

# Singlet-Exciton Energy Transfer in Tetracene-doped Anthracene Crystals as Studied by Time-Resolved Spectroscopy

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The time-resolved sensitized fluorescence of tetracene-doped anthracene crystals following a two-photon picosecond-pulse excitation was investigated experimentally as a function of dopant concentration and temperature. Even at the optimum time resolution achieved in these experiments (about 5 ps) the time dependence of the host fluorescence was always purely exponential, that of the guest fluorescence a superposition of two exponentials. Thus no time dependence of the energy-transfer rate could be identified. The temperature dependence of the energy-transfer rate is explained tentatively in terms of a "hopping model" (hopping time  $t_h \approx 5.8 \cdot 10^{-14}$  s) and thermal reactivation from shallow exciton traps (trap depth  $43 \text{ cm}^{-1}$ ) in the vicinity of the guest molecules.

In pure anthracene crystals the intrinsic exciton lifetime (observed at 20 K) is  $(5.0 \pm 0.5) \text{ ns}$ . At higher temperatures it increases to about 15.5 ns at 300 K due to reabsorption processes. Below 20 K it decreases to about 1.5 ns at 1.6 K because of exciton trapping at shallow X-traps (trap depth  $23 \text{ cm}^{-1}$ ). When using conventional one-photon excitation exciton-exciton annihilation was observed with an annihilation constant  $\gamma_{ss} \approx 1.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ .

## 1. Introduction

The investigation of sensitized fluorescence is a well established method for the study of energy transfer processes in organic molecular crystals. Anthracene crystals doped with tetracene were the first systems to be studied in this regard. For the interpretation of the experimental results the so-called hopping model [1] has been quite successful. The applications of this model to various experiments in different crystals have been reviewed by Wolf [2]. More sophisticated theoretical models have been discussed extensively in various reviews [3–6].

Initiated by the early activities on time-resolved spectroscopy of the sensitized fluorescence in doped crystals [7] the question was posed whether the hopping model is adequate to explain the experimental observations. Starting from this model one can interpret the experiments in terms of a rate of energy transfer.

One of the basic problems in this context is the question whether a time-independent rate of energy transfer is adequate to account for the experimental results. Furthermore, if a time-dependence is ob-

served, is it correctly explained by the Chandrasekhar-Smoluchowski theory [8, 9] or are extended theories required such as a "generalized random walk" model, the "long-range resonance transfer" model [7] or the "generalized master equation" approach [5], and do they adequately account for the observations?

Since the influence of such time dependencies should reveal itself more significantly as the time resolution is improved, the progress in time-resolving spectroscopic techniques has recently stimulated considerable activities in the field of time resolved investigations of the sensitized fluorescence [10–13]. The results of these various efforts were quite contradictory. However, since the experimental parameters (temperature, guest concentration, excitation conditions) in the various experiments were different, it is very difficult to compare the different results.

In previous experiments we have attempted to obtain a complete set of experimental data for naphthalene doped with anthracene covering a wide range of temperature and concentration [11]. Whereas in the high and medium concentration limit the experiments could be interpreted using a time-independent energy transfer rate, the low-concentration, low-temperature results apparently re-

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quired the assumption of a time-dependent rate of energy transfer, formally equivalent to that used by Powell and coworkers. However, when attempting to interpret these results in the Chandrasekhar-Smoluchowski picture, it was necessary to assume that both, the trapping radius of the guest molecules and the diffusion constant were dependent on the guest concentration, a hypothesis which evidently is unreasonable.

The aim of the present work was to establish whether the time dependence of the sensitized fluorescence in tetracene-doped anthracene following a picosecond pulse excitation necessitated the assumption of a time-dependent rate of energy-transfer anywhere in the accessible range of temperature (1.6 to 300 K) and of concentration ( $1 \cdot 10^{-6}$  to  $2.3 \cdot 10^{-3}$  mole/mole). Since the anthracene excited-state lifetime is only about 5 ns, a high time resolution was required. In the present experiments an optimum time resolution of about 5 ps was established. The most important result of this systematic

study is that *at no concentration and at no temperature within the above mentioned limits the experimental results forced us to invoke a time-dependent rate of energy transfer.*

Based on some preliminary experiments we suppose that the apparent time dependence reported in [11], as mentioned above, must be attributed to a partial saturation of the guest molecules and a resulting exciton-excited-guest annihilation, even at low-intensity two-photon excitation [14]. Conclusive experiments concerning this point are currently in preparation.

## 2. Experimental Procedure

The experimental setup was virtually identical to the one described in detail in reference [15]. For convenience in Fig. 1 we repeat the schematic diagram of the apparatus:

Picosecond transients were studied by exciting the crystals with single pulses of a mode-locked Nd-

