ENERGY TRAPPING PROCESSES IN AROMATIC CRYSTALS

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ABSTRACT

Excitons in ideal aromatic crystals are delocalized. So far no experimental evidence for self trapping of excitons is known. Trapping of energy is possible in mixed crystals or in crystals containing defects. Disturbed exciton states due to the presence of foreign molecules or due to structural defects (the so-called X-traps) are the most characteristic type of defects in aromatic crystals. Some spectroscopic experimental data on X-traps are collected and discussed. The most sensitive method for detecting traps is that of sensitized delayed fluorescence. The kinetics of sensitized delayed fluorescence is discussed and compared with that of prompt fluorescence. Trap concentrations as low as 10^{-10} mol/mol can be detected using delayed fluorescence.

I. THE IDEAL CRYSTAL

The *energy levels* of an ideal aromatic crystal, like naphthalene or anthracene, lie in bands: valence bands, exciton bands and conduction bands. Energy is completely delocalized in the ideal crystal.

The time scale for *transitions* is determined by the electronic structure of these bands, and by the transition matrix elements. Transitions between these crystal states are:

Absorption from the ground state S_0 to excited states S_i.
Fluorescence from the lowest excited singlet state S_1 to S_0. The lifetime of S_1 is typically between 5 and 500 nsec.
Internal conversion between different excited S states or triplet (T) states. These processes occur in less than 0.1 nsec.
Intersystem crossing between the singlet and the triplet manifold. The typical time constants are 100–1000 nsec.
Phosphorescence from the lowest excited triplet state T_1 to the ground state S_0. The lifetime of T_1 is typically between 1 and 10^4 msec and is determined by radiationless processes.

Energy storage for times longer than 0.5 μsec is possible only in the T_1 band. Energy relaxation between the energy bands (internal conversion) is due to exciton–phonon interaction. Trapping processes, which are able to localize energy at specific sites in the perfect crystal are unknown so far. There is no experimental evidence for the self trapped exciton, which was first discussed by Frenkel[1], and later by Sidman[2].

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Self trapping of an exciton is a process in which the exciton induces a lattice relaxation, which should be responsible for some energy loss, for a Stokes–shift between absorption and emission and, perhaps, for some kind of localization of the exciton. Among the well investigated crystals only in anthracene is there a Stokes–shift between the maxima of S_0–S_1 absorption and S_1–S_0 emission, even after exclusion of other traps (*Figure 1*)[3,4].
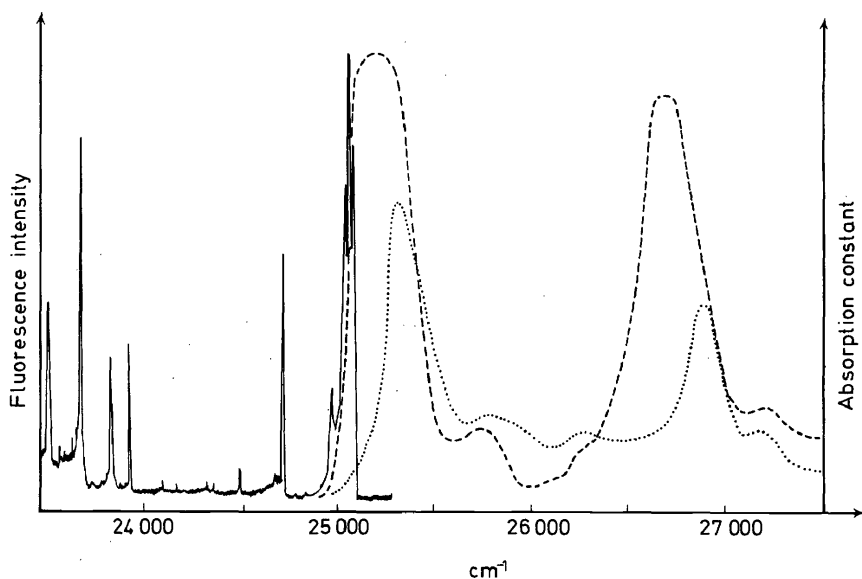

Figure 1. Absorption (right) and fluorescence (left) spectrum of crystalline anthracene near 0.0 of the lowest singlet transition. After references 3 and 4. 4.2°K. The absorption spectrum is given parallel to axes b (– – –) and a (. . . .). The 0.0 line in emission at 25097 cm^{-1} is not visible due to reabsorption. The first strong emission line is the 0.0 line of the X_1-series[4]

But this Stokes–shift gives no evidence for exciton self trapping. The shift has been explained by the specific exciton band structure in anthracene[4] and the k-selection rule. An alternative explanation makes use of special surface states[5].

In conclusion, the problem of traps and trapping is a problem of the real, imperfect crystal.

II. THE REAL CRYSTAL

For the spectroscopist, the main difference between the ideal and the real crystal is the existence of traps in the latter. Very often emission spectra are, more or less, only trap spectra because of the high sensitivity of the sensitized fluorescence.

Exciton traps are sites capable of holding energy that, otherwise, propagates through the lattice. Traps are localized, non–periodic states in the crystal. Their time scale is determined by the specific electronic structure of the trap.

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Traps change the spectral energy distribution in spectra, especially in fluorescence. Traps change the time dependence of electronic population and depopulation processes in the crystal.

Traps are interesting:

as probes for measuring intrinsic properties of the host crystal, for instance the phonon structure of the host crystal from the phonon wings, which accompany guest fluorescence lines in mixed crystals[6].
in themselves, because they are responsible for electronic and optical properties of the mixed or real crystal, which are different from those of the pure or ideal host crystal.

In the following two specific topics are discussed in detail: the so called X-traps, and the kinetics of trap-induced delayed fluorescence.

III. DIFFERENT KINDS OF TRAPS

In organic crystals, three types of traps have been observed and discussed so far:

1. *Guest molecules*, like the oldest example, tetracene in anthracene. The guest molecule can be identified by its spectral properties, which are different from those of the host crystal. Guest molecules are traps, if their S_1 state is lower than the host crystal S_1 exciton band. If these guest molecules are deep traps ($\Delta E \gg kT$), sensitized fluorescence is observed.

