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## Energy Transfer by Excitons in a Tetracene-Doped Anthracene Crystal

By

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A new interpretation is proposed of experimental data found by Powell on fluorescence decay of donor and acceptor molecules in binary tetracene-anthracene solid solution. Intense direct excitation of acceptor molecules by X-rays is assumed and a new exact relation between fluorescence decay laws of acceptor and donor molecules is derived. Using this relation it is shown that the experimental data may be satisfactorily described under the assumption that the direct impurity excitation efficiency is about four orders higher than for molecules of the host substance. Such a difference may be explained by the impurity large capture cross section of charge carriers produced by X-rays.

Дана новая интерпретация экспериментов, проведенных Пауэлом с сотрудниками, по изучению законов спада флуоресценции акцепторных молекул и основного вещества в органических кристаллах. Главная идея состоит в возможности прямого возбуждения молекул акцептора при использованном в этих экспериментах возбуждении X-лучами. Получено новое точно соотношение связывающее законы свечения основного вещества и примеси. На основе этого соотношения и ранее полученного закона спада свечения основного вещества с учетом передачи энергии электронного возбуждения молекулам акцептора показано, что экспериментальные результаты можно удовлетворительно объяснить в предположении, что вероятность возбуждения молекулы примеси X-лучами примерно на четыре порядка превышает вероятность возбуждения молекулы основного вещества. Такое различие объясняется тем, что примесные молекулы могут обладать большим сечением захвата носителей заряда, генерируемых X-лучами высокой энергии, и высокой эффективностью многофоновых процессов при последующем переходе примесной молекулы в нижайшее возбужденное синглетное состояние.

### 1. Introduction

In the last few years the experimental results and their interpretation in the paper by Powell et al. [1, 2] have been widely discussed. This discussion was caused by the statement in [1, 2], that the behaviour of the acceptor and donor fluorescence decay laws  $n_D(t)$  and  $n_A(t)$  may be explained only on the basis of Förster's theory with extremely large donor-acceptor energy transfer radius  $R_0 = 108 \text{ \AA}$ , whereas the experimental value of  $R_0$  found in [3] from the overlap integral of light emission and absorption spectra is equal only to  $19 \text{ \AA}$ . It is clear that the assumption of the overlap integral being 50000 times larger than the measured one requires rather a serious reconsideration of the existing theory of sensitized fluorescence in solids.

Selsby and Swenberg [4] made an attempt to "modify" the exciton diffusion theory [5 to 7] and proposed the expression  $K = 4\pi DR_0 \exp(-t/\tau_D)$  for the exciton capture rate instead of the well-known formula  $K = 4\pi DR_0$ , where  $D$

is the exciton diffusion coefficient. Such an approach was criticized by Powell and Kepler [8] who showed its inconsistency. Elliot [9] also rejected the explanation proposed in [4] and presented his own version of the exciton diffusion theory introducing Wigner-Seitz cells of different volume and averaging the energy transfer rate over a random distribution of cell sizes in a crystal. This approach may be hardly justified because such an averaging procedure corresponds, in fact, to averaging over different impurity concentrations and, consequently, has no concern to the problem with a fixed acceptor concentration. Therefore, it is clear that the expressions for  $n_A(t)$  and  $n_D(t)$  found in [9] were incapable to describe the experimental data of [1].

Below we point out that the results of [1] may be explained with reasonable values of  $R_0$  and the exciton diffusion coefficient  $D$  if one assumes that the efficiency of direct excitation of tetracene molecules in an anthracene crystal by 600 keV X-rays is four orders of magnitude higher than that for host molecules. The reason for such an assumption may be the following.

X-rays produce both excited acceptor and donor molecules and charge carriers. Due to high electron and hole mobility ( $\mu \approx 1$  cm/Vs and  $D \approx 3 \times 10^{-2}$  cm/s [10]) the process of their migration and trapping by the acceptor molecules may be a very effective channel for optical excitation of these molecules.