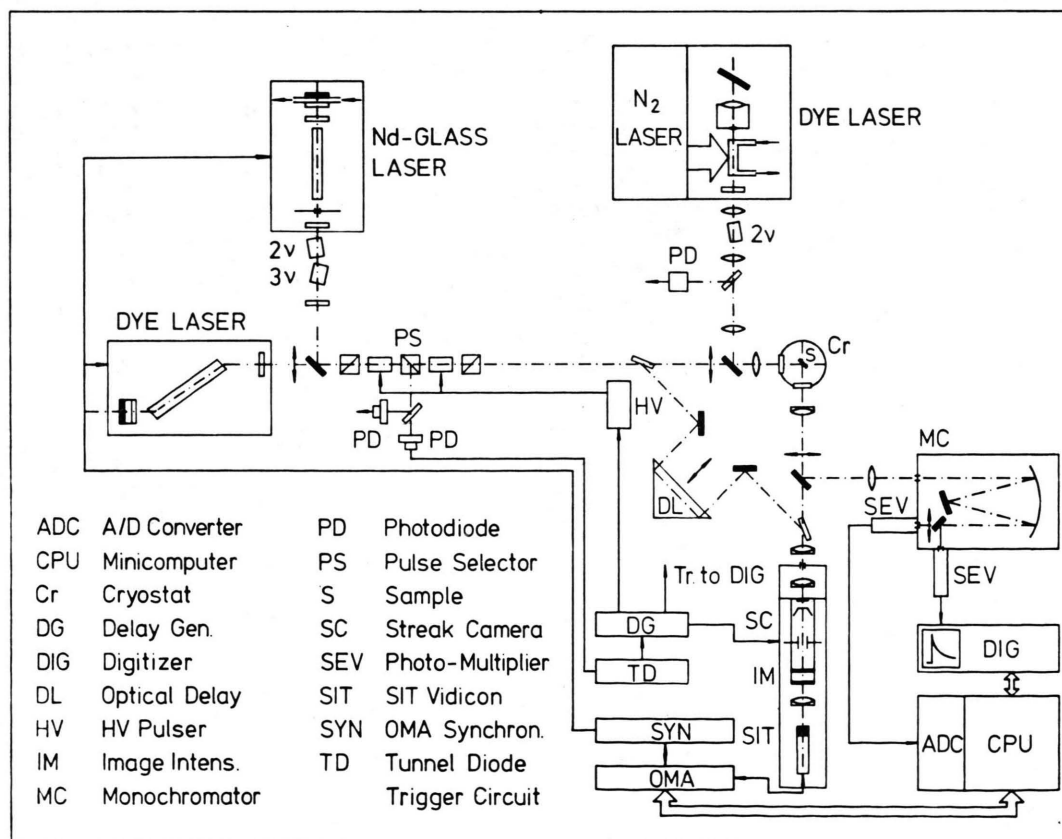


Fig. 1. Schematic diagram of the experimental setup.

glass laser (system 2000, JK) or with harmonics thereof. In some experiments we used single pulses from a passively mode-locked flash-lamp pumped dye laser (SUA 33, Electro Photonics) for excitation. The time dependence of the resulting fluorescence was recorded using a picosecond streak-camera (Imacon 675/II, Hadland) the output of which was monitored with an optical multichannel analyzer (1205 A with SIT-vidicon, PAR) and processed using an on-line computing system (2117 F, Hewlett Packard). The overall time resolution of this setup was 5ps (Nd-glass) and 10ps (dye-laser), respectively. The dynamical range at these resolutions was 24. Additional specifications of the setup are given in [15].

Nanosecond events were excited with a nitrogen-laser/dye-laser combination (M 100 and FL 100 A, Lambda Physics) and recorded using a fast photomultiplier (C 31024, RCA) and a transient digitizer (R 7912, Tektronix).

Stationary fluorescence spectra were studied by exciting the samples with a mercury high pressure lamp (HBO 200, Osram) and recording the spectra using a medium-resolution monochromator (HRP, 0.6 m focal length, Jobin Yvon) and a low-noise photomultiplier (6255 B, S 13 cathode, EMI). All stationary spectra reported in this work were corrected for the overall spectral response of the setup.

In the time resolving experiments host and guest fluorescence were separated using special filter combinations: When monitoring the host fluorescence a combination of a type 7-59 filter (Corning) and a GG 400 (Schott) was added in front of the detector, for the guest fluorescence a GG 445 (Schott) was combined with a saturated solution of  $\text{CuSO}_4$  in water (2 cm).

Sample temperatures between 1.7 and 300 K could be established using either a helium bath cryostat or a continuous-flow helium cryostat.

The crystals were grown by the Stuttgarter Kristall-Labor. The anthracene raw material was purified by sublimation and subsequent zone-refining (180 passes). Single crystals were grown using the Bridgman method. For the doped crystals tetracene was added to the melt at concentrations of  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  and  $10^{-6}$  mole/mole, respectively.

For the interpretation of the experimental results an accurate determination of the actual guest concentration in the sample is essential. This determination can be accomplished by determining the

quantum flux ratio of the guest and the host fluorescence, respectively, since this quantity is uniquely related to the guest concentration. However, since in previous publications [1, 16] conflicting results were reported for the relation between the quantum flux ratio and the guest concentration, a careful redetermination of this relation had to be performed. In these experiments first the quantum flux ratio of the particular sample under consideration was determined. To illustrate the procedure, Fig. 2 presents the fluorescence spectra of anthracene crystals doped with different amounts of tetracene. The spectra were obtained at 60 K and are corrected for the overall spectral response of the setup. We define the quantum flux ratio as

$$Q_G/Q_H = \int_G I_G(\bar{\nu}) d\bar{\nu} / \int_H I_H(\bar{\nu}) d\bar{\nu}, \quad (1)$$

where  $I(\bar{\nu})$  is the fluorescence intensity at wave number  $\bar{\nu}$ , the subscripts G and H symbolize guest and host, and  $\int_G$  or  $\int_H$  indicate an integration over the spectral ranges relevant for the respective fluorescence intensities ( $16\,800$  to  $20\,400\text{ cm}^{-1}$  for the guest fluorescence and  $20\,400$  to  $25\,000\text{ cm}^{-1}$  for the host fluorescence). Following the determination of this quantity for small samples of various dopant concentrations (2 mm diameter in order to avoid the influence of guest-concentration inhomoge-