2. *Self trapping*. This process has been discussed in section I.

3. *Disturbed exciton states in the crystal, X-traps*. These X-traps are very characteristic defects in organic crystals. The name X-series has been coined for vibronic series in the luminescence spectra of crystals which are identical with the intrinsic host emission, but red shifted by a certain amount of energy[7]. This is the emission from disturbed regions of the crystal.

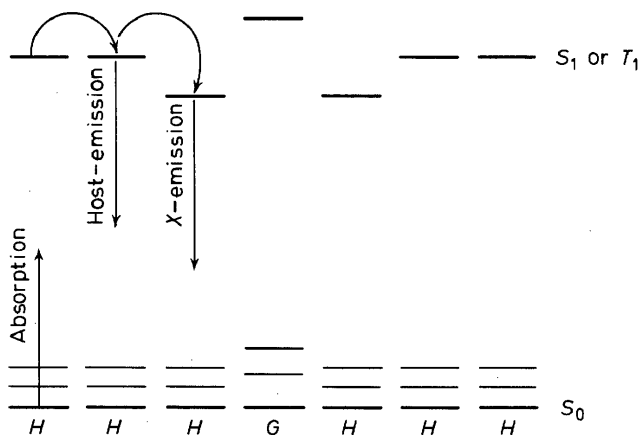The perturbation can be due to the presence of *foreign molecules* (impurities

Figure 2. Energy level scheme of a host (*H*) crystal with guest (*G*) molecules, which induce X-traps. For simplification, the host exciton band is approximated by the individual molecule energy levels

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or guest molecules) in the matrix, which cannot act as traps themselves, because the energy of their lowest S_1 state is higher than the bottom of the host S_1 band. But host molecules around these impurities are shifted in energy and can act as energy traps. A schematic energy level diagram for X-traps is shown in *Figure 2*. These impurity-induced X-traps can be removed partially or completely by crystal purification.

The second possible reason for X-series can be *structural defects* or dislocations in the lattice. These X-traps are insensitive towards purification processes, but they can be removed by annealing.

It is impossible to understand most of the spectroscopic solid-state properties of organic crystals without taking into account these X-traps. They are the analogues of the so called α and β-bands in alkali halides[8], which have been well known for nearly forty years.

It is important to notice that the X-traps, which have been found so far, are always relatively shallow traps. At room temperature they are more or less ineffective.

IV. EXAMPLES OF X-TRAPS IN OPTICAL SPECTRA

In this section are collected some experimental data on X-traps in different crystals, and identified by different methods.

In the fluorescence spectrum of naphthalene crystals of high purity, 4 main series of lines have been identified[7]: one of them, with 0.0 at 31 474 cm^{-1}, is the emission originating from the exciton band S_1. The other three, with 0.0 at 31 444, 31 418 and 31 395, are emission series originating from naphthalene molecules with an S_1-level $\Delta E = 30, 56$ and 79 cm^{-1}, respectively, below the bottom of the naphthalene exciton band.

The perturber which induces the 30 cm^{-1} X-trap has been identified as thionaphthene. The other perturbers are impurities X, unidentified so far. This is the reason for the name X-trap. All the X-series have the vibronic progressions characteristic of the naphthalene molecule. The X-series are identical in energy with the naphthalene series, but shifted to lower energy by ΔE. The lines of the X-series are much sharper than the lines in the host series.

In contrast to these impurity-induced X-traps, β-methyl-naphthalene in naphthalene is a real trap, with 0.0 at 31 059 cm^{-1} and a vibronic structure of the fluorescence spectrum characteristic of the β-methyl-naphthalene molecule.

On can create additional X-traps by introducing *structural imperfections* into the crystal. In naphthalene this has been investigated using plastic deformation[9]. In the fluorescence spectrum of plastically deformed naphthalene crystals, one observes three different characteristic structures:

1. One sharp X-series, shifted 165 cm^{-1} to lower energies (0.0 at 31 309 cm^{-1}).
2. A continuous background (called subnaphthalene series in reference 9).
3. Emission typical of excimers with the maximum at about 24 000 cm^{-1}.

These three types of spectra can be reduced in intensity by annealing. In some cases, annealing is improved by simultaneous excitation with light[9]. The relative intensity of the different spectra is a function of temperature, corresponding to the different trap depth.

The fluorescence spectrum of extremely pure anthracene crystals also contains many lines which are due to X-traps. In addition to the intrinsic fluorescence, originating at $25\,097$ cm^{-1}, X-series are observed[10] with 0.0 at $25\,074$, $25\,030$, $24\,850$ and $24\,823$ cm^{-1}. Similar observations are reported by other authors[11, 12].

X-traps are present also in the *triplet state* T_1. It is much easier to observe them via delayed fluorescence than directly by phosphorescence spectra. In naphthalene, the following triplet state X-traps have been identified[13]: thionaphthene introduces an X-trap with $\Delta E = 45$ cm^{-1}, durene one at 60 cm^{-1}, and other X-traps are present which have not been identified so far[14]. As in the singlet state, β-methyl-naphthalene is a guest molecule, not an X-trap, with $\Delta E = 240$ cm^{-1}. In anthracene crystals, the trap[10] X_4 which is 274 cm^{-1} below the S_1 exciton band is also an X-trap in the triplet state, with[15] $\Delta E = 24$ cm^{-1}.

