

PHOTOGENERATION OF CURRENT CARRIERS IN CRYSTALLINE TETRACENE
IN A MAGNETIC FIELD

B. S. YAKOVLEV, L. I. NOVIKOVA, and E. L. FRANKEVICH

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

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The effect of a magnetic field on the photoconductivity of a tetracene film is investigated. Comparison of the results with the published data on the effect of a magnetic field on the fluorescence of tetracene shows that the effect of the field on the photocurrent is due to at least two different processes. One of these processes is connected with the "sensitivity" of fluorescence to the magnetic field, and the other is apparently connected with the participation of Wannier-type excitons in the generation of current carriers. With decreasing temperature, the contribution of the first process to the variation of the photocurrent in a magnetic field decreases, whereas the contribution of the second process increases.

SEVERAL papers^[1-3] were dedicated to the investigation of the effect of a magnetic field on the photoconductivity of tetracene, where the variations of the magnitude of the photocurrent were several per cent in fields of $H \sim 2$ kG. It was shown^[2] that this effect was connected with the influence of the magnetic field on the process of carrier photogeneration. At present, however, the nature of this influence has not yet been completely clarified. It is known that the photogeneration of carriers in tetracene is through excitons.^[4] Therefore the influence of a magnetic field on the rate of arbitrary processes in which excitons take part may, in principle, explain the changes in the photocurrent. Shortly after the influence of a magnetic field on the photoconductivity of several concentrated aromatic substances^[1] was detected, an assumption was put forward^[5] that this effect is connected with the participation of Wannier-type excitons in the generation of the carriers. The lifetimes of these excitons was found to change in a magnetic field. Lately, in investigations of the influence of a magnetic field on the luminescence of molecular crystals,^[6-9] it became necessary to consider other processes "sensitive" to the magnetic field. One of these processes may be the formation of a singlet exciton during the annihilation of two triplet excitons,^[6] i.e., the inverse process of the decay of a singlet exciton into two triplet excitons.^[8]

In the present paper, on the basis of temperature and kinetic investigations of the effect of a magnetic field on the photoconductivity of tetracene, we discuss the role of different excited states in the process of carrier formation and in the "sensitivity" of the photocurrent to a magnetic field.

EXPERIMENT

The photoconductivity was measured on tetracene films 2-5 μ thick. The films were placed between two aluminum electrodes. The preparation of the specimens was described in an earlier paper.^[10] Brand KhCh (chemically pure) tetracene was twice recrystallized in xylene and sublimated in vacuum. The irradiation

of the specimens was made by monochromatic light in the wavelength range $380 < \lambda < 600$ nm. The light was passed through the semi-transparent positive electrode. The light intensity was 10^{11} - 10^{14} photons/cm² \times sec. The photocurrent was measured in a vacuum of 10^{-4} Torr. The specimen was placed in a specially constructed cell so that its temperature could be raised from 90°K to 310°K. In this temperature range the lux-ampere characteristics were linear; the dependence of the steady-state photocurrent on temperature showed an exponential character. The calculated activation energy of the photocurrent per kT was found to be 0.09-0.02 eV and within these limits was independent of the wavelength of the exciting radiation. A magnetic field up to 2 kG was set up by a direct-current electromagnet.

RESULTS

Figure 1 shows different types of observed time dependences of the change $\Delta I(t)$ of the steady-state photocurrent I on the applied magnetic field. It is necessary to stress that when the light intensity was increased from L by an amount ΔL ($\Delta L/L \sim 10^{-2}$), the photoresponse curve always had the form of curve 3. The appearance of a current "spikes" in the $\Delta I(t)$ curve of type 1 is not caused by an electric pulse induced when the current in the magnet is switched on and is independent of the mutual orientation of H and I . The relative magnitude of the "spike" $(\Delta I_0 - \Delta I_{st})/\Delta I_{st}$, where ΔI_0 and ΔI_{st} are the maximum and steady-state variations of photocurrent, respectively, decreased with increasing L or with increasing voltage V applied

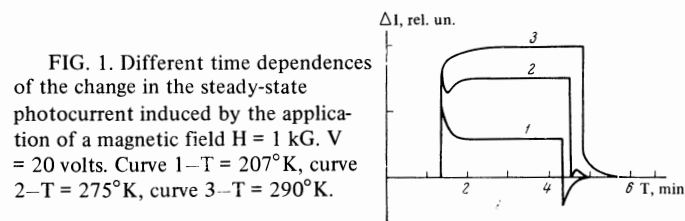


FIG. 1. Different time dependences of the change in the steady-state photocurrent induced by the application of a magnetic field $H = 1$ kG. $V = 20$ volts. Curve 1— $T = 207^\circ\text{K}$, curve 2— $T = 275^\circ\text{K}$, curve 3— $T = 290^\circ\text{K}$.