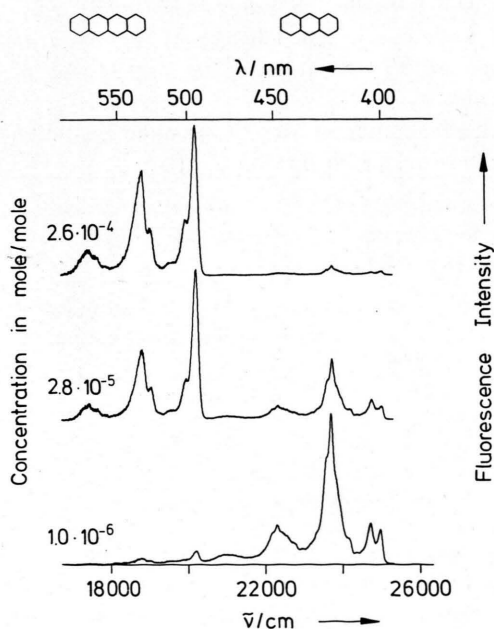


Fig. 2. Fluorescence spectra of tetracene-doped anthracene for various dopant concentrations at  $T = 60\text{ K}$ .



neities) these samples were dissolved in spectroscopic-quality n-heptane and the resulting absorption spectrum in the tetracene absorption range was compared to that of a solution of tetracene at a known concentration. In this way it was possible to relate the observed quantity  $Q_G/Q_H$  directly to the guest concentration in the sample

$$Q_G/Q_H = (9.8 \cdot 10^4 \pm 30\%) c_G, \quad (2)$$

where  $c_G$  is the guest concentration in mole guest/mole host. The limits of error quoted in (2) represent only the errors in the relative magnitude of the concentration of various samples, the absolute value may be off by up to a factor of two. (The result is in excellent agreement with that obtained earlier by Schmillen and Falter [16].)

### 3. Experimental Results

#### 3.1. Fluorescence Spectra of Pure Anthracene

It is well known that the fluorescence spectra of anthracene depend critically on the crystals quality and purity [17, 18] as well as on the excitation wavelength. In this section we compare the fluorescence spectra obtained with excitation light at 313 nm obtained from a mercury lamp and that obtained with a two-photon excitation with light from a pulsed dye laser ( $\lambda = 600$  nm). Figure 3 presents a comparison between the fluorescence spectra obtained in both cases. The labeling of the impurity lines given in Fig. 3 follows the assignment of Glockner and Wolf [17].

Several advantages of the two-photon excitation techniques are evident from Figure 3:

- (1) The broad background fluorescence, characteristic for samples of low crystallographic quality is significantly reduced.
- (2) No fluorescence of the X-traps X3 and X4 is observed when using two-photon excitation.
- (3) The fluorescence of defect B is reduced by a factor of 5.
- (4) Chemical impurities (series C, 2-hydroxyanthracene) show up only very weakly in the two-photon fluorescence spectrum.

These observations prove that the influence of both, chemical and structural defects on the fluorescence spectra is enhanced in the region near to the surface of the crystal. Therefore most of the time-resolved experiments were performed using a two-

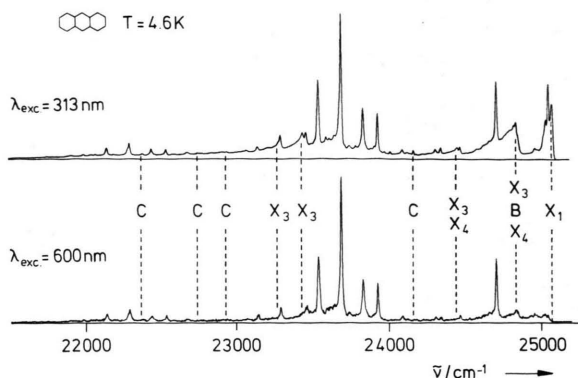


Fig. 3. Fluorescence spectra of pure anthracene at 4.2 K following one-photon excitation at  $\lambda_{exc} = 313$  nm and two-photon excitation at  $\lambda_{exc} = 600$  nm, respectively. The notation of the defect lines follow the assignment of Glockner and Wolf [17].

photon excitation with single pulses from a mode-locked dye laser. In this way a homogeneous bulk excitation was guaranteed thus avoiding undesired influence of both, surface defects and annihilation phenomena (see appendix). On the other hand, the influence of reabsorption is more pronounced than with conventional one-photon excitation. Therefore, for the interpretation of the experimental results reported in the following sections, this effect had to be taken into account. Finally errors in the lifetime measurements due to stimulated emission [19, 20] were eliminated by working below the threshold of the excitation power.

#### 3.2. Time Dependence of the Fluorescence of Pure Anthracene Crystals Following Two-Photon Pulse Excitation

The fluorescence decay of pure anthracene crystals is significantly different for one- and two-photon excitation, respectively. In this section we present results on the fluorescence decay of pure anthracene crystals following a two-photon excitation with single pulses from a mode-locked dye laser at a wavelength of 614.5 nm. It has been shown by Bergman and Jortner [21] that light at this wavelength induces a vibronically-allowed two-photon transition  $^1A_{1g} \longleftrightarrow B_{3u}^-$ . Using the two-photon "absorption cross section" of  $3 \cdot 10^{-49}$  cm<sup>4</sup> s per photon [21] and the maximum flux of  $10^{27}$  cm<sup>-2</sup> s<sup>-1</sup> available in our experiments one can estimate the two-photon absorption length to be about 0.8 cm. Thus the excitation density obtained in this way can be considered as a homogeneous bulk excitation, and the



resulting exciton density of about  $10^{16} \text{ cm}^{-3}$  is below the critical density, above of which annihilation processes become relevant. To exclude such effects the available photon flux was reduced at least by a factor of 10 in all two-photon induced experiments concerning the time dependence of the fluorescence of doped crystals.