In addition to the unperturbed exciton emission of the host and X-series, the spectrum of delayed fluorescence in anthracene and naphthalene crystals contains a continuous background, which is due to a continuous energy distribution of traps[14, 15]. All types of trap spectra are much more pro-
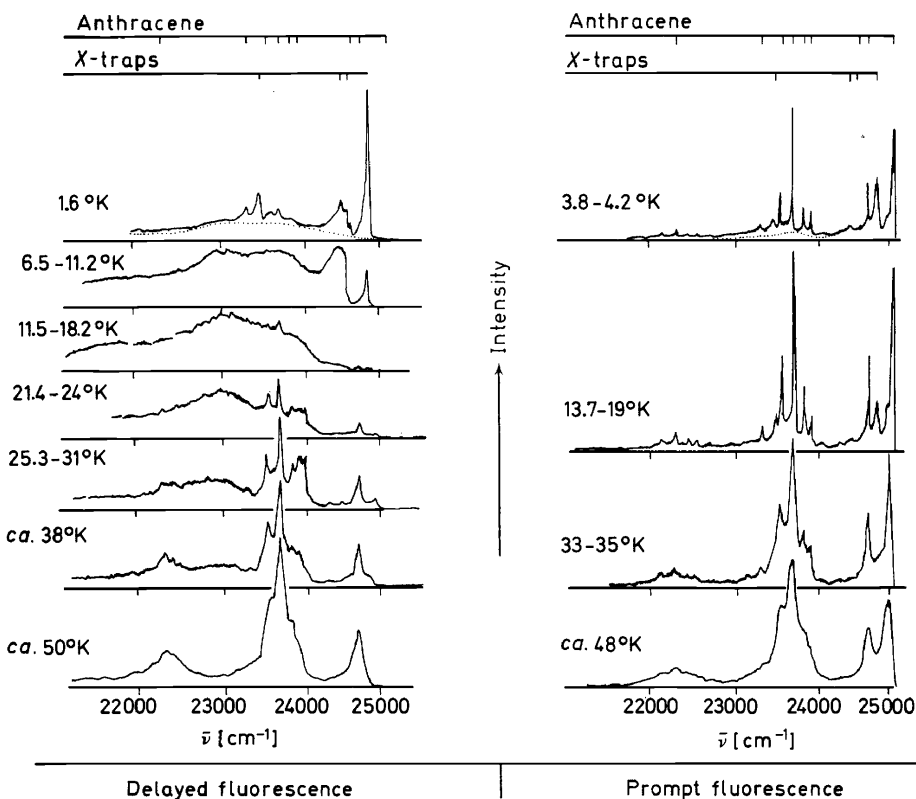

Figure 3. Spectrum of delayed and prompt fluorescence of very pure anthracene crystals between 1.6 and 50°K. From reference 15
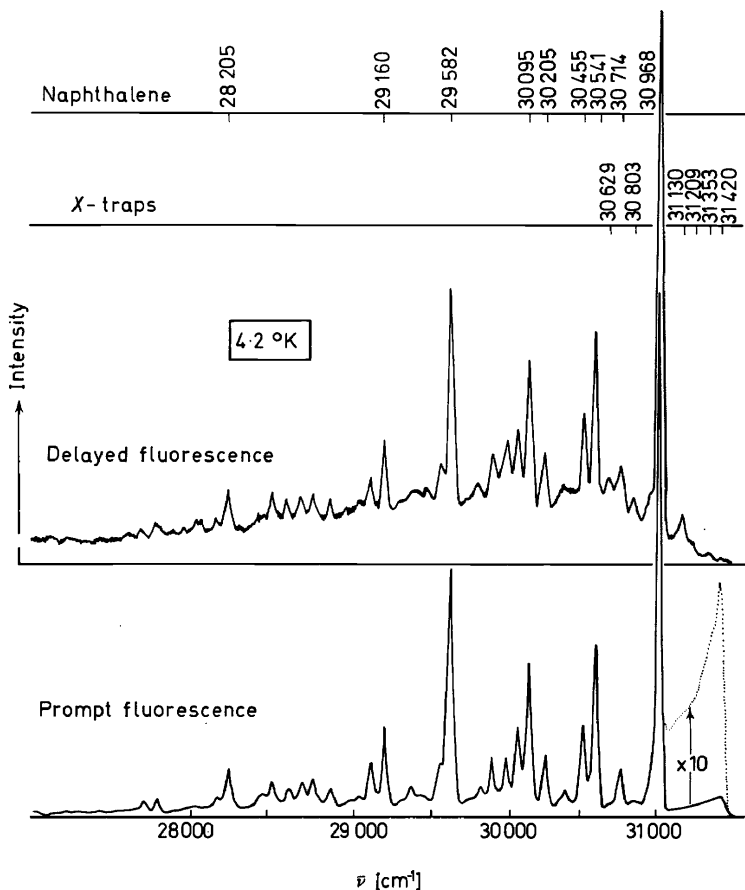
Figure 4. Spectrum of delayed and prompt fluorescence of a very pure naphthalene crystal at 4.2°K. From reference 15

nounced in delayed fluorescence than in prompt fluorescence—an observation which will be discussed in section VI. The trap spectra disappear with increasing temperature when the traps are thermally depopulated. *Figure 3* shows the temperature dependence of delayed and prompt fluorescence in pure anthracene crystals. In delayed fluorescence the trap emission is much more pronounced than in prompt fluorescence. A plot of the X-trap emission relative to the continuous background versus temperature (*Figure 5*) can be used to determine the trap depth ΔE.

X-traps are also observable in *phosphorescence*. In pyrazine crystals at 4.2°K two X-series have been observed[16]. Azumi called them impurity induced resonance defects.

V. X-TRAPS IN ESR SPECTRA

X-traps can be identified and are important also in *ESR spectra of the metastable triplet state* T_1 at low temperature. A good example is quinoxaline
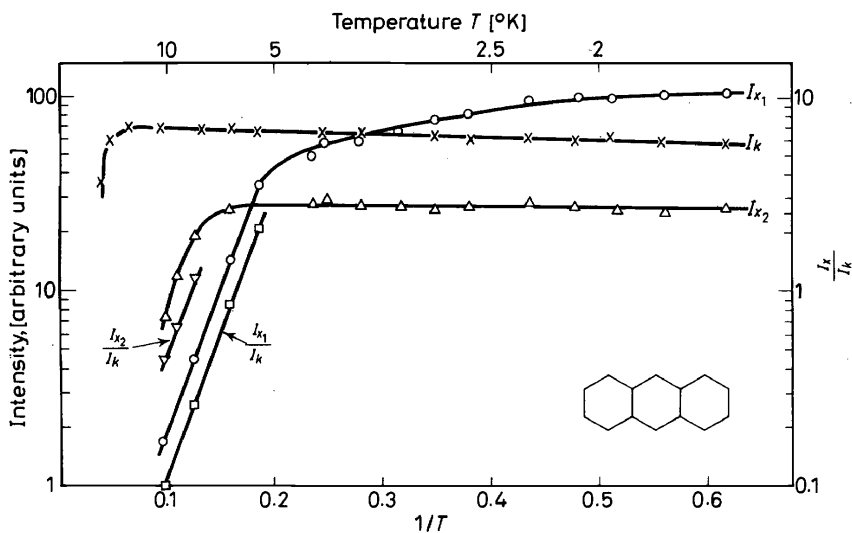
Figure 5. Temperature dependence of the intensity I of the series X_1, X_2 and the continuum K in the delayed fluorescence spectrum of anthracene crystals between 1.6 and 20°K. Determination of the trap depth ΔE. From reference 15