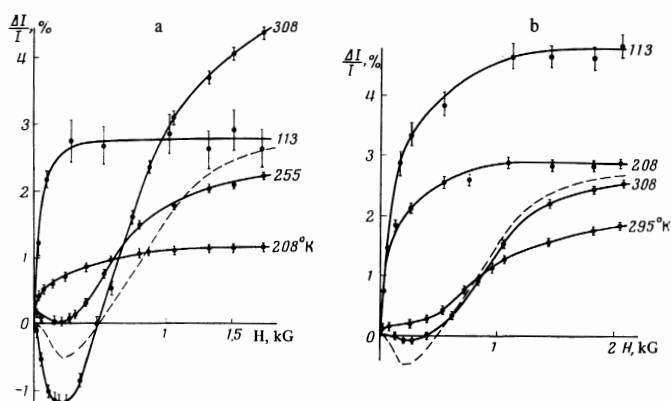


FIG. 2. The dependence of the relative change of the photocurrent in a magnetic field on the magnetic field strength for two specimens. Dashed line— $\Delta L/L = f(H)$ taken from [9], in relative units.

to the electrodes. In the case when $\Delta I(t)$ followed curve 3, the magnitude of $\Delta I_{st}/I$ was independent of L (L changed by three orders of magnitude) and of V .

Two of the most outstanding results of the $\Delta I/I = f(H)$ dependences obtained from two different specimens are shown in Figs. 2a and 2b. At high temperatures ($T = 290^\circ\text{K}$), when the $\Delta I/I = f(H)$ dependence was "saturated" at $H \gtrsim 2$ kG, $\Delta I(t)$ had the form of curve 3 of Fig. 1. The appearance of the "rapidly saturating" region of $\Delta I/I = f(H)$ was accompanied by the formation of "spikes" in the $\Delta I(t)$ dependence.

Figures 3 and 4 represent the dependence $\Delta I/I$ ($H \approx 2$ kG) on temperature and on the wavelength of light at $T = 210^\circ\text{K}$. The points on the curves correspond to the steady-state values of ΔI .

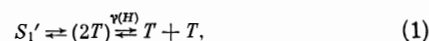
DISCUSSION

1. The Processes of "Magnetosensitivity" of the Photocurrent

The interpretation of the effect of a magnetic field on the photocurrent, presuming that Wannier-type excitons (Π) take part in the generation of the photocurrent, is based on the fact that mixing of the wavefunctions of the triplet and singlet states takes place in a magnetic field. This causes a change in the effective lifetime of the exciton.^[5] Since an optical transition from the

ground state S_0 to Π is hardly possible, it was assumed^[5] that Π are formed as a result of conversion of the excitation from a singlet excited state into a singlet Wannier-type exciton (Π_1). With this scheme of Π formation, the magnetic field causes a decrease in the density of the singlet part of Π and, in the case of the existence of a reverse transition $\Pi_1 \rightarrow S_1$ it can only decrease the population of S_1 and cause a decrease of fluorescence ($S_1 \rightarrow S_0$) in a magnetic field.

The detection of an increase in intensity of fluorescence of tetracene in a magnetic field^[7] necessitated the search for another process with the participation of a fluorescent state (S'_1) "sensitive" to the magnetic field. Such a process, as suggested by Geacintov and Pope,^[8] is the decay of S'_1 into two triplets excitons (T). Investigations^[8,9] of the temperature dependence of the change ΔL of the fluorescence (L) in a magnetic field ($\Delta L/L$ decreases and L increases with decreasing temperature) led to the conclusion that the process $S'_1 \rightarrow T + T$ needs activation energy and apparently follows the scheme



where $2T$ is a state preceding the decay of S'_1 to T and $\gamma(H)$ is a constant of the reaction rate and depends on the magnetic field.

