

## TRIPLET EXCITON FUSION IN ORGANIC MIXED CRYSTALS: THE NAPHTHALENE AS HOST AND CHRYSENE AND 1,2,5,6-DIBENZANTHRACENE AS GUESTS SYSTEM

B. BONNO, F. GÉRARDOT, J. L. LAPORTE and Y. ROUSSET

*Laboratoire d'Optique Moléculaire, Université de Reims, BP 347, 51062 Reims Cédex  
(France)*

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### Summary

In the present paper we describe phosphorescence and delayed fluorescence spectra of naphthalene crystals containing various concentrations of chrysene and 1,2,5,6-dibenzanthracene (DBA). For each sample, delayed emission intensities were measured by means of optical spectroscopy and were investigated as a function of temperature in the range 77 - 300 K.

A generalized  $n$ -trap mixed-crystal kinetic model including quadratic terms is proposed in order to explain the experimental results. Quadratic terms take into account triplet exciton homofusion and heterofusion (free and trapped excitons). Under photostationary conditions, the values of the exciton and trap populations are deduced from numerical solutions of the coupled equations describing these populations. The values obtained are used to calculate delayed emission intensities.

Assuming that the energy variation in the excited triplet state is due to radiative traps we obtain good agreement between the experimental results and the calculated values. The unknown concentration of DBA in chrysene is estimated.

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### 1. Introduction

In organic crystals, triplet excitons have a relatively large diffusion length. This fact allows us to study extended regions on the crystal and by this means we can advantageously use the triplet exciton in the study of molecular crystal defects.

It is well known that the defects in this kind of crystal are mostly chemical impurities and structural deformations. These defects constitute traps for the crystal energy. Trapped triplet excitons can fuse with crystal-free excitons. The delayed fluorescence resulting from these processes is a useful tool in the study of crystals and has been extensively used in the study of a large variety of mixed crystals [1 - 9].

In a previous paper we have presented the results of our investigation on biphenyl crystals doped with naphthalene [10]. In these crystals the only triplet exciton trap is the naphthalene triplet state. Good agreement between experimental and theoretical results was obtained by the introduction of bimolecular terms in the kinetics.

In the present paper we investigate naphthalene host-chrysene and 1,2,5,6-dibenzanthracene (DBA) guest systems at temperatures between 77 and 300 K. In these crystals several known traps exist whose concentration may be modified as wished.

The experimental results agree with those calculated from a generalized *n*-trap mixed-crystal kinetic model.

## 2. Experimental details

Commercially available naphthalene was purified by zone refining before use. Chrysene and DBA from the Eastman Organic Chemical Laboratory were used without purification. The polycrystalline samples used were prepared by melting.

We have studied three kinds of mixed crystals.

(1) Sample 1 contained  $10^{-5}$  mol DBA per mole of naphthalene.

(2) Sample 2 contained  $10^{-4}$  mol chrysene per mole of naphthalene. Several researchers [11] have shown that chrysene is always contaminated by DBA. Thus, this sample contained an unknown but certainly very small amount of DBA.

(3) Sample 3 was obtained from sample 2 by the introduction of  $10^{-5}$  mol DBA per mole of naphthalene. Given the low concentration of DBA in chrysene we may consider that the DBA concentration in this sample is  $10^{-5}$  mol DBA per mole of naphthalene.

The samples were excited using a 200 W mercury lamp (Philips CS 200 W-2) filtered at 3130 Å by a monochromator. The delayed luminescence was separated from the prompt fluorescence with a Becquerel-type phosphoroscope. Luminescence was detected photoelectrically using an M 25 Huet monochromator with a resolution of  $30 \text{ cm}^{-1}$  and an R 928 Hamamatsu photomultiplier.

The crystals were mounted on a holder and were placed inside an optical cryostat. The temperature of the cryostat was monitored by means of a platinum resistor in contact with the crystal holder.