From this point of view the mechanism of the sensitized fluorescence under X-ray irradiation may be considered crudely having two stages proceeding differently in time. The first stage (fast) is the generation of excited acceptor and donor molecules by electron-hole recombination. The second one (slow) is the diffusion and the resonance transfer of excitons to acceptor molecules. It is well-known that the quantum yield of sensitized fluorescence may approach unity at very low concentrations of acceptor molecules, i.e. a large fraction of excitons are trapped by acceptor molecules. By analogy one may assume that trapping of electron-hole pairs by the acceptor molecules at the first stage may be as efficient as the resonance trapping of localized excitons in the second stage.

Although one may think that in the interpretation presented below one unreasonably high parameter  $R_0$  in the Kepler-Powell theory has been replaced by another one, the assumption of high direct excitation efficiency of tetracene molecules by X-rays seems more reasonable because it does not require reconsideration of the existing theory of sensitized fluorescence in solids.

The high efficiency of charge carrier trapping by tetracene molecules may be revealed in experiments in the study of X-ray excited electron-hole recombination in molecular crystals like [10]. Such experiments seem to be of great interest.

## 2. Relation between the Host and Impurity Fluorescence Decay Laws

Let us find an exact relation between the functions  $n_A(t)$  and  $n_D(t)$ . These functions are expressed through the probabilities  $\varrho_n(t)$  and  $\varrho_m(t)$  to find the electronic excitation on the donor molecule  $n$  and on the acceptor molecule  $m$  in a binary solid solution as follows:

$$n_D(t) = \frac{1}{N} \sum_{\{n\}} \varrho_n(t), \quad n_A(t) = \frac{1}{N} \sum_{\{m\}} \varrho_m(t), \quad (1)$$

where  $N$  is the total number of molecules, and the line above denotes the averaging over the random distribution of impurity molecules in a crystal. Introducing  $G_D(t)$  and  $G_A(t)$ , the generation rates of excited donor and acceptor molecules by an external source, one may write the following kinetic equations for the functions  $\varrho_n(t)$  and  $\varrho_m(t)$ :

$$\left. \begin{aligned} \frac{d\varrho_n(t)}{dt} &= G_D(t) - \frac{\varrho_n(t)}{\tau_D} - \sum_{\{m\}} W_{nm}^{DA} \varrho_n(t) + \sum_{\{n'\}} W_{n'n}^{DD} (\varrho_{n'}(t) - \varrho_n(t)) , \\ \frac{d\varrho_m(t)}{dt} &= G_A(t) - \frac{\varrho_m(t)}{\tau_A} + \sum_{\{n\}} W_{nm}^{DA} \varrho_n(t) , \end{aligned} \right\} \quad (2)$$

where  $W_{nm}^{DA}$  and  $W_{n'n}^{DD}$  are the donor-acceptor and donor-donor rates of excitation transfer between molecules at crystal sites  $n$  and  $m$ , respectively.

Let us first consider a simple case when  $G_D(t) = \delta(t)$  and  $G_A(t) = 0$  ( $\delta(t)$  is the Dirac function). From (1) and (2) one obtains the following relation:

$$\frac{d}{dt} (e^{t/\tau_D} n_D^{(0)}(t)) = -e^{t(\frac{1}{\tau_D} - \frac{1}{\tau_A})} \frac{d}{dt} (e^{t/\tau_A} n_A^{(0)}(t)) . \quad (3)$$

To prove it we introduce the functions  $\tilde{\varrho}_n(t) = \varrho_n(t) \exp(t/\tau_D)$ ,  $\tilde{\varrho}_m(t) = \varrho_m(t) \times \exp(t/\tau_A)$  and using (2) formulate the equations

$$\left. \begin{aligned} \frac{d\tilde{\varrho}_n(t)}{dt} &= - \sum_{\{m\}} W_{nm}^{DA} \tilde{\varrho}_n(t) + \sum_{\{n'\}} W_{n'n}^{DD} (\tilde{\varrho}_{n'}(t) - \tilde{\varrho}_n(t)) , \\ e^{t(\frac{1}{\tau_D} - \frac{1}{\tau_A})} \frac{d\tilde{\varrho}_m(t)}{dt} &= \sum_{\{n\}} W_{nm}^{DA} \tilde{\varrho}_n(t) . \end{aligned} \right\} \quad (4)$$