Figure 4 presents some results of such experiments at various temperatures. At all temperatures one observes a purely exponential decay of the anthracene fluorescence following a two-photon pulse excitation. The decay time, however, decreases linearly with temperatures from 15.5 ns at 300 K to 9.7 ns and 6.2 ns at 150 K and 60 K, respectively, and approaches a limiting value of 5 ns at 20 K. Below 10 K the decay time drops steeply to about 1.5 ns at 1.6 K.

The weak temperature dependence of the observed decay time between 20 K and 300 K is caused by the temperature dependence of the spectral overlap between the absorption and the emission spectra. The temperature variation of the overlap factor  $S(T)$ , which is essentially the integral over the product of the normalized absorption and emission spectra [22], can be determined by comparing the one-photon induced (surface) and the two-photon induced (bulk) emission spectra [14] using the following technique: It can be shown that at a homogeneous two-photon bulk excitation the influence of reabsorption is independent of time. It can be splitted into a factor  $K$ , which depends only on the sample geometry and into the contribution due to the overlap between absorption and emission  $S(T)$ . For identical sample orientation and thickness

$K$  is a constant. The overlap factor  $S(T)$  can then be determined experimentally by comparing the steady state spectra at one and two-photon excitation [14]:

$$S(T) = \frac{\int F^{1\nu}(\bar{\nu}, T) d\bar{\nu}}{\int F^{2\nu}(\bar{\nu}, T) d\bar{\nu}}, \quad (3)$$

where  $F^{1\nu}(\bar{\nu}, T)$  and  $F^{2\nu}(\bar{\nu}, T)$  are the fluorescence spectra at one-photon and two-photon excitation, respectively. By applying this procedure we obtain for  $S(T)$  the respective numbers 0.22, 0.14, 0.05 and 0.01 at 300 K, 150 K, 60 K and 20 K. Thus at 20 K the influence of reabsorption on the observed decay time is negligible, and the measured value represents the intrinsic exciton lifetime. The gentle increase of the fluorescence decay time with temperature can be attributed to the change in the overlap factor, whereas the intrinsic lifetime is independent of temperature within the limits of error:

$$\tau_0 = 5.0 \pm 0.5 \text{ ns.}$$

The steep decrease in the observed fluorescence decay time below 20 K can be explained, if one assumes that there are short lived shallow traps for the excitons present in the crystal. An optimum fit of the predictions based on this model to the experimentally determined temperature dependence assigns a trap depth of about  $27 \text{ cm}^{-1}$  and a lifetime of about 1.5 ns to these traps. It is possible that these traps are identical with those from which the line labelled X1 in Fig. 3 originates ( $\Delta E(\text{X1}) = 23 \text{ cm}^{-1}$  [17]).

The fluorescence decay of pure anthracene crystals following a one-photon pulse excitation has been studied previously by various authors [12, 20, 23–27]. If this technique is used, the experimental observations are much more complicated, since the excitons are created close to the surface at a high concentration. This causes annihilation processes [28–31]. In order to avoid these complications in the experiments concerning the sensitized fluorescence of doped crystals we always used a two-photon excitation as described in this section. Results obtained on pure anthracene crystals when using one-photon pulse excitation are presented in the appendix.

### 3.3. Time Dependence of the Sensitized Fluorescence of Tetracene-Doped Anthracene Crystals Following Two-Photon Pulse Excitation

This section presents a summary of experimental observations obtained for the range of temperature

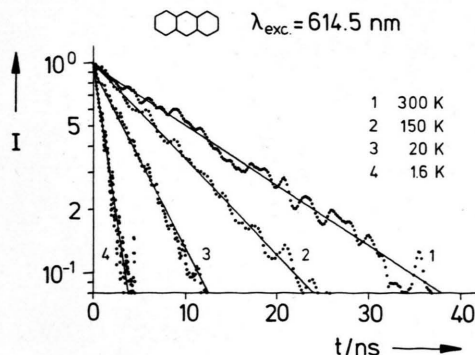


Fig. 4. Decay of the integral fluorescence of pure anthracene crystals following two-photon pulse excitation at various temperatures ( $\lambda_{\text{exc}} = 614.5 \text{ nm}$ , pulse duration: 10 ps, pulse energy:  $100 \mu\text{J}$ , initial exciton density:  $\leq 10^{16} \text{ cm}^{-3}$ ).

from 1.6 to 300 K and of dopant concentration from  $1 \cdot 10^{-6}$  to  $2.3 \cdot 10^{-3}$  mole tetracene per mole anthracene. The concentrations were always determined in situ on the particular sample by determining the quantum-flux ratio in the stationary spectra (see section 2).

Figure 5 presents as an example the respective time dependencies obtained on the sample with the highest dopant concentration ( $2.3 \cdot 10^{-3}$  mole/mole) at 1.6 K. The host-fluorescence (Fig. 5 a) rises within less than 10 ps, the overall response time of the setup. Following this the host fluorescence decays exponentially with a time constant of 70 ps. The full line in Fig. 5 a is a convolution of this exponential with the temporal response function of the entire setup.

