Two-photon transitions to highly excited states in anthracene crystals*

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The two-photon absorption spectrum at room temperature for the creation of singlet excitons and of electron-hole pairs in anthracene crystals has been determined over the two-photon energy range 3.9–5.0 eV. Within a fairly large experimental error, no structure was observed in the wavelength dependence of the two-photon absorption spectrum for the creation of singlet excitons, but the number of electron-hole pairs created increased by more than an order of magnitude between 4.0 and 4.6 eV. The energy dependence of the increase in the number of electron-hole pairs is approximately that expected for transitions to a wide band with an energy gap of about 4.1 eV.

INTRODUCTION

The electronic states of organic molecular crystals have been the subject of intensive study in recent years. The lowest-energy excited states are known to be low-lying exciton states and both the singlet and the triplet states have been very extensively studied.[1] In anthracene crystals the triplet-exciton band begins at 1.8 eV and the singlet-exciton band begins at 3.2 eV. Photoconduction studies[2] have shown that above these bands intrinsic generation of electron-hole pairs begins near 4.0 eV but because of large extinction coefficients at these energies and because of persistent extrinsic carrier generation by surface effects, very little is known about the wavelength dependence of carrier generation and what is known is the subject of controversy. Some believe that the carriers are generated by autoionization of high-lying exciton states[3] and others believe that the carriers are generated by direct transition to a continuum state.[4,5] A well-established fact which tends to muddy the water is that, by whatever mechanism the carriers are generated, the vast majority of free electron-hole pairs created immediately recombine in a process referred to as geminate recombination.[6,7] Extensive studies of the drift mobility of electrons and holes in anthracene have been carried out[8] and the geminate-recombination process is well understood in terms of these results.

In this paper some results of experiments using two-photon transitions to highly excited states are presented. Peticolas,[9] using a ruby laser, was the first to report two-photon excitation of anthracene crystals. Since then Fröhlich and Mahr[10] have studied two-photon absorption over the two-photon energy range 3.20–4.25 eV, Webman and Jortner[11] studied the energy range from 3.10 to 3.5 eV, and very recently, Bergman and Jortner[12] extended these studies to 5.2 eV. Carrier generation by two-photon absorption was first reported by Strome[13] and very recent results have been reported by Bergman and Jortner.[14]

The work reported here consists of a detailed study of the wavelength dependence of both two-photon exciton generation and two-photon carrier generation over the two-photon energy range 3.9–5.0 eV. The results strongly favor carrier generation by direct two-photon excitation to a broad continuum of states. In this work no evidence was found for a two-photon-excited exciton state between 3.9 and 5.0 eV. Theoretical calculations have indicated that one might be found around 4.8 eV and recent experimental work[12,13] has indicated that one exists near 4.1 eV.

EXPERIMENTAL

The dye laser used for these studies was the commercially available Dial-a-Line system in which dye cells are pumped with a pulsed nitrogen laser. The output of the dye laser was passed through a monochromator to eliminate unwanted wavelengths and the size of the beam at the crystal was varied from experiment to experiment with lenses. Typically, the laser output was 100 μJ/pulse and the laser was operated at either 1 or 10 pulses/sec. The pulse length varied with dye cell and laser adjustments but was typically around 5 nsec. The fluorescent light emitted by the anthracene crystal was measured with photomultipliers and, for the carrier-generation experiments, the crystal was mounted between conducting glass electrodes. All signals were averaged on a Fabritek signal averager to separate weak signals from the noise and to average out pulse-to-pulse variations in laser output. The crystals used were cleaved from Harshaw crystals and the light was always incident normal to the *ab* plane.

A wide variety of phenomena involving the excited states of anthracene crystals have been identified and an important experimentally observable characteristic which helps unscramble the various processes is the laser-intensity dependence of the phenomena. In the case of singlet-exciton generation it was found in the present experiments that the prompt fluorescence intensity varied as the square of the laser intensity over the complete

two-photon energy range studied. These results were interpreted to mean that the dominant process for exciton creation was two photon absorption. At room temperature, where these experiments were carried out, direct one-photon absorption to the first-excited singlet state began to compete with the second-order process above 4900 Å. These experiments were limited to two-photon energies of 5.0 eV by this process. The intensity of the prompt fluorescence was determined by integrating the photomultiplier current during the pulse.

