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Delayed Fluorescence and Triplet Excition Kinetics in Tetracene Doped Anthracene Crystals

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The triplet exciton kinetics in the host–guest system anthracene-tetracene is studied. Intensity and time dependence of the delayed fluorescence emission of both host and guest are investigated for guest concentrations between 10^{-8} and 10^{-5} mol/mol. The host triplet state is excited using a xenon arc lamp or a krypton ion laser for steady state and a specially shaped xenon flash or a pulsed ruby laser for the transient measurements. The guest concentrations are measured down to 5×10^{-9} mol/mol with an accuracy of 20% by observing the prompt guest fluorescence excited directly with a suitable line of an argon ion laser.

For relative guest concentrations smaller than 2×10^{-7} mol/mol the measurements can be described satisfactorily by assuming that the guest molecules act as traps with a lifetime of 0.8ms, a trapping rate for the host excitons of $\gamma^* N$ with $\gamma^* = 1.8 \times 10.^{11}$ cm^{3}s^{-1} (N = density of guest molecules), and a detrapping rate of about 100s^{-1}. The analysis involves host-host as well as host-guest annihilations. The observed magnetic field dependence of the delayed fluorescence (directional resonances) agrees with the kinetic measurements. At higher guest concentrations additional traps govern the triplet kinetics.

1. INTRODUCTION

Impurities or guest molecules can significantly influence the triplet energy transfer phenomena in an organic host crystal. The most striking effect of certain guest molecules is their ability to trap host excitons and thus influence the triplet kinetics at guest concentrations as low as 10^{-9} mol/mol.[1,2] The trapped excitons may be thermally released or decay to the ground state. It is also possible that they are annihilated by interaction with a free host exciton; a process which can lead to delayed guest fluorescence.

Rise and decay of the delayed fluorescence gives detailed information about the trapping, detrapping and annihilation processes which the triplet excitons undergo. If the fluorescence does not decay with a single exponential function but rather with a composition of several exponentials, we get information about the traps involved in the triplet kinetic, since each additional characteristic decay time corresponds to a new trap species.

As reported previously,[3] the decay of the delayed fluorescence in the host-guest system anthracene-tetracene contains in fact more than one decay time. In this paper we will present detailed and more complete measurements of the time dependence of the delayed fluorescence in this system over a broad range of guest concentrations between 10^{-8}-10^{-5} mol/mol. The measurements include studies of the delayed host and guest fluorescence for different excitation methods (ruby laser, xenon flash, xenon arc lamp and krypton ion laser). Since the magnetic field dependence of the delayed fluorescence has proved to give good information about annihilation processes[4-7] we also use magnetic field experiments to clarify and check the conclusions we obtain from the time dependence.

A model is presented which satisfactorily describes the experimental findings for guest concentrations smaller than 2×10^{-7} mol/mol. The problems arising at higher guest concentrations are discussed. Since detrapping is a thermally activated process the temperature dependence of the delayed fluorescence intensity is usually investigated.[8-11] It will be shown that in our case the temperature dependence gives practically no information about the involved annihilation and trapping processes (cf. Figure 6).

So far most studies of the triplet kinetics in mixed organic crystals were done at high doping levels ($> 10^{-4}$ mol/mol,[8, 9, 12])where guest-guest interactions are the dominating processes. In this case the host fluorescence is hardly observed either because the host triplets are not excited at all or because their density is strongly reduced by trapping effects. Since much smaller guest concentrations are used in our experiments it is possible to investigate the host fluorescence as well as the guest fluorescence. In order to study very low doping levels a new method has been used to measure the guest concentration down to 5×10^{-9} mol/mol with an accuracy of 20%.

To our knowledge, time resolved spectroscopy has so far never been used to study the triplet kinetics in lightly doped crystals, i.e. in crystals where the lifetime of the free triplets is between 10^{-6} and 10^{-3} sec and it is the first time that the time dependence of both host and guest fluorescence has been analysed.

2. EXPERIMENTAL PROCEDURE

Scintillation grade anthracene from different supliers was used as starting material. The material was zone-refined in two steps with a total of up to 60 passes. The crystals were grown by the Bridgman method. The guest material (tetracene) was added to the growing tube in crystalline form or dissolved in benzene.

The lifetime of pure undoped anthracene was determined to be 20 msec.

Guest concentration in the crystal was evaluated in a new way. We excited the guest directly with the 4579-Å-line of an argon ion laser and not via energy transfer. Fortunately, anthracene does not absorb at this wavelength. The energy is too low to excite the anthracene singlet state (E = 3.15 eV) and too high to excite the anthracene triplet state (E = 1.83 eV), but just right to excite the fluorescent tetracene singlet state (E = 2.4 eV). This has been controlled experimentally: pure crystals showed fluorescence signals corresponding to not more than 10^{-10} mol/mol fluorescent impurities, which is reasonable even for high purity crystals. If anthracene singlets would have been excited, the long wavelength part of the anthracene fluorescence would have given a much larger signal. Anthracene Raman lines limited the accuracy of these measurements. For high doping levels the guest concentration was determined by comparing the fluorescence intensity of a known crystal weight dissolved in benzene with the fluorescence intensity from standard solutions. For weakly doped crystals we assumed that the tetracene concentration was proportional to the observed tetracene (crystal-) fluorescence.

In our earlier experiments[3] we used a phosphoroscope arrangement which is commonly used for studying triplet kinetics in doped organic crystals. The advantage of this method is that host triplets can be formed via intersystem crossing from the host singlets thus giving a high triplet population. Especially in doped crystals, a high triplet excitation efficiency is required since the yield of delayed fluorescence is up to 10^6 times smaller than in pure crystals for the same excitation level. However, both the use of a phosphoroscope and indirect population via the first excited singlet have serious disadvantages. Using the strongly absorbed singlet excitation, we get a non-uniform distribution of excitons in the crystal and diffusion terms may come into the triplet kinetic equations. As pointed out by Ern [10] there is an inherent loss of information by using a phosphoroscope since we can observe only a part of the fluorescence decay, i.e., we lose an initial dead time of some 100μs of the decay and the whole buildup. In doped crystals however, there are fast components just at the beginning of the decay which can make up over 90% of the delayed fluorescence intensity.