The guest fluorescence (Fig. 5 b) rises exponentially with the host fluorescence decay time (70 ps) and then decays exponentially with a time constant of 14.6 ns. This decay process is too slow to show up on the time scale of this figure. Both curves in

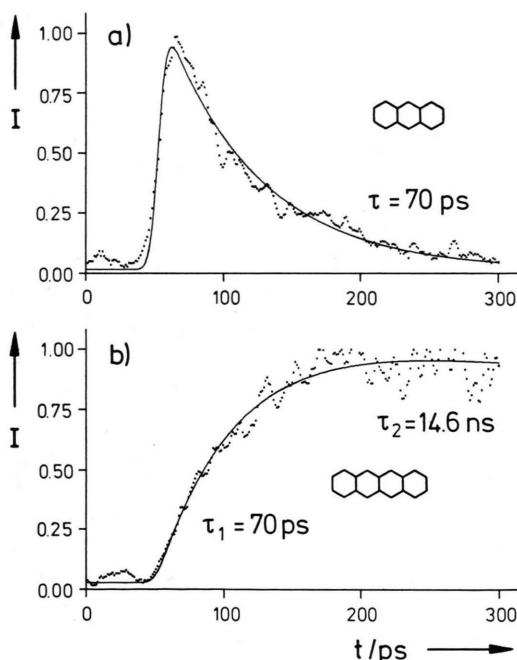


Fig. 5. Time dependence of the sensitized fluorescence of tetracene-doped anthracene ( $c_G = 2.3 \cdot 10^{-3}$  mole/mole) at 1.6 K following two-photon pulse excitation ( $\lambda_{\text{exc}} = 614.5$  nm, pulse duration 10 ps, pulse energy  $10 \mu\text{J}$ , initial exciton density  $10^{15} \text{ cm}^{-3}$ ). a) Host fluorescence; b) Guest fluorescence. The guest fluorescence rise time is identical to the host fluorescence decay time. The guest fluorescence decay is too slow to show up on the time scale of this figure.

this figure were obtained by averaging over 10 individual shots.

The time dependencies obtained at lower dopant concentrations are qualitatively similar to Figure 5. The rise time of the guest fluorescence is always identical to the host-fluorescence decay time, which at low concentrations approaches the decay time of the pure anthracene fluorescence. The decay time of the guest fluorescence is identical to the lifetime of the excited guest molecules. (The latter statement is based on measurements of the guest fluorescence decay following a selective excitation of the guest molecules with a laser pulse at 482 nm. The lifetime of tetracene molecules in their excited state turns out to depend only weakly on the temperature:  $(17.3 \pm 2) \text{ ns}$  at 300 K and  $(14.6 \pm 2) \text{ ns}$  at 1.6 K).

Figure 6 presents a compilation of the anthracene decay constants (which are identical to the tetracene rise times) for various concentrations obtained in the temperature range between 1.6 K and 300 K. We observed in all cases an exponential decay of the host fluorescence, and an exponential rise of the guest fluorescence followed by an exponential decay, provided the two-photon excitation intensity was low enough to avoid annihilation and guest saturation (see Section 4).

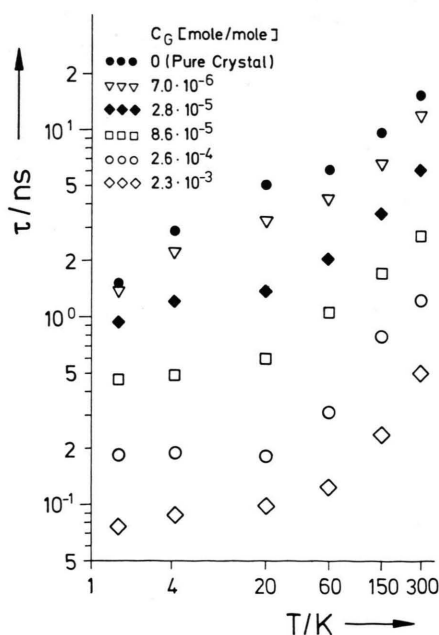


Fig. 6. Survey of the observed host fluorescence decay times (= guest fluorescence rise times) for various temperatures and dopant concentrations.

#### 4. Discussion

The basic aim for this work was to answer the question to which extent time-resolved studies of the sensitized fluorescence can contribute to the understanding of the energy transfer process. From this point of view the experiments performed on the pure anthracene crystal should be considered only as a source of necessary background information. Therefore in this section we will discuss only the results on the doped crystals. Comments required for the understanding of the results on the pure crystal have been included in the sections describing the experimental results.

The pertinent question through many different time-resolving experiments on the sensitized fluorescence was in principle the question, whether the host fluorescence decays exponentially and the guest fluorescence rises exponentially and decays also exponentially or if there are significant deviations from this behaviour [3]. A purely exponential time dependence is predicted by the most simple model, which assumes a rate of energy transfer from the host-excitons to the guest molecules which is independent of time. This model is illustrated in Fig. 7: Excitons are created by the excitation pulse at a rate  $I(t)$  via vibronic levels. Following their relaxation to the bottom of the exciton band (which is assumed to occur very rapidly), they can decay either via radiative or non-radiative processes ( $k_H^{0*}$  and  $k_H^{0'}$ , respectively) or they can transfer their energy to guest molecules (rate constant  $k_{HG}$ ). The radiative and non-radiative decay rates of the guest

molecules are labeled  $k_G^*$  and  $k_G'$ , respectively. Figure 7 also indicates the position of the respective energy levels for tetracene-doped anthracene. If  $k_{HG}$  is in fact independent of time the rate equations for the excited state populations can be solved easily, at least for the decay process following a homogeneous excitation with a short pulse. This yields for the host and the guest fluorescence intensities