## 3. Results

The naphthalene-DBA mixed crystal (sample 1) delayed luminescence spectra are shown in Figs. 1(a) and 1(b). At 250 K (Fig. 1(a)) the emission spectrum begins at 4000 Å ( $25\,000 \text{ cm}^{-1}$ ) and we only observe the delayed fluorescence of DBA. As the temperature decreases the DBA phosphorescence

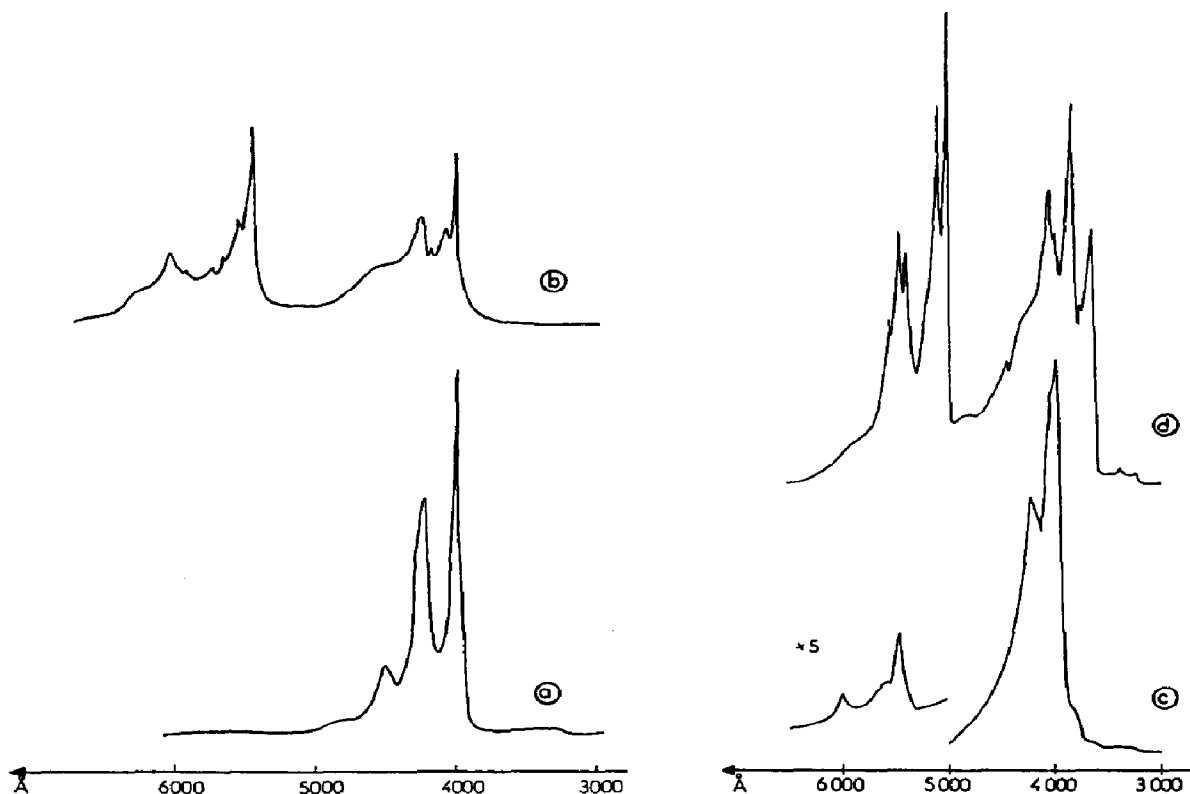


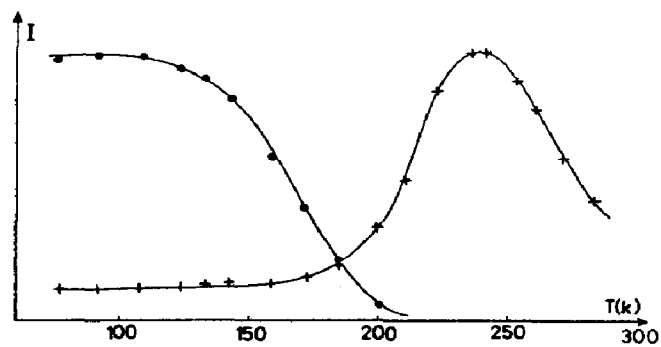
Fig. 1. Delayed emission spectra: (a) and (b) naphthalene-DBA mixed crystal (sample 1) at 250 K and at 77 K; (c) and (d) naphthalene-chrysene mixed crystal (sample 2) at 180 K and at 77 K.

appears and its spectrum begins at  $5490 \text{ \AA}$  ( $18\,210 \text{ cm}^{-1}$ ). At the final temperature (77 K) the phosphorescence and delayed fluorescence intensities are equal in magnitude (Fig. 1(b)).