How is this process connected with the "sensitivity" of the photocurrent to the magnetic field? The answer to this question can be obtained if a comparison of $\Delta L/L = f(H)$ and $\Delta I/I = f(H)$ is made. The $\Delta L/L = f(H)$ dependence taken from [9] is represented by the dashed line in Fig. 2. It is known that the shape of this curve is independent of temperature (290 – 210°K)^[7] and apparently is the same for tetracene polycrystalline films^[7] and single crystals.^[9]

The comparison of $\Delta I/I = f(H)$ and $\Delta L/L = f(H)$ shown in Fig. 2 and the examination of the kinetics of photocurrent changes upon application of a magnetic field give rise to the following conclusions.

a) The $\Delta I/I = f(H)$ dependence does not coincide, generally speaking, with the $\Delta L/L$ dependence; only at high temperatures ($T \sim 290^\circ\text{K}$) are $\Delta I/I$ and $\Delta L/L$ similar in shape. In the general case the observed dependence on the field can be represented as the result of a superposition of two dependences, one of which has the form $\Delta L/L = f(H)$ and is "saturated" in fields $H \geq 2$ kG, and the other is similar to $\Delta I/I = f(H)$ at $T < 210^\circ\text{K}$ (Fig. 2) and saturates in fields $H \approx 0.4$ kG. From this conclusion it follows that there exist essentially, at least two processes contributing to the creation of magnetic sensitivity of the photocurrent. Process I is the very process which causes the changes in fluorescence in a magnetic field. This process, as far as we know, follows the mechanism of Geacintov and Pope scheme [scheme (1)]. Process II is connected with the "magnetosensitivity" of fluorescence.

b) With decreasing temperature, the contribution of process I to the change in photocurrent in a magnetic field decreases and practically vanishes at $T \leq 200^\circ\text{K}$. The contribution of process II increases. The dotted line in Fig. 3 shows the course of $\Delta I/I$ determined by process I. Its temperature dependence coincides with dependence.^[8]

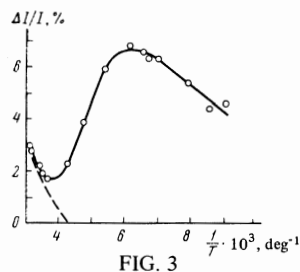


FIG. 3

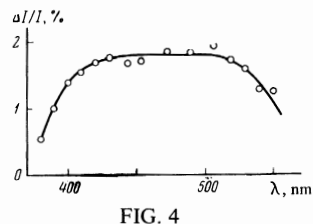


FIG. 4

FIG. 3. Temperature dependence of the change of the photocurrent in a magnetic field.

FIG. 4. Dependence of the relative change of photocurrent in a magnetic field $H = 2$ kG on the wavelength of the light exciting the photocurrent.

c) The presence of process II is accompanied by the appearance of "oscillations" on the $\Delta I(t)$ curve. The shape of the $\Delta I(t)$ curve due to process I has the appearance of curve 3 (Fig. 1), coinciding in shape with the curve of photoresponse for increasing light intensity. The differences in shape in the $\Delta I(t)$ curves due to the influence of either process I or process II prove the differences in the mechanism of generation of current carriers.

2. Excited States in Process I

Investigations of the basic spectral dependences of I and $\Delta I/I$ ($H \approx 8$ kG) at $T = 290^\circ\text{K}$ under the same experimental conditions have previously shown^[11] that the photogeneration ($400 < \lambda < 540$ nm) of carriers in tetracene essentially takes place on the electrode (or in layers close to the electrode) and that the magnetosensitive excitons, which may be presumed to be of the Wannier-type, possess the following properties: a) they cause the generation of holes by decaying on the electrode and b) they create "non-magnetosensitive" excitons having a longer diffusion path.

The foregoing division of the mechanisms of magnetosensitivity of the photocurrent allows us to attribute these properties to fluorescent states whose concentration changes in a magnetic field, i.e., S_1' in scheme (1). In this case it follows from property (b) that S_1' are formed from the other non-magnetosensitive excitons. This conclusion was confirmed by the study of the luminescence of tetracene ($T \sim 290^\circ\text{K}$)^[12-14] which shows that the fluorescence maximum is shifted (by approximately 10^3 cm⁻¹) towards the red side of the relatively long-wavelength peak in the absorption spectrum. The intensity distribution in the spectra is such that the distance between vibrational sub-levels in the excited states is larger than in the ground state.

Apparently, excitons of one type (S_1) are first created under the action of light in tetracene. Their radiation lifetime is large in comparison with the transition time needed for transformation into the S_1' -type exciton (or localized excitation) that is responsible for the fluorescence.

The larger diffusion length of S_1 compared with S_1' [property (b)], under the condition that the carriers are created with the help of both S_1 and S_1' , explains the small magnetic effect on the photocurrent ($\Delta I/I \sim 2-6\%$) compared with the effect on fluorescence ($\Delta L/L \sim 15-40\%$).