In anthracene the presence of triplet excitons leads to delayed fluorescence.[15] Delayed fluorescence consists of the same spectrum of light as that of prompt fluorescence but the time period over which the light is emitted is much longer than the 25-nsec singlet exciton lifetime. It has been shown that two triplet excitons, which have lifetimes on the order of 25 msec, can mutually annihilate creating a singlet exciton which, with a very high probability, radiatively decays essentially immediately, thereby creating a fluorescence photon. Therefore, the intensity of the delayed fluorescence depends on the square of the triplet-exciton concentration. If the concentration of triplet excitons is directly proportional to the intensity of the incident laser light, as would be the case for direct one photon creation, the delayed fluorescence signal will vary as the square of the incident laser light. If, on the other hand, the triplet exciton concentration varied with the square of the laser light intensity, as it would for example, if intersystem crossing from two-photon-excited singlet states were the dominant generation mechanism, then the delayed fluorescence intensity would vary as the incident laser intensity to the fourth power. In the present experiment it was found that the delayed fluorescence intensity varied as the square of the incident light intensity at all wavelengths. The delayed-fluorescence signal was separated from the prompt signal by opening a shutter between the crystal and the photomultiplier about 1 msec after the laser pulse. The triplet-exciton lifetime depends on crystal purity but is typically 15–25 msec.

Preliminary experiments indicated that there was very little variation in the two-photon absorption coefficient for the creation of singlet excitons over the energy range covered in this experiment, so to test this hypothesis, the ratio of the delayed fluorescence to the prompt fluorescence was measured as a function of wavelength. If this hypothesis were true, this ratio would reproduce the variation of fluorescence intensity with wavelength of exciting light previously reported for experiments with incoherent light.[16] One problem encountered in this experiment was that the time dependence of the laser pulse varied considerably from dye cell to dye cell and to some extent with wavelength and laser adjustments. This variation created problems because the prompt fluorescence intensity I_p depends on the laser intensity $I_L(t, r)$ as

$$I_p = K \int \int I_L^2(t, r)\, dv\, dt$$

and the delayed fluorescence intensity I_D varies as

$$I_D = \int K' [\int I_L(t, r)\, dt]^2\, dv$$

if we assume that diffusion of triplet excitons out of the illuminated volume is not important. Therefore, an effort was made to adjust the laser in such a fashion that the time dependence of the laser pulse, as observed with a fast photodiode and a Tektronix model No. 519 oscilloscope, was the same at all wavelengths.

The results of the experiment in which the ratio of the delayed fluoresence to the prompt fluorescence was measured as a function of wavelength are shown in Fig. 1. The data in the top part of the figure were taken with the electric vector of the polarized light parallel to the b axis and the data in the bottom part of the figure were taken with the electric vector parallel to the a axis. The

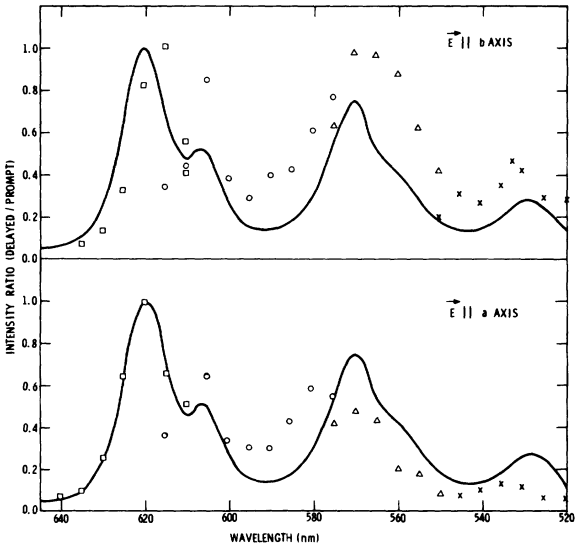

FIG. 1. Ratio of the delayed fluorescence to the prompt fluorescence wavelength. Different symbols represent data taken with different dye cells in the dye laser. The data in the top part of the figure were taken with the electric vector of the incident light parallel to the crystal b axis, and that in the bottom part, with the electric vector parallel to the a axis. The maximum ratio with the electric vector parallel to the b axis was about ten times smaller than the maximum ratio with the electric vector parallel to the a axis. The solid lines are data from Ref. 16 and are the observed delayed fluorescence intensity vs incoherent exciting light wavelength.

ratio with the electric vector parallel to the *b* axis was about ten times smaller than the ratio with the electric vector parallel to the *a* axis near 620 nm, as expected based on the polarization ratio for two photon absorption reported later in this paper and on the polarization ratio previously reported for direct absorption to the triplet state.[16] All the data agree quite well with the previously observed wavelength dependence strongly indicating that there is very little, if any, structure over the wavelength range investigated in the two-photon absorption cross section for the creation of singlet excitons.