in a naphthalene matrix[17]. In a matrix of normal naphthalene (N-h$_8$), quinoxaline introduces an X-trap with $\Delta E = 60$ cm^{-1}. The ESR spectrum observed at low temperature ($< 4.2°$K) (*Figure 6*) is therefore due to naphthalene molecules. This is demonstrated by the hyperfine structure of the ESR spectrum. The hyperfine structure is due to the four equivalent α protons in the naphthalene molecule. The hyperfine structure due to the β-protons cannot be resolved. According to the angular dependence of the ESR-spectrum, the misorientation of the X-trap naphthalene molecule is less than 2°. In addition, the ESR spectrum shows no indication of any delocalization of the triplet energy. This means that the X-trap is probably only *one* very slightly disturbed naphthalene molecule in the vicinity of the quinoxaline molecule. With increasing temperature the ESR signal vanishes due to thermal detrapping (*Figure 7*).

In contrast to N-h$_8$, quinoxaline in perdeutero-naphthalene is a real trap. The ESR spectrum of N-d$_8$ crystals doped with quinoxaline is therefore a quinoxaline spectrum. The hyperfine structure is typical of two equivalent α protons and four equivalent β-protons (*Figure 6*).

ESR and ENDOR spectroscopy is a powerful method for getting very detailed information on the structure of X-traps. Other X-traps which have been identified, using ESR-spectroscopy, are due to quinazoline and thionaphthene in naphthalene and dibenzothiophene and carbazole in fluorene[18].

Theoretical calculations on the electronic structure of disturbed exciton states were first published by Merrified[19]. A very detailed comprehensive review is given by Rice and Jortner[20]. Many new experimental data have been collected in the meantime. It seems worthwhile to use these data as a
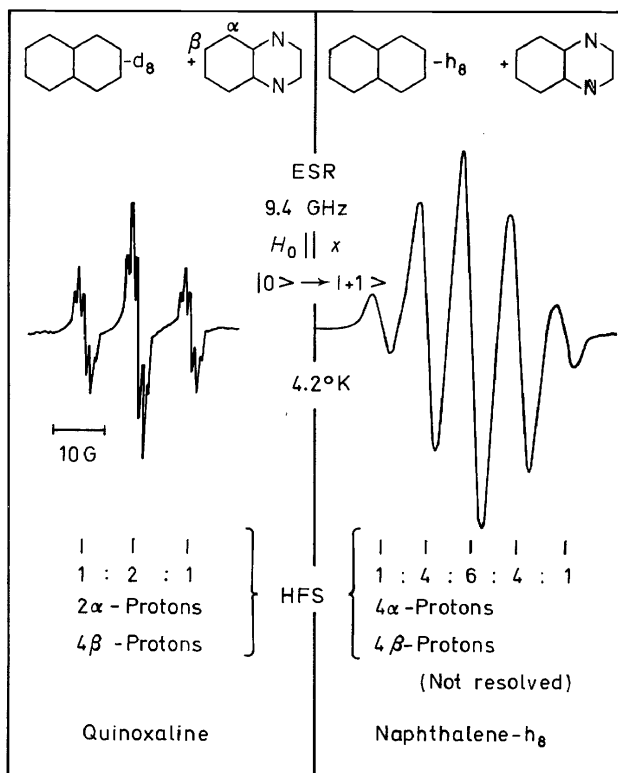
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Figure 6. Hyperfine structure of one ESR-line ($\Delta m = 1$ transition) in the ESR spectrum of the triplet state of quinoxaline in perdeutero-naphthalene (left), and of the X-trap which is induced by quinoxaline in nahpthalene (right). The quinoxaline concentration was the same in both crystals. The hyperfine structure is characteristic of quinoxaline (left) and of naphthalene (right). (This figure was kindly supplied by M. Schwoerer)

basis for more detailed theoretical work, which could help us to get a better understanding of the nature of these defects in molecular crystals. In semi-conducting materials, like silicon and germanium, similar disturbed exciton states are known. An empirical rule has been proposed[21], which correlates the trap depth and the physical nature of the perturber.

In a series of recent papers, Jortner et al.[22] have treated the X-trap problem theoretically in a very detailed manner. They have shown that X-trapping is due to the solvent shift terms. An X-trap host molecule is just a host molecule in a different environment. It seems worthwhile to apply these calculations to the experimental data collected above.

In *Table 1* experimental data on X-traps in naphthalene and anthracene crystals are collected.

VI. KINETICS OF TRAPPING PROCESSES

Trapping processes are responsible for the well known phenomenon of

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Table 1. Some X-traps in naphthalene and anthracene and their trap depths, ΔE, in the singlet and in the triplet state

Matrix	Perturber	ΔE in S_1 cm^{-1}	ΔE in T_1 cm^{-1}	References
Naphthalene				
	thionaphthene	30	45	7, 13
	unknown impurity	56		7
	unknown impurity	79		7
	structural defect	165		9
	continuum	continuous		9
	durene		60	13
	quinoxaline		*ca.* 60	17
	unknown	144		14
	unknown	268	23	14
	unknown	346	32	14
Anthracene				
	unknown defects	23		10
	or impurities	67		10
		247		10
		274	24	10, 15
	continuum	continuous		

sensitized fluorescence, where low concentrations of impurity molecules are able to convert the host fluorescence into guest (impurity) emission. The delayed fluoresence is even more sensitive towards impurities, because of the effectiveness of energy transfer, and sensitized delayed fluorescence is a method for detecting impurities or traps in concentrations a hundred times lower than is sensitized prompt fluorescence.