In order to avoid these disadvantages we excite the host triplets via the $S_0 \rightarrow T_1$ transition. Although the absorption coefficient for this forbidden transition is small, we can populate the triplets using a very intense light source such as a xenon flash, a ruby laser or a krypton ion laser. Since the ruby laser pulse is very short, ($\simeq$ 40 ns), we can approximate it in the kinetic equations by a delta function. To reach a steady state population of the triplet states the exciting light pulse should be much longer. The pulse of a xenon flashlamp would be long enough (some ms), but since it has a complicated pulse shape, analysis of the experimental curves would be quite difficult. To get fluorescence signals which are easy to analyse mathematically we therefore constructed an apparatus which gives a square wave flash.[13] In experiments with the krypton ion laser a rotating disk chopper produced the desired square wave excitation.

If not stated differently the exciting light was incident normal to the ab-plane of the crystals, fluorescence observed in the direction of the a axis and the experiments were done at room temperature.

The delayed fluorescence was detected by a cooled photomultiplier using suitable interference filters to select the host or the guest fluorescence. Three interference filters in series were needed to separate host and guest fluorescence as well as to reject the exciting light. These filters attenuated light outside the 430 to 460 nm and 480 to 510 nm bands (for the host and the guest fluorescence, respectively) more than five orders of magnitude. The host fluorescence was completely separated from the guest fluorescence, but the guest fluorescence always contained a fraction (5%) of the host-fluorescence from the long wavelength tail of the anthracene fluorescence. In order to measure the spectrum of the delayed fluorescence (Figure 1) a monochromator was used instead of the filters. The characteristics of these filters and the spectral sensitivity of the

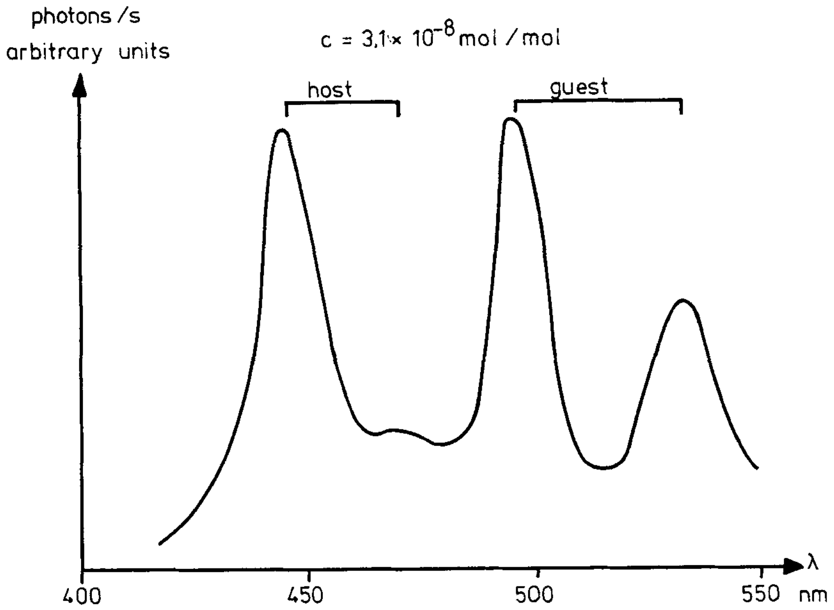

FIGURE 1 Delayed fluorescence emission spectrum of an anthracene crystal doped with 3.1×10^{-8} mol/mol tetracene. Excitation: 900-W xenon arc lamp combined with a Schott RG 610 filter to eliminate all wavelengths shorter than 600 nm. The signal is corrected for photomultiplier and spectrometer spectral sensitivity.

photomultiplier were measured to get comparable values of the host and guest fluorescence intensities. This calibration is accurate only to a factor of two, but most results discussed later are independent of it. For high guest concentrations the signals were corrected for singlet energy transfer as well using the transfer constant $k = 6 \times 10^4$ given by Benz and Wolf.[14] Steady state measurements were made with the photon counting technique, and transient measurements with a signal averager (50μs/point) or with a transient recorder (100ns/point).

For the magnetic field experiments a light guide separated the crystal from the photomultiplier to avoid any influence of the magnetic field on the detector system. A 4.2 kG permanent magnet was used to produce the magnetic field.

3. MODEL FOR THE TRIPLET EXCITON KINETICS

The kinetics of triplet excitons in our crystals can be described by a model similar to the one introduced by Siebrand[15] to explain the temperature dependence of delayed fluorescence in pure anthracene crystals. The model introduces m different triplet traps N_i ($i = 1, \ldots m$). Kinetic equations for the triplet densities n_i ($i = 0$ for the host and $i = 1, \ldots, m$ for the traps N_i) are then given by:

$$\frac{dn_i}{dt} = \alpha_i \, I(t) + \sum_{k=0}^{m} q_{ki} \, n_k \quad , \qquad (1)$$

where $I(t)$ = incident light intensity, and α_i = absorption coefficient of N_i. The term within the summation describes monomolecular decays, trapping and detrapping processes. Figure 2 shows the processes included in Eq. (1) if we have only one trap ($m = 1$). Since the experimentally observed delayed fluorescence is

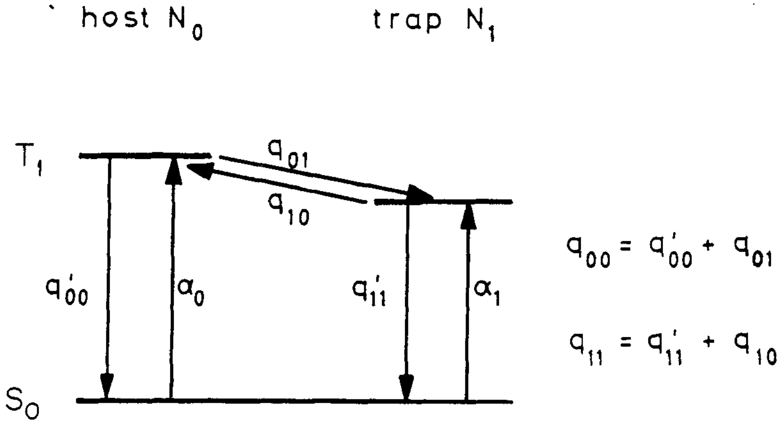

FIGURE 2 The processes described by Eq. (1) if only one trap is considered.

