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The Involvement of Triplet Excitons in the Surface Carrier Generation in Anthracene

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Abstract—It is demonstrated that triplet excitons are directly involved in the surface photo-carrier generation in anthracene. The result is obtained by altering the concentration ratio of singlet to triplet excitons with high energy radiation.

1. Introduction

In aromatic hydrocarbon organic crystals, photoinjection can be obtained with photons of energy less than the energy needed for ionization of the ground state. The feature that makes these crystals unusual is the participation of the Frenkel excitons in the photogeneration processes. In anthracene, photocarrier generation have been reported essentially for every process involving excitons and photons with a combined energy greater than 4 eV.[1,2,3,4]

The single photon extrinsic carrier generation at the surface of anthracene crystals is attributed to singlet exciton – surface impurity interaction. Supporting evidence for this mode of carrier generation is the well documented data that the spectral dependence of the steady state photoinjection current in the singlet absorption region is symbatic with the absorption spectra (maxima and minima at the same wave length in either spectrum) while the fluorescence quantum

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yield is antibatic with the absorption spectra. Accordingly, the singlet excitons diffuse to the surface and are annihilated there non-radiatively by impurities. The annihilation of the excitons by surface impurities generate free carriers that can be injected into the crystal. The closer to the surface are the excitons generated the more will reach it, hence, the current increases with the the increase of the absorption coefficient and the fluorescent yield decreases. However, this model of singlet exciton–impurity interaction is not in accord with data observed in the bulk where direct evidence was given for triplet exciton–trapped electron[5] and triplet exciton–trapped hole[6] interaction, but no direct evidence could be obtained for singlet exciton–trapped carrier interaction.

Our aim is to demonstrate that triplet excitons are directly involved in the single photon extrinsic carrier generation in anthracene. This conclusion is based on results showing a decrease in the density of the photo-carriers generated due to the selective reduction of the triplet concentration with the aid of high energy radiation.

2. Experimental

Transient photoinjection currents were measured in melt grown anthracene crystals of thicknesses of the order of 10^{-1} cm, sandwiched between two electrodes, one of which is transparent, by the following methods: (1) Applying a steady voltage across the crystal and then illuminating it by a microsecond duration light pulse; (2) Illuminating the crystal with a highly absorbed steady light (singlet absorption band) and then applying a microsecond rise time step function voltage pulse; and (3) Illuminating the crystal with a microsecond rise time step function light pulse, followed by a step function voltage pulse applied at different time intervals after the onset of the light pulse. The microsecond rise time step function light pulse was obtained by inserting a thin graphite film in the path between the steady light source and the crystal and then punching a hole in the graphite film by a Q-switched laser.[7] The polarity of the applied field in all the experiments was such that hole current was measured.

The crystals were irradiated from a ^{60}Co source at a rate of 560 rads/min. Experiments were made on crystals which were irradiated

through the conducting glass and on crystals in which the electrodes were removed during the irradiation. The results were not affected by the irradiation mode, and the reproducibility of the current was not impaired by the successive removal of the electrodes.

3. Results and Discussion

Transient photoinjection current curves obtained by illuminating the crystal first with steady light and then applying a voltage pulse, are shown in Fig. 1 for several irradiation doses. The initial value of the current in all the curves is well below the space-charge limita-