This is demonstrated by *Figures 8* and *9*. *Figure 8* shows the fluorescence spectrum of a mixed crystal naphthalene with 2×10^{-7} parts of anthracene. Whereas in prompt fluorescence the anthracene concentration is too low to convert much of the naphthalene emission into anthracene fluorescence and anthracene emission is almost absent, in delayed fluorescence the anthracene emission is more intense than that of naphthalene. Energy transfer can be measured quantitatively by determining the *quantum ratio* Q_G/Q_H (guest quanta divided by host quanta) as a function of guest concentration. This quantum ratio is, according to *Figure 9*, 100 times higher in delayed fluorescence than in prompt fluorescence. Also *Figures 3* and *4* demonstrate the much higher sensitivity of delayed fluorescence than of prompt fluorescence towards impurities and traps.

In this section, the effectiveness of delayed sensitized fluorescence is calculated and compared with that of sensitized prompt fluorescence.

The kinetics of population and depopulation of traps, which can be guest molecules or X-traps, is described in the following general scheme (*Figure 10*):

1. Excitons are created by absorption of light of intensity I with absorption coefficient α_S or α_T. Exciton bands S_1 or T_1 are populated by internal conversion and intersystem crossing.
2. Excitons can decay with emission of a photon, radiatively, into the ground state S_0 with a rate constant k_H^* for singlets and β_H^* for triplets.
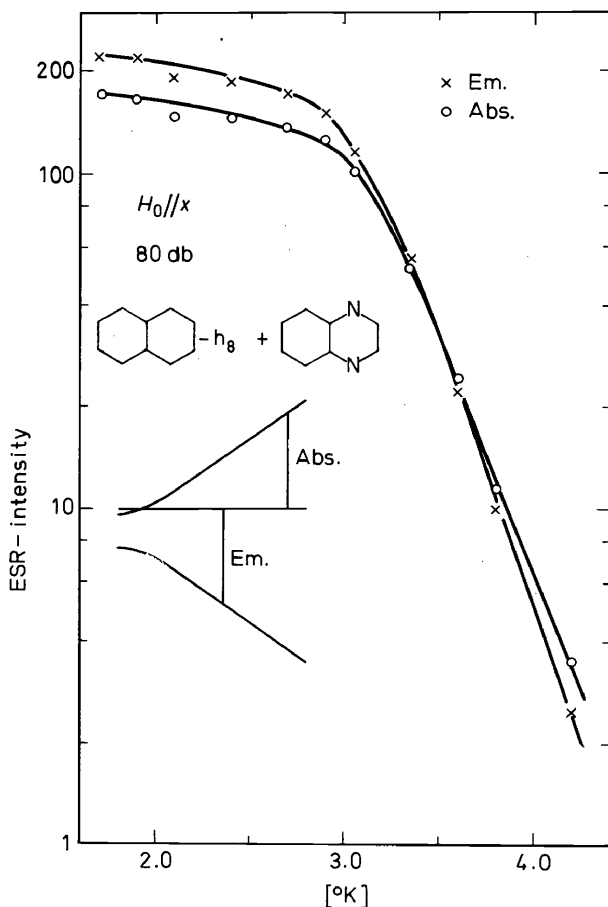
Figure 7. Temperature dependence of the intensity of the two ESR lines of the *X*-trap induced in naphthalene by quinoxaline. One of the two lines is emissive due to optical spin polarization. (This figure was kindly supplied by M. Schwoerer)

3. Radiationless processes are competitive, with rate constants k'_H and β'_H; $k = k' + k^*$, $\beta = \beta' + \beta^*$.
4. Excitons can relax into traps, which are ΔE lower in energy with a rate constant k_{HG} and β_{HG}.
5. Traps can be thermally depopulated back into the exciton band, if the temperature is high enough.
6. Traps ca. be depopulated by emission of a photon radiatively into the ground state S_0, rate constant k^*_G.
7. Traps can be depopulated nonradiatively k'_G.
8. Triplet traps can be depopulated by triplet–triplet annihilation, annihilation coefficient γ_G.
9. Triplet annihilation is also effective in the T_1 exciton band, without traps, annihilation coefficient γ.
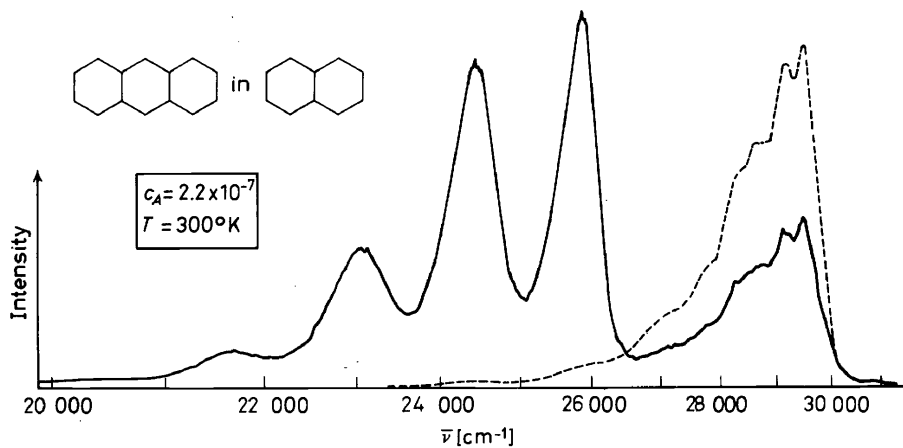
Figure 8. Spectrum of prompt (broken line) and delayed (full line) fluorescence in a naphthalene crystal containing 2.2×10^{-7} parts of anthracene, at room temperature. Anthracene emission is below $26\,500$ cm^{-1}. From reference 15
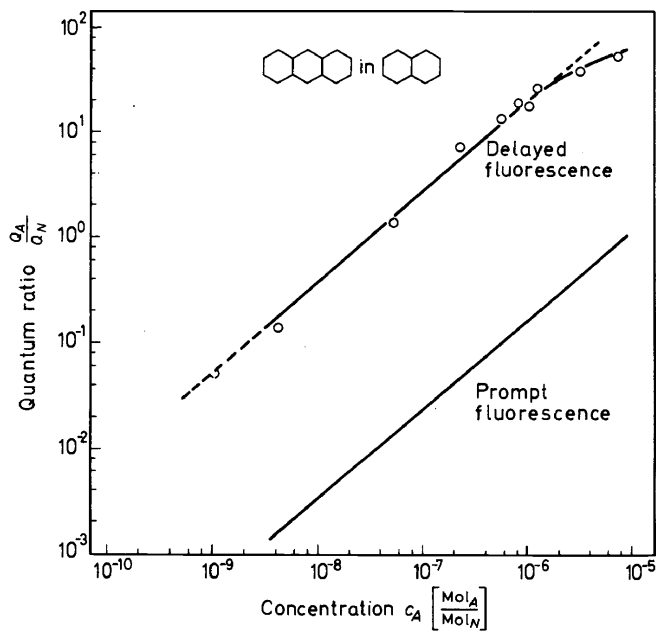

