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Generation of Electrons and Holes in Anthracene by Ruby Laser Light†‡

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Abstract—The number of carriers generated in an anthracene crystal by a pulse of light from a Q-spoiled ruby laser has been investigated. The number observed far exceeds the number expected on the basis of existing theoretical predictions, varies approximately as the intensity of the laser light cubed and increases exponentially with increasing temperature as $e^{-T_0/T}$ where $T_0 = 2 \times 10^3$ °K. The carriers are generated uniformly throughout the volume of the crystal. A neodymium laser pulse of the same energy density produced no detectable signal so it is concluded that the carriers are not produced by the electric field associated with the light pulse.

Introduction

The fact that electrons and holes can be created in anthracene by light from a ruby laser has been reported in several papers recently.[1–3] In the early papers[1] the photocurrent was attributed to direct excitation of localized anthracene ions or trapped carriers by the incident photons. In reference 2, a Q-spoiled ruby laser was used rather than a normal pulsed laser and with the higher light intensity, effects were seen which were interpreted in terms of carrier creation by two photon absorption. In the most recent work,[3] it was asserted that evidence was obtained which showed that the carriers were generated by exciton–exciton annihilation[4, 5] after the excitons had been created by two photon absorption.[6, 7]

It was this last observation which prompted the work presented in this paper. The possibility of carrier creation by exciton–exciton annihilation has been considered for sometime[8] and recently very

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good agreement between theory[4] and experiment[5] has been obtained. However, when attempts were made to calculate the number of carriers created in an experiment using light of a wavelength different from that of reference 5, very serious difficulties arose.[9]

It appeared, therefore, that the observation of carrier generation by ruby laser light might be able to resolve this problem. Two photon absorption leading to creation of excitons has been observed in several laboratories and is a well established process. The results reported by Hasegawa and Yoshimura[3] were not convincing, however, primarily since the data were taken with such high carrier concentrations that electron hole recombination played a major role in the photocurrent pulses observed.

In this paper, we report on experiments performed at considerably lower carrier densities. The results disagree with those obtained by Hasegawa and Yoshimura and do not support the exciton–exciton mechanism for carrier creation. However, the observations do not necessarily disprove the possibility of the exciton–exciton mechanism since the number of carriers created by the laser light far exceeds the number predicted by this theory.

Experimental Techniques

The experimental technique used is similar to that used in previous experiments to study the drift mobility of electrons and holes in anthracene.[10] The light from a ruby laser created a small number of electrons and holes in a crystal which was placed between two pieces of conducting glass. The conducting glass plates, between which a voltage was applied, acted like the plates of a parallel plate capacitor. The lifetime of the electrons and holes was sufficiently long that they were all swept out of the crystal by the applied field and the number of carriers created was kept sufficiently small so that recombination and the electric field set up by the displacement of the charge was negligible. The number of carriers created was determined by measuring the amount of charge swept out of the crystal after a pulse of light.

The ruby laser used was a TRG Model 104 Q-spoiled laser which puts out approximately 0.15 joules in a pulse 40 nsec long. The intensity of the light was reduced by filters and by using a plano concave lens, focal length = -48 mm, to spread the laser beam to a larger diameter. The negative lens not only reduced the light intensity but provided essentially uniform intensity over the surface of the crystal. The absolute intensity of the light was

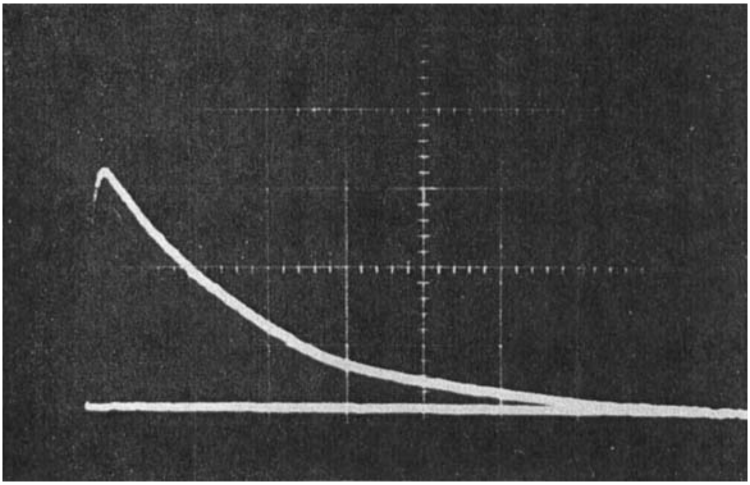

Figure 1. A typical photocurrent pulse with 1400 volts applied to a crystal 1.27 mm thick. Each major division on the horizontal scale corresponds to 5 μsecs.

measured with a ballistic thermopile. Since, as will be pointed out later, the main source of disagreement between the results reported here and those of reference 3 is in the magnitude of the light intensity, considerable care was taken in its measurement. Experiments were performed both without the plano-convex lens and with the anthracene crystal 20 cm from the lens with essentially identical results and the calibration of the ballistic thermopile was checked by comparing it to another calibrated ballistic thermopile.