proportional to the square of the exciting light, we can omit biexcitonic processes and trap saturation effects in the kinetic equations.[16]

The solutions of Eq. (1) are:

- for the rise (index r) of the triplet populations
  ($I(t) = 0$ for $t < 0$, and $I(t) = I$ for $t > 0$):

$$n_{ri}(t) = n_{io}\,(1 - \sum_{k=0}^{m} a_{ik}\, e^{-\lambda_k \cdot t}) \tag{2}$$

- for the decay (index d) of the triplet populations
  ($I(t) = I$ for t < 0, and $I(t) = 0$ for $t > 0$):

$$n_{di}(t) = n_{io} \sum_{k=0}^{m} a_{ik}\, e^{-\lambda_k \cdot t} \tag{3}$$

The introduced parameters are:

n_{io} = steady state triplet concentration. The n_{io} are steady state solutions of Eq. (1), taking $I(t) = I$.

λ_k = decay rate constants, depending only on q_{ik} from Eq. (1).

a_{ik} = weight factors for the various decays, depending upon q_{ik} and α_i from Eq. (1).

Note that for any time t the following relationship holds:

$$n_{ri}(t) + n_{di}(t) = n_{io} = \text{const.} \tag{4}$$

One can get Eq. (4) directly from Eq. (1), if one examines the functions

$$z_i(t) = n_{ri}(t) + n_{di}(t)$$

These functions obey Eq. (1) with the boundary conditions

$$z_i(\text{o}) = n_{io}$$

These are just the boundary conditions for the steady state solutions z_i = const. The observed delayed host (ϕ_A) and guest (ϕ_T) fluorescence is given by

$$\phi_A \propto \sum_{i \geqslant k} f_{ik}\;\gamma_{ik}\, n_i\, n_k \tag{5}$$

$$\phi_T \propto \sum_{i \geqslant k} f_{ik}\;\gamma_{ik}\, n_i\, n_k \tag{6}$$

where f_{ik} and f'_{ik} are the fractions of the annihilations between a triplet T_i and a triplet T_k that lead to host- and to guest-fluorescence respectively. γ_{ik} is the corresponding annihilation rate constant. Eq. (5) and (6) include host–host, host–trap and trap–trap annihilation processes.

4. THE INFLUENCE OF TRAPS ON THE DELAYED FLUORESCENCE

We want to discuss first the necessary conditions under which a triplet trap can be observed at all. Observable effects which are due to traps are: changes of the triplet kinetics (i.e. of triplet concentrations and decay rates) or additional new triplet annihilation processes which may even lead to trap fluorescence.

A direct method to find trap effects is therefore to search for new decay rates in the fluorescence decay curves. This method works if the influence of the trap on fluorescence is large. Smaller influences can be detected if the traps, in addition to normal trapping processes, are directly excited by the incident light. According to Eq. (1) the triplet densities are proportional to the incident light intensity I. A variation of I changes the yield of the fluorescence but not its time dependence. However, if the spectral distribution of the exciting light is changed, the time dependence may change as well if the trap absorption spectrum (described by $\alpha_i(\lambda)$)differs from the host absorption spectrum $\alpha_0(\lambda)$. Even rotating the polarisation of the exciting light might therefore influence the triplet kinetic. Since one compares measurements made on the same crystal, one can detect very small effects with this method.

The magnetic field dependence of the delayed fluorescence on the other hand is a convenient tool to demonstrate the influence of traps (and of guests) on triplet annihilation processes.[5] If it changes with varying guest concentration one can conclude that new annihilations due to a new trap occur. The angles at which these new directional resonances are observed may even give information about the nature of the trap involved.

Finally one can get information about traps by measuring the efficiency of delayed fluorescence as a function of guest concentration. A trap can lower or enhance the efficiency by acting as a sink or as a reservoir for triplet excitons respectively.

Note that all these methods described yield more information than the temperature dependence of delayed fluorescence (see Figure 6).

5. DISCUSSION OF THE EXPERIMENTAL RESULTS

5.1 Delayed fluorescence at small guest concentrations

All our experiments indicate that at guest concentrations smaller than $c_k = 2 \times 10^{-7}$ mol/mol only one trap is important. Yet even with one trap there are several adjustable parameters left in the kinetic analysis for fitting the experimental rise and decay curves. Fortunately the magnetic field measurements help to decide which processes are responsible for the observed fluorescence. A substitutionally introduced guest molecule has two possible orientations in the lat-

