GENERATION OF CHARGE CARRIERS IN ANTHRACENE WITH POLARIZED LIGHT

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Intrinsic photogeneration of charge carriers in anthracene single crystals occurs with photon energies in excess of 4 eV[1-4]. The mechanism of this process, however, is not well understood. The interpretation of the wavelength dependence of this current in particular is difficult.[2] Two maxima in the photocurrent appear, one at 4.4 eV[1,2,4] and the other at 5.4 eV.[2] The 4.4 eV maximum appears in a region of low absorption coefficient ($k \sim 16{,}000$ cm^{-1}) and the other maximum in wavelength region where $k \sim 113{,}000$ cm^{-1}. It has been proposed that bulk generation of carriers in anthracene proceeds by direct excitation into a conduction band. On this basis an inverse dependence on k of the bulk generated photocurrent was predicted,[4,5] which seems to explain the wavelength dependence of the 4.4 eV maximum,[5] but not that of the 5.4 eV peak.[2] In order to ascertain the dependence of ~~the~~ bulk generated photocurrent on k we studied the relative quantum efficiency of the photocurrent at fixed wavelength as a function of the angle θ between the electric vector of ~~the~~ polarized light and the b crystalline axis. The extent of variation of k with θ depends on the wavelength,[6] being

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8

largest at 37,300 cm^{-1} in the wavelength region of interest to us (32,000 - 46,000 cm^{-1}). The bulk generated current, designated by i^-, was measured in a sandwich arrangement with water electrodes with the illuminated side of the crystal at a negative potential (i^+ is the photocurrent with the illuminated side at a positive potential and is mostly due to an extrinsic surface generation of carriers[2,7]). Studies of i^+ and i^- as a function of k usually involve changing the excitation wavelength; this simultaneous change of photon energy as well as of k, introduces an uncertainty in the interpretation of the results. However, by using polarized light, k can be varied conveniently by changing θ, whereas the photon energy remains constant. In our experiments the exciting light was polarized by means of a Glan-Taylor prism. Both i^+ and i^- were studied as a function of θ at different wavelengths in the range indicated above. The results at 37,300 cm^{-1} (4.6 eV where maximum variation of k with θ occurs) are shown in figure 1. k (θ) was calculated from the data of Lyons and Morris[6] who give values of the molar extinction coefficient ϵ parallel to the b and a crystalline axes. Using $k = 2.303\, c\epsilon$ ($c = 7.0$ mol l^{-1}, molar concentration of solid anthracene), the expression $k(\theta) = k_b \cos^2\theta + k_a \sin^2\theta$ was used to calculate k(θ), where k_b and k_a are the absorption coefficients parallel to the b and a axes respectively.

Since i^+ depends on a diffusion of excitons to the surface where they dissociate,[2,7] this current is a strong function of k(θ). i^-, however, which is a bulk generated current is fairly independent of k (θ). This is also the case for the entire wavelength range investigated and has been verified for eight other crystal surfaces, the variation never exceeding ± 10% at any wavelength. It is conceivable that triplet excitons with a long diffusion length could reach the back side of the crystal to produce hole injection. This would be an i^- current independent of θ, but would exhibit all the characteristics of the extrinsic i^+ current. Such a process should therefore saturate with voltage[8], which is not observed.[2] This possibility can therefore be ruled out.

It is evident from these results that the wavelength dependence of i^- cannot be attributed to a dependence on k^{-1} as proposed by other workers.[4,5] We shall now restate the two possible mechanisms for intrinsic carrier generation[2] and attempt to distinguish the most probable one in view of our present findings.

I. Direct band to band (BB) transition,[4,5] characterized by an absorption coefficient α (cm^{-1}).

II. Autoionization (AI)[7,2] - light absorption of appropriate energy generates excited bound molecular states which have sufficient energy to ionize, the probability being φ. The absorption coefficient for the autoionization state is k' cm^{-1}; the total absorption coefficient for a crystal is thus $k = k' + \alpha$. AI, however, may not necessarily lead to free carrier formation where the electron is free of the coulomb field of its parent ion.[7] The mean free path of the electron may be so small[9] that the kinetic energy of the electron is degraded before it can escape, leading to its recapture by the parent ion[7] (first-order recombination); a recombination between free holes and electrons is second-order. When the electron and hole densities are comparable, the latter implies that the photocurrent depends on the square-root of the light intensity I_o as long as the photocurrent is field dependent. We observe, however, that i^- depends linearly on I_o although it is also field dependent.[2] Furthermore, second-order recombination is ruled out by the low carrier densities in our experiments,[7] (10^5-10^6 cm^{-3}).

AI may produce quasi-free electron states from which free carriers are produced subsequently under the influence of temperature T or applied field E with probability γ (E,T). The effect of E on carrier generation has been proposed by us for tetracene[7] and by other workers for anthracene.[10] If free carriers are not formed, the quasi-free electron state decays via the charge-transfer exciton state observed by Pope and Burgos,[3] in which the hole and electron are on adjacent molecules.

A consideration of steady state kinetics of formation of free carriers and their disappearance at the electrode in absence of second-order recombination, leads to the following expression for i^-:

$$i^- = \frac{eI_o}{k}\gamma(E,T)\left[\alpha + \varphi k'\right] \qquad (1)$$

Both generation mechanisms (BB) and (AI) have been assumed with the generalization that quasi-free electron states may also be formed by the BB mechanism[9] in which case α must also be multiplied by γ (E,T). e is the electronic charge. We shall now examine mechanisms I and II in context of equation (1). If BB transitions prevail over the AI transition, $\alpha >> \varphi k'$ and i^- should vary as k^{-1} unless $\alpha \propto k \approx k$. The latter would imply that absorption of light in anthracene occurs mostly to crystal continuum states. A detailed interpretation of the anthracene crystal spectrum by Lyons and Morris,[6] however, shows that it can be explained in terms of excited electronic states of the anthracene molecule. Even if $\alpha \propto k$, it is highly unlikely that $\frac{\alpha}{k}(\theta)$ is a constant at all wavelengths which would have to be the case to explain the θ independence of i^-.