The above results were confirmed by measuring the absolute magnitude of the two photon absorption coefficient for the creation of singlet excitons versus wavelength. These experiments were made difficult by the very small size of the laser beam. The beam size had to be kept small in order to have sufficient peak light intensity so that two photon absorption could be observed. By scanning the laser beam with a 25-μm-diam pinhole and observing the light intensity passed by the pinhole with a photodiode, it was determined that the beam diameter at the half-intensity points was about 400 μm. For these measurements the light passed by the pinhole was spread out with a negative lens so that it hit the cathode of the photodiode over a wide area. For the absolute magnitude experiments the laser beam was passed through a 400-μm-diam hole before impinging on the crystal. The intensity and time dependence of the light beam incident on the crystal was measured with a photodiode and these measurements were carried out without the crystal present. The amount of two photon absorption was determined by measuring the number of fluorescence photons emitted by the crystal with a photomultiplier. This photomultiplier was calibrated by measuring the number of photons emitted by the crystal when it was excited with a known number of photons at 4150 Å. Photons of this wavelength excite the crystal directly to the first excited singlet state with a quantum efficiency of one. Except for surface quenching effects it is believed that the quantum efficiency for emission of fluorescence photons is independent of wavelength and for this study we used a value of 0.7 for that quantum efficiency.[17]

The results of the experiment to measure the absolute magnitude of the two photon absorption coefficient are shown in Fig. 2. These experiments were carried out with polarized light with the electric vector parallel to the *b* axis of a 2-mm-thick crystal. The order in which the wavelength settings were chosen was randomized in order to minimize errors associated with the way the laser was set up. The experimental error was large but over this wavelength range the median value of the two photon absorption rate constant

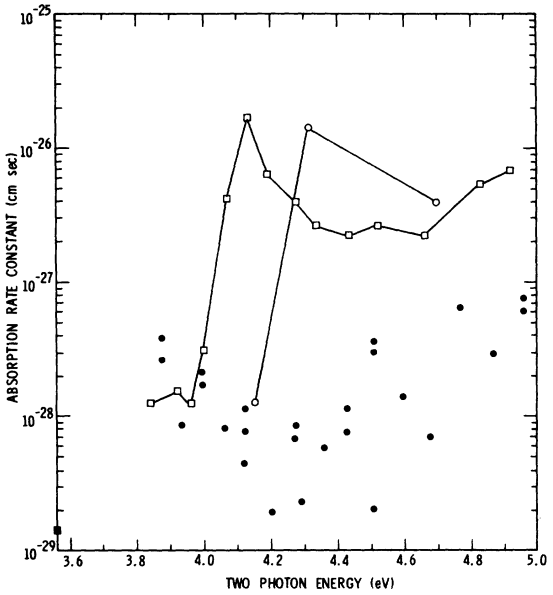

FIG. 2. Absolute magnitude of the two photon absorption rate constant versus two photon energy. The solid circles are the data taken in the present experiments, with the electric vector of the incident light parallel to the *b* crystal axis, the solid square at the two photon energy 3.56 eV is from Hall, Jennings, and McClintock [Phys. Rev. Lett. 11, 364 (1963)], the open circles are from Ref. 13, and the open squares are from Ref. 12. The data of Ref. 10 are not shown but they are in agreement with the present data in the region up to 4.25 eV where there is overlap. Reference 10 indicates that there is a drop of a factor of 10 in the absorption coefficient in going from 3.75 to 4.2 eV.

was found to be about 1×10^{-28} cm sec. As the experiment in which the ratio of the delayed fluorescence to the prompt fluorescence was measured showed, there is very little variation with wavelength but there is some suggestion of an increasing absorption coefficient at the two extremes of the wavelength range studied.

