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Positive Magnetic Effect on Photo-Enhanced Current in Anthracene. A Novel Determination of Triplet-Triplet Annihilation Rate Constant

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It has been observed that under certain conditions (light intensity, field strength, etc.) the photoenhanced current (PEC) increases on application of external magnetic field. This anomalous positive magnetic effect is accounted for in terms of a competition between triplet-triplet and triplet-doublet reactions. Numerical simulation shows that the observed anomaly is possible for a rather limited range of parameter values. Hence, the analysis of the effect offers a good chance to check the magnitude of the triplet-triplet annihilation rate constant γ_{TT}. The currently accepted value of $\gamma_{TT} = 2 \times 10^{-11}$ cm^3 s^{-1} is confirmed.

INTRODUCTION

External magnetic field often affects photoconductivity in organic materials. Various mechanisms are possible. The most established mechanism is the one involving the detrapping of carriers (which are magnetically doublet) due to triplet excitons. The spin selective process

Triplet + Doublet
→ Electronically excited doublet

is influenced by an external magnetic field in a similar fashion to triplet-triplet annihilation. Johnson and Merrifield[1] have shown that the general feature of the magnetic field effect is understood in terms of the level crossing of spin sublevels of the annihilating triplet pair. Suna[2] has elaborated the theory by taking the dimensionality of triplet motion into account. An extension of the idea to triplet-doublet (TD) pair has been done by

Geacintov *et al.*[3] and by Bouchriha *et al.*[4] The spin wavefunctions of a TD pair, which is going to annihilate, are written, in the high field limit, as

$$\left|1, \frac{1}{2}\right\rangle, \quad \left|1, \frac{-1}{2}\right\rangle, \quad \left|0, \frac{1}{2}\right\rangle, \quad \left|0, \frac{-1}{2}\right\rangle, \quad \left|-1, \frac{1}{2}\right\rangle$$

$$\text{and} \quad \left|-1, \frac{-1}{2}\right\rangle.$$

At zero magnetic field all six wavefunctions have equal doublet character, whereas at high field only four of them have doublet character. The key idea in understanding the magnetic field effect on reaction rate is that what one observes is the sum of the reactions of different spin states. The rate constant k_2 of the reaction

$$T + D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (T, D) \xrightarrow{k_2} D^*$$

is the sum over spin states which have finite doublet (i.e., product of the reaction) character. The rate of the annihilation becomes smaller as a magnetic field is applied and the doublet character concentrates into fewer spin states. A further decrease of the reaction rate occurs at a certain specific crystal orientation relative to the magnetic field at which spin states $|1, -1/2\rangle$ and $|0, 1/2\rangle$, and $|-1, 1/2\rangle$ and $|0, -1/2\rangle$ come into degeneracy. For this orientation linear combination of these spin states are the eigenstates, and there are only two states which have sizable doublet character.

In the course of investigating the carrier generation mechanism near the surface of anthracene crystals, we have often observed an increase of the photocurrent on applying a magnetic field, while the above theory predicts a decrease. It will be shown in this article that this apparently anomalous effect is a result of the competition between triplet-triplet (TT) and triplet-doublet (TD) reactions. It is possible, by making use of this competition, to determine the relative magnitude of γ_{TT} and γ_{TD}. Since a relatively reliable measurement of γ_{TD} is possible, this approach serves as a novel route to assess γ_{TT}.

EXPERIMENTAL

Anthracene (Tokyo Kasei Co.) was treated with maleic anhydride to remove tetracene which is present as an impurity and was zone refined. Single crystals grown from ethanol solutions were used for the measurements.

Photocurrent was measured with an electrometer and a stabilized voltage source. A 500 W Xenon lamp was used as the light source, together with a monochromator (Bausch & Lomb, high intensity) or suitable interference filters. In some measurements a He-Ne laser (Nippon Electric Co., 5 mW) was used. Cuprous iodide electrodes were prepared as described.[5] They made ohmic contact to the anthracene crystals. The performance of the CuI contacts was satisfactory and reproducible. Sample specimen was placed between pole pieces of an electromagnet which could be rotated.

Triplet lifetime for each crystal was measured with a mechanical chopper combined with a gated photon counting system. We call it a "photon counting Boxcar". Delayed fluorescence was viewed from the thin edge of the crystals. It is necessary to keep the concentration of triplet excitons low enough so that the contribution of the bimolecular process is negligible. As a result the exciting light intensity has to be kept low and delayed fluorescence is correspondingly very weak if the excited volume is small. The above instrument is sensitive enough to enable the measurement of the lifetime in a crystal the thickness of which is several tens of micrometers which is needed for the photocurrent measurements. The decrease of the triplet lifetime due to the injected charge was monitored with this apparatus in order to be sure that the space charge limited current (SCLC) condition is really fulfilled.