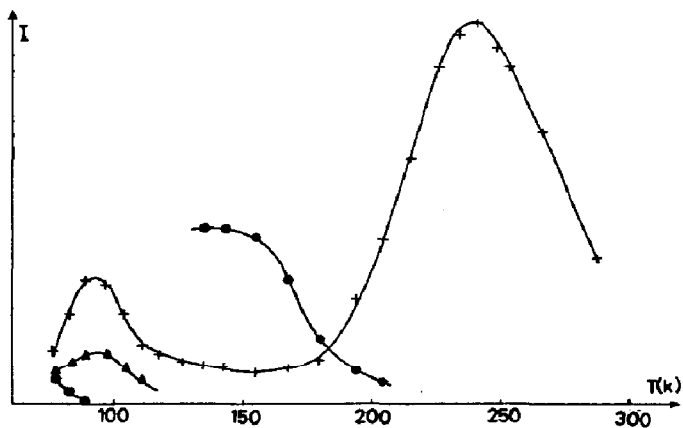
In Fig. 2(a) we report the evolution of DBA phosphorescence and delayed fluorescence intensities as functions of temperature.

In the other samples, spectral analysis and intensity evolution allow the unambiguous identification of the following five emission bands in the spectrum: (i) naphthalene delayed fluorescence beginning at  $3180 \text{ \AA}$  ( $31\,450 \text{ cm}^{-1}$ ); (ii) chrysene delayed fluorescence and phosphorescence beginning at  $3630 \text{ \AA}$  ( $27\,550 \text{ cm}^{-1}$ ) and  $5045 \text{ \AA}$  ( $19\,820 \text{ cm}^{-1}$ ) respectively; (iii) DBA delayed fluorescence and phosphorescence beginning at  $4000 \text{ \AA}$  ( $25\,000 \text{ cm}^{-1}$ ) and  $5490 \text{ \AA}$  ( $18\,210 \text{ cm}^{-1}$ ) respectively.

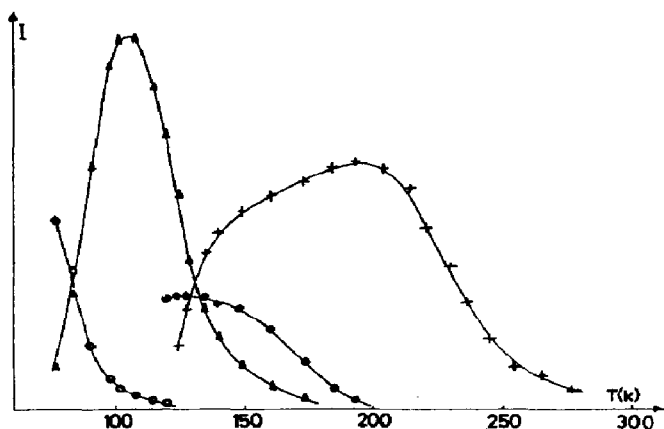
The delayed luminescence of the naphthalene-chrysene mixed crystal (sample 2) is shown in Figs. 1(c) and 1(d). This sample contains an unknown quantity of DBA. We observe delayed fluorescence and phosphorescence of DBA at 180 K (Fig. 1(c)). The emission spectrum at 77 K is shown in Fig. 1(d). In the UV region, we notice that the naphthalene delayed fluorescence intensity is very weak. Also, the chrysene phosphorescence emission is so intense that it masks the DBA phosphorescence. Between  $3500$  and  $5000 \text{ \AA}$



(a)



(b)



(c)

**Fig. 2.** Temperature dependence of delayed luminescence intensities of (a) naphthalene-DBA mixed crystal (sample 1), (b) naphthalene-DBA-chrysene mixed crystal (sample 3), (c) naphthalene-chrysene mixed crystal (sample 2): +, delayed fluorescence of DBA; ●, phosphorescence of DBA (enlarged ten times in (a), (b) and (c)); ▲, delayed fluorescence of chrysene (enlarged ten times in (b) only); ○, phosphorescence of chrysene.

the observed spectrum is a superposition of chrysene and DBA delayed fluorescence spectra.

In the naphthalene-DBA-chrysene mixed crystal (sample 3) we observe the five emission bands.

In Figs. 2(b) and 2(c) we show the luminescence intensities as a function of temperature. The very weak intensity of the naphthalene delayed fluorescence is omitted.

