INVESTIGATION OF THE MECHANISM OF CARRIER PRODUCTION IN ANTHRACENE BY USING THE EFFECT OF VARIATION OF PHOTOCONDUCTIVITY IN A MAGNETIC FIELD

E. L. FRANKEVICH and I. A. SOKOLIK

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor December 15, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 1189-1195 (May, 1967)

The variation of the photoconductivity of anthracene single crystals in a magnetic field is investigated. The relative contributions of singlet and triplet molecular excitons to carrier-production processes can be varied by employing intermittent illumination. The relative change of the photocurrent in a magnetic field, $\Delta i/i$, is zero if light pulses of duration shorter than 0.1—1 msec are employed. This indicates that short light pulses do not result in filling of ortho- and para-states of the charge-transfer excitons with an equal probability. These states are responsible for the variation of photoconductivity in a magnetic field. With growth of the light pulse duration $\Delta i/i$ tends to the value obtained with continuous illumination. This signifies that triplet molecular excitons which combine with either singlet or triplet excitons, participate in the carrier generation.

THE first investigations of the effect of the change of photoconductivity of single crystals of anthracene in a magnetic field[1,2] have shown that when the crystal is illuminated through a transparent electrode, application of a magnetic field causes a decrease in the photocurrent. The relative change in the photocurrent, $\Delta i/i$, increases from zero with increasing light intensity, reaching a limiting value of ~8%. The change of the photoconductivity in the magnetic field was attributed in[2] to the shift of the ψ-functions of the para- and ortho-states with m = 0 of the positronium-like charge-transfer excitons of the transport (Wannier excitons). Recently direct experimental proof has been obtained for the existence of transfer excitons in anthracene[3]. It must be noted that, unlike the positronium atoms, there can be no mixed ψ-functions of the ortho- and para-states of transfer excitons in a magnetic field, if the effective masses (and consequently the magnetic moments) of the electron and of the hole are equal, for in this case the total-spin and magnetic-moment operators commute. This pertains not only to the S-state but also to the higher excited states of the transfer excitons. The fact that the change in the photoconductivity in the magnetic field is observed as a result of mixing of the ψ-functions of the ortho- and para-states is evidence of presence of a magnetic moment both in ortho- and in the para-state of the transfer exciton. Inasmuch as the lifetimes of the excitons in the

ortho- and para-states are different, a change in the total stationary concentrations of the excitons can take place in a magnetic field. The change will be negative only if the stationary concentration of the ortho-excitons (with the longer lifetimes) with m = 0 is higher in an illuminated sample in the absence of a magnetic field than that of the para-excitons. It was indicated in[2] that this is possible if the source of the transfer excitons is such that it populates with equal probability their ortho- (with m = 0) and para-states. With this, since the lifetime of the excitons is longer in the ortho-state than in the para-state, the stationary concentration of the former will be larger. It was proposed[2] that such a source may be provided by molecular-exciton recombination which produces either transfer excitons directly, or free carriers which subsequently recombine to synthesize the transfer excitons.

The present paper is devoted to an experimental investigation of the processes that lead to a predominant population of the ortho-states of the transfer excitons.

To check on the hypothesis concerning the nature of the processes of transfer-exciton formations, we have used the method of intermittent photoionization in a magnetic field, which has made it possible to vary the relative roles of the singlet and the triplet molecular excitons in the formation of the carriers and to trace the corresponding
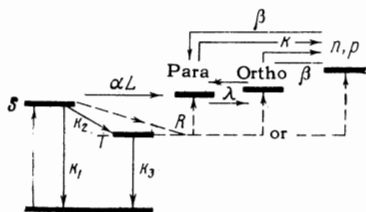
FIG. 1. Transitions between excited and ionized states. The dashed lines denote possible ways of equally-probable population of the ortho- and para-states of the transfer excitons in recombination processes. The notation is given in the text.

variations of the magnetic effect ($\Delta i/i$).