RESULTS AND DISCUSSION

As mentioned in the Introduction the magnitude of the magnetic field effect on the photocurrent was found to be sensitive to the conditions such as applied voltage, the light intensity and the nature of the contacts. We have made a systematic investigation of the condition under which a positive magnetic field effect (i.e. increase of a photocurrent on application of a magnetic field) occurs. Following electrode materials were examined: Water, aqueous solution of Ce^{4+}, iodine in aqueous KI solution, and solid CuI. It can be said that for all the systems investigated a positive magnetic field effect was observed when the triplet exciton concentration was high, and when the concentration of the space charge was not very high. A typical set of results is shown in Figures 1 and 2. These measurements were made on a 35 μm thick crystal (grown from solution, triplet lifetime 5 ms) with CuI as a hole injecting electrode.

Among the electrodes examined CuI is most convenient and gives results which allow quantitative treatment. Liquid electrodes are superb in that they make homogeneous contact over the contact area, but they tend

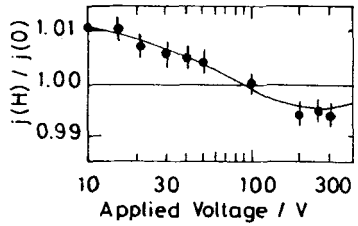

FIGURE 1 Magnetic field effect on SCLC of an anthracene crystal as a function of applied voltage. Electrode, CuI; crystal thickness, 35 μm; magnetic field strength, 5 kG; light intensity, 10^{16} photons/cm^{2}s.

to show saturation at relatively low current levels (typically less than 10^{-5} A/cm^2). Evaporated metal films often make point contacts which lead to field injection that has been evidenced by irregular light emission. Accordingly, one has to be careful whether SCLC condition is realized. A large current density alone provides no guarantee for a space charge limited current. Cuprous iodide is an exception. It makes a good electrical contact to several organic crystals (anthracene,[5] tetracene,[6] and pyrene[4]) reproducibly. Currents as high as 10^{-2} A/cm^2 can be drawn without any indication of saturation. With this electrode the SCLC is easily realized. This is confirmed by the decrease of triplet lifetime on applying the electric field (Figure 3). When charge carriers are present in a crystal the stationary concentration of triplet excitons T is given by the rate equation

$$\alpha I - \beta T - \gamma_{TT} T^2 - \gamma_{TD} TD = 0 \qquad (1)$$

where I is the light intensity, T is the triplet concentration and D is the doublet concentration. The first term is the generation of excitons by light absorption, the second term is the monomolecular decay, the third term is the mutual annihilation of triplet excitons, and the last term is the annihilation of triplet excitons by the presence of doublets (charge carriers). The external magnetic field influences T *via* γ_{TT} and γ_{TD}. Absorption coefficient

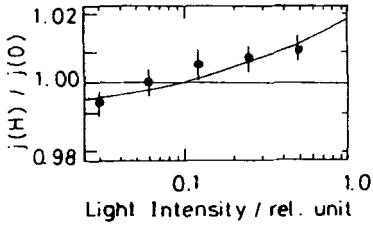

FIGURE 2 Magnetic field effect on SCLC of the same crystal as in Figure 1 as a function of light intensity. Electrode, CuI; magnetic field strength, 5 kG; applied voltage, 30 V.

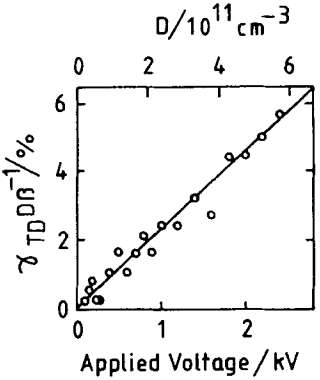

FIGURE 3 Shortening of the triplet exciton lifetime due to injected charge (D). Crystal thickness, 1.2 mm; decay rate constant, $\beta = 80\ s^{-1}$. From the slope of the line one obtains $\gamma_{TD} = 0.9 \times 10^{-11}\ cm^3\ s^{-1}$.