As shown in Fig. 2 the present data disagree with both those of Bergman and Jortner[12] and those of Strome.[13] It should perhaps be pointed out that polarization is not a possible source of the discrepancies noted since, as will be shown later, the fact that the data were taken with the electric vector of the incident light parallel to the *b* crystal axis makes the data high with respect to other polarizations. The present data are in excellent agreement with the data of Fröhlich and Mahr.[10] The Fröhlich-Mahr experiment was carried out using a two beam technique, one of which was a high-intensity neodymium laser beam and the other a low-intensity variable-wavelength light beam. As a result, before comparison, the experimental data has to be corrected for a dominant resonance denominator $(E_{GI}-h\nu_v)^2$, which appears in the sec-

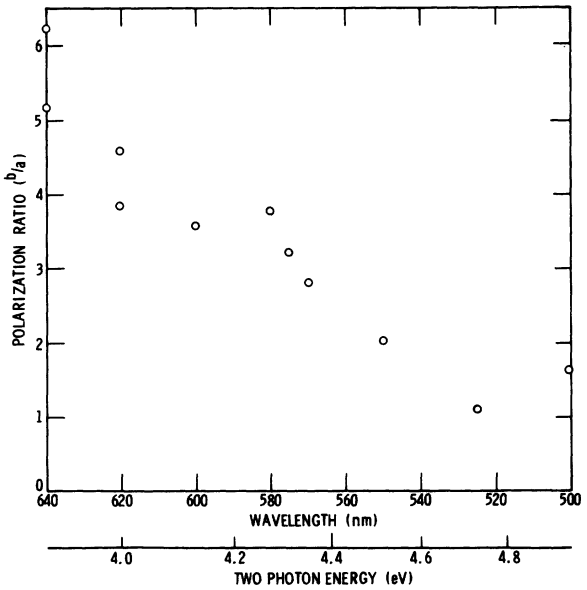

FIG. 3. Ratio of the two-photon absorption rate constant with the electric vector parallel to the b axis to that with the electric vector parallel to the a axis vs wavelength of two-photon energy.

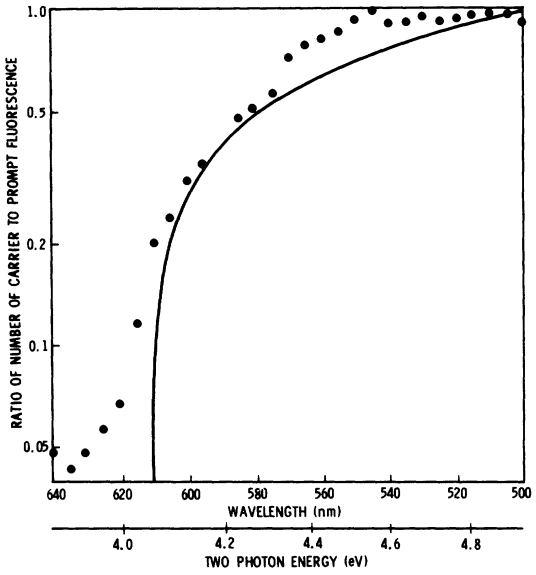

FIG. 5. Ratio of the number of carriers produced to the prompt fluorescence vs wavelength. The solid curve varies as $(E-E_G)^{1/2}$ with $E_G = 4.1$ eV and was set equal to 1.0 at 500 nm.

ond-order perturbation theory where E_{GI} is the difference in energy between the ground state and an intermediate state which is involved in the transition and $h\nu_v$ is the energy of the variable energy photons. Frölich and Mahr assumed that the intermediate state was 3.125 eV above the ground state and this assumption gives excellent agreement with the present results. Their data indicate that there is a drop of a factor of 10 in the two-photon absorption coefficient in going from 3.75 to 4.2 eV and the absolute magnitude found agrees with the results of the present work.

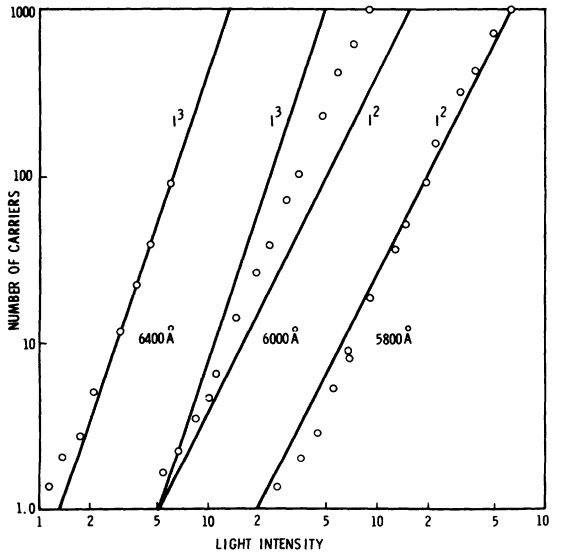

FIG. 4. Laser light intensity dependence of the number of carriers generated at 640, 600, and 580 nm. The abscissa is an arbitrary log scale and the solid lines represent either an intensity, I, cubed, or squared dependence, as marked.