$$I_H(t) = I_H^0 e^{-(k_H^{0*} + k_{HG})t}, \quad (4)$$

$$I_G(t) = I_G^0 [e^{-(k_H^{0*} + k_{HG})t} - e^{-k_G t}], \quad (5)$$

where

$$k_H^0 = k_H^{0*} + k_H^{0'}, \quad k_G = k_G^* + k_G', \quad I_H^0 = I_H(0)$$

and

$$I_G^0 = \frac{k_{HG}}{k_G - k_H - k_{HG}} \frac{k_G^*}{k_H^*} I_H^0.$$

It has been pointed out in great detail by Powell and Soos [7] that even in the most simple models (hopping or diffusion model)  $k_{HG}$  is not expected to be time independent. Numerous more sophisticated models for the energy transfer process have been proposed [3–6]. From the point of view of this work they have all in common that they predict time-dependent energy-transfer rates after a creation of host excitons with an (ideally  $\delta$ -shaped) light pulse. This feature on the other hand should change the observed time dependencies of host and guest fluorescence from the behaviour predicted by (4) and (5) and its influence should show up the more significant the better the time resolution is.

In the experiments reported in Sect. 3.3. no significant deviations from the simple exponential behavior could be detected, provided additional processes like annihilation or saturation were carefully avoided. Thus there is no evidence that time dependent contributions must be included into the energy-transfer rate. It is therefore reasonable to interpret the experimental observations on the basis of (4) and (5). In particular we can determine the energy transfer rate by comparing the anthracene-fluorescence decay time in the doped crystal with that in the pure crystal (see Figure 6). In the range of concentrations between  $1 \cdot 10^{-6}$  and  $2.6 \cdot 10^{-4}$  mole/mole this quantity is proportional to the guest concentration as predicted by a simple hopping model:

$$k_{HG} = k_{HG}^0 c_G. \quad (6)$$

In Fig. 8 the quantity  $k_{HG}^0$ , as defined in (6), is

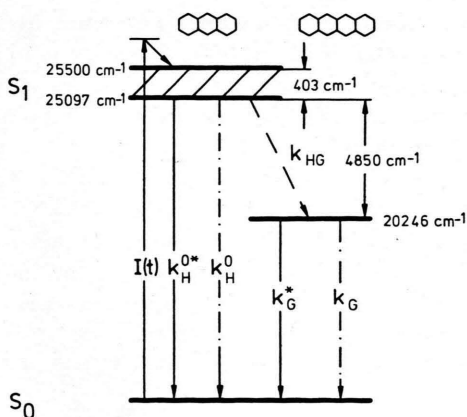


Fig. 7. Schematic energy level diagram of the electronic singlet state of tetracene-doped anthracene. The relevant transitions involved are indicated with their respective rate constants.  $k_H^{0*}$  and  $k_G$  are called  $k_H^{0'}$  and  $k_G'$  in the text.



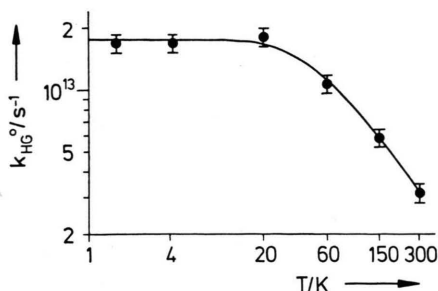


Fig. 8. Temperature dependence of the normalized energy-transfer rate,  $k_{HG}^0 = k_{HG}/c_G$  for tetracene-doped anthracene. The full line is obtained from fitting the solutions of the rate equations based on the model presented in Fig. 9 to the experimental time dependencies. (Fitting parameters:  $k_{HT} = 1/t_h = 1.7 \cdot 10^{13} \text{ s}^{-1}$ ,  $\varepsilon = 43 \text{ cm}^{-1}$ ).

plotted as a function of temperature. At low temperatures ( $T < 20 \text{ K}$ )  $k_{HG}^0$  approaches a limiting value of  $1.7 \cdot 10^{13} \text{ s}^{-1}$ , at higher temperatures it decreases significantly. At the highest concentration ( $2.3 \cdot 10^{-3} \text{ mole/mole}$ ) the energy transfer becomes less effective. This observation may be explained by assuming that at this concentration the guest molecules are no longer distributed homogeneously in the crystal.

Tentatively these observations might be interpreted in terms of a simple hopping model, although it should be emphasized that the only direct experimental information is the fact that no deviations from the exponential behavior of (4) and (5) can be detected within the experimentally accessible range of concentration, temperature and time resolution. This is equivalent to the statement that no time dependence of the energy transfer rate could be identified.

In the simple hopping model  $k_{HG}^0$  is directly related to the hopping time,  $t_h \approx 1/k_{HG}^0$ . If we restrict ourselves to the asymptotic low-temperature value, this yields  $t_h \approx 5.8 \cdot 10^{-14} \text{ s}$  or a diffusion constant  $D \approx a^2/6 t_h \approx 0.8 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . (For this rough estimate we have assumed that the step width is equal to the nearest neighbour distance  $a = 5.24 \text{ \AA}$ , and that the trapping radius  $R \approx a$ .)

