

## TRANSFER OF EXCITATION ENERGY IN ANTHRACENE TO NEW-TYPE EXCITONS

E. L. Frankevich and B. M. Romyantsev  
 Institute of Chemical Physics, USSR Academy of Sciences  
 Submitted 25 February 1969  
 ZhETF Pis. Red. 9, No. 7, 424-428 (5 April 1969)

The known types of excited states in anthracene single crystals are the singlet and triplet molecular excitons, the study of which has been the subject of many papers (see, for example, [1]). In molecular crystals, as noted by Lyons [2], there may be another type of exciton, with charge transfer (or of the Wannier type). Investigations by one of the authors with co-workers, devoted to the study of the influence of magnetic field on the photoconductivity [3, 4] and delayed fluorescence [5, 6] of anthracene, lead to the conclusion that excitons with charge transfer are produced when free electrons and holes recombine. The electrons and holes themselves can be produced in the anthracene during the course of annihilation of two triplet molecular excitons [4]. In connection with this conclusion, the authors have undertaken an investigation of the diffusion of this new type of excitons and the energy transfer by them. The investigation was carried out with single crystals grown from chromatographically treated anthracene purified by zone melting. An "excitation detector" layer, containing tetracene molecules, was deposited on the rear surface of the single crystal with area 40 mm<sup>2</sup>. It is known [7] that these molecules luminesce when excited at energies higher than 2.35 eV. The anthracene single crystal, with initial thickness 3 mm, was excited with flashes of 5 msec duration from the side opposite to that of the detector. Light with wavelengths 3900 - 4100 Å was used. A photomultiplier was used to register the delayed fluorescence  $L_s$  of the anthracene-plus-detector system. The separation of the crystal-excitation processes and the registration of the delayed fluorescence were effected by a phosphoroscope described in [8]. Inasmuch as the fluorescence of the anthracene occurred predominately at 4200 Å, and that of the tetracene at 5000 Å, we could register either the delayed fluorescence of the tetracene  $L_{st}$  (using OS-11 or ZhS-18 filters), or the total delayed fluorescence of the anthracene and tetracene  $L_{sa} + L_{st} \approx L_{sa}$ . The excitation of the detector alone produced practically no delayed fluorescence. The intensities  $L_{st}$  and  $L_{sa}$  were measured at 0.4 msec after the termination of the excitation pulse. Figure 1 shows a plot of  $L_{st}/L_{sa}$  against the crystal thickness (curve 1). The thickness was varied by successively cleaving the illuminated surface of the crystal along the ab plane. The exciting-light intensity (I) in these experiments was such that the triplet molecular exciton produced by inter-combination transitions from the singlet excitons were lost in the annihilation processes ( $I \gg 10^{15}$  quanta/cm<sup>3</sup> sec). In this case  $L_{sa} = I$ . Curve 2 of Fig. 1 was obtained under the same conditions as curve 1, but for the case when the excitation detector was separated from the rear surface of the crystal by an air gap of approximately 0.01 cm. It is seen that in the latter case the ratio  $L_{st}/L_{sa}$  is not zero, but does not depend on the crystal thickness d.

Our interpretation of the observed change of  $L_{st}/L_{sa}$  with d (curve 1) is that when  $d < 1$  mm the excitons with charge transfer, generated by the light near the illuminated surface of the crystal, reach the rear surface and excite the tetracene molecules. The form of curve 2 indicates that the tetracene is also excited by other processes (mainly, apparently, by

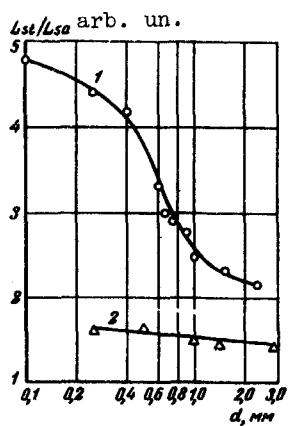


Fig. 1

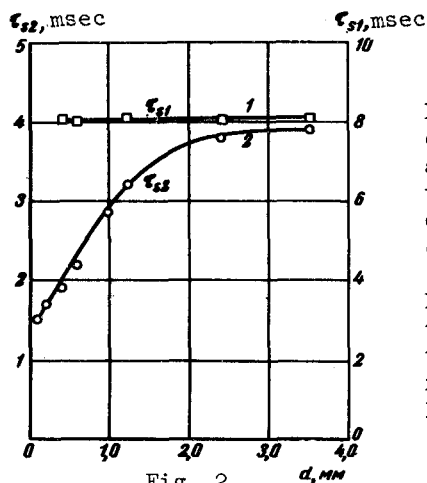


Fig. 2

Fig. 1. Intensity ratio  $L_{st}/L_{sa}$  of delayed fluorescence of tetracene and anthracene vs. anthracene-crystal thickness: 1 - excitation detector in contact with crystal surface, 2 - no contact.

Fig. 2. Characteristic times  $\tau_{s1}$  and  $\tau_{s2}$  of delayed fluorescence vs. crystal thickness at different exciting-light intensities: 1 - low intensity,  $L_{sa} \sim I^2$ , 2 - high intensity,  $L_{sa} \sim I$ .

the delayed fluorescence of the anthracene), but this excitation is practically independent of the crystal thickness.