Figure 1 shows a level and transition scheme illustrating the possible mechanisms for the formation of transfer excitons and carriers. If the transfer excitons are produced only from the singlet excitons $^1S_0$, then they have equal stationary concentrations in the ortho- and para-states[1][2]. Recombination of molecular excitons can result, with equal probability, in either ortho- (with m = 0) or para- transfer excitons. It is easy to show that their stationary concentrations in the presence of the singlet and recombination sources will not be equal to each other. The magnetic effect, $\Delta i/i$, is determined, assuming the mechanism indicated in Fig. 1 for the formation and recombination of the carriers, by the relative difference in the filling of the ortho- (with m = 0) and para-states of the transfer excitons:

$$4\frac{\Delta i}{i} = \frac{\Delta n}{n_{\psi_0}} = \frac{R/4\tau_t}{aL(\lambda + k/4) + R(\lambda + k/4 + 1/4\tau_t)}$$
$$= \frac{AR}{BaL + CR}. \tag{1}$$

In formula (1), $\Delta n = n_{\psi_1} - n_{\psi_0}$ is the difference of the stationary concentrations of the excitons in the ortho- (m = 0) and para-states; R is the rate of recombination of the molecular excitons, which leads to the appearance of transfer excitons (or to the appearance of free carriers); aL is the rate of filling of the para-states of the transfer excitons from the singlet source (L—intensity of the incident light); τ_t—lifetime of the transfer excitons in the para-state prior to the annihilation with formation of a singlet exciton; k—rate constant of the dissociation of transfer excitons with formation of free carriers; λ—rate constant of the ortho—para transition. In the derivation of this formula it was assumed that $\tau_t \ll \tau_0$, where τ_0 is the lifetime of

---

[1] Inasmuch as they do not produce a magnetic effect here, our conclusions will be valid also in the case when the single molecular excitons produce carriers directly, for example, by dissociating on the impurities.

the excitons in the ortho-state. As follows from (1), the presence of only the singlet source (R = 0) leads to $\Delta i/i = 0$; inclusion of the recombination source leads to the appearance of a magnetic effect which reaches a limiting value $R \gg aL$.

An investigation of the dependence of $\Delta i/i$ on L in[2] has confirmed the general form of (1). The use of intermittent photoionization in the present work has made it possible to vary independently the recombination and the singlet sources of transfer excitons.

According to the scheme shown in Fig. 1, the stationary concentrations of the molecular excitons can be expressed in the following manner: $n_S = k_1^{-1}L$ and $n_T = Lk_2/k_1k_3$ (neglecting triplet-triplet annihilation). The rate of formation of the transfer para-excitons from the singlet source is $aL = a'n_S$, where a' is the rate constant for the formation of transfer excitons from singlet excitons.

The rate of formation of transfer excitons in recombination is given by

$$R_{ST} = \gamma_{ST}'(k_2/k_1^2k_3)L^2 \text{ for } S+T \text{ recombination,}$$
$$R_{TT} = \gamma_{TT}'(k_2/k_1k_3)^2L^2 \text{ for } T+T \text{ recombination,}$$
$$R_{SS} = \gamma_{SS}'k_1^{-2}L^2 \text{ for } S+S \text{ recombination.}$$

In these formulas γ' are the rate constants for carrier production in the corresponding recombination processes.

If the sample is illuminated with rectangular light pulses of duration τ and repetition period T, then the ratio of the average concentrations of the triplet and singlet molecular excitons does not change if only linear exciton-annihilation processes occur. However, in view of the fact that the molecular excitons form transfer excitons (or carriers) in second-order processes, the ratio of the rates of filling of the states of transfer excitons from the recombination and singlet sources becomes a function of τ and T. For intermittent illumination formula (1) is rewritten in the form

$$\frac{\Delta i}{i} = \frac{Af(\tau, T)R/aL}{B + Cf(\tau, T)R/aL}, \tag{2}$$

where

$$f(\tau, T) = \frac{(R)_{int}}{(aL)_{int}} \frac{aL}{R}.$$

The form of the function f(τ, T) is determined by the kinetics of accumulation and annihilation of the molecular excitons. In first-order annihilation of molecular excitons the average value of aL under intermittent illumination conditions will be