The light from a ruby laser is very weakly absorbed in an anthracene crystal, the absorption coefficient[11] being approximately

10^{-5} cm^{-1}, and therefore the carriers are presumably produced uniformly throughout the bulk of the crystal. That this is the case can be seen from the shape of the photocurrent pulse observed. A typical photocurrent pulse is shown in Fig. 1. This pulse is expected to be the sum of two triangular-shaped pulses produced by the drift of the holes and electrons to the appropriate electrode if the carriers are created uniformly throughout the crystal. Figure 1 is in very good agreement with the shape predicted and the drift mobility of the carriers determined from pulses like that shown was found to be 0.7 cm^2/v sec and 0.35 cm^2/v sec for holes and electrons, respectively, values which are in excellent agreement with those published for the direction perpendicular to the *ab* plane.[12] The light was incident on the crystal perpendicular to the *ab* plane and the electric field was applied parallel to the direction of propagation of the light.

The crystals used were grown from the melt from zone refined synthetic anthracene.

Experimental Results and Discussions

With a light intensity of 2×10^{23} photons cm^{-2} sec^{-1}, a carrier density of 3.4×10^{8} cm^{-3} was observed. The number of carriers created varied approximately as the intensity of light cubed and varied exponentially with temperature as $e^{-T_0/T}$ with $T_0 = 2 \times 10^3$ °K. Typical intensity dependence results are shown in Fig. 2 and the temperature dependence is shown in Fig. 3.

According to the theory of carrier generation by exciton–exciton interaction, the number of carriers generated per unit volume by this process in a pulse type experiment is

$$n = \int_0^\infty \beta N^2 \, dt$$

where β is the exciton–exciton interaction rate constant leading to free carrier pairs and N is the concentration of singlet excitons. If it is assumed that a light pulse from the ruby laser is a square pulse of amplitude I photons cm^{-2} sec^{-1} and width Δt and that the exciton lifetime, τ, is small compared to Δt, then during a laser pulse $N = \alpha I^2 \tau$ where α is the two-photon absorption rate constant. The exciton lifetime is not small compared with Δt but the error

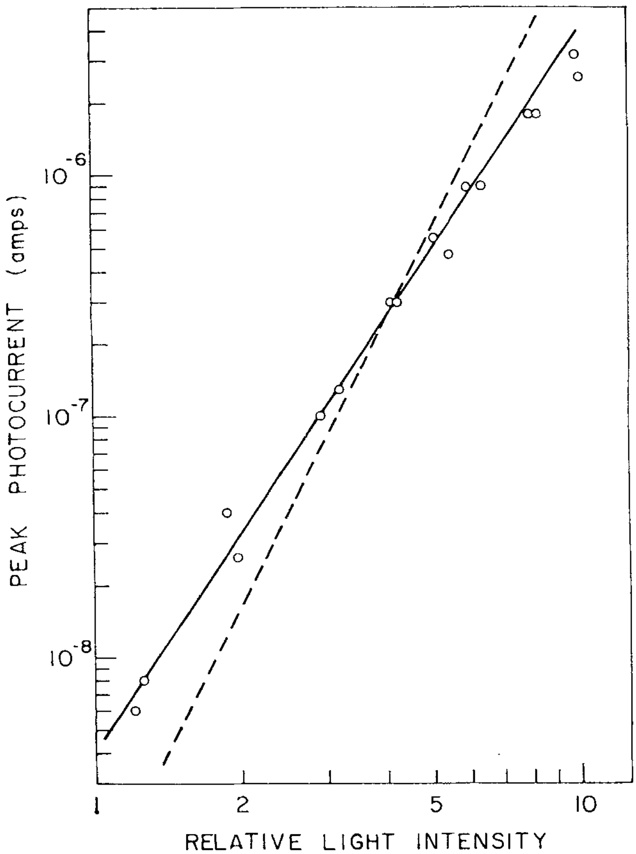

Figure 2. Intensity dependence of the number of electron-hole pairs created. The solid line is drawn for an intensity cubed dependence and the dashed line for an intensity to the fourth power dependence.

caused by this approximation is relatively small and, as will be seen below, is obviously negligible compared to the discrepancy which has been observed between theory and experiment. With these approximations, the number of carriers produced by a pulse of light from a ruby laser is $n=\beta \Delta t \alpha^2 \tau^2 I^4$. Using the values $\beta = 5 \times 10^{-12}$ cm^3 sec^{-1},[5] $\Delta t = 4 \times 10^{-8}$ sec, $\alpha = 1.26 \times 10^{-29}$ cm sec,[7] $\tau = 2.6 \times 10^{-8}$ sec,[13] and $I = 2 \times 10^{23}$ cm^{-2} sec^{-1}, the number of carriers created by a pulse of ruby laser light is calculated to be 34 cm^{-3}. This is seven orders of magnitude smaller than the number