The polarization ratio of the two photon absorption coefficient was measured and the experimental results are shown in Fig. 3. The experimental results were obtained by measuring the number of fluorescence photons emitted by the crystal with the electric vector of the incident light parallel and perpendicular to the b crystal axis. The measurement was made four times at each wavelength with the crystal rotated through 90° after each measurement to average out crystal shape and edge effects.

The intensity dependence of carrier generation was measured and varied with wavelength as shown in Fig. 4. At the higher photon energies the number of carriers generated varied as the intensity squared indicating two-photon generation but at the lowest photon energies the dominant mechanism for carrier generation, particularly at the higher light intensities, is two-photon generation of singlet excitons followed by exciton photoionization.[18,19] This process leads to the observed intensity cubed dependence. In order to minimize the influence of this third-order process all the carrier generation wavelength dependence data were taken at as low a light intensity as possible which still allowed the observation of carrier generation at the low-photon energies. Since it was

fairly well established that the two photon absorption coefficient varied very little with wavelength, the wavelength dependence of carrier generation was determined by measuring the ratio of the magnitude of the photocurrent pulse to the magnitude of the prompt fluorescence pulse. The experimental results are shown in Figs. 5 and 6. The data in Fig. 5 were taken with unpolarized light and that in Fig. 6 with polarized light. The solid curves in Figs. 5 and 6 vary as $(E-E_0)^{1/2}$ with E_0 equal to 4.1 eV and they are normalized to the experimental data at the highest energies.

One of the difficulties encountered in obtaining the experimental data on carrier generation was that it was very difficult to eliminate the effect of an extrinsic surface generation process. Considerable care was required to keep the crystal surface sufficiently clean.

The electric field dependence of carrier generation was measured and an attempt was made to detect a wavelength dependence of the electric field dependence as previously reported by Batt *et al.*[6] using one-photon excitation. The number of carriers generated was found to depend on the electric field and the dependence was consistent with previous results,[6,7] however, the accuracy of the measurements was quite poor and no wavelength dependence was observed.

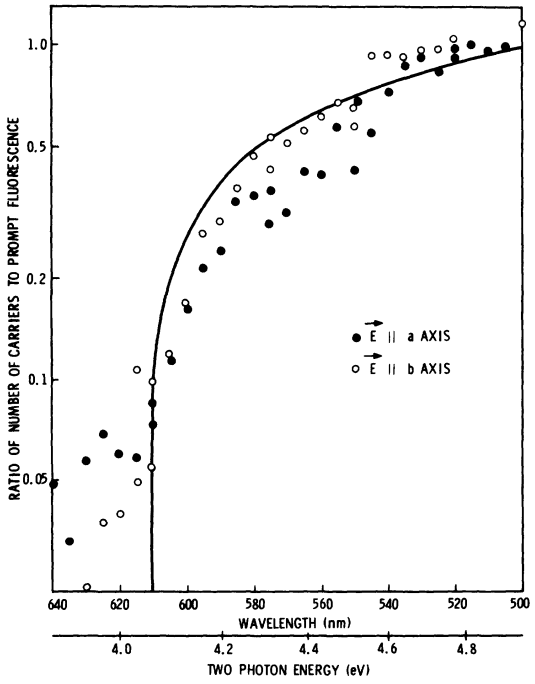

FIG. 6. Ratio of the number of carriers produced to the prompt fluorescence versus wavelength using polarized light. The solid curve varied as $(E-E_G)^{1/2}$ with $E_G=4.1$ eV and was equal to 1.0 at 500 nm. Solid circles give the data taken with the electric vector of the incident light parallel to the *a* axis and open circles are for data taken with the electric vector parallel to the *b* axis.

As with the two photon absorption coefficient data, the wavelength dependence of carrier generation reported here disagrees with that reported in two previous publications, one by Strome[13] and one by Bergman and Jortner.[14] Strome reported a very large peak in the photocarrier generation coefficient at about 4.3 eV which was not observed in the present work, and, if the ratio of his photocarrier generation coefficient to his fluorescence photon generation coefficient is taken as a function of wavelength as was done in the present experiments, his data indicate that this ratio is increasing with decreasing energy between 4.32 and 4.14 eV in contrast to the results reported here. Bergman and Jortner[14] reported a sharp rise in the two-photon carrier generation coefficient at 4.04 eV and attributed it to the onset of the conduction band. In addition, they reported structure in the two photon generation coefficient which they interpret as evidence for narrow vibronic components of the valence and conduction bands. No such structure was observed in the present work. It is perhaps worth pointing out that Bergman and Jortner also did not observe the peak in the photogeneration coefficient reported by Strome.

