the low-temperature fluorescence spectrum with $\Delta E_1 = \bar{\nu}_{0M} - \bar{\nu}_{01} = 191$ cm^{-1} [5]. The fluorescence spectrum is similar to that of anthracene, so that $F_1(\bar{\nu}) \simeq F_M(\bar{\nu} + \Delta E_1)$.

($^1X_2$). In melt-grown anthracene crystals at 4.2°K at least 70% of the total fluorescence yield is a structureless emission $F_2(\bar{\nu})$, attributed to dislocations [6]. A similar, but less intense, emission is observed in vapour-grown crystals [5]. $F_2(\bar{\nu})$ is excited at $\bar{\nu} \geqslant \bar{\nu}_{0M} - 100$ cm^{-1} [6] so that the $^1X_2$ trap depth $\Delta E_2 \simeq 100$ cm^{-1}. $F_2(\bar{\nu})$ originates near $\bar{\nu}_{0M}$, it has a maximum at about $\bar{\nu}_{0M} - 1400$ cm^{-1}, and it extends to about $\bar{\nu}_{0M} - 7400$ cm^{-1}, beyond the limit of $F_M(\bar{\nu})$ [3]. The fluorescence spectrum is similar to that of an excimer or sandwich dimer. It has been reported that $\tau_2 \simeq 15$ ns [7].

($^1X_3$). A structured emission $F_3(\bar{\nu})$, attributed to point defects, occurs in melt-grown and vapour-grown anthracene crystals at 4.2°K [6]. $F_3(\bar{\nu})$ has rather broad maxima at 24820, 24460, 23900, 23000, 21500 and 19100 cm^{-1}. The emission may be excited at $\bar{\nu} \geqslant \bar{\nu}_{0M} - 2300$ cm^{-1} [6], so that the $^1X_3$ trap depths extend down to at least $\Delta E_3 = 2300$ cm^{-1}.

($^1X_4$). A structureless emission $F_4(\bar{\nu})$, attributed to disordered crystal regions, occurs in melt-grown and vapour-grown anthracene crystals at 4.2°K with excitation at $\bar{\nu} < \bar{\nu}_{0M}$ [6]. With excitation at $\bar{\nu} = \bar{\nu}_{0M} - 1100$ cm^{-1}, $F_4(\bar{\nu})$ decreases monotonically with $\bar{\nu}$ [6]. It is concluded that the $^1X_4$ trap depths extend down to at least $\Delta E_4 = 1100$ cm^{-1}.

Other defect species have been observed, but not categorised. We may divide the principal guest species in a "pure" anthracene crystal into two groups:

(a) shallow traps ^1X_S of depth $\Delta E_S \sim 100 - 300$ cm^{-1}, which include $^1X_1$ and $^1X_2$; and

(b) deep traps ^1X_D of depth $\Delta E_D \sim 1000 - 3000$ cm^{-1}, which include $^1X_3$ and $^1X_4$.

$[^1X_S]$ is expected to be lower for vapour-grown than for melt-grown crystals of the same purity, because of the much lower values of $[^1X_2]$ in the former case.

Absorption. The reabsorption probabilities a_{MM} and a_{nM} $[^1X_n]$ depend on the crystal thickness, and on the overlap of $F_M(\bar{\nu})$ with $\kappa_M(\bar{\nu})$ and $\kappa_n(\bar{\nu})$ $[^1X_n]$, respectively. The total crystal absorption spectrum at $\nu < \nu_{0M}$ is

$$\kappa(\bar{\nu}) = \kappa_M(\bar{\nu}) + \sum_n \kappa_n(\bar{\nu})[^1X_n] \tag{17}$$