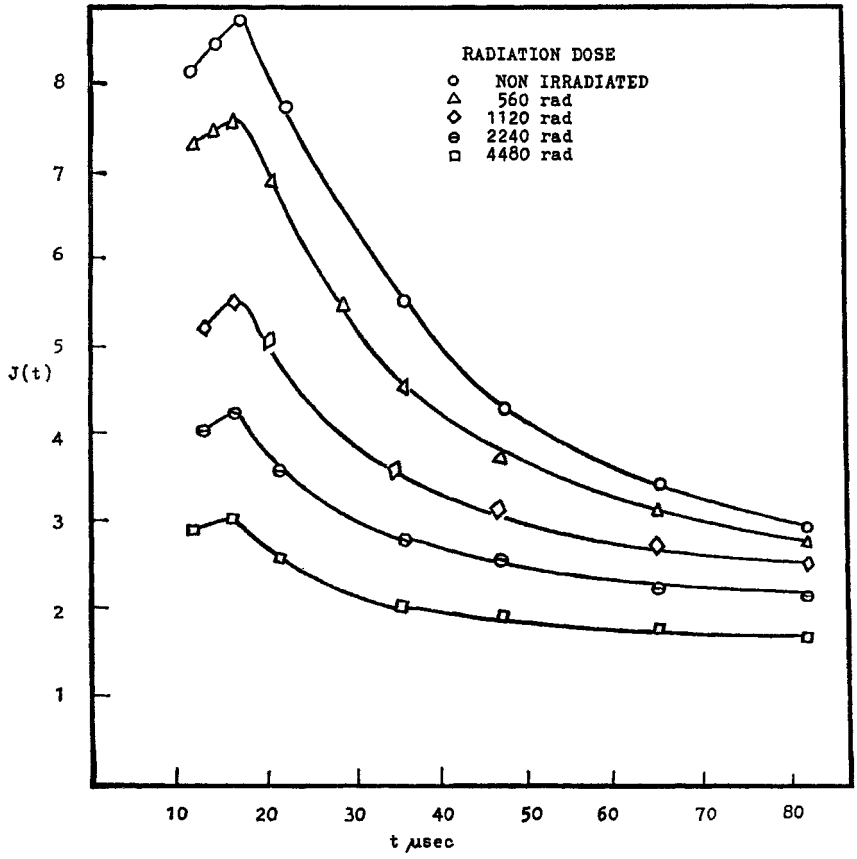

Figure 1. Current vs. time for different radiation dose.

tion. By increasing the irradiation dose the current decreases. This current decrease can be attributed either to an increase in the concentration of the surface traps or to the reduction of the carrier generation rate.

The effect of surface trapping on injection current is shown in Fig. 2. These curves were obtained by the successive application of a step function light and voltage pulse. The lower curve was obtained by applying first a step function voltage pulse to the crystal and then illuminating it with a step function light pulse. The five upper curves were obtained by delaying the application of the voltage