One of the mechanisms of energy transfer to the tetracene can, in principle, be the diffusion of the triplet molecular excitons, accompanied by triplet-pair annihilation near the rear surface of the crystal. In this case, singlet excited states of the anthracene will be produced and will give up their energy to the tetracene. Arguments against the mechanism of the remote energy transfer observed by us are the following facts: we investigated the influence of the thickness of the anthracene single crystal (without the detector) on the characteristic decay time of the delayed fluorescence of the anthracene at different excited-light intensities  $I$ . It is known that at low  $I$  loss of triplet molecular excitons occurs in monomolecular processes, and that the delayed fluorescence  $L_{sa}$  nearly equals  $I^2$  and decreases exponentially, after the termination of the excitation, with a characteristic time  $\tau_{s1} \approx \tau_T/2$ , where  $\tau_{si}$  is the lifetime of the triplet molecular excitons. At high values of  $I$ , the lifetime of the triplet is short and is determined by the annihilation processes:  $L_{sa} \sim I$ , and the decay of  $L_{sa}$  is either hyperbolic (if the lifetime of the triplet exceeds the lifetime of the other excited states produced upon annihilation of the triplets) or exponential with a characteristic time  $\tau_{s2}$  equal to the lifetime of the excited states produced upon annihilation of the triplets (if this lifetime is larger than the lifetime of the triplets) [8]. Figure 2 shows how the thickness of the crystal influences  $\tau_{s1}$  and  $\tau_{s2}$ . Curve 1 was plotted at an excitation intensity such that  $L_{sa} \approx I$  and the decay of the delayed fluorescence is exponential. According to the conclusions of [8], this decay is determined by the lifetime of the triplet excitons with charge transfer. The thickness of the crystal, according to Fig. 2, influences only  $\tau_{s2}$ , from which it follows that the excited states produced upon triplet annihilation, i. e., excitons with charge transfer, have a much larger diffusion length than the triplet molecular excitons. (We recall that the direct products of the annihilation of the triplets are, according to [4, 6, 8], a hole and an electron, and excitons with charge transfer are produced upon their recombination. But at high exciton concentrations the lifetime of the electrons and holes with respect to recombination is much shorter than the lifetimes of the excitons, and does not come into play in the kinetics of the delayed fluorescence). This conclusion agrees

with the obtained diffusion length of the triplet molecular excitons, which, according to [9, 10], equals  $10^{-3}$  cm, much less than the crystal dimensions employed by us.

Thus, the results of the present investigation show that in anthracene there exist long-lived highly mobile excited states, which are produced by recombination of electrons and holes (by annihilation of triplet molecular excitons), and which apparently are triplet excitons with charge transfer and are characterized by the following parameters: lifetime 4 msec, diffusion length  $\approx 0.03$  cm, and energy  $E > 2.35$  eV.

- [1] R. Knox, *Exciton Theory* (Russ. Transl.), Mir, 1966.
- [2] L. E. Lyons, *J. Chem. Soc.*, 5001 (1957).
- [3] E. L. Frankevich and E. I. Balabanov, *ZhETF Pis. Red.* 1, No. 6, 33 (1965) [*JETP Lett.* 1, 169 (1965)].
- [4] E. L. Frankevich and I. A. Sokolik, *Fiz. Tverd. Tela* 9, 1945 (1967) [*Sov. Phys.-Solid State* 9, 1532 (1968)].
- [5] E. L. Frankevich and B. M. Romyantsev, *ZhETF Pis. Red.* 6, 553 (1967) [*JETP Lett.* 6, 70 (1967)].
- [6] E. L. Frankevich and B. M. Romyantsev, *Zh. Eksp. Teor. Fiz.* 53, 1942 (1967) [*Sov. Phys.-JETP* 26, 1102 (1968)].
- [7] J. Ferguson, *Austr. J. Chem.* 9, 160 (1956).
- [8] E. L. Frankevich and B. M. Romyantsev, *Phys. Stat. Sol.* 30, 329 (1968).
- [9] V. Ern, P. Avakian, and R. E. Merrifield, *Phys. Rev.* 148, 862 (1966).
- [10] M. Levin, J. Jortner, and A. Szoke, *J. Chem. Phys.* 45, 1591 (1966).

#### FLUCTUATION STRUCTURE OF A GIANT LIGHT PULSE AND ITS VARIATION WHEN PASSING THROUGH A NON-LINEAR ABSORBER

N. G. Basov, Yu. A. Drozhbin, P. G. Kryukov, V. B. Lebedev, V. S. Letokhov, and Yu. A. Matveets

P. N. Lebedev Physics Institute, USSR Academy of Sciences  
Submitted 27 February 1969  
*ZhETF Pis. Red.* 9, No. 7, 428-432 (5 April 1969)

1. Great interest attaches to an investigation of the process of formation of ultra-short pulses of light in a laser with a nonlinear absorber [1]. In [2], attention was called to the important role which may be played by intensity fluctuations of multimode radiation in the formation and development of ultrashort pulses in such a laser. Such fluctuations are the result of interference of radiation with random phases in a very large number of modes.

In the present investigation we used apparatus with high temporal resolution ( $10^{-11}$  sec) to observe fluctuations of multimode radiation of a ruby laser, and the process of separation of the most intense fluctuation peaks in multiple passes through a nonlinear absorber (cryptocyanine).

2. The experimental setup is shown in Fig. 1. The source of the multimode radiation was a ruby laser (1) Q-switched by a Kerr cell (pulse duration 15 - 20 nsec, resonator length 60 cm, width of emission spectrum 1 - 2  $\text{cm}^{-1}$ ). An amplifier using a ruby crystal (2) made it possible to regulate the pulsed radiation power.

A system of two diaphragms (3) of 1 mm diameter, spaced 1.5 meters apart, produced a wave that was plane within the diffraction limitations. With the aid of two parallel mirrors (4) ( $R = 64\%$ , distance 1.5 meters) the light pulse was made to pass several times through two cells with cryptocyanine solution (5). To compensate for the loss in the mirror and in the