Nakada [8] has observed $\kappa(\bar{\nu})$ at $\bar{\nu} < \bar{\nu}_{0M}$ for crystal anthracene with *a*- and *b*-polarised light normal to the (*ab*) crystal plane from 93 to 353°K. $\kappa_M(\bar{\nu})$ may be separated into three components, $\kappa_{0M}(\bar{\nu})$ due to the 0-0 absorption band edge, and $\kappa_{1M}(\bar{\nu})$ and $\kappa_{2M}(\bar{\nu})$ due to the 1-0 and 2-0 absorption hot bands, respectively. $\kappa_{0M}(\bar{\nu})$ obeys the Urbach rule [9],

$$\kappa_{0M}(\bar{\nu}) = \kappa_{0M}(\bar{\nu}_0)\exp[-\alpha\,\mathrm{hc}(\bar{\nu}_0 - \bar{\nu})/\mathrm{k}T] \tag{18}$$

where hc$\bar{\nu}$ is the photon energy, hc$\bar{\nu}_0$ is the extrapolated (0-0 absorption transition) photon energy at 0°K, and $\kappa_{0M}(\bar{\nu}_0)$ and α are constants. $\kappa_{1M}(\bar{\nu})$, evaluated [8] from $\kappa(\bar{\nu}) - \kappa_{0M}(\bar{\nu})$, is a diffuse band with a maximum at $\bar{\nu}_1$ given by the Boltzmann relation,

$$\kappa_{1M}(\bar{\nu}_1) = \kappa'_{1M}\exp[-\mathrm{hc}(\bar{\nu}_0 - \bar{\nu}_1)/\mathrm{k}T] \tag{19}$$

with $\kappa'_{1M} \simeq \kappa_{0M}((\bar{\nu}_0)$ and $(\bar{\nu}_0 - \bar{\nu}_1) \simeq 1300\ \text{cm}^{-1}$, corresponding to the dominant CC vibrational mode. The 2-0 absorption hot band $\kappa_{2M}(\bar{\nu})$, which lies beyond the limit $(\kappa(\bar{\nu}) \geqslant \sim 1\ \text{cm}^{-1})$ of Nakada's observations [8], will be a similar diffuse band with a maximum at $\bar{\nu}_2$ given by

$$\kappa_{2M}(\bar{\nu}_2) = \kappa'_{2M} \exp[-hc(\bar{\nu}_0 - \bar{\nu}_2)/kT] \tag{20}$$

with $\kappa'_{2M} \cong \kappa_{0M}(\bar{\nu}_0)$ and $(\bar{\nu}_0 - \bar{\nu}_2) \cong 2(\bar{\nu}_0 - \bar{\nu}_1) \cong 2600\ \text{cm}^{-1}$.

$\kappa_M(\bar{\nu})$ at $\bar{\nu} < \bar{\nu}_{0M}$ is strongly temperature-dependent. $\kappa_{2M}(\bar{\nu})$ is negligible ($< 1\ \text{cm}^{-1}$) at 353°K, and $\kappa_{1M}(\bar{\nu})$ becomes negligible below about 150°K [8]. The magnitude of $\kappa_{0M}(\bar{\nu})$ and its overlap with the 0-0 fluorescence band also decrease with T, and at low temperatures a_{MM} tends to zero.

The absorption spectrum $\kappa_n(\bar{\nu})$ of each guest species ^1X_n is red-shifted relative to the absorption spectrum $\kappa_M(\bar{\nu})$ of the host crystal by the trap depth ΔE_n. If it is assumed that the absorption spectra of 2-MA and the anthracene defects are similar to that of anthracene, then

$$\kappa_n(\bar{\nu}) \cong \kappa_M(\bar{\nu} + \Delta E_n) \tag{21.n}$$

The total crystal absorption at $\bar{\nu} < \bar{\nu}_{0M}$ is thus

$$\kappa(\bar{\nu}) = \kappa_{0M}(\bar{\nu}) + \kappa_{1M}(\bar{\nu}) + \kappa_{2M}(\bar{\nu}) + \sum_n \kappa_M(\bar{\nu} + \Delta E_n)[^1X_n] \tag{22}$$

Each guest species contributes

$$\kappa_n(\bar{\nu})[^1X_n] = \kappa_M(\bar{\nu} + \Delta E_n)[^1X_n] \tag{23.n}$$

to the absorption between $\bar{\nu}_{0M}$ and $\bar{\nu}_{0M} - \Delta E_n$. Unlike $\kappa_M(\bar{\nu})$, the guest absorption is practically independent of temperature, since the guest hot band absorption is negligible.