Figure 9. Quantum ratio Q_A/Q_N in naphthalene crystals with different anthracene concentrations, delayed and prompt fluorescence. The concentration was measured by absorption. From references 14 and 15
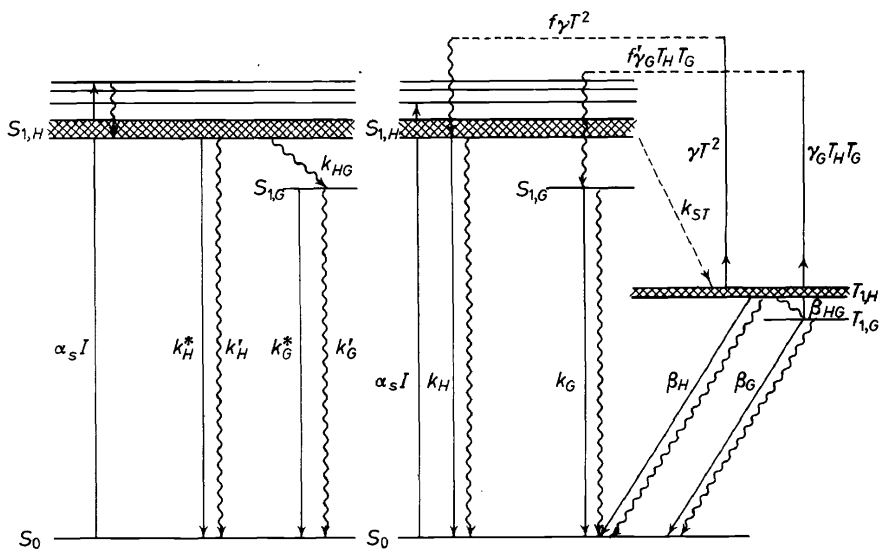
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Figure 10. Kinetics of sensitized prompt fluorescence (left) and sensitized delayed fluorescence (right) for a host–guest system

The process which determines the effectiveness of traps is mainly process 4, the exciton capture by traps. During their lifetimes excitons scan the crystal for traps. The concentration of traps, the exciton lifetime and the diffusion rate of the exciton determine, therefore, the capture probability.

Many different models for exciton motion have been discussed in the past. It seems that the very simple hopping model is a quite adequate description[23], at least as long as energy transfer is concerned. In this model the exciton jumps statistically from molecule to molecule in the lattice with a characteristic hopping time t_h. This time is related to the diffusion coefficient D by an expression of the form[23] $t_h = \pi D R N_H$; R = defect radius, N_H = number of host molecules per cm^3. The number of lattice sites visited during the lifetime is given by the quotient lifetime divided by hopping time (if one neglects the probability of visiting the same site more than once)[24]. This model has been discussed in great detail by Suna recently[25]. In prompt fluorescence one measures the singlet traps which are populated by the scanning exciton, in delayed fluorescence the triplet traps.

The quantum ratio of guest to host emission is calculated in the following way (*Figure 10*):

A. Prompt fluorescence

The rate equations for host and guest singlet excitons S_H and S_G (number of excited states per volume) are in the deep trap limit ($\Delta E \gg kT$), neglecting intersystem crossing into the triplet state,

$$\frac{dS_H}{dt} = \alpha_s I - k_H S_H - k_{HG} S_H \tag{1}$$

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$$\frac{dS_G}{dt} = k_{HG}S_H - k_G S_G \tag{2}$$

The quantum flux Q_H, Q_G (number of quanta per volume and sec) is given by

$$Q_H = k_H^* S_H \tag{3}$$

$$Q_G = k_G^* S_G \tag{4}$$

In the stationary case, $dS/dt = 0$, one gets from (2)

$$\frac{S_G}{S_H} = \frac{k_{HG}}{k_G} \tag{2a}$$

and finally the quantum ratio

$$\left(\frac{Q_G}{Q_H}\right)_{\text{prompt fluorescence}} = \frac{k_G^*}{k_H^*} \times \frac{k_{HG}}{k_G} \tag{5}$$

(5) can also be written in the form

$$\left(\frac{Q_G}{Q_H}\right) PF = \eta_G \frac{k_{HG}}{k_H^*} \tag{5a}$$

$$\eta_G = \text{quantum yield of the guest fluorescence}$$

In the hopping model, the simplest assumption for the transfer rate constant k_{HG} is

$$k_{HG} = \frac{c_G}{t_{h,\,\text{singlet}}} \tag{6}$$

$$c_G = \text{guest concentration in mol/mol}$$

$$t_h = \text{hopping time}$$

With (5) and (6) one gets as quantum ratio

$$\left(\frac{Q_G}{Q_H}\right)_{\text{prompt fluorescence}} = \frac{\eta_G c_G}{k_H^* t_{h,\,\text{singlet}}} = K_{\text{singlet}} \times c_G \tag{7}$$

$$K = \text{transfer constant as defined in reference 23.}$$

Equation (6) is based on the following simplifications:

1. It is assumed that transfer of excitation is by hopping from molecule to the nearest neighbour molecule, and that the capture cross section is the same for host and guest molecules. The validity of this assumption is questioned by new experiments of Baessler et al.[32].