3. Excited States in Process II

From Fig. 4 it is apparent that the magnetic effect at 210°K , which is governed, as was shown previously, by the "magnetosensitive" process II, is independent of the energy of light quanta in the interval 2.4-3.1 eV. Since the activation energy of the photocurrent is $\Delta E \leq 0.1$ eV, the excited states connected with process II have an energy $E \leq 2.5$ eV. In agreement with^[4], the energy needed for the formation of free charges in tetracene is $E \approx 3.1$ eV. Therefore these states take part in the formation of current carriers by interacting with impurity molecules or with the electrode.

The appearance of "spikes" in curve $\Delta I(t)$ during the action of process II demonstrates apparently its

connection with volume creation of carriers. In this case the generation of carriers by ionization of impurity molecules cause the accumulation of space charge that reduces the photocurrent. The time necessary to set up a steady-state current is defined by the Maxwell relaxation time, which depends on L and V .

The "magnetosensitive" states connected with process II may apparently be the Wannier-type excitons generated from singlet excitons S_1 or "hydrogen-like" states (a trapped electron (M^-) and a hole (p) weakly bound to it), produced upon interaction of S_1 and/or S_1' excitons with the impurity. The effective lifetimes of such states change in a magnetic field, owing to the mixing of the wave-functions of the triplet and singlet states.^[5]

To summarize, it is possible to propose the following picture of the excited states in tetracene (Fig. 5). Absorption of light produces excitons in the lower excited singlet state S_1 (2.4 eV^[4]). The radiative lifetime of S_1 is large compared with the time of transition into the state S_1' , which is responsible for the "magnetosensitivity" of fluorescence, or into the "hydrogen-like" singlet state Π_1 (Wannier-type exciton or the system of a trapped electron bound to a hole). The energy of the Π and S_1' states is less than 2.5 eV; the diffusion length of S_1 is greater than that of S_1' ; the symbol \nrightarrow means that the process has low probability. The generation of carriers p takes place on the electrode with participation mainly of excitons S_1 and S_2 , and in the volume with the participation of the states Π . The change in concentration of S_1' in a magnetic field, which is connected^[8] with the magnetic-field dependence of the rate of decay of S_1' into two triplet excitons (T), give rise to one type of magnetosensitivity of the photocurrent (process I). The change in the effective lifetime of the Π states in a magnetic field leads to process II.

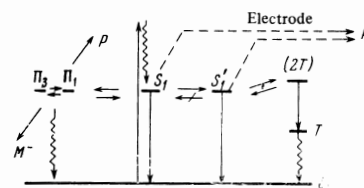


FIG. 5. Scheme of excited states. Explanation in text.

¹E. L. Frankevich and E. I. Balabanov, ZhETF Pis. Red. 1, No. 3 35 (1965) [JETP Lett. 1, 93 (1965)].

²E. L. Frankevich, E. I. Balabanov, and G. V. Vsel'yubskaya, Fiz. Tverd. Tela 8, 1970 (1966) [Sov. Phys.-Solid State 8, 1567 (1966)].

³B. A. Rusin and E. L. Frankevich, Phys. St. Solid. 33, 885 (1969).

⁴N. Geacintov, M. Pope, and N. Kallman, J. Chem. Phys. 45, 2643 (1966).

⁵E. L. Frankevich, Zh. Eksp. Teor. Fiz. 50, 1226 (1966) [Sov. Phys.-JETP 23, 814 (1966)].

⁶R. E. Merrifield, J. Chem. Phys. 48, 4318 (1968).

⁷J. Donini, Compt. rend. 266 AB 1618 (1968)

⁸N. Geacintov, M. Pope, and F. Vogel, Phys. Rev. Lett. 22, 593 (1969).

⁹R. E. Merrifield, P. Avakian, and R. P. Croff, Chem. Phys. Lett. 3, 155 (1969).

¹⁰E. L. Frankevich and E. I. Balabanov, Phys. St. Solid. **14**, 523 (1966).

¹¹B. S. Yakovlev and E. L. Frankevich, Fiz. Tverd. Tela **11**, 1975 (1969) [Sov. Phys.-Solid State **11**, 1588 (1970)].

¹²A. F. Prikhot'ko and A. F. Skorobogat'ko, Opt. Spekt. **20**, 62 (1966).

¹³Y. A. Katul and A. B. Zahlen, J. Chem. Phys. **47**, 1012 (1967).

¹⁴A. A. Karraz and A. B. Zahlen, J. Chem. Phys. **48**, 1242 (1968).

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