In the technical fluorescence spectrum of a 1 cm thick melt-grown anthracene crystal at room temperature, the 0-0, 0-1 and 0-2 fluorescence bands are eliminated or strongly attenuated by the reabsorption which extends to about 3000 cm^{-1} below $\bar{\nu}_{0M}$ [10]. $\kappa_{1M}(\bar{\nu})$ and $\kappa_{2M}(\bar{\nu})$ are inadequate to account for the magnitude and extent of the reabsorption, which is partly due to the absorption $\kappa_D(\bar{\nu})$ of the deep traps ^1X_D [4]. The reabsorption data indicate that ΔE_D extends down to 3000 cm^{-1}.

The excitation of $F_3(\bar{\nu})$ and $F_4(\bar{\nu})$ at $\bar{\nu} < \bar{\nu}_{0M}$ in anthracene crystals at 4.2°K [6] provides evidence for $\kappa_D(\bar{\nu})$. The magnitude of $\kappa_D(\bar{\nu})[^1X_D]$ can be estimated from Nakada's data [8]. With b-polarised light $\kappa(\bar{\nu}) \cong 2\ \text{cm}^{-1}$ at $\bar{\nu}_{0M} - 2200\ \text{cm}^{-1}$ is practically independent of temperature from 93 to 263°K, and it is therefore equated to $\kappa_D(\bar{\nu})[^1X_D]$. If $\kappa_{0M}(\bar{\nu}_0) = 6 \times 10^4\ \text{cm}^{-1}$ for crystal anthracene [8] is taken as the maximum value of $\kappa_D(\bar{\nu})$ at $\bar{\nu} < \bar{\nu}_{0M}$, then $[^1X_D] \geqslant 3.3 \times 10^{-5}$ mole/mole. A similar value of $[^1X_D] \geqslant 4 \times 10^{-5}$ mole/mole has been estimated previously from fluorescence reabsorption data [4]. Observations of the low temperature absorption spectra of anthracene crystals at $\bar{\nu} < \nu_{0M}$ are required to obtain fuller data on the defect absorption spectra.

FLUORESCENCE OF ANTHRACENE CRYSTALS

Three effects influence the host crystal fluorescence,

(a) host crystal absorption (a_{MM}),
(b) host-guest exciton transfer ($\sum_n \sigma_{nM} [^1X_n]$), and
(c) guest reabsorption ($\sum_n a_{nM} [^1X_n]$).

The lifetime τ_M^t (8) is affected by (a) and (b), the spectrum $F_M^t(\bar{\nu})$ and its area A_M^t (10) are affected by (a) and (c), and the quantum yield Φ_{FM}^t (9) is affected by all three factors. Thus τ_M^t and $F_M^t(\bar{\nu})$ appear the most useful parameters to study.

The host and guest fluorescences occur in the same spectral region. The total fluorescence spectrum

$$F^t(\bar{\nu}) = \Phi_{FM}^t F_M^t(\bar{\nu}) + \sum_n \Phi_{Fn}^t F_n(\bar{\nu}) \tag{24}$$

is difficult to resolve into its components, since each component spectrum is either a complex sequence of bands or a broad continuum. Although the low-temperature anthracene crystal fluorescence spectrum has been studied for many years, only recently has 2-methylanthracene ($^1X_1$) been identified as an inherent component [5]. It is thus difficult to determine $F_M^t(\bar{\nu})$ from observations of $F^t(\bar{\nu})$.

The total fluorescence response function is

$$i^t(t) = i_M(t) + \sum_n i_n^t(t) \tag{25}$$

$$= A\exp(-k_M^t t) + \sum_n B_n \exp(-k_n t) \tag{26}$$

Here each component is represented by a single decay parameter, and there is little difficulty in identifying the major component k_M^t ($= 1/\tau_M^t$). Measurements of τ_M^t provide the simplest means of studying the influence of host crystal reabsorption and host-guest exciton transfer on the host crystal fluorescence.