$$(aL)_{int} = aL\tau/T. \tag{3}$$

Under the same conditions we have

$$(R)_{int} = R\frac{\tau}{T}\left[1 - \frac{t}{\tau}(1 - e^{-\tau/t})\right] \qquad (4)$$

and consequently

$$f(\tau, T) = 1 - \frac{t}{\tau}(1 - e^{-\tau/t}). \qquad (5)$$

We see therefore that $f(\tau, T)$ tends from zero to unity with increasing τ, and when $\tau = t$ (t—lifetime of the molecular exciton: $t = 1/k_1$ for singlet excitons and $t = 1/k_3$ for triplet excitons) we have $f(\tau, T) = e^{-1}$.

If the transfer excitons (or carriers) are produced by recombination of singlet molecular excitons $(S + S)$, then $f(\tau, T)$ approaches unity when $\tau \gtrsim 10^{-8}$ sec; for the processes $S + T$ and $T + T$, this will occur when $\tau \sim 10^{-2}-10^{-3}$ sec.

It should be noted that at high light intensities (more than 10^{13} quanta/cm³sec) the loss of triplet excitons in anthracene is accompanied by first-order processes with mutual annihilation of the triplet excitons[4,5]. Under these conditions, the lifetime of the triplet excitons becomes a function of their concentration (and consequently, in the case of intermittent illumination, also a function of τ). The function $f(\tau, T)$ has in this case a more complicated form than (5), but its main characteristics remain the same: it increases from zero to unity with increasing τ, and its magnitude is commensurate with unity at $\tau = t$. If the triplet excitons are lost predominately in annihilation processes, then their stationary concentration becomes proportional to $L^{0.5}$, and consequently under these conditions $R_{ST} \sim L^{1.5}$ and $R_{TT} \sim L$.

PROCEDURE

We used single crystals grown at NRC (Canada) from a melt of chromatographically-treated and zone-purified anthracene. We used also crystals obtained from the melt in the Laboratory of X-ray Structure Analysis of the Institute of Inorganic Elementary Compounds of the USSR Academy of Sciences. The crystals were grown from synthetic anthracene recrystallized from alcohol. Photoconductivity was measured with direct current in sandwich-type samples (volume conductivity). The samples, whose thickness was 0.5—1.5 mm, were placed in the gap of an electromagnet. The photocurrent i was measured with the magnetic field turned off. The changes in the photocurrent Δi were registered after turning on a magnetic field (H = 3000 Oe). This field strength corresponded to the maximum possible magnetic effect. Three types of illuminated electrode were used: a grid
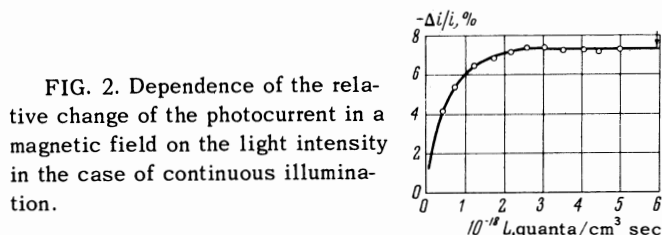
FIG. 2. Dependence of the relative change of the photocurrent in a magnetic field on the light intensity in the case of continuous illumination.

covered with silver paste, a sputtered semitransparent layer of aluminum, and a liquid contact constituting 0.1 M solution of Na_2SO_4 in water. The second electrode was in all cases silver paste covering on the sample.