2. It is assumed that the probability for the hopping exciton to meet a guest molecule is proportional to the guest concentration. Due to the possibility that the excitation is able to visit one lattice site more than once, this assumption is valid only at low concentrations[24].

Equation (7) has been derived and verified in the system anthracene/tetracene[26]. In this system, the measured transfer constant $K_{singlet}$ in the equation $Q_G/Q_H = K \times c_G^p$, is $(6 \pm 3) \times 10^4$, with the exponent $p = 0.8 \pm 0.2$. K-values in other systems have the same order of magnitude[23]. At a guest concentration of $c_G = 10^{-7}$, the quantum ratio is 0.01. Therefore it is possible to detect traps and impurities using sensitized fluorescence at concentrations down to $10^{-7} - 10^{-8}$.

Using equation (7), the hopping time t_h can be calculated. For the system anthracene in naphthalene, the following value has been measured:

$$K_{singlet} = 10^5 \ (Figure \ 9)$$

Taking η_G (anthracene in naphthalene) $= 1$ and k_H^* (naphthalene, room temperature) $= 2 \times 10^6$ sec^{-1}, one gets for naphthalene

$$t_{h,singlet} = 5 \times 10^{-12} \ sec \ (\pm 50\%)$$

Equations (1)–(7) are valid for a two component system, host and guest. If there are other traps present with a trap depth comparable to kT, then the apparent quantum ratio is a function of temperature[23, 26]. By this freezing of energy transfer one can measure trap concentrations down to approximately 10^{-7}.

B. Delayed fluorescence

Again we discuss only a two component system (guest and host), and we assume homogeneous excitation. If one excites into the singlet state, the following rate equations describe the time dependence of concentration of triplet excitons, T_H and T_G (Figure 10):

$$\frac{dT_H}{dt} = \eta_{ST}\alpha_S I - \beta_H T_H - \beta_{HG} T_H - \gamma_G T_H T_G - \gamma T_H^2 \tag{11}$$

$\eta_{ST} = $ quantum yield for intersystem crossing

$$\frac{dT_G}{dt} = \beta_{HG} T_H - \beta_G T_G - \gamma_G T_H T_G \tag{12}$$

If one excites directly into the triplet state, one has to replace the expression $\eta_{ST}\alpha_S I$ in (11) by $\alpha_T I$.

At low concentration, delayed host fluorescence is entirely due to host/host annihilation, and delayed guest fluorescence entirely due to host/guest annihilation. Therefore the rate equations for singlet excitons created by triplet–triplet annihilation are:

$$\frac{dS_H}{dt} = \tfrac{1}{2}f\gamma T_H^2 - k_H S_H \tag{13}$$

$$\frac{dS_G}{dt} = \tfrac{1}{2}f'\gamma_G T_H T_G - k_G S_G \tag{14}$$

f and f' are the fraction of triplet–triplet annihilation processes which result in singlet states S_1. f and f' are near[27] 0.4.

In the stationary case,

$$\frac{\mathrm{d}T_H}{\mathrm{d}t} = \frac{\mathrm{d}T_G}{\mathrm{d}t} = \frac{\mathrm{d}S_H}{\mathrm{d}t} = \frac{\mathrm{d}S_G}{\mathrm{d}t} = 0.$$

Saturation of traps is neglected. Using equations (3), (4), (13) and (14), one gets the quantum ratio:

$$\left(\frac{Q_G}{Q_H}\right)_{\text{Delayed fluorescence}} = \frac{\eta_G}{\eta_H} \times \frac{f'\gamma_G}{f\gamma} \times \frac{T_G}{T_H} \tag{15}$$

The triplet concentrations T_G and T_H are a function of the intensity I of the exciting light. At low excitation intensities (or low stationary triplet concentrations), the triplet lifetime is determined by monomolecular decay, at high excitation intensities by bimolecular annihilation. The two limiting cases have to be discussed separately.

α. *Weak excitation*, $\beta_G T_G \gg \gamma T_G T_H$

Equation (12) transforms into

$$\frac{T_G}{T_H} = \frac{\beta_{HG}}{\beta_G} \tag{12a}$$

Equation (12a) is completely analogous to the singlet state equation (2a), and the quantum ratio is independent of I:

$$\frac{Q_G}{Q_H} = \frac{\eta_G f'\gamma_G}{\eta_H f\gamma} \frac{\beta_{HG}}{\beta_G} \tag{15a}$$

In the hopping model, the transfer rate is given by

$$\beta_{HG} = \frac{c_G}{t_{h,\text{ triplet}}} \tag{16}$$

and finally one gets the quantum ratio

$$\left(\frac{Q_G}{Q_H}\right)_{\substack{\text{Delayed fluorescence,} \\ \text{weak excitation}}} = \frac{\eta_G f'\gamma_G}{\eta_H f\gamma} \frac{c_G}{\beta_G t_{h,\text{ triplet}}} \tag{17}$$

$$= K_{\text{triplet}} \times c_G$$

Comparing equations (7) and (17) one realises immediately that the ratio of the transfer constants $K_{\text{triplet}}/K_{\text{singlet}}$ is determined by the ratio

$$\frac{k_H^* t_{h,\text{singlet}}}{\beta_G t_{h,\text{ triplet}}}$$

Now the experimental results (*Figure 9*) are compared with equation (17). In the system anthracene in naphthalene, the experimentally determined transfer constant is roughly

$$K_{\text{triplet}} = 3 \times 10^7 \, (Figure\ 9)$$

We use the following approximate numerical values:

$\eta_G = 1^{28}$, $\eta_H = 0.2^{28}$, $f = 0.4^{27}$, $\gamma = 3.5 \times 10^{-12}$ cm^3 sec^{-1} ^{14}, and we assume without experimental proof that $f = f'$ and $\gamma = \gamma_G$; $\beta_G = 300$ sec^{-1} ^{14}. So we get the triplet hopping time t_h:

$$t_h = 5 \times 10^{-11} \text{ sec } (\pm 50\%)$$

This value is consistent with results from ESR[29] and NMR[30] measurements.