In the first equation (4) the source  $G_D(t) = \delta(t)$  is taken into account by the initial condition  $n_D(0) = 1$  ( $n_A(0) = 0$ ). Multiplying equations (4) by  $1/N$ , summing the left-hand and right-hand sides over  $n$  and  $m$ , respectively, and averaging one obtains (3).

Taking into account the initial condition  $n_D(0) = 1$  and  $n_A(t) = 0$  from (3) we obtain

$$n_A^{(0)}(t) = - \int_0^t dt' e^{\frac{t'-t}{\tau_A}} \left[ \frac{n_D^{(0)}(t')}{\tau_D} + \frac{d}{dt'} n_D^{(0)}(t') \right] . \quad (5)$$

The expression in brackets on the right-hand side of (5) is proportional to the electronic excitation transfer rate from donor molecules to acceptor ones. Actually, in the absence of transfer  $n_D^{(0)}(t) = \exp(-t/\tau_D)$  and this expression becomes zero. The exponential  $\exp((t' - t)/\tau_A)$  describes the radiative decay of acceptor excitation created at the time  $t'$ .

It is easy to generalize the result (5) for a case when the generation rates  $G_D(t)$  and  $G_A(t)$  are arbitrary functions. We give the final result

$$n_A(t) = \int_0^t dt' e^{\frac{t'-t}{\tau_A}} G_A(t') - \int_0^t dt' e^{\frac{t'-t}{\tau_A}} \int_0^{t'} dt'' G_D(t'') \left[ \frac{n_D^{(0)}(t' - t'')}{\tau_D} + \frac{d}{dt'} n_D^{(0)}(t' - t'') \right] . \quad (6)$$

The first term in (6) describes the decay of the acceptor molecule excitation produced at their direct excitation by an external source. The second one

describes the decay of excited acceptor molecules created due to energy transfer from donor molecules. With  $n_D^{(0)}(t)$  the function  $n_D(t)$  may be expressed as

$$n_D(t) = \int_0^t G_D(t') n_D^{(0)}(t - t') dt'. \quad (7)$$

The explicit form of the function  $n_D(t)$  has been determined in a number of papers (see, for example, [5]) in the case of the dipole-dipole energy transfer with account for exciton diffusion in the crystal. In [7] the following simple interpolation formula for  $n_D^{(0)}(t)$  was proposed:

$$n_D^{(0)}(t) = \exp \left\{ -\frac{t}{\tau_D} - \frac{4\pi R_0^3}{3\Omega} c_A \sqrt{\frac{t}{\tau_D}} \left[ 1 + 1.15 \frac{l}{R_0} \sqrt{\frac{t}{\tau_D}} \right] \right\}, \quad (8)$$

where  $\Omega$  is the volume of the crystal elementary cell. This approximation of  $n_D^{(0)}(t)$  describes the results of a precise computation of  $n_D^{(0)}(t)$  with an accuracy of 15% for an arbitrary ratio of the exciton diffusion length  $l = \sqrt{D\tau_D}$  to the effective energy transfer radius  $R_0$  [7].