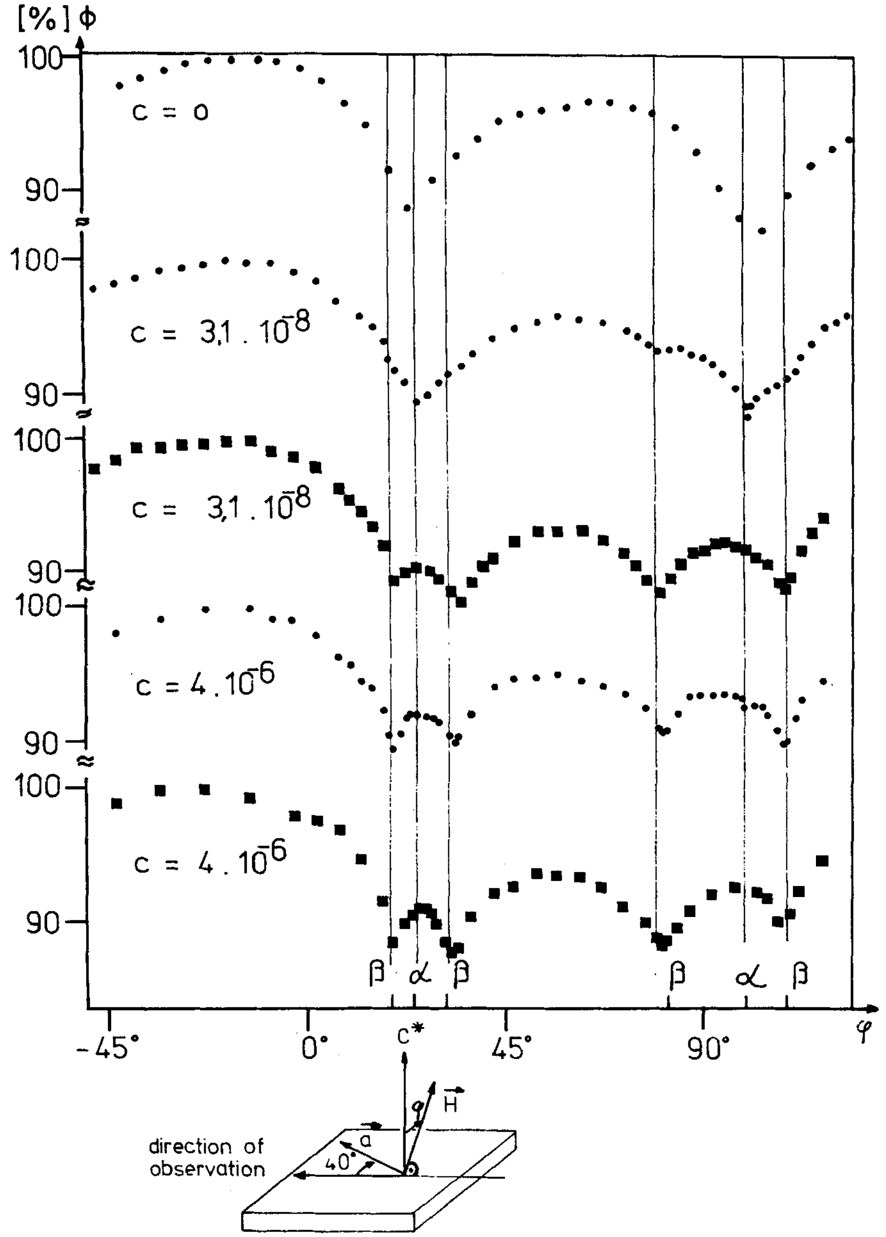

FIGURE 3 The steady state delayed fluorescence intensity ϕ as a function of the direction of a magnetic field of 4.3 kG for a pure $c = 0$, a lightly and a heavily doped crystal. The fluorescence yield of host (●) and guest (■) are normalised to 100% at the maximum. The crystal a-axis encloses an angle of 40° with the direction of observation and the magnetic field H is rotated in a plane perpendicular to this direction. ϕ is the angle between the c^*-axis and H. The angles α and β of the directional resonances are computed with the theory of Johnson and Merrifield.[22, 23] The α's correspond to host–host and the β's to host-guest annihilations. The accuracy of the intensity is 0.3% and that of the angles is 2°.

tice of the anthracene host. The finestructure tensor of the triplet state of such a guest is diagonal in these two directions. The tensor of the free triplet exciton is diagonal in a third direction which is an average over the two possible orientations. The triplet–triplet annihilation probability depends on the mutual orientation of the fine-structure tensors of the two triplets. Therefore, in a doped crystal, three different types of annihilations and their corresponding resonances should be observed in a magnetic field if the crystal contains substitutionally introduced guests which act as exciton traps; namely free–free, free–guest with orientation 1 and free–guest with orientation 2. This was observed first by Groff *et al.*[5] The guest fluorescence in Figure 3 also shows resonances at the angles corresponding to free–guest annihilation for substitutionally introduced traps with a D/E ratio corresponding to that of anthracene[17] or tetracene[18] (D and E are the fine-structure constants).

On the other hand, the host fluorescence in Figure 3 displays resonances typical for the annihilation of two free triplets but also additional weak resonnances at the angles corresponding to free–guest annihilations. We can therefore learn from these measurements that the host fluorescence originates from both free–free and free–guest annihilations. The guest fluorescence is primarily due to free–guest annihilations although small contributions of host–host annihilations cannot be completely ruled out. Having identified the nature of the annihilation processes in this way we can now use these results for fitting the measured time dependence of the delayed fluorescence signals (Figure 4a and 4b) which gives us numerical values for the various rate constants.

At small doping levels two decay times are observed (Figure 4a), indicating that only one trap which is probably the guest is important. With this assumption one can use Eqs. (1) to (6) to fit the four experimental curves in Figure 4 for each crystal (rise and decay of both host- and guest-fluorescence respectively). Figures 4a and 4b show such a fit which is best if one assumes that 72% of the host fluorescence is due to free–free and 28% due to free–trap annihilations, and that 17% of the guest fluorescence is due to free–free and 83% due to free-trap annihilations. If $q_{00} \simeq q_{01}$, i.e. all vanishing host triplets appear as trap triplets, one can obtain from this fit the values of the annihilation rate constants given in Table 1. If the above assumption does not hold then $q_{00} > q_{01}$ and the values in Table 1 for $f_{01} \times \gamma_{01}$ and $f_{01} \times \gamma_{01}$ are lower limits.