The samples were illuminated with a 400-watt incandescent lamp, and also with a DKSSh–1000 lamp. A set of filters was used to separate the 3000—4200 Å spectral region, and in most cases the 7000—11000 Å region was also present. The total light flux was measured with an actinometer. The area of the illuminated electrodes was ~ 0.3 cm² for the solid electrodes and 0.1 and 0.2 cm² for the liquid ones. The light producing the photoconductivity was absorbed in a layer $\sim 10^{-4}$ cm thick, corresponding to an average energy-absorption rate of 5×10^{18} quanta/cm³sec (the calculation was made for $\lambda = 3700$ Å, maximum light intensity, and attenuation of the intensity in the crystal by a factor of e). A rotating disc with a variable-width slit was used to produce intermittent illumination. The disc rotated at 20—40 rpm. The pulse duration was determined with the aid of a photocell and an oscilloscope. Periodic pulses of 10^{-6} sec duration were generated with an IFK-120 lamp.

The photocurrent was measured with an ÉMU-3 electrometric amplifier equipped with a potentiometer circuit (to measure changes of large photocurrents). The stability of the photocurrent made it possible to measure its variation within 0.05%. The measurements were made in air; control experiments in vacuum did not lead to noticeable changes in the results.

RESULTS

Figure 2 shows the relative change of the photocurrent, $\Delta i/i$, against the light intensity (continuous
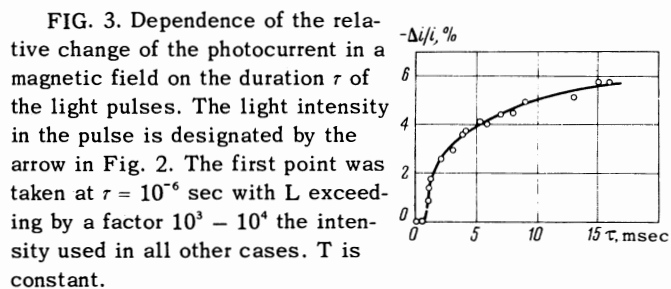
FIG. 3. Dependence of the relative change of the photocurrent in a magnetic field on the duration τ of the light pulses. The light intensity in the pulse is designated by the arrow in Fig. 2. The first point was taken at $\tau = 10^{-6}$ sec with L exceeding by a factor $10^3 - 10^4$ the intensity used in all other cases. T is constant.

illumination). This curve was obtained with single-crystal anthracene and a liquid contact. The crystal voltage was 300 V, and the positive potential was on the illuminated side of the crystal. Figure 3 shows a plot of $\Delta i/i$ against the duration of the illumination pulses, obtained under the same conditions. The intensity of the light incident on the crystal during the time of the pulse was ~6 × 10^{18} quanta/cm^3sec, and corresponded to the point marked by the arrow in Fig. 2. The form of the plot of $\Delta i/i$ against τ was practically the same for different crystals and electrodes. The shortest employed pulse duration was 10^{-6} sec. Even when the light intensities exceeded the values used in all other cases by 10^3—10^4 times there was no magnetic effect here.

Since the magnetic effect is connected with the influence of the magnetic field on the rate of carrier production, it is significant that the lux-ampere characteristics of the crystal, taken at different illumination conditions (constant and intermittent), were identical. The measurements of the average photocurrent through the sample obtained as functions of the light intensity for constant and intermittent illuminations (for different τ) have shown that they are actually described by a single law. This result enables us to compare magnetic effects registered under different illumination conditions.

DISCUSSION OF RESULTS

The main conclusion that can be drawn from the absence of the magnetic effect when light pulses of duration is shorter than 0.1—1.0 msec are used is that long-lived triplet molecular excitons take part in the generation of the carriers (or of the transfer excitons)[2]. The f(τ, T) curve, the form of which was determined from the experimental dependence of $\Delta i/i$ on τ with the aid of Eq. (2), is shown in Fig. 4. The same figure shows the f(τ, T) curve calculated from Eq. (5) for different values of t. We see that the forms of the calculated and experimental curves do not agree. It follows therefore that the kinetics of accumulation of excitons is not described by the exponential dependence assumed in the derivation of (5).