### 3. Comparison with Experiment

Formulae (6) to (8) may be used for calculating the functions  $n_D(t)$  and  $n_A(t)$ . For comparison with experiment information is needed on the following parameters: donor and acceptor molecule radiative lifetimes  $\tau_D$  and  $\tau_A$ , effective radius  $R_0$  of energy transfer, exciton diffusion length  $l$ , and generation rates  $G_D(t)$  and  $G_A(t)$ . Below we shall discuss in detail the laws of tetracene (acceptor) molecule fluorescence  $n_A(t)$  in an anthracene (donor) crystal  $n_D(t)$ , measured by Powell and Kepler [1] at relative impurity concentrations  $c_A = 10^{-6}$  and  $83 \times 10^{-6}$ . Let us determine the parameters needed from the following physical considerations:

1. The radiative lifetime of donor molecules  $\tau_D$  and the localized exciton diffusion length  $l$  may be extracted from the experimental data on the anthracene fluorescence decay law  $n_D(t)$ . In fact, at a sufficiently large exciton diffusion length  $l$  ( $l \gg R_0$ ) the value of decay time of donor molecules  $\tau$  is determined according to [7] by the following expression:

$$\frac{1}{\tau} = \frac{1}{\tau_D} \left[ 1 + 2.04 \frac{4\pi R_0^3}{3\Omega} \left( \frac{l}{R_0} \right)^{3/2} c_A \right]. \quad (9)$$

Introducing into (9)  $R_0 = 19 \text{ \AA}$  [3] and  $\tau = 3$  and 26 ns at  $c_A = 10^{-6}$  and  $83 \times 10^{-6}$  [1], respectively, one obtains from (9)  $\tau_D = 28.7$  ns and  $l = 1060 \text{ \AA}$ .

2. The way of  $\tau_A$ -determination proposed in [1] seems to us unconvincing. In [1] the value of  $\tau_A$  was considered a fitting parameter whereas it may be obtained directly from the data for  $n_A(t)$  at highest acceptor concentration, i.e. at  $c_A = 83 \times 10^{-6}$ . In fact, at this concentration the lifetime of excited donor molecules is very short due to rather fast donor-acceptor excitation transfer and is equal to about 3 ns. In this case the decay law of acceptor fluorescence will be simply  $n_A(t) \approx \exp(-t/\tau_A)$ . The value of  $\tau_A$  determined in such a way appears to be  $\tau_A = 16$  ns, that is somewhat larger than the value of  $\tau_A = 13$  ns assumed in [1]. A larger value of  $\tau_A$  permits to obtain a better description of the  $n_A(t)$  behaviour at large  $t$ .

3. In our opinion there is no reason at present to doubt the well-known procedure of  $R_0$ -determination from the light emission and absorption spectra

overlap integral (see the discussion of this problem in [11]). Therefore, for  $R_0$  we adopted the value  $R_0 = 19 \text{ \AA}$  in agreement with measurements of [3].

4. For an accurate calculation of the functions  $n_D(t)$  and  $n_A(t)$  one needs a detail form of the functions  $G_D(t)$  and  $G_A(t)$ , that would best describe the experimental arrangement. In view of [4] we chose  $G_D(t)$  in the form  $G_D(t) = \exp(-(t - t_0)/(\Delta t)^2)$  with  $t_0 = 2.5 \text{ ns}$  and  $\Delta t = 2.0 \text{ ns}$ . The function  $G_A(t)$  was chosen in the form  $G_A(t) = \alpha c_A G_D(t)$ , where  $\alpha$  is the ratio of direct excitation probabilities of acceptor and host molecules. In our computations  $\alpha$  is the only fitting parameter, the value of which was chosen to get the best coincidence of the theoretical and experimental curves for the functions  $n_D(t)$  and  $n_A(t)$ .

#### 4. Computation Results and Conclusions

The computation results for the functions  $n_D(t)$  and  $n_A(t)$  are shown in Fig. 1 and 2 at  $\alpha = 1.8 \times 10^4$ . It is seen that under the assumption of direct excitation of acceptor molecules by X-rays a rather satisfactory description of the experimental data [1] can be obtained without using a value of  $R_0$  many times exceeding the value found from the overlap integral of optical spectra. The value of  $\alpha = 1.8 \times 10^4$  does not seem to be in contradiction with the supplementary experimental evidence, found in [1]: at  $c_A = 10^{-5}$  about 50% of the total fluorescence intensity comes from tetracene, whereas the part of the directly excited tetracene molecules is only 18% at  $\alpha = 1.8 \times 10^4$  and  $c_A = 10^{-5}$ .