A simple proof can be given to show that in our case the anthracene host fluorescence does not originate exclusively from mutual annihilation of free anthracene triplets. Regardless of how many traps are involved it follows from Eq. (4) that $\phi_{\text{decay}} = (\sqrt{\phi_0} - \sqrt{\phi_{\text{rise}}})^2$ should hold if free-free annihilation is the only process that can lead to host fluorescence. In the experimental curve however, the actual rise is slower than is expected from the decay curve according to this relation (Figure 4b). This clearly indicates that host-trap annihilations

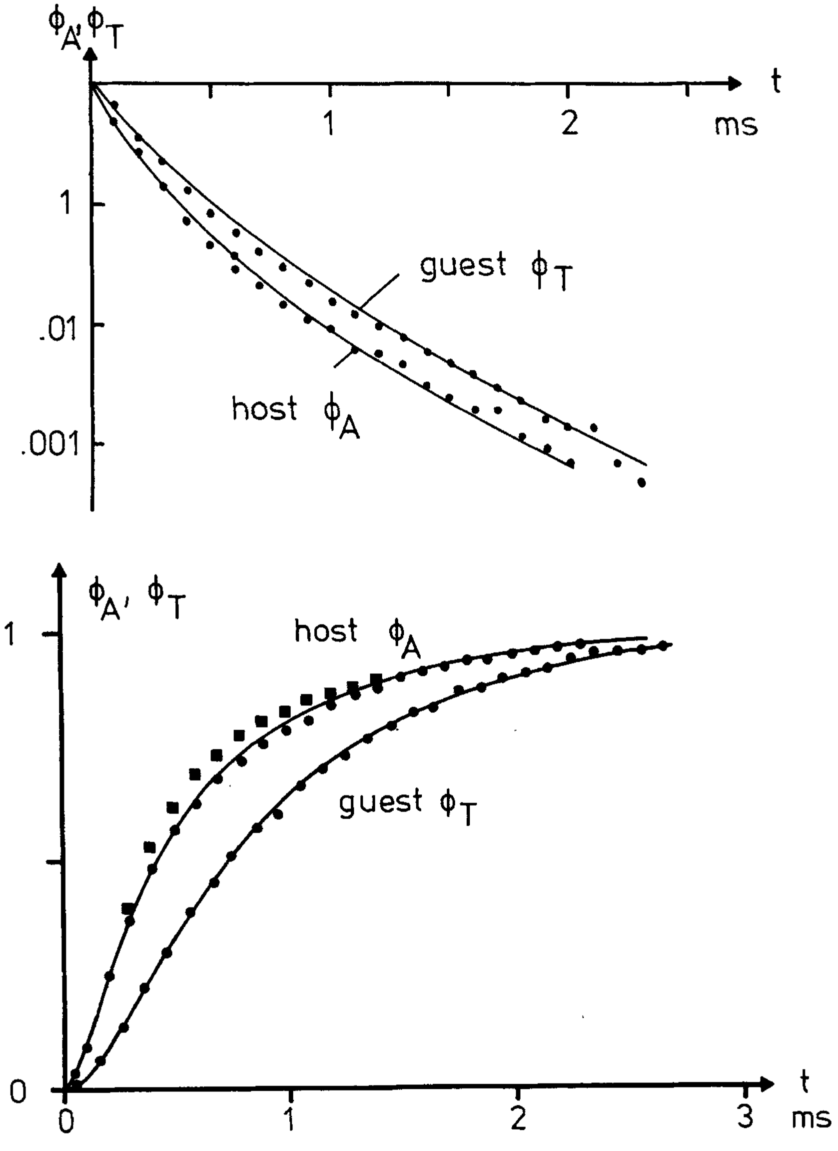

FIGURE 4 Comparison between the experimental curves (.) and the calculations (-) of the time dependence of delayed fluorescence. (a) Decay of the anthracene (ϕ_A (t)) and the tetracene ($\phi_T(t)$) fluorescence on a logarithmic scale. (b) Build-up of the anthracene ϕ_A and tetracene ϕ_T fluorescence on a linear scale. The values of the annihilation rate constants used for the fits in Figure 4a and 4b are listed in Table 1. For comparison the ■ indicate the rise of the host computed from the decay by using Eq. (4) under the assumption that only host-host annihilations lead to host fluorescence.

TABLE 1

The table lists the parameters q_{00}, q_{10} and q_{11} introduced in Eq. (1) computed from the time dependent measurements of the crystals with low quest concentrations, and the annihilation rate constants of eqs. 5 and 6 as used in the fit of Figure 4. For the evaluation of the annihilation constants the ratio ϕ_A/ϕ_T which is known only to a factor of two has been used. The values of q_{10}, $f_{01}\,\gamma_{01}$ and $f'_{01}\,\gamma_{01}$ are lower limits if the equation $q_{01} \cong q_{00}$ does not hold, i.e. if the tetracene molecules are not the only traps that influence the host triplet concentration. The direct triplet decay q'_{00} (Figure 2) yields a negligible contribution to q_{00} in the guest concentration region studied (10^{-8} to 10^{-7} mol/mol).

Rate constant for	Experimental value
Decay of free triplets (N = density of guest molecules)	$\lvert q_{00}\rvert = \gamma^* N; \gamma^* = (1.8 \pm 0.4)\ 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$
Decay of guest triplets	$\lvert q_{11}\rvert = 1.2 \pm 0.2\ \mathrm{ms}^{-1}$
Detrapping	$q_{10} = 0.18 \pm 0.1\ \mathrm{ms}^{-1}$
Host–host annihilations leading to guest fluorescence	$f'_{00}\,\gamma_{00} = 0.5\, f_{00}\,\gamma_{00}$
Host–guest annihilations leading to host fluorescence	$f_{01}\,\gamma_{01} = 0.1\, f_{00}\,\gamma_{00}$
Host–guest annihilations leading to guest fluorescence	$f'_{01}\,\gamma_{01} = 0.7\, f_{00}\,\gamma_{00}$

can also contribute to the host fluorescence at guest concentrations as low as 3×10^{-8} mol/mol.

The fit gives the different decay rates of the free and the trapped excitons. Similar fits can be made for all crystals with guest concentrations smaller than c_k. The results are listed in Table 1. It turns out that the decay rate of the trapped excitons q_{11} is approximately independent of the guest concentration c and that the decay rate of the free host excitons q_{00} is proportional to c ; $q_{00} = \gamma^* N$, where N = density of guest molecules and $\gamma^* = (1.8 \pm 0.4) \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. This value is close to that of the bimolecular annihilation rate constant $\gamma = 2 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$,[19] indicating that the cross section for trapping is equal to the cross section for annihilation. This above mentioned proportionality between q_{00} and the guest concentration holds even for high guest concentrations if one identifies q_{00} to be the decay rate corresponding to the first fast decay observed in the ruby laser experiments (Figure 5).