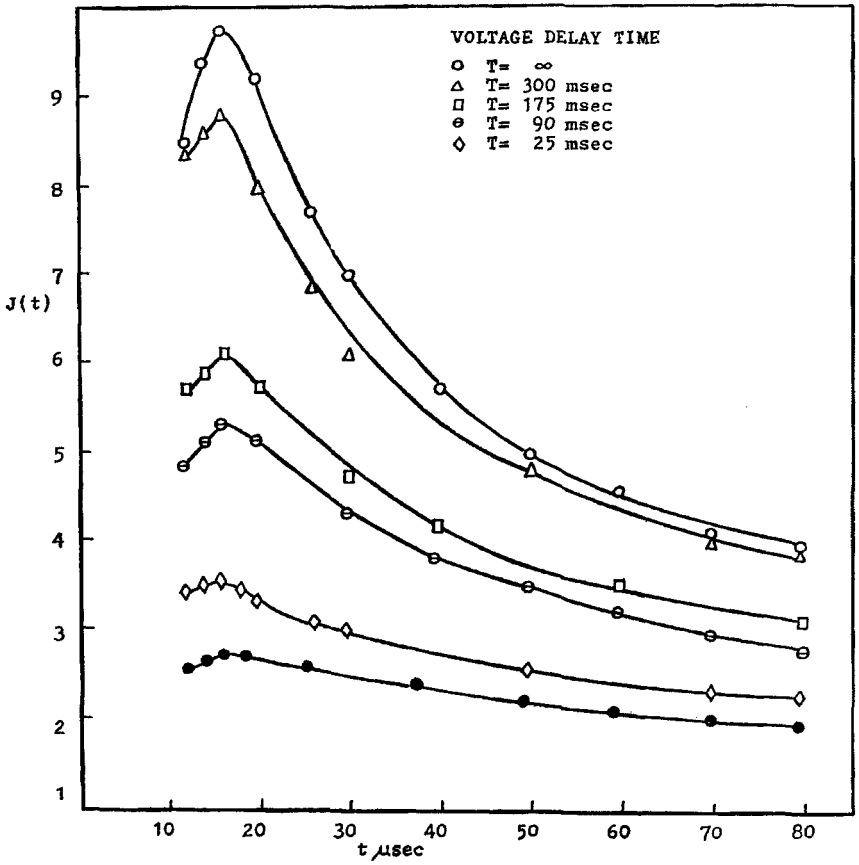

Figure 2. Current vs. time for different voltage delay times. The lowest curve was obtained by applying the voltage before the light.

pulse for 25; 90; 175; 300; and 1000 milliseconds respectively, after the onset of the light pulse.

Due to fast trapping and a slow release process at the surface, the magnitude of the carrier reservoir generated by the light increases with time until a steady state is reached. The initial value of the current depends on the magnitude of the reservoir at the time the current measurement starts. If the voltage is on when the step function light is applied (lower curve), the current measurement starts at the onset of the light pulse. If the crystal is illuminated before the voltage is applied (upper curves), the current measurement starts at the onset of the voltage. Due to the creation of a reservoir during the delay time interval, the current is larger the longer is the time elapse between the application of the light pulse and the voltage pulse. The saturation value of the current is reached when the application of the voltage is delayed for several seconds.

Though the intensity of the continuous light used for obtaining the step function light pulse is very high, about 10^{18} photons cm^{-2} sec^{-1}, it is small compared to the intensity of the short duration high intensity light pulses, about 10^{22} photons cm^{-2} sec^{-1}, used in experiments of transient space-charged limited currents. Hence, the injection rate is small and the current is electrode limited. The increase of the current until the first transit time is due to the increase of the charge density in the crystal during this time period.

A decrease in the injection current curves similar to those in Figs. 1 and 2 can be obtained also by reducing the carrier generation rate. As mentioned in the introduction, the symbatic behaviour of the spectral dependence of the photoinjection current and the antibatic behaviour of the fluorescent quantum yield with the absorption spectra, led to the conclusion that the single photon extrinsic carrier generation is due to singlet surface impurity interaction. In the bulk, triplet exciton trapped carrier interaction was observed directly. However, singlet exciton trapped carrier interaction could not be observed. It was also demonstrated that the triplet exciton trapped electron interaction generates free electrons.[5] The experimental results in the bulk, led to the anticipation that triplet excitons should be involved also in the process of photo-generation at the surface. The method by which the existence of triplet trapped carrier interaction was demonstrated in the bulk is not sensitive

enough when applied to the surface region. Triplets in the bulk are generated directly by weakly absorbed light. The density of singlets generated in this case by triplet interaction is about 10^6 times smaller than the density of the triplets even at very high light intensities when the difference between the densities is the smallest. In measurements at the surface region, the singlets are generated directly by the strongly absorbed light. The triplets are generated by the singlet triplet intersystem crossing with a yield of less than 1%. Due to the long life time of the triplets, the density of the singlets is smaller also in this case. However, even at very low light intensities when the triplet life time is determined by the monomolecular decay, the density of the triplets is only about 300 times larger than the density of the singlets. The trapped carrier exciton interaction rate constant contains the product of the density and the velocity of the excitons. The velocity of the singlets is about 100 times larger than that of the triplets. Hence, the method used in the bulk, where large difference between the densities of singlets and triplets can be obtained, can not be applied at the surface without ambiguity.