The process of exciton diffusion over donor molecules leads to the exponential form of the  $n_D(t)$  function. The essential feature of Förster-Dexter's theory is the nonexponential behaviour of the fluorescence decay curve for  $n_D(t)$ . But the data of [1], plotted in semilogarithmic scale, demonstrate the exponential

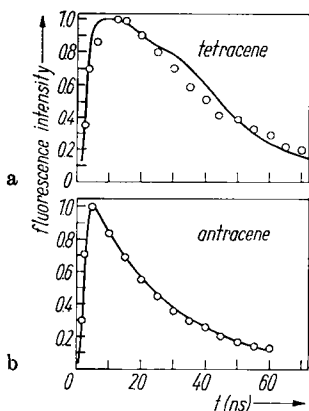


Fig. 1

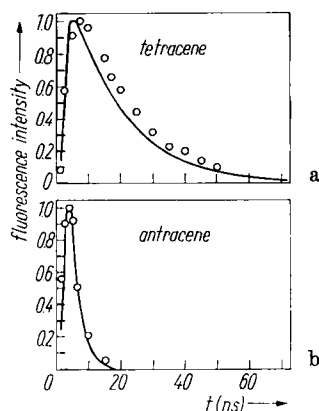


Fig. 2

Fig. 1. Time dependence of the fluorescence intensity in anthracene doped with 1 ppm tetracene. The points plotted are taken from [1]; the curves correspond to a)  $n_D(t)$  and b)  $n_A(t)$  calculated using formulae (6) to (8)

Fig. 2. Time dependence of the fluorescence intensity in anthracene doped with 83 ppm tetracene. The points plotted are taken from [1]; the curves correspond to a)  $n_D(t)$  and b)  $n_A(t)$  calculated using formulae (6) to (8)

character of  $n_D(t)$ . The data of [12] and [13] also confirm such a behaviour. This experimental evidence seems to exclude the use of Förster's theory with an extremely large  $R_0$  for the explanation of electronic excitation transfer from anthracene to tetracene impurity molecules in the experiment.

### References

- [1] R. C. POWELL and R. G. KEPLER, Phys. Rev. Letters **22**, 636, 1232 (1969).
- [2] R. C. POWELL, Phys. Rev. B **2**, 1159, 1207, 2090 (1970); **4**, 628 (1971).
- [3] Y. TAKAHASHI and M. TOMURA, J. Phys. Soc. Japan **31**, 1100 (1971).
- [4] R. G. SELSBY and C. E. SWENBERG, phys. stat. sol. (b) **50**, 235 (1972).
- [5] M. YOKOTA and O. TANIMOTO, J. Phys. Soc. Japan **22**, 779 (1967).
- [6] C. E. SWENBERG and W. T. STACY, phys. stat. sol. (b) **36**, 717 (1969).
- [7] S. I. GOLUBOV and YU. V. KONOBEEV, phys. stat. sol. (b) **56**, 69 (1973); **70**, 373 (1975).
- [8] R. C. POWELL and R. G. KEPLER, phys. stat. sol. (b) **55**, K89 (1973).
- [9] R. A. ELLIOTT, phys. stat. sol. (b) **67**, K65 (1975).
- [10] R. C. HUGHES, J. chem. Phys. **55**, 5442 (1971).
- [11] S. I. GOLUBOV and YU. V. KONOBEEV, phys. stat. sol. (b) **71**, 777 (1975).
- [12] M. D. GALANIN, S. D. KHAN-MAGOMETOVA, and Z. A. CHIGIROVA, Izv. Akad. Nauk SSSR, Ser. fiz. **39**, 1807 (1975).
- [13] M. TOMURA, E. ISHIGURO, and N. MATAGA, J. Phys. Soc. Japan **25**, 1439 (1968).

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