At 77 K the chrysene and DBA phosphorescence mean lifetimes are 2 s and 0.25 s respectively. The naphthalene delayed fluorescence mean lifetime is  $0.15 \times 10^{-3}$  s at 300 K for pure naphthalene crystals.

#### 4. Interpretation and discussion

Processes involved in triplet state population in an  $n$ -trap mixed crystal are shown in Fig. 3 for the  $j$ th trap triplet state ( $1 \leq j \leq n$ ). Since the trap concentration is low, we have omitted the direct light absorption by traps. The population of traps takes place by a relaxation from the exciton states to these traps.  $K_{oj}$  and  $K_{ij}$  are the release rate and the trapping rate respectively for the trapping level  $j$ . The exciton bandwidth is denoted  $\Delta\epsilon$ , and  $\Delta E_j$  is the  $j$ -trap depth. We have neglected the exciton bandwidth ( $\Delta\epsilon < 10 \text{ cm}^{-1}$  [12]) which is small compared with the trap depth ( $\Delta E > 1000 \text{ cm}^{-1}$ ) and we have assumed Arrhenius' law, *i.e.*  $K_{oj} = K_{oj}^\infty \exp(-\Delta\epsilon_j/kT)$ .

$K_{ij}$  is related to  $K_{oj}^\infty$  by the equation  $K_{oj}^\infty = C_j K_{ij}$  where  $C_j$  is the guest-to-host molecule number ratio [13, 14].  $K_e$  and  $K_{ij}$  are the unimolecular decay rate constants for free and trapped triplets respectively.  $\gamma$  is the bimolecular rate constant for free triplet-free triplet fusion and  $\alpha_j \gamma$  is that for free triplet-trapped triplet state fusion. The exciton creation rate is given by the pumping rate  $P$ .

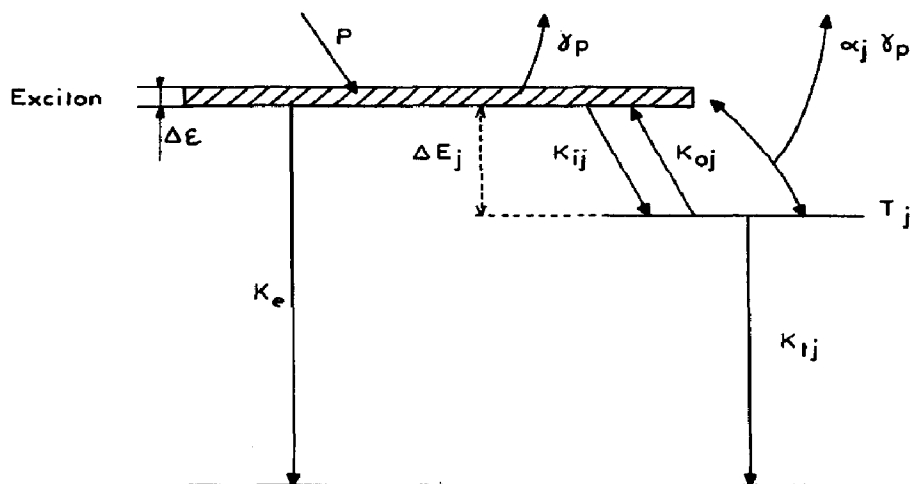


Fig. 3. The kinetic model.

The dynamics of the exciton- $j$ th trap system can be described by the coupled kinetic equations for  $N_e$  (the number of excitations in the exciton level) and  $N_{tj}$  (the number of excitations in the  $j$ th trap level). Hence

$$\frac{dN_e}{dt} = P + \sum_{j=1}^n K_{oj}N_{tj} - N_e(K_e + \sum_{j=1}^n K_{tj}) - \gamma N_e(N_e + \sum_{j=1}^n \alpha_j N_{tj})$$

$$\frac{dN_{tj}}{dt} = N_e K_{tj} - N_{tj}(K_{oj} + K_{tj}) - \gamma \alpha_j N_e N_{tj}$$

If we assume photostationary conditions we obtain an equation of the  $(n + 2)$ th degree for  $N_e$ . Such an equation may be solved by iteration. The delayed fluorescence intensity as a function of  $N_e$  and  $N_t$  is usually written as follows:

$$I_{DF} = \frac{1}{2} \gamma (N_e^2 + N_e \sum_{j=1}^n \alpha_j N_{tj})$$

This equation is to be used when only homogeneous excitations are present. It does not work in our case where the triplet excitons are created by an intersystem crossing. Moreover, in these samples a large energy migration [15] makes the calculations for the energy distribution practically impossible. Because of this fact and because the delayed fluorescence emission process is independent of energy density we consider  $P$  as a macroscopic parameter.