DISCUSSION

As has been noted above, the results reported here disagree with both those reported by Strome[13] and those reported by Bergman and Jortner[12,14] and the origin of the discrepancies between the results of the different groups is not known. In an attempt to make the results of this paper more credible the following points are stressed. In the present work, considerable care was taken to take into account both the temporal and the spatial variation in the laser beam and to carry out measurements keeping these two factors as constant as possible. To this end, in all experiments where it was possible, a second order phenomena was used as a reference in the belief that this procedure would minimize this type error. Second, the high-repetition-rate dye laser used in the present experiments made possible signal averaging techniques and other diagnostics such as measurements of spatial intensity variations in the laser beam. And finally, it was found that the carrier generation experiments were hindered by surface generation phenomena and considerable care had to be taken to keep the surface sufficiently clean so that the surface-generation phenomena did not dominate.

There are two primary conclusions that can be drawn from the present work if the experimental results are accepted. The first is that there is very little, if any structure in the two photon absorption coefficient between two-photon energies

of 3.9 and 5.0 eV and the second is that two-photon-excited carrier generation begins at about 4.1 eV and the cross section for carrier generation increases approximately as $(E-E_G)^{1/2}$, where E is the photon energy and E_G is 4.1 eV.

The two-photon absorption coefficient data are in very good agreement with the data of Fröhlich and Mahr[10] in the region where the data overlap, both in magnitude of the coefficient and magnitude of the polarization ratio and Fröhlich and Mahr concluded that there was a two photon excited state at 3.58 eV. Even though the magnitude of the absorption coefficient does not change appreciably above 3.9 eV according to the present experimental results, there is a very significant decrease in the polarization ratio. This latter result might be an indication that the state which is being excited by two photon absorption at the higher energies is no longer a molecularlike exciton state but is, in fact, a broad continuum something like that discussed by Hernandez.[4] Excitation to a broad continuum would result in the creation of singlet excitons because of geminate recombination. There was no evidence in the absorption spectrum for a state near 4.8 eV as suggested by Hernandez and Gold.[20]

In the case of carrier generation, there has been considerable discussion regarding whether a transition to an exciton state which subsequently autoionizes is involved or whether the transition is a direct transition to a continuum. Druger[21] recently discussed the theoretical situation with respect to one photon transitions.

The data reported here are not conclusive but they do support direct transitions to a broad continuum in the case of two-photon carrier generation. In the simplest case of allowed direct transitions between parabolic bands, the absorption coefficient can vary as $(E-E_G)^{1/2}$, where E is the incident photon energy and E_G is the energy gap.[22] The experimental data presented here do appear to be consistent with such a variation. Also, the polarization ratio data indicate that near 3.9 eV the two photon absorption process for the creation of singlet excitons is still dominated by a polarized molecular state but at higher energies the polarization ratio decreases toward one as might be expected for a broad continuum of fairly isotropic crystal states. As stated earlier, two-photon transitions to free-electron states in anthracene would lead primarily to singlet exciton states because of geminate recombination.

One reason that exciton autoionization has been invoked by some is that theoretical investigations of the band structure have indicated that the bands in anthracene are very narrow and experimental investigations have confirmed that the bands of states in which electron and hole transport occurs are very narrow. Therefore, if the broad continuum proposed here exists, the lifetime of the electron in this state has to be very short so that significant transport occurs only in a narrow band of states, created perhaps by polaron effects.[23] Another reason that autoionization of excitons was invoked for carrier generation is that the quantum efficiency for carrier generation has been found to be small for all mechanisms of generation so far investigated.[5] The quantum efficiency was not measured in the course of this investigation but if we take the photocarrier generation coefficient previously reported[13,15] for 5300 Å and compare it to the absorption coefficient reported in this paper, the quantum efficiency is found to be between 10^{-2} and 10^{-3}. Geminate recombination can easily account for these values and the fact that the number of carriers generated depends on the applied electric field as predicted by this theory is a strong indication that this is the correct interpretation.

ACKNOWLEDGMENT

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