---

[2]The triplet molecular excitons are at present the only type of exciton whose lifetime lies in the region 10^{-3} sec. It is possible, however, that the triplet transfer excitons are also long-lived, but even then their existence would be revealed in experiments with intermittent illumination only in the case when the recombination of these excitons plays a role in the photoconductivity.
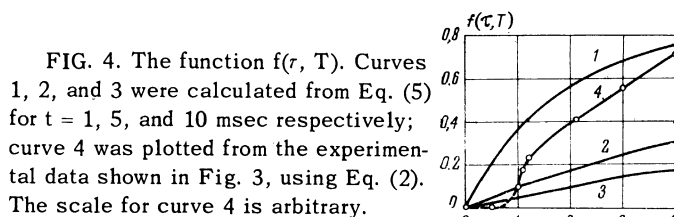

FIG. 4. The function f(r, T). Curves 1, 2, and 3 were calculated from Eq. (5) for t = 1, 5, and 10 msec respectively; curve 4 was plotted from the experimental data shown in Fig. 3, using Eq. (2). The scale for curve 4 is arbitrary.

We have noted earlier that at high light intensities the triplet excitons are lost not only as a result of nonradiative decays, but also through mutual annihilation[4,5]. The function f(τ, T) becomes too complicated to be expressed exactly in analytic form, but its main features can be understood from the following considerations: in the presence of annihilation the lifetime of the triplet excitation becomes a function of the concentration and consequently of τ. With increasing τ, the time t, which at first is equal to $1/k_3$, becomes equal to $1/(k_3 + r\tau)$, where r is a proportionality coefficient which approximately relates n_T and τ. The decrease of t with increasing τ, as follows from (5), produces an inflection on the f(τ, T) curve in the region where the loss of triplet excitons through annihilation becomes commensurate in rate with the nonradiative decay of the excitons. Such an inflection was actually observed on the experimental f(τ, T) curve (Fig. 4). It was also noted that when light of high intensity is used, the inflection shifts towards smaller τ. This indicates that under our conditions the loss of triplet molecular excitons is essentially due to their mutual annihilation.

Thus, we arrive at the conclusion that triplet excitons take part in the process of carrier production (or production of transfer excitons) in anthracene. At those light intensities for which the recombination creation of carriers becomes predominant (> 10^{13} quanta/cm^3sec according to the data of Kearns[4]), the triplet excitons themselves are lost predominantly through the annihilation process. Unfortunately, an analysis of the experimental f(τ, T) curve does yields no clue as to whether the second partner in the recombination process that produces the carriers is the triplet or the singlet exciton. The results can be interpreted in different fashion when both free carriers and transfer (excitons (which then disintegrate into free carriers) are produced in the recombination process. It should be noted that while there are theoretical grounds for expecting the triplet recombination products to be transfer excitons[6], there is no direct experimental information.

CONCLUSIONS

1. The use of the method of intermittent illumination in the investigation of the magnetic effect has confirmed the hypothesis, advanced in[2], that the process leading to equally-probable population of the ortho- (with m = 0) and para-states of the transfer excitons is recombination.

2. It is shown that at least one of the excitons participating in the recombination process leading to the direct formation of carriers (or transfer excitons) is the triplet molecular exciton.

The authors are grateful to Professor W. G. Schneider (Canada) and also Professor A. I. Kitaĭgorodskiĭ and his co-workers for supplying the anthracene single crystals.

[1] E. L. Frankevich and E. I. Balabanov, FTT 8, 855 (1966), Soviet Phys. Solid State 8, 682 (1966).

[2] E. L. Frankevich, JETP 50, 1226 (1966), Soviet Phys. JETP 23, 814 (1966).

[3] G. A. Gerhold, J. Chem. Phys. 45, 1889 (1966).

[4] D. Kearns, J. Chem. Phys. 39, 2697 (1963).

[5] H. Sternlicht, G. C. Neiman, and G. W. Robinson, J. Chem. Phys. 38, 1326 (1963).

[6] J. Jortner, S. A. Rice, J. L. Katz, and S. Choi, J. Chem. Phys. 42, 309 (1965).