It thus appears that the experimental facts can be much better described by the AI than by the BB mechanism. In this case i^- is proportional to $\gamma(E,T)\ \varphi\ k'/k$; $\gamma(E,T)\varphi$ determines the quantum efficiency of intrinsic carrier generation and $k' \approx k$, thus satisfying the experimental requirement that i^- is independent of $k(\theta)$. We further conclude that an inverse dependence of the photocurrent on k is not a criterion for bulk generation as proposed by Chaiken and Kearns.[4]

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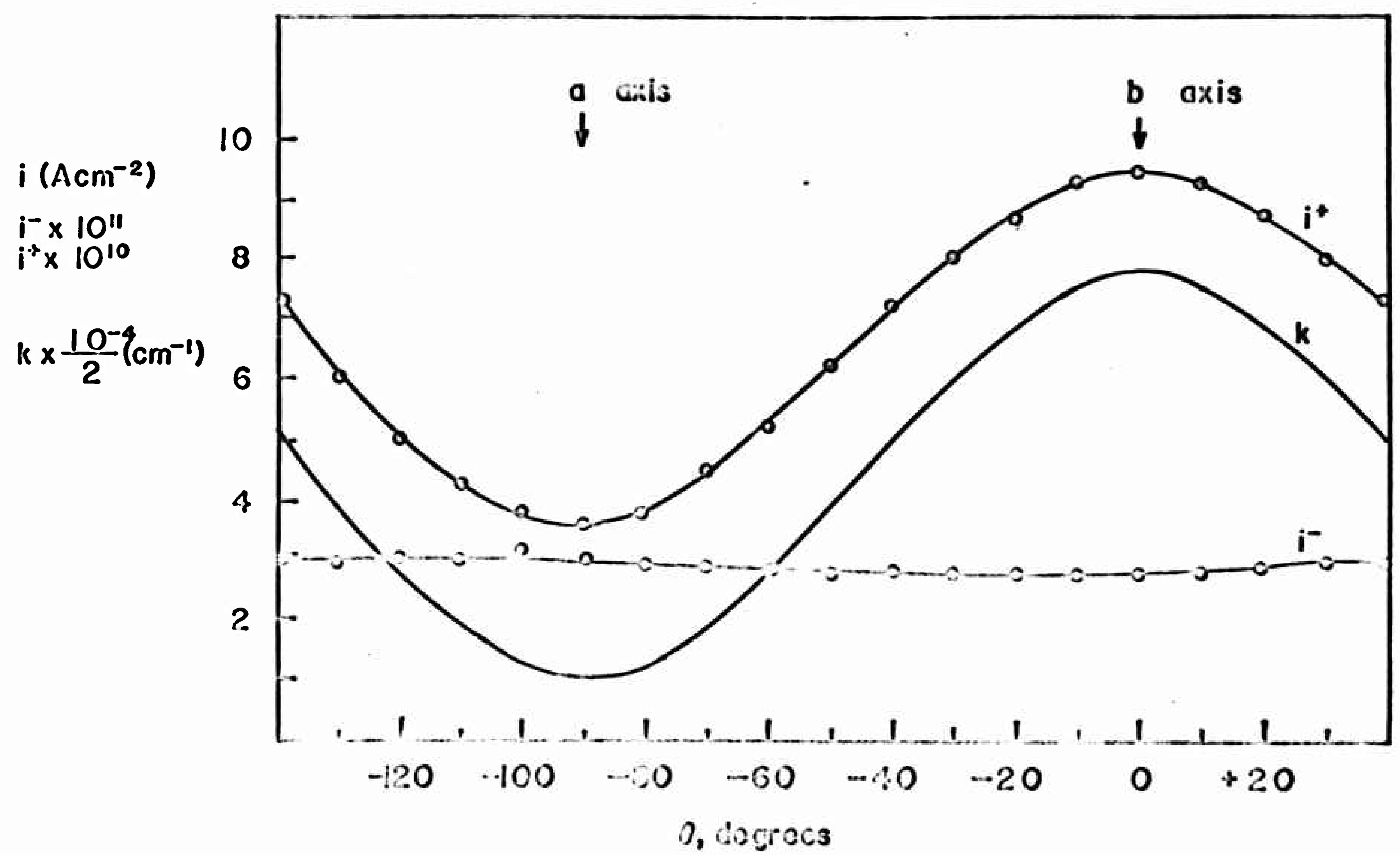
a axis
b axis
10
8
6
4
2
i (Acm^{-2})
i^{-} x 10^{11}
i^{+} x 10^{10}
k x $\frac{10^{-4}}{2}$ (cm^{-1})
i^{+}
k
i^{-}
-120
-100
-80
-60
-40
-20
0
+20
θ, degrees

FIGURE 7

FIGURE I. Photocurrents in anthracene single crystal (35 microns thick) and absorption coefficient k as function of angle θ between electric vector of exciting polarized light and b crystal axis. Wavelength corresponds to photon energy of 4.6 eV (37,300 cm^{-1}). Light intensity 1.5×10^{11} quanta $cm^{-2} sec^{-1}$, field intensity 40,000 volts cm^{-1}