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Delayed Fluorescence and Triplet Lifetime in Tetracene Crystals

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In crystalline tetracene the combined energy of two triplet excitons slightly exceeds the energy of the lowest singlet state (2.4 eV) (1). Therefore delayed fluorescence (DF) should be observable (2). Groff, Avakian, and Merrifield (3) have confirmed this recently. The present note reports on the lifetime of triplet excitons in tetracene crystals which can be inferred from the time decay of DF after excitation with a laser pulse.

Sublimation grown crystals, 50 to 100  $\mu\text{m}$  thick, were mounted in a cryostat under vacuum ( $10^{-6}$  Torr) or under an inert atmosphere. Measurements were done between 220 and 300  $^{\circ}\text{K}$ . Light of a giant pulse ruby laser generated a uniform concentration of triplet excitons via direct  $S_0 - T_1$  absorption.<sup>1)</sup> The intensity was varied with neutral density filters. DF-light emitted from the crystal passed through a light guide and was detected with a RCA 6655 A photomultiplier connected to an oscilloscope. The time constant of the circuit was less than 1  $\mu\text{s}$ . Combined cutoff and interference filters (Schott) provided spectral separation of exciting and emitted light. Background emission in the absence of a crystal was negligible.

After cessation of the laser pulse DF is observed. Its spectral distribution is identical with the fluorescence spectrum of crystalline tetracene (4, 5). Fig. 1 shows a typical decay curve. It consists of an initial hyperbolic part and an exponential tail. It can be described in terms of the familiar kinetic equations (2)

$$[\dot{T}] = -\beta[T] - k_t [T]^2 \quad (1)$$

and

$$\Phi = \frac{1}{2} f \eta k_t [T] \quad (2)$$

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1)  $T_1$  formation via the  $S_1$ -state populated by double photon absorption can be neglected as evidenced by the quadratic intensity dependence of DF.

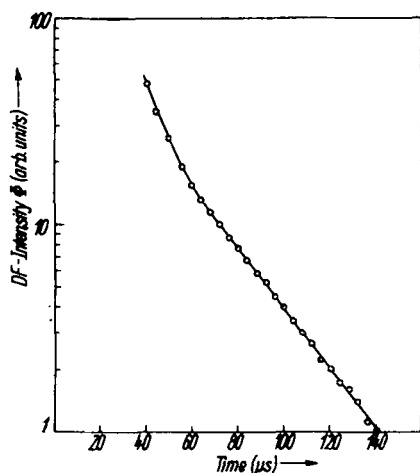


Fig. 1

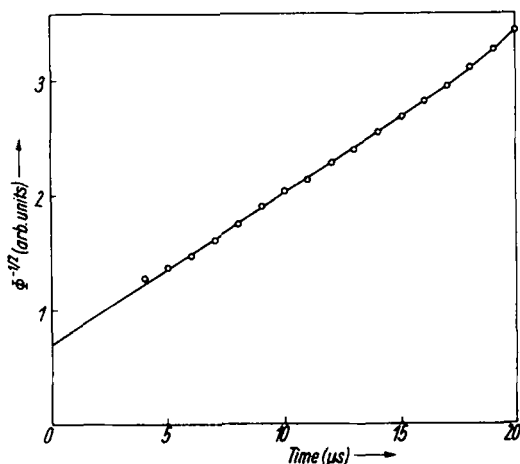


Fig. 2

Fig. 1. Decay of the delayed fluorescence emitted from a tetracene crystal after laser excitation

Fig. 2. Reciprocal square-root of DF intensity vs. time

$[T]$  is the concentration of triplet excitons,  $\beta^{-1} = \tau$  their lifetime,  $\gamma_t$  the total rate constant for bimolecular triplet reaction,  $f$  the fraction of triplet encounters leading to formation of an  $S_1$  state,  $\eta$  the quantum yield for fluorescence and  $\Phi$  the intensity of DF. Surface quenching can be neglected since the thickness of the crystal is large compared with the diffusion length of triplet excitons ( $l = 0.4 \mu\text{m}$ ) (6). In the limit  $\beta n \gg \gamma_t n^2$ , i.e. low excitation density or an observation time  $t > \beta^{-1}$ , solution of equations (1) and (2) <sup>2)</sup> yields

$$\Phi(t) = \frac{1}{2} f \eta \gamma_t n_o^2 \exp\left(-\frac{t}{2\tau}\right). \quad (3)$$

The quadratic relationship between  $\Phi$  and  $n_o$ ,  $n_o$  being proportional to the excitation  $I$ , was verified. Analysis of a series of decay curves obtained with different crys-

2) More accurately triplet formation via fission of singlet states (see. (1) and (9)) generated by TT-reaction must be taken into account. This leads to a correction factor  $(1-f)$  for  $\gamma_t$  at room temperature.

tals gave an average triplet lifetime  $\tau = (58 \pm 5) \mu\text{s}$  in fairly good agreement with a previous estimate (6). Between 220 and 300 °K no temperature dependence of  $\tau$  was found. However,  $\Phi$  showed the expected increase (4) as the temperature was lowered.

Since the triplet lifetime in anthracene crystals is known to depend on crystal purity and perfection the question arises whether or not the above value for  $\tau$  refers to an intrinsic radiationless transition. At present no definite answer can be given. The fact, however, that a polycrystal of low mechanical quality gave the same value for  $\tau$  seems to indicate that imperfections do not play an important role in the triplet decay process. Furthermore, the ratio of the triplet diffusion lengths in anthracene and tetracene is about 60. This means that the concentration of quenching centers required to reduce  $\tau$  by a given factor is about three orders of magnitude higher in tetracene than it in anthracene. It is unlikely that the "quality" of the crystals used in the present investigation is three orders of magnitude less than that of good anthracene crystals. However, since for tetracene in solid solution  $\tau = 800 \mu\text{s}$  has been reported (7), a substantial medium effect on the triplet lifetime must be present if  $58 \mu\text{s}$  represents an intrinsic value for crystalline tetracene.

For short times DF-decay is determined by triplet-triplet annihilation. From equations (1) and (2) it follows:

$$\left( \frac{\Phi}{\Phi_0} \right)^{-1/2} = 1 + n_0 \gamma_t t = 1 + \alpha_{ST} \gamma_t I t. \quad (4)$$

$n_0$  denotes the initial triplet concentration,  $\alpha_{ST}$  the singlet-triplet absorption coefficient,  $I$  the photon density at the crystal. Fig. 2 shows the experimental verification. With  $I = (8 \pm 2) \times 10^{17} \text{ quanta cm}^{-2}$  the slope of the straight line yields  $\alpha_{ST} \gamma_t = (1.9 \pm 0.3) \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . Assuming  $\alpha_{ST} = 3 \times 10^{-4} \text{ cm}^{-1}$ ,  $\gamma_t$  becomes  $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . This value is between those reported by Pope et al. (8) and Groff et al. (3). An independent measurement of the triplet concentration  $n_0$  which is necessary to determine  $\gamma_t$  more precisely is underway.

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