Reabsorption. The host-guest excition transfer is described by the parameter

$$z = \sum_n \sigma_{nM} [^1X_n] \tag{27}$$

Equation (8) may be rewritten as

$$\tau_M^t = \frac{\tau_M'}{1 - a_{MM}' \Phi_{FM}} \tag{28}$$

analogous to (1), where $\tau'_M = \tau_M / (1+z)$ and $a'_{MM} = a_{MM} / (1+z)$. τ'_M is the fluorescence lifetime corrected for reabsorption, but not for exciton trapping. τ'_M and $a'_{MM}\ \Phi_{FM}$ may be determined from observations of τ_M^t for crystals of different thickness d of the same purity and growth method, with similar values of z. Such measurements have been made by Powell [11] for anthracene crystals of $d = 56$ to $470\ \mu$m at 4, 100 and 300°K. Analysis of his data in terms of (28) leads to the following conclusions.

(i) The host crystal reabsorption of the thinnest ($d = 56\ \mu$m) crystal is small ($a'_{MM}\ \Phi_{FM} = 0.02 - 0.04$) from 4 to 300°K.

(ii) The host crystal reabsorption of the thickest ($d = 470\ \mu$m) crystal is small ($a'_{MM}\ \Phi_{FM} = 0.065$) up to 100°K, but it increases to $a'_{MM}\ \Phi_{FM} = 0.50$ at 300°K.

(iii) The "zero-thickness" lifetime $\tau'_M = 6.5$, 10.5 and 11.0 ns at 4, 100 and 300°K, respectively. This temperature dependence of τ'_M is due to the temperature-dependent host-guest exciton transfer z and to any intrinsic temperature dependence of τ'_M.

Host-guest exciton transfer. The influence of this process on the anthracene crystal fluorescence can be studied by observation of τ_M^t, or preferably τ'_M, as a function of T. Tomura *et al.* [12] attributed an observed decrease of τ'_M from 10 ns at room temperature to about 6 ns 100°K to the presence of two Davydov states with different decay times in thermal equilibrium. The present interpretation in terms of host-guest exciton transfer is preferred.

For a 56 μm anthracene crystal Powell [11] observed τ_M^t ($\cong \tau'_M$) from 4 to 100°K. Between 30 and 80°K τ_M^t increases sigmoidally from its 4°K value of 6.6 ns to its 100°K value of 10.5 ns. The data were fitted to a single shallow trap relation, equivalent to (16), with $\Delta E_S = 250$ cm^{-1} and $[{}^1X_S] = 1.8 \times 10^{-4}$ mole/mole [11].

Munro *et al.* [3] observed a more complex temperature dependence of τ_M^t ($\cong \tau'_M$) for a thin anthracene sublimation flake. τ_M^t rises sigmoidally from $(\tau_M^t)_0 \sim 5$ ns at 4°K to a plateau of $(\tau_M^t)_1 \sim 6$ ns at 75 to 140°K, and it then rises to a second plateau of $(\tau_M^t)_2 \sim 10.5$ ns at 300°K. The data are consistent with a system containing shallow and deep traps $[{}^1X_S]$ and $[{}^1X_D]$ respectively. From (16), neglecting $a_{MM}\ \Phi_{FM}$ since the crystal is thin, we obtain

$$(\tau_M^t)_0 = \frac{\tau_M}{1 + \sigma_{SM}^0\,[{}^1X_S] + \sigma_{DM}^0\,[{}^1X_D]} \tag{29}$$

$$(\tau_M^t)_1 = \frac{\tau_M}{1 + \sigma_{DM}^0\,[{}^1X_D]} \tag{30}$$

$$(\tau_M^t)_2 = \tau_M \tag{31}$$

Comparison with the data [3] gives $\tau_M = 10.5$ ns, σ°_{DM} $[^1X_D] = 0.75$ and σ°_{SM} $[^1X_S] = 0.35$. For host-guest transfer from anthracene to tetracene (^1Y), values of $\sigma_{YM} \cong 4 \times 10^4$ are obtained [13]. The assumption that $\sigma^{\circ}_{DM} = \sigma^{\circ}_{SM} = \sigma_{YM}$ gives $[^1X_D] \cong 2 \times 10^{-5}$ mole/mole and $[^1X_S] \cong 9 \times 10^{-6}$ mole/mole. ^1X_D is identified with $^1X_3$ and $^1X_4$ defects, and ^1X_S with $^1X_1$ (2-methylanthracene) and possibly some $^1X_2$ defects.