Our value of γ^* is in fair agreement with the value reported by Groff *et al.*[5] $\gamma^* = 3.7 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, but is much larger than the value reported by Baessler *et al.*[20], $\gamma^* = 5.8 \times 10^{-14}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Since the latter value has been measured at high guest concentrations ($c > 10^{-6}$ mol/mol), traps may well simulate a longer free triplet lifetime. At high guest concentrations mathematical descriptions of

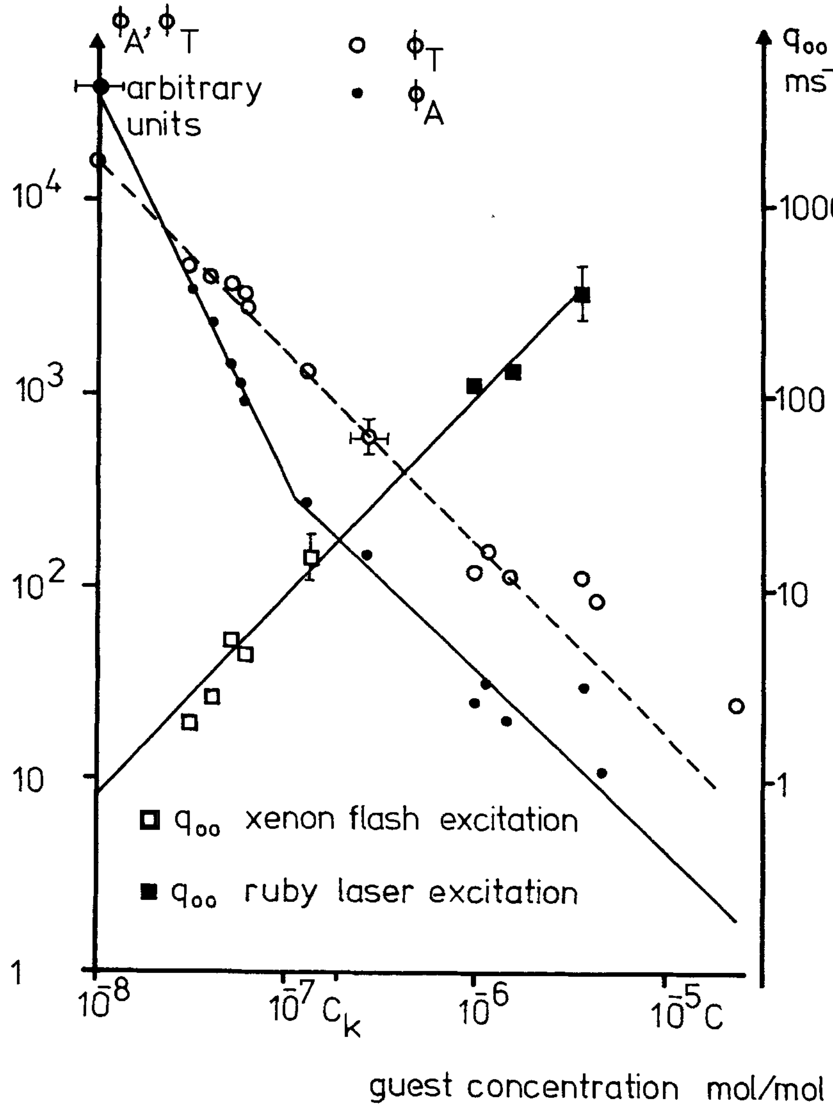

FIGURE 5 Host (ϕ_A) and guest (ϕ_T) steady state delayed fluorescence intensity and inverse triplet lifetime q_{00} as a function of the guest concentration c. Extreme care was taken to use identical geometry for all crystals. The correction factors used to account for the different spectral overlap of the fluorescence with the filters and with the photomultiplier are accurate to a factor of two. For comparison the values of ϕ_A and q_{00} as measured for a pure crystal are: $\phi_A = 8.7 \times 10^6$ and $q_{00} = 0.05\ ms^{-1}$.

triplet dynamics become very complicated and observed decay rates naturally less meaningful (see Sect. 5.2).

The fits also yield an estimation for the detrapping rate constant: $q_{10} \geq (.18 \pm 0.1)\text{ms}^{-1}$. This value is larger than one would expect from the host-guest triplet energy separation ΔE if the traps are tetracene molecules:[10] $q_{10} = \gamma^* M \exp^{-\Delta E/kT} \simeq 0.03\ \text{ms}^{-1}$. Regardless of this discrepancy we have good reasons to assume that the observed traps are the guest molecules since

a) they are present in all tetracene doped anthracene crystals,

b) annihilations with trapped excitons lead to tetracene fluorescence,

c) the trap density is proportional to the guest concentration,

d) the trap is introduced substitutionally into the host.

Detrapping processes as well as host–trap annihilations leading to host fluorescence are both highly improbable if one takes the value of the triplet energy measured in pure tetracene crystals as the triplet energy of the guest. If the energy of the tetracene triplet state is slightly higher when embedded in the anthracene host crystal, both processes would become more probable.

Dependence of the fluorescence yield on the guest concentration agrees with the above results: host fluorescence ϕ_A varies as c^{-2} with the guest concentration c (Figure 5) and guest fluorescence ϕ_T as c^{-1}. One would expect this result if ϕ_A is primarily due to free–free and ϕ_T to free–trap annihilations, as it follows from the magnetic field experiments as well as from the time dependent measurements.

5.2 Delayed fluorescence at high guest concentrations

At guest concentrations above $c_k = 2 \times 10^{-7}$ mol/mol new phenomena are observed. They indicate that new kinds of traps become important. As discussed in Sect. 4, dependence of the triplet kinectics upon the spectrum of exciting light is a very strong indication of the presence of a new trap. Figure 7 shows the rise of delayed fluorescence for three different excitation spectra: Two different laser lines and a xenon flashlamp were used as excitation sources. One of the two laser lines at 6764 Å lies at a maximum, the other at 6471 Å at a minimum of the anthracene triplet absorption spectrum.[21] If there are traps absorbing in this region their presence should be observable preferably at 6471 Å. For the xenon flash with a broader spectrum the rise lies in between the two curves observed with laser excitation as one would expect. A similar effect is shown in Figure 8 where the host-guest fluorescence intensity ratio ϕ_A / ϕ_T is plotted versus guest concentration. Again the curve corresponding to the xenon arc excitation lies between the two other curves.