The ratio of the triplet to singlet concentration can be altered by gamma irradiation. Irradiating anthracene with gamma rays, singlet and triplet quenching centers are induced.[8,9] The quenching centers reduce the life times of the excitons, hence, their steady state concentrations are also reduced. While an irradiation dose of several hundred rads reduces considerably the concentration of the triplets, an irradiation dose of several hundred thousand rads are needed for a similar reduction in the singlet concentration. Hence, irradiating the crystal with small radiation doses, the triplet concentration is reduced without changing the concentration of the singlets. The current curves in Fig. 1 were obtained by illuminating the crystal for a long time before applying the voltage, therefore, at the onset of the current the singlet and triplet excitons are in their steady state concentrations. The small irradiation doses for which the current decreases indeed indicate that triplet excitons are directly involved in the surface carrier generation.

Radiation induces also carrier trapping centers which in turn causes to a reduction of the free carrier concentration.[10] A detectable increase in the density of carrier traps is induced by an ir-

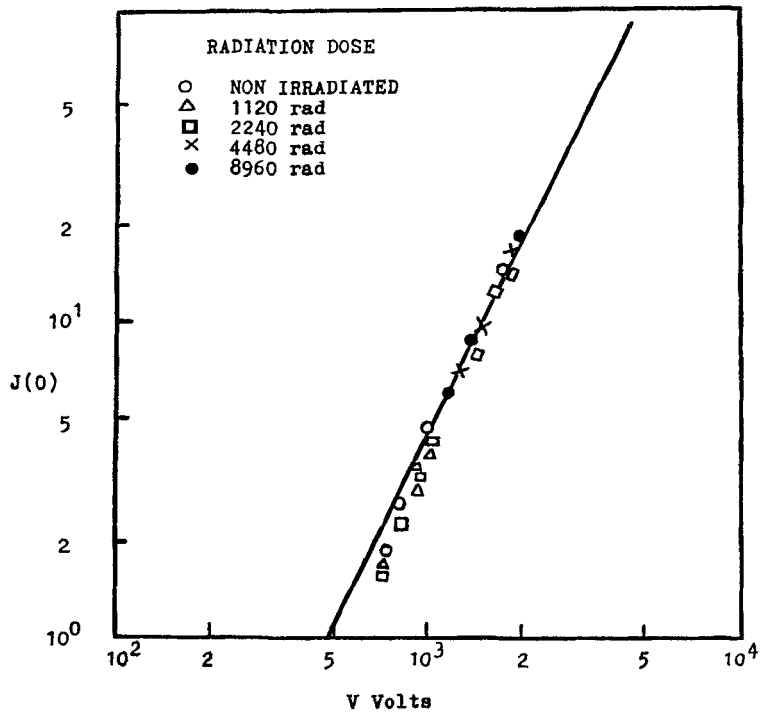

Figure 3. Initial value of the current vs. voltage for different radiation dose.

radiation dose of several thousand rads. That the lowering of the current in Fig. 1 is not due to an increase in the density of the surface traps induced by the radiation can be seen from Fig. 3, where the initial value of the current due to a short duration light pulse versus voltage is shown on a log-log scale. The V^2 dependence is typical for these curves even though the current is not space-charge limited.[11] The duration of the light pulse is short compared to the triplet life time, hence, at the onset of the current the triplet concentration is not in its steady state and therefore independent of the life time. The initial values of these current pulses are not affected by irradiation doses up to 10^4 rads. If the lowering of the current curves on Fig. 1 were due to an increase in the density of the surface traps and not due to a decrease in the generation rate, then the current in Fig. 3 should have been affected similarly.

The experimental evidence given in Figs. 1 and 3, demonstrates

that triplets are directly involved in the surface photo-carrier generation process in anthracene. Triplet surface impurity interaction can not explain the spectral response of the photoinjection current and the related fluorescence quantum yield results. The mechanism for the involvement of the triplets in the surface carrier generation process remains open. The known[1] linear dependence of the current on the light intensity is not in accord with a singlet-triplet interaction model, however, it is also not inconsistent unless the process is controlled by the concentration of the singlets. This is possible since the density of the singlets is about 300 times smaller than the density of the triplets. However, it would be difficult to account, by this mechanism, for the symbatic behavior of the photocurrent and the antibatic behavior of the fluorescence with the absorption spectra.

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