The observed temperature dependence of  $k_{HG}^0$  may be accounted for by extending the model in the following way (see Fig. 9): We assume that the exciton trapping at the guest molecules takes place via a trapping energy level, which is slightly below the exciton level by an amount  $\varepsilon$ . As soon as the exciton falls into such a localized pre-trapping state, it is trapped in an "energy funnel", in which

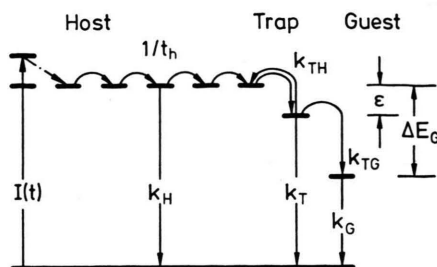


Fig. 9. Schematic energy level diagram for the exciton-trap-guest model defining the relevant rates involved in this model.

it can only decay into states with lower energy levels and a greater degree of localization, except if thermal reactivation via exciton-phonon interaction takes place and promotes the exciton into energetically higher mobile states. For the experiments reported in this work it is reasonable to make the following assumptions:  $k_H \approx k_T$ ,  $k_{TG} \approx k_{HT}$  and  $c_G \approx c_T \lesssim 10^{-4} \text{ mole/mole}$ . Using these assumptions it can be shown that the respective rate constants for trapping and detrapping are related to each other by

$$k_{TH} = k_{HT} \exp(-\varepsilon/kT). \quad (7)$$

The resulting rate equations for  $n_H$ ,  $n_T$  and  $n_G$  can be solved easily and the results can be compared to the experimentally observed time dependencies. In order to account for the observed temperature dependence  $\varepsilon$  is used as a fitting parameter. The full line in Fig. 8 has been obtained in this fashion by assuming that  $k_{HT} \approx k_{HG}^0 = 1/t_h = 1.7 \cdot 10^{13} \text{ s}^{-1}$  and  $\varepsilon \approx 43 \text{ cm}^{-1}$ .

(For the three-species rate equations a third exponential is expected in the solutions analogous to (4) and (5). However, it can be shown that under the present experimental conditions its contribution is too small to be detectable.)

Thus it is possible to account for the observed temperature dependence within the framework of the hopping model. The nature of the pre-trapping state is unknown. Possible candidates are, for instance, X-traps in the vicinity of the guest molecules or vibronic levels of the guest molecules.

## 5. Conclusions

In some of the previous work apparent deviations of the exponential behavior according to (4) and (5) have been reported [7, 11]. Most of the other

authors [10, 12, 13, 31–33] have reported pure exponentials. Powell and coworkers have interpreted their results in terms of a time-dependent rate of energy transfer. However, already in the work of Ref. [11] these ideas led to inconsistencies: Deviations from the exponential behavior were detected only at low temperatures ( $T \approx 60$  K) and at low dopant concentrations ( $c_G < 5 \cdot 10^{-6}$  mole/mole). In order to get agreement between the calculated and the measured curves unreasonable assumptions had to be made: Both, the trapping radii and the diffusion constant had to be assumed to be strongly dependent on the concentration. In view of the present results we have carefully reexamined the experimental conditions used in reference [11, 14]. Although exciton-exciton annihilation processes were carefully avoided by applying the two-photon excitation technique it is likely that at the lowest concentrations a partial saturation of the guest molecules and a subsequent annihilation of excitons with excited guest molecules occurred. This process might have led to an incorrect interpretation of the non-exponential behavior by attributing it to a time-dependent rate of energy transfer. Preliminary results seem to support this suspicion. A careful repeat of the experiments on naphthalene including the investigation of such non-linear effects is currently under way.

The fact that no time dependence of the energy-transfer rate is observed is not surprising in view of the present results: The experimental observations are consistent with the assumption of a trapping radius in the order of  $5 \text{ \AA}$  and a diffusion constant of about  $0.8 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . Using these numbers one can estimate that the  $\sqrt{t}$ -term in the Chandrasekhar-Smoluchowski picture should become comparable to the leading time-independent part only for times  $\leq 10^{-13} \text{ s}$ , a time scale which is far below the experimental time resolution.

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## Appendix

### Time Dependence of the Fluorescence of Pure Anthracene Crystals Following One-Photon Pulse Excitation

Contrary to the two-photon excitation experiments on pure anthracene crystals (Sect. 3.2.), when using one-photon excitation one observes in most cases a non-exponential decay. The details of this decay depend on the excitation intensity as well as on the wavelength of both, excitation and fluorescence. In this appendix we summarize the experimental results obtained at 300 K.

Figure 10 presents the fluorescence decay observed on the fluorescence line at 420 nm for different excitation intensities following an excitation with pulses obtained from a nitrogen laser (337 nm, 2.5 ns). There are strong deviations from an exponential behavior, which are the more pronounced the higher the excitation intensities are. The fitting curves were calculated using the procedure described below.

The reasons for the non-exponentiality of the fluorescence decay have been studied in numerous investigations [27–30]. It has been attributed primarily to non-radiative exciton-exciton annihilation processes which occur in the course of the exciton diffusion. For this bimolecular reaction it is reasonable to postulate that this process yields a time dependence of the exciton density  $n(z, t)$  following pulse excitation, which is governed by the following differential equation:

$$\frac{dn(z, t)}{dt} = -n(z, t)/\tau_0 - \gamma_{ss} n^2(z, t) + \alpha_0 I_0(t) e^{-\alpha_0 z} \quad (\text{A } 1)$$

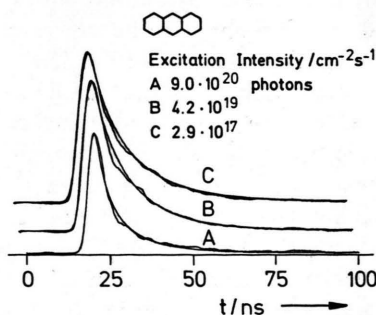


Fig. 10. Anthracene-fluorescence decay ( $\lambda = 420 \text{ nm}$ ) at 300 K for one-photon excitation ( $\lambda_{\text{exc}} = 337 \text{ nm}$ ) at various excitation intensities. The fitting curves are numerical solutions of Eq. (3) with  $\tau_0 = 12 \text{ ns}$ ,  $\gamma_{ss} = 1 \cdot 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  and  $\alpha_0 = 1 \cdot 10^4 \text{ cm}^{-1}$ .