As to the magnetic field measurements, host and guest fluorescence have almost the same magnetic field dependence as shown in Figure 3. One would expect therefore, that in both cases the fluorescence originates from the same annihilation process which would mean that the time dependence should be the same as well. This however is not the case as seen in Figure 7. With an introduction of a new trap this discrepancy can be removed by assuming that this trap has the same fine-structure tensor and the same orientation in the host lattice as the guest but different kinetic parameters.

The fluorescence yield of the host and guest fluorescence is plotted against the guest concentration in Figure 5. Again one can observe that for $c > c_k$ new effects become important, since ϕ_A decreases slower than c^{-2} above c_k. The decay rate q_{00} however, shown on the same figure, still increases proportionaly to c which corresponds to a steady decrease of the free host triplet concentration. To explain the high host fluorescence yield we have to look for a new source of excitons, either free or trapped ones. Traps can act in this way. If the lifetime of the trapped excitons is longer than the lifetime of the free excitons, the overall triplet population (host and trap) is enhanced and therefore the observed host fluorescence can be higher than it would be without the trap present.

As long as we cannot study the triplet kinetics as a function of the excitation spectrum to get the trap absorption spectrum, it is difficult to get more quantitative data about this trap. To do this one would need an extremely intense light source since the fluorescence of heavily doped crystals is 10^6 times smaller than that of pure crystals as shown in Figure 5.

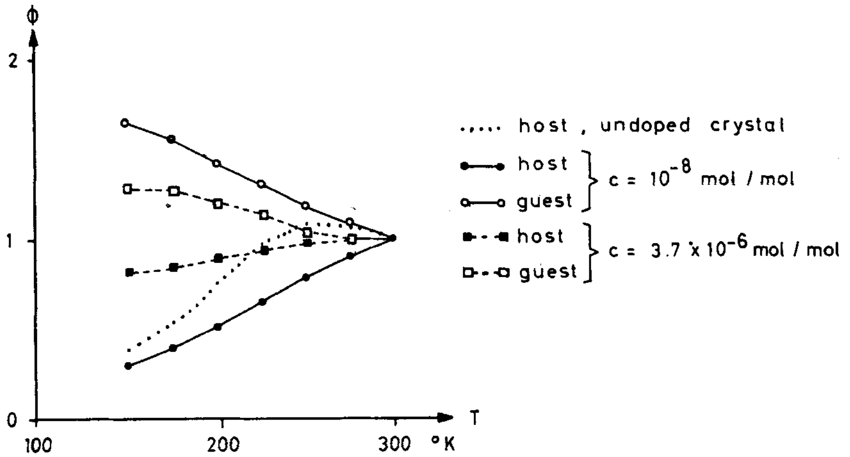

FIGURE 6 Host and guest fluorescence intensity ϕ as a function of the temperature T for a pure, a lightly and a heavily doped crystal. The signal is normalised to 1 at T = 300 °K. Excitation: 1000 w xenon arc lamp with a Schott RG 610 filter.

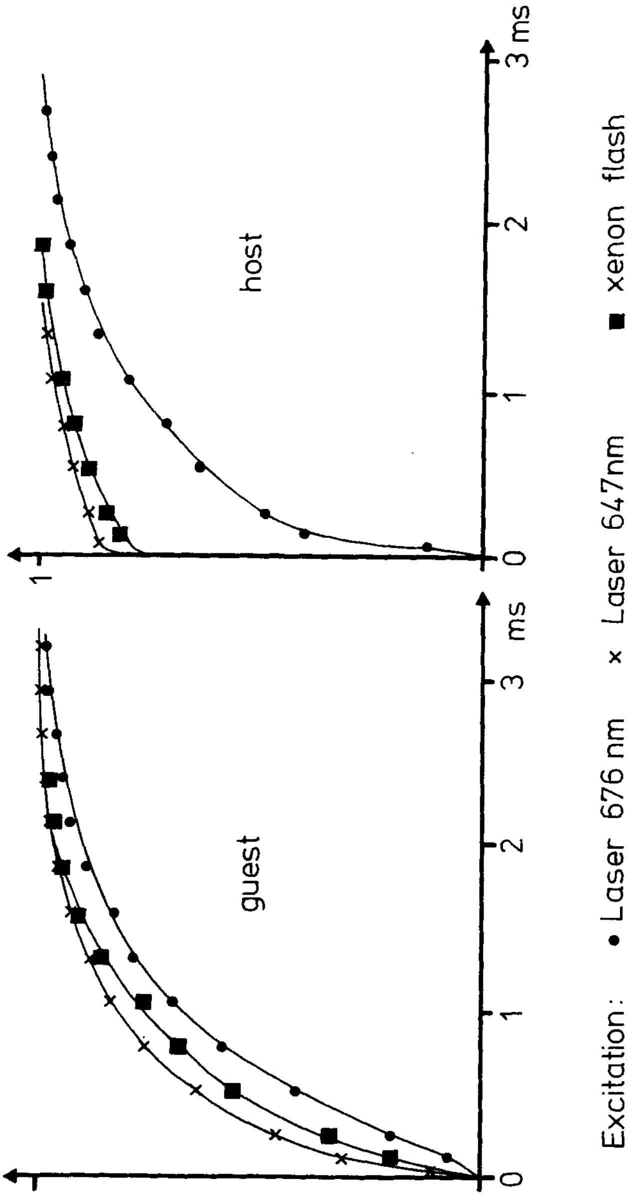

FIGURE 7 The rise of the delayed fluorescence for excitation with two different krypton ion laser lines and with a xenon flash combined with a Schott RG 610 filter. The signals are normalised to 1 for steady state conditions ($t \to \infty$). The 676 nm line of the laser falls on a maximum, the 647 nm line on a minimum of the singlet–triplet absorption spectrum of anthracene.[20]

To summarise the results, we can say that at high guest concentrations a new triplet trap governs the triplet kinetics and the delayed fluorescence of the host. The guest fluorescence is less affected by it. The trap can be an intrinsic anthracene property as well as a consequence of the guest molecules. Since its influence begins at guest concentrations where the triplet lifetime of the host is about 30μs, one can assume that the trap lifetime has the same order of magnitude. Unfortunately, at high guest concentrations our experimental accuracy is not good enough to seperate such an additional decay time from the two decay times already present.