Now we are able to discuss the *limiting sensitivity* of sensitized delayed fluorescence for detecting impurities. Since the transfer constant $K = 3 \times 10^7$, the quantum ratio equation (17) is 0.01 at $c_G = 3 \times 10^{-10}$. Consequently, using delayed fluorescence, one is able to detect anthracene in naphthalene at concentrations as low as 10^{-10}, more than two orders of magnitude lower than using prompt fluorescence. This is mainly due to the long lifetime of the triplet traps, β_G in equation (17), since the hopping time t_h is 10 times longer for triplet excitons than for singlets. Similar conclusions have been derived for the mixed system anthracene in phenanthrene[31].

β. *Strong excitation,* $\beta_G T_G \ll \gamma_G T_G T_H$

From equation (12) one gets

$$T_G = \frac{\beta_{HG}}{\gamma_G} \tag{12b}$$

and from (15)

$$\left(\frac{Q_G}{Q_H}\right)_{\substack{\text{Delayed fluorescence} \\ \text{strong excitation}}} = \frac{\eta_G f'}{\eta_H f \gamma} \frac{\beta_{HG}}{T_H} \tag{15b}$$

In this case, the quantum ratio is dependent on the intensity of excitation I. In the limiting case of high intensity and low guest concentration, $T_H \simeq (\alpha I/\gamma)^{\frac{1}{2}}$. Therefore the quantum ratio is proportional to $I^{-\frac{1}{2}}$. This is demonstrated in *Figure 11*.

In *multi-component* systems the intensity relations are much more complex because there is competition between different traps. The extremely high sensitivity of sensitized delayed fluorescence is valid apparently only at not too low temperatures, where the X-traps and all kinds of shallow traps are no longer effective. In the system naphthalene + β-methyl-naphthalene, the quantum ratios for prompt and for delayed fluorescence at 4.2°K are nearly equal[14]. This is due to the presence of X-traps in naphthalene, and to the introduction of additional shallow traps when doping naphthalene with β-methylnaphthalene. These shallow traps are responsible for the very strong temperature dependence of delayed fluorescence intensity below 100°K (*Figure 12*).

Since X-traps are always present even in pure crystals, and since trapping processes can be so tremendously effective, it seems justified to say that one can hardly overestimate the importance of traps and trapping processes in organic molecular crystals.
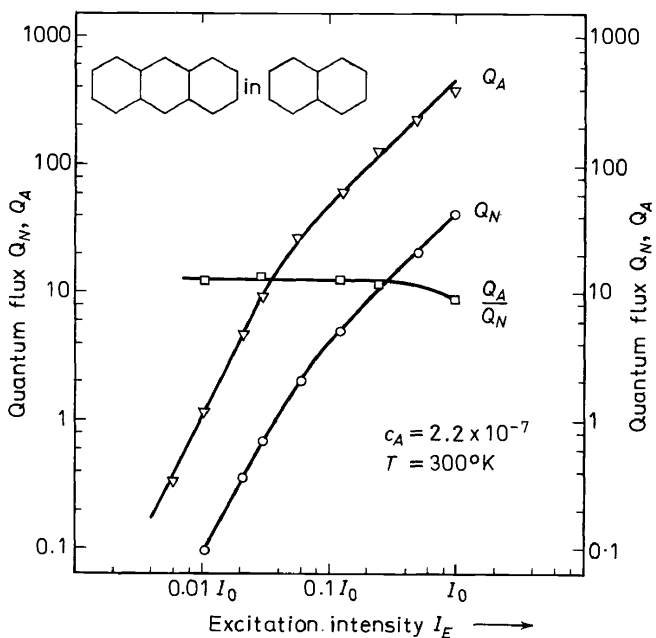
Figure 11. Quantum flux Q_A and Q_N and quantum ratio Q_A/Q_N of delayed fluorescence in naphthalene crystals containing 2.2×10^{-7} parts of anthracene, as a function of excitation intensity I, room temperature. From reference 14
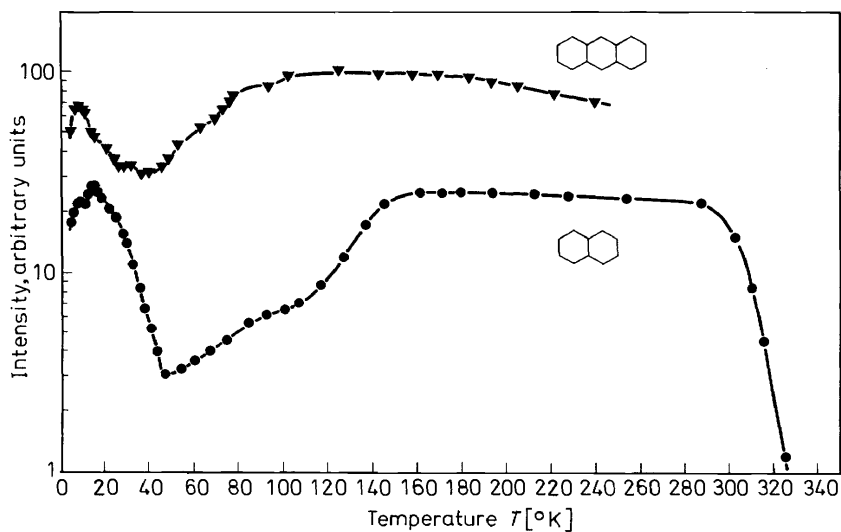

Figure 12. Integral intensity of delayed fluorescence in typical very pure anthracene and naphthalene crystals as a function of temperature. From reference 15

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