Munro *et al.* [3] also observed the temperature dependence of τ^t_M for a melt-grown anthracene crystal. (The same data were earlier attributed [14] to "a defect-free (*sic*) anthracene flake," but the later assignment is probably the correct one.) In this case τ^t_M rises linearly $(\tau^t_M)_0 \cong 5$ ns at 4°K to a plateau of $(\tau^t_M)_1 \sim 8$ ns from 75 to 140°K, and it then rises to a maximum of $(\tau^t_M)_2 \sim 17$ ns at 300°K. The higher value of $(\tau^t_M)_2$ is due to host reabsorption, but since the latter is small at $T \leqslant 100$°K, its effect on $(\tau^t_M)_0$ and $(\tau^t_M)_1$ may be neglected. The higher value of $(\tau^t_M)_1$ is attributed to an increased value of $[^1X_S] \cong 3 \times 10^{-5}$ mole/mole, due to a higher concentration of $^1X_2$ defects. The linear non-sigmoid dependence of τ^t_M in the 4-75°K region is consistent with the presence of at least two guest species ($^1X_1$ and $^1X_2$) of different ΔE_S.

Molecular fluorescence lifetime. The above results indicate that the net host-guest exciton transfer is small in anthracene crystals at room temperature, so that the unitary relations (1) – (3) can be used to correct for reabsorption. Such an analysis [15] of the 1962 data gave a value of $\tau_M = 11 \pm 1$ ns, and all subsequent data, including those already cited [3, 11, 12], appear consistent with this value. It corresponds to a radiative lifetime $\tau_{FM} = 1/k_{FM} = 12 \pm 1$ ns for crystal anthracene. This agrees with the experimental values of $\tau_{FM} = 15 - 20$ ns for anthracene in fluid solutions [13] and plastic solutions [3], when allowance is made for the higher refractive index of the crystal [16], and it also agrees with the theoretical value obtained from the integrated absorption spectrum [16].

In contrast, Munro *et al.* [3] concluded from their data cited above that $\tau_M = 6 \pm 1$ ns for crystal anthracene, irrespective of the crystal growth method or the temperature. There are several errors in their analysis and presentation. They treated the crystals as unitary systems, using (3) and (1) to evaluate a_{MM} and τ_M respectively, although the fluorescence spectrum $F^t(\bar{\nu})$ and response function $i^t(t)$ included prominent guest fluorescence components, and although $F^t(\bar{\nu})$ and $i^t(t)$ were not observed under identical excitation conditions. The reduction of τ^t_M from 10.5 ns to ~ 6 ns for a thin anthracene crystal at 300° K [3] corresponds from (28) to $a'_{MM}\,\Phi_{FM} \cong 0.43$; Powell [11] and other observers [15] obtained $a'_{MM}\,\Phi_{FM} = 0.02$-$0.04$. The fluorescence spectra were plotted as accumulated areas [3], a procedure which reduces the spectral resolution, obscures the distinction between host and guest fluorescence, and inhibits comparison with conventional spectra. The accumulated area crystal spectra are incorrectly plotted, since they are all blue-shifted by about 100Å [3]. Due to this the 2° K crystal spectrum accumulates 40% of its area at $\bar{\nu} > \bar{\nu}_{0M}$, its normal origin. a_{MM} was determined from S/L, where S and L are the spectral areas below and above $\lambda_n = 4370$Å, which was taken as the reabsorption limit [3]. The "zero-absorption" value of $S/L = (S/L)_0$ was determined from measurements on dilute liquid and plastic solutions of anthracene and on thin anthracene crystals, and "the results from all specimens were comparable and gave $(S/L)_0 = 0.15 \pm 0.01$" [3]. The effects on (S/L) of guest fluorescence, temperature, or the ~ 1500 cm^{-1} crystal-to-solution red shift of $F_M(\bar{\nu})$, were not discussed. Since reabsorption reduces S/L, it is to be expected that $S/L \leqslant (S/L)_0 = 0.15$. The fluorescence spectra of a sublimation flake "free of defects" at 295° K (Figure 3a) and of a dilute plastic solution of anthracene (Figure 4) give values of $S/L > 1.0$ and $S/L \cong 100$, respectively [3]. It is concluded that the spectral data of Munro *et al.* [3] are unreliable, and that the value of τ_M derived therefrom may be disregarded. Their values of τ_M^1 are consistent with those of other observers.