A number of researchers [1, 4] have observed that the maximum of the delayed fluorescence intensity occurs in the same temperature range where the phosphorescence disappears. For our samples this phenomenon was also observed. We relate the variations in the delayed fluorescence intensity to the population of chrysene and DBA triplet states.

Experimentally measured energy states are shown in Fig. 4. The naphthalene non-radiative triplet exciton is located at  $21\,210\text{ cm}^{-1}$  [16].

Many of the kinetic rate constants needed for the delayed fluorescence intensity have been determined experimentally. For naphthalene-DBA (sample 1) and naphthalene-DBA-chrysene (sample 3) mixed crystals, the characteristics of the trap, *i.e.* depth, concentration and mean lifetime are known.

The deactivation rate constant  $K_e$  of the triplet exciton and the homofusion rate constant  $\gamma$  are supposed to be the same as for pure crystals. The  $K_e$  is deduced from the delayed fluorescence mean lifetime; thus,  $K_e = 3333\text{ s}^{-1}$  and  $\gamma = 2 \times 10^{-12}\text{ cm}^3\text{ s}^{-1}$  [17].

Two more assumptions are made in order to reduce the number of parameters: (i) the same detrapping rate constant is assumed for chrysene and for DBA; (ii) the same value is taken for the heterofusion and homofusion rate constant, namely  $\alpha_j = 1$  [9, 18, 19]. With these assumptions, for samples 1 and 2, the fit depends only on the detrapping rate constant  $K_o^\infty$  and on the exciton density  $P$ .

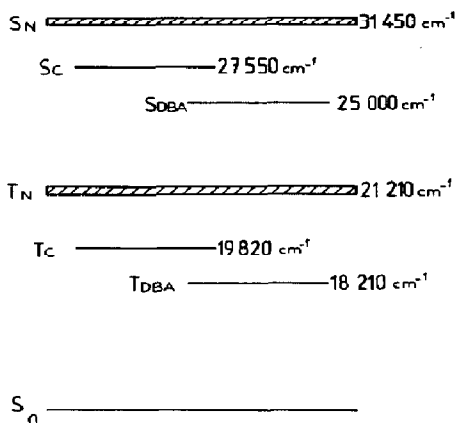


Fig. 4. Energy levels of naphthalene (host)-chrysene and DBA (guests) mixed crystal.

For naphthalene-DBA (sample 1) and for naphthalene-DBA-chrysene (sample 3) crystals the best agreement between calculated and experimental curves is obtained for  $K_0^\infty = 2 \times 10^{10} \text{ s}^{-1}$  and  $P = 1.5 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$ . These results are shown in Figs. 5(a) and 5(b).

As previously stated, the naphthalene-chrysene mixed crystal contains an unknown amount of DBA. With the above values of  $K_0^\infty$  and  $P$ , the fit with experimental curves depends only on the DBA concentration  $C$ . Figure 5(c) shows the best fit using  $C = 0.5 \times 10^{-6} \text{ mol DBA per mole of naphthalene}$ .

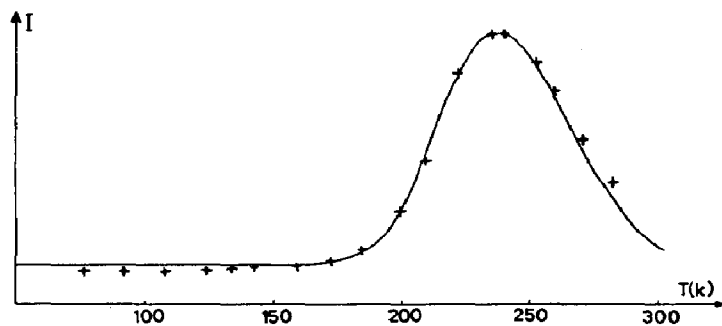
In an earlier paper, Talapatra and Misra [11] studied the naphthalene-chrysene crystal. We note that if the luminescence emissions are qualitatively similar, the relative intensities and the intensity variation as a function of the temperature are very different from those we have observed for the same crystal.