(α) and monomolecular decay rate constant (β) are not affected by the external magnetic field. The magnitude of the photocurrent j_{ph}, in the case of SCLC, is expressed as[7]

$$j_{ph} = (9\varepsilon\varepsilon_0\mu/8H)N_{eff}^{1/l}[A(\lambda)I/v\sigma]^{1-1/l}V^2/L^3 \tag{2}$$

where ε is the dielectric constant of the crystal, μ is the mobility of carriers, H is the trap density, N_{eff} is the effective density of states in the conduction band (or the valence band for holes), $A(\lambda)I$ is the rate of carrier release from traps, $v\sigma$ is the trapping rate, V is the applied voltage, and L is the crystal thickness. The parameter l characterizes the distribution of trap depths. For most crystals studied l was found to be 5 to 6. In the case where carriers are generated through detrapping by triplet excitons

$$j_{ph} \propto [A(\lambda)]^{1-1/l} = [\gamma_{TD}TD]^{1-1/l} \tag{3}$$

holds. Photocurrent is influenced by magnetic field through γ_{TD} and T (which is sensitive to magnetic field, as stated above). We have calculated, according to Eqs. (1) and (3), how the photocurrent is influenced by the magnetic field as a function of the light intensity and the electrical field strength. Figure 4 shows the result. Following parameters are used. $\beta = 160\ s^{-1}$, $\gamma_{TT} = 2 \times 10^{-11}\ cm^3\ s^{-1}$, $\gamma_{TD} = 1 \times 10^{-11}c\ m^3\ s^{-1}$, $\gamma_{TT}(H{=}5\ kG)/\gamma_{TT}(H = 0) = -0.2$, $\gamma_{TD}(H = 5\ kG)/\gamma_{TD}(H = 0) = -0.07$, $L = 35\ \mu m$. These parameters, except γ_{TT}, which is adopted from Ref. (8), have been measured with crystals used in this work.

It may be seen that the calculation reproduces the observation (Figures 1 and 2) quite well. This, together with more or less qualitative observations

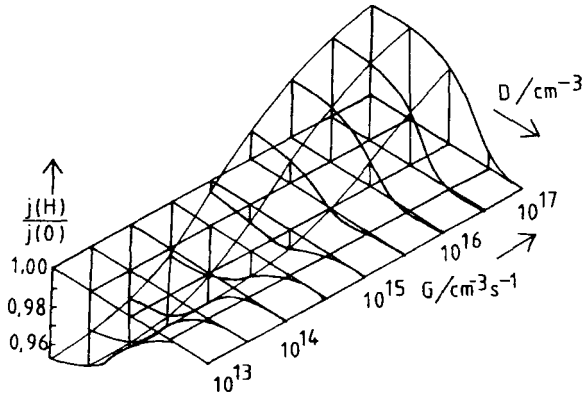

FIGURE 4 Magnetic field effect on SCLC for H = 5 kG calculated with Eqs. (1), (3), and (4). Crystal thickness, 35 μm. Note that the reversal of the sign of $j(H)/j(o)$ as the charge carrier concentration (D) increases is only detectable in a very limited range of the generation rate (G), i.e. around 3×10^{15} cm^{-3} s^{-1}.

employing liquid electrodes, shows that the observed positive magnetic field effect on the photocurrent is a result of the competition between TT and TD reactions. A positive magnetic field effect is observed when the concentration of triplet excitons is so high that TT annihilation is the dominant decay route for triplets. The magnetic field effect diminishes and changes sign as the concentration of charge carriers increases so that the TD reaction dominates over the TT reaction.

A relatively reliable measurement of γ_{TD} is possible if one has an ideally ohmic contact at hand. One knows then the concentration of charge carriers, D, in the crystal,

$$D = 3\varepsilon\varepsilon_0 V/2eL^2 \tag{4}$$

from SCLC theory[7] and γ_{TD} is determined by measuring the change of $\beta_{eff} = \beta + \gamma_{TD}D$ as a function of D (Figure 3). We obtained $\gamma_{TD} = (1.0 \pm 0.4) \times 10^{-11}$ cm^3 s^{-1} with differently prepared crystals with thicknesses ranging from 3×10^{-3} to 1×10^{-1} cm.

The determination of γ_{TT} has been, on the other hand, much more indirect. The product $\alpha\gamma_{TT}$ can be obtained from various processes involving bimolecular decay of delayed fluorescence. The absorption coefficient α is, however, extremely small (estimated to be 10^{-3} to 10^{-4} cm^{-1} with anthracene) and a direct measurement is usually not feasible. It may be seen from Figure 4 that the change of the sign of the magnetic field effect with electric field occurs for a rather limited range of light intensity. The competition between TT and TD reactions gives us a good chance to check

the relative magnitude of γ_{TT} and γ_{TD}. The success of Figure 4 in explaining the results shown in Figures 1 and 2 gives an additional support to the value of γ_{TT} of 2×10^{-11} cm^3 s^{-1} for anthracene, which is currently accepted.

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