TIME DEPENDENCE OF HOST-GUEST EXCITON TRANSFER

It has been implicitly assumed that $k_{nM}[^1X_n]$, the net rate of host-guest exciton transfer, is time-independent. This assumption, which allows (4) and (5.n) to be integrated to yield the simple exponential functions (6) and (12.n), needs to be considered.

Soos and Powell [17] have observed that the host-guest exciton transfer rate parameter k_{YM} (t) in tetracene-doped anthracene crystals and other mixed crystals is time-dependent. It may be described either by a generalized random-walk model [17], or by the time-dependent Smoluchowski relation for a diffusion-controlled process [13],

$$k_{YM}(t) = 4\pi c_M D R \; \{1 + R(\pi D t)^{-1/2}\} \qquad (32)$$

$$= k_{YM}(1 + a\,t^{-1/2}) \qquad (33)$$

where D is the $^1M^*$ diffusion coefficient, R is the host-guest interaction distance, c_M is the host crystal concentration in molecules/cm^3, k_{YM} is the photostationary host-guest exciton transfer rate parameter and

$$a = R(\pi D)^{-1/2} \qquad (34)$$

is the transient coefficient. The transient and photostationary components of $k_{YM}(t)$ are equal at a time

$$\Delta t = a^2 = R^2/\pi D \qquad (35)$$

after δ-function excitation of $[^1M^*]_0$ at time $t = 0$.

In tetracene-doped anthracene crystals values of $R \sim 60\text{-}160$Å and $D \sim 1.6\text{–}9.6 \times 10^{-5}$ cm^2 s^{-1} are obtained [17], corresponding to $\Delta t \simeq 10$ ns. The high values of R are attributed to extensive defect regions, induced by the distortion of the host crystal lattice in the vicinity of each guest molecule, and which function as extended exciton trapping regions. The guest-induced defects have been observed spectroscopically [5]. The high defect concentration in a doped crystal reduces D, since exciton trapping and subsequent thermal detrapping reduce the $^1M^*$ exciton mobility.

In a "pure" anthracene crystal the host-guest interaction is probably collisional with $R \sim 6\text{-}10$Å, and the relatively low concentration of exciton traps increases D to $\sim 10^{-4}$ cm^2 s^{-1} [13]. These values correspond to $\Delta t \sim 10\text{-}30$ ps, three orders of magnitude less than in tetracene-doped anthracene crystals. The transient effects in the exciton transfer rate in "pure" crystals are restricted to $t < 0.1$ ns, and the time-independent model provides adequate descriptions of the fluorescence response functions, as observed with nanosecond time resolution, and of the photostationary behaviour.

Mixed crystal fluorescence studies are normally undertaken to elucidate the properties of the host crystal. It is therefore important that the guest species used as a probe should cause minimal perturbation of the host crystal. The defect and impurity species naturally present in "pure" anthracene crystals produce the minimum perturbation. It is, however, difficult to separate the guest and host fluorescences, except at low temperatures. The $^1X_2{}^*$ defect fluorescence is most readily resolved, since its structureless spectrum F_2 $(\bar{\nu})$ is relatively intense, it underlies the structured host spectrum F_M $(\bar{\nu})$ and extends to lower $\bar{\nu}$, and its lifetime $\tau_2 \sim 15$ ns differs from τ_M. The use of a guest species, which is isomorphic with the host crystal and which has more distinctive fluorescence characteristics, is an attractive alternative. A non-isomorphic guest, such as tetracene in anthracene, introduces such major perturbations that there is little relation between the properties of the perturbed host crystal and those of an unperturbed "pure" crystal.