We observed that the delayed fluorescence intensity is strongly dependent on the DBA concentration. In this way the behaviour of delayed fluorescence as a function of the temperature reported by Talapatra and Misra can be deduced from the kinetics with  $C = 5 \times 10^{-6}$ . This result agrees with the experimental observations. The DBA delayed fluorescence and phosphorescence intensities are stronger than those of the naphthalene-chrysene crystals studied in this paper.

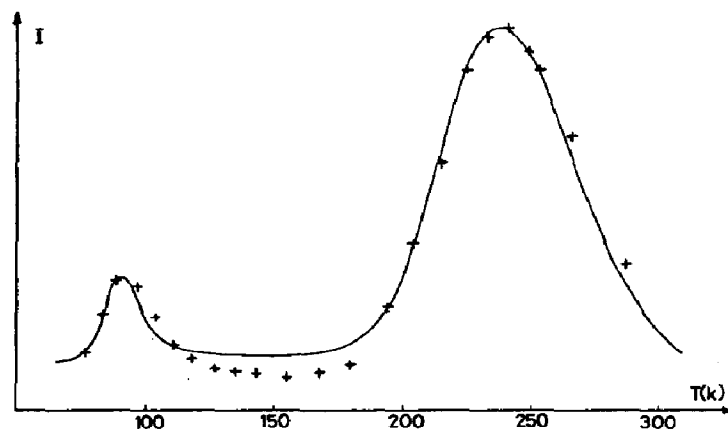
Talapatra and Misra [11] have concluded that in the temperature range 77 - 300 K a non-radiative trap exists at a depth of  $450 \text{ cm}^{-1}$  but its concentration is unknown. The trap mean lifetime, deduced from the delayed fluorescence, is estimated by these researchers to be 1.4 s. We have introduced this non-radiative trap into our kinetics with a concentration equal to the chrysene concentration. The delayed fluorescence dependence on the temperature is not affected.

## 5. Conclusion

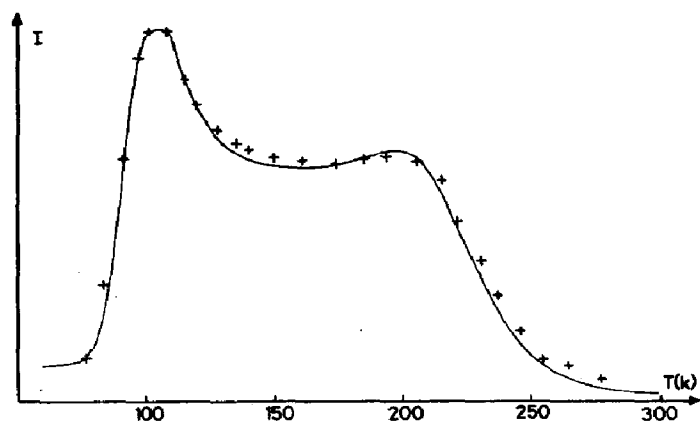
We have assigned the delayed fluorescence intensity behaviour of naphthalene (host)-chrysene and DBA (guests) mixed crystals to observed



(a)



(b)



(c)

Fig. 5. Experimental delayed fluorescence fitting for (a) naphthalene-DBA mixed crystal (sample 1), (b) naphthalene-DBA-chrysene mixed crystal (sample 3), (c) naphthalene-chrysene mixed crystal (sample 2): +, experimental values; —, theoretical curves.

traps. Trap depths correspond to chrysene and DBA energy states which are below the naphthalene exciton energy ( $\Delta E = 1390 \text{ cm}^{-1}$  for chrysene and  $\Delta E = 3000 \text{ cm}^{-1}$  for DBA).



According to a simple kinetic model the fit of the experimental curves is obtained in each case for  $K_0^\infty = 2 \times 10^{10} \text{ s}^{-1}$  and  $P = 1.5 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$ . The unknown DBA concentration in chrysene has been estimated to be  $0.5 \times 10^{-2}$  mol DBA per mole of chrysene.

We obtain good agreement between calculated and experimental curves for all our samples over the entire temperature range. These results justify the various approximations used in delayed-fluorescence calculations. However, because of these various approximations, the values deduced from the kinetic analysis must only be taken as orders of magnitude.

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