5.3 Temperature dependence of the delayed fluorescence

A qualitative confirmation that detrapping processes are involved in the kinetics of doped crystals is given by the temperature dependence of the delayed fluorescence (Figure 6). The guest fluorescence decreases and host fluorescence increases with increasing temperature as one would expect if detrapping processes are playing a role, i.e. if q_{10} increases with increasing temperature. Analysing the transient measurements of the same two crystals shown in Figure 6 one finds that the proportion of the slow component in the decay is smaller for the higher doped crystal. But this slow component is temperature dependent since it is due to thermally released excitons, so a less pronounced temperature dependence of the highly doped crystal as shown in Figure 6 is reasonable.

6. CONCLUSION

To understand the delayed fluorescence in doped organic crystals it is necessary to investigate in detail the triplet kinetics as well as the magnetic field dependence of the delayed fluorescence of host and guest. Using these two methods we have demonstrated that a tetracene molecule in an anthracene host crystal acts as a triplet trap with a lifetime of 0.8 ms and a trapping cross-section equal to that for anthracene triplet annihilation. This trap is the only one observed at relative tetracene concentrations smaller than 2×10^{-7} mol/mol. Both, host–host and host–guest annihilations can lead to host as well as to guest fluorescence. There is evidence that triplet excitons trapped at tetracene molecules in the anthracene lattice have a somewhat higher energy than the triplet state in pure tetracene crystals since considerable thermal detrapping is observed as well as anthracene–tetracene annihilations which lead to anthracene fluorescence.

At higher guest concentrations an additional trap appears and influences the transient measurements and the host fluorescence yield. Direct evidence for this trap is the dependence of the triplet kinectics upon the spectrum of the incident light.

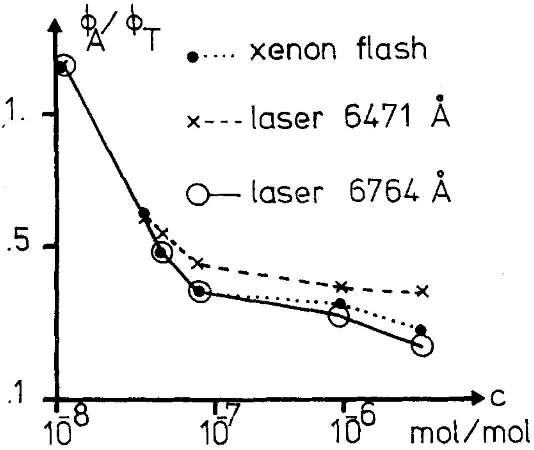

FIGURE 8 The dependence of the host to guest delayed fluorescence intensity ration (Q_A/Q_T) plotted as a function of the guest concentration c for the three different excitations used in Figure 7.

The nature of this new trap is not known except that it absorbs the exciting light and that it has a long enough lifetime to reach triplet densities comparable with the density of the free triplets.

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References

1. K. W. Benz, W. Häcker, H. C. Wolff, *Z. Naturforsch.* 25a, 657, (1970).
2. G. C. Smith, *Phys. Rev.* 166, 839, (1968).
3. H. P. Schwob, J. Fünfschilling, I. Zschokke-Gränacher, *Mol. Cryst. and Liq. Cryst.* 10, 39, (1970).
4. R. C. Johnson, R. E. Merrifield, P. Avakian, R. B. Flippen, *Phys. Rev. Lett.* 19, 285, (1967).
5. R. P. Groff, R. E. Merrifield, P. Avakian, Y. Tomkievicz, *Phys. Rev. Lett.* 25, 105, (1970).
6. R. F. Merrifield, *Pure and Appl. Chem.* 27, 481, (1971).
7. P. Avakian, A. Suna, *Mat. Res. Bull.* 6, 891, (1971).
8. Noboru Hirota, *J. Chem. Phys.* 43, 335, (1965).
9. T. N. Misra, S. P. McGlynn, *J. Chem. Phys.* 44, 3816, (1966).
10. V. Ern, *Mol. Cryst. and Liq. Cryst.* 18, 1, (1972).
11. E. M. Yee, M. A. El-Sayed, *J. Chem. Phys.* 52, 3075, (1970).
12. B. N. Srinivasan, M. Kinoshita, J. W. Rabalais, S. P. McGlynn, *J. Chem. Phys.* 48, 1924, (1968).

13. J. Fünfschilling, I. Zschokke-Gränacher, Rev. Sci. Instrum. **45**, 598, 1974
14. K. W. Benz, H. C. Wolf, *Z. Naturforsch.* **19a**, 177, (1964).
15. W. Siebrand, *J. Chem. Phys.* **42**, 3951, (1965).
16. D. H. Goode, F. R. Lipsett, *J. Chem. Phys.* **51**, 1222, (1969).
17. D. Haarer and H. C. Wolf, *Mol. Cryst. and Liq. Cryst.* **10**, 359, (1970).
18. L. Yarmus, J. Rosenthal and M. Chopp, *Chem. Phys. Letters* **16**, 477, (1972).
19. P. Avakian, R. E. Merrifield, *Mol. Cryst.* **5**, 37, (1968).
20. H. Baessler, G. Vaubel and H. Kallmann, *J. Chem. Phys.* **53**, 370, (1970).
21. P. Avakian, E. Abramson, R. G. Kepler and Caris, *J. Chem. Phys.* **39**, 1127 (1963).
22. R. C. Johnson and R. E. Merrifield, *Phys. Rev.* **B1**, 896, (1970).
23. M. Chabr, J. Fünfschilling and I. Zschokke-Gränacher *Chem Phys. Lett.* **25**, 387, 1974