In this equation  $\tau_0$  is the intrinsic exciton lifetime,  $\gamma_{ss}$  the annihilation constant,  $\alpha_0$  the absorption coefficient at the wavelength of the excitation light (intensity  $I_0$ , direction of incidence:  $z$ , perpendicular to the crystal surface). In (A 1) the influence of reabsorption does not show up directly. It can be accounted for by attributing different "effective decay times" to the individual fluorescence bands:

$$\begin{aligned}\tau_0(420 \text{ nm}) &= 12 \text{ ns}, \quad \tau_0(445 \text{ nm}) \\ &= \tau_0(470 \text{ nm}) = 22 \text{ ns},\end{aligned}$$

(see below).

Equation (A 1) can be solved in closed form only for  $\delta$ -shaped excitation pulses and spatially uniform initial exciton densities ( $\alpha_0 z \ll 1$ ) to yield

$$n(t) = n(0) e^{-(t/\tau_0)} / \{n(0) \gamma_{ss} \tau_0 (1 - e^{-(t/\tau_0)}) + 1\}. \quad (\text{A } 2)$$

Using one-photon excitation, however, one always creates strongly spatially inhomogeneous initial exciton densities. This fact can be accounted for, by solving (A 1) for a fixed coordinate  $z$ , according to the actual initial density  $n(z, 0)$  and superimposing the individual contributions for the whole fluorescent volume. Because in the experiments laser pulses of a nitrogen laser with finite pulse width were used, (A 1) was solved numerically for each  $z$ -value, by assuming a Gaussian excitation pulse of pulsewidth 2.5 ns.

Since the exciton density is proportional to the fluorescence intensity it is possible to test the calculated curves by comparing them to the experimentally determined fluorescence decay. The fitting curves given in Fig. 4 were calculated using the sketched procedure. Similar agreement between the experimentally observed fluorescence decay and the fitting curves was obtained for all anthracene fluorescence lines and all accessible excitation intensities, if the effective decay times quoted above and an annihilation constant,  $\gamma_{ss} = 1 \cdot 10^8 \text{ cm}^3 \text{ s}^{-1}$  were used. (Kenkre [5, 34, 35] has pointed out that this usual procedure may be seriously incorrect in the case of strong inhomogeneities. Thus the quoted number should be considered only as an estimate.)

A further complication in the evaluation of the experimentally observed time dependencies following one-photon pulse excitation is illustrated in Fig. 11: At low enough excitation intensities ( $n \leq 3 \times 10^{15} \text{ cm}^{-3}$ ) the anthracene fluorescence decay can be fitted with a superposition of two ex-

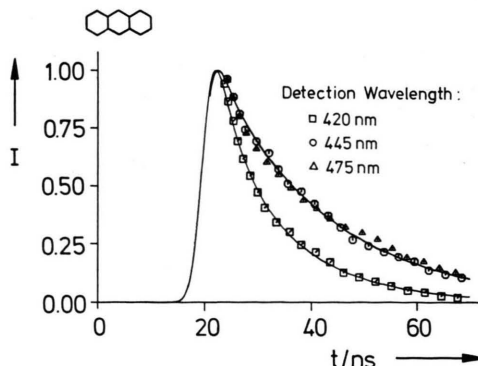


Fig. 11. Anthracene-fluorescence decay following low-intensity one-photon excitation detected on the three dominant fluorescence bands at 300 K ( $\lambda_{exc} = 337 \text{ nm}$ , exciton density  $< 10^{15} \text{ cm}^{-3}$ ).

ponentials within the limits of error, however, the time constants are different for different fluorescence bands: The longer (dominant) of the two time constants is 12 ns at 300 K for the emission band at 420 nm, whereas the corresponding time constants observed on the fluorescence bands at 445 nm and 475 nm has a value of 22 ns. Similar observations have been reported by various authors [13, 20, 23 – 26].

Qualitatively this observation can be explained using the following arguments (for a quantitative interpretation see Ref. [14, 25 – 27, 36]): Immediately following the pulse excitation excited molecules exist only in a thin layer at the surface of the crystals (about  $10^{-4} \text{ cm}$ ). When they decay via photon emission the front of the excitation moves into the bulk of the crystals due to reabsorption processes caused by the spectral overlap between absorption and fluorescence spectra. Since reabsorption processes are much more important for the line at 420 nm than for those at longer wavelengths (because of the stronger overlap), this results in a reduction of the intensity of the line at 420 nm compared to that of the longer-wavelength lines in the course of the motion of the excitation front into the crystal. Thus, due to the initially inhomogeneous exciton production, the short wavelength line decays faster than those at longer wavelengths, a fact, which partially cancels the familiar prolongation of the observed decay time, which results from reabsorption processes. This effect can be treated quantitatively by adding a reabsorption term, which depends on the fluorescence wavelength and the



spatial distribution of the excited states. However, since in this work the experiments relevant for the energy transfer have been performed using two-photon excitation, this procedure is not outlined here.

For the interpretation of the annihilation experiments it is sensible to use the "effective decay times" quoted above, since they describe the time evolution of excited molecules which contribute to the fluorescence in the respective spectral range.

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