Acknowledgments

This work was initiated during a visit to the Department of Chemistry, University of Queensland, Brisbane, Australia, and I wish to express my appreciation to Professor L. E. Lyons and his colleagues for their hospitality. I am also indebted to Dr. D. F. Williams, National Research of Canada, Ottawa, for some helpful comments.

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APPENDIX

Relations (1) and (2) were originally derived [1, 2] from the $^1M^*$ decay rate,

$$-\frac{d[^1M^*]}{dt} = (k_M - a_{MM}\, k_{FM})[^1M^*] = k_M^\dagger\, [^1M^*] \qquad (1A)$$

the fluorescence photon escape rate,

$$\frac{d[h\nu_M]}{dt} = (1 - a_{MM})\, k_{FM}\, [^1M^*] \qquad (2A)$$

and the resultant fluorescence response function,

$$i_M^\dagger(t) = (1 - a_{MM})\, k_{FM} \exp(-k_M^\dagger t) \qquad (3A)$$

Substitution of $\tau_M = 1/k_M$, $\tau_M^\dagger = 1/k_M^\dagger$ and $\Phi_{FM} = k_{FM}/k_M$ in (1A) gives (1). Integration of (3A)

$$\Phi_{FM}^\dagger = \int_0^\infty i_M^\dagger(t)\, dt \qquad (4A)$$

gives (2).

This derivation implicitly assumes that a_{MM} is time-independent, an assumption which is not often valid in practice. It will be shown that (1) and (2) do not depend on this assumption. $[^1M^*]_1$, $[^1M^*]_2$ and $[^1M^*]_p$ refer to the primary, secondary and p^{th} generations of excited molecules, $[h\nu_M]_1$, $[h\nu_M]_2$ and $[h\nu_M]_p$ to their corresponding fluorescence photons, and a_1, a_2 and a_p to the corresponding absorption probabilities of these photons. In the general case (1A) is replaced by a series of rate equations,

$$-\frac{d[^1M^*]_1}{dt} = k_M[^1M^*]_1 \tag{5A.1}$$

$$-\frac{d[^1M^*]_2}{dt} = k_M[^1M^*]_2 - a_1 k_{FM}[^1M^*]_1 \tag{5A.2}$$

$$-\frac{d[^1M^*]_p}{dt} = k_M[^1M^*]_p - a_{p-1} k_{FM}[^1M^*]_{p-1} \tag{5A.p}$$

Summation of the complete series gives

$$-\frac{d[^1M^*]}{dt} = (k_M - a_{MM} k_{FM})[^1M^*] \tag{1A}$$

where

$$[^1M^*] = \Sigma[^1M^*]_p \tag{6A}$$

$$a_{MM} = \frac{\Sigma a_p[^1M^*]_p}{[^1M^*]} \tag{7A}$$

In a similar manner (2A) is replaced by a series of equations,

$$\frac{d[h\nu_M]_1}{dt} = (1 - a_1)k_{FM}[^1M^*]_1 \tag{8A.1}$$

$$\frac{d[h\nu_M]_p}{dt} = (1 - a_p)k_{FM}[^1M^*]_p \tag{8A.p}$$

Summation of the complete series gives

$$\frac{d[h\nu_M]}{dt} = (1 - a_{MM})k_{FM}[^1M^*] \tag{2A}$$

where

$$[h\nu_M] = \Sigma[h\nu_M]_p \tag{9A}$$

Thus the general case yields (1A) and (2A), leading to (3A), (1) and (2). a_{MM}, which is defined by (7A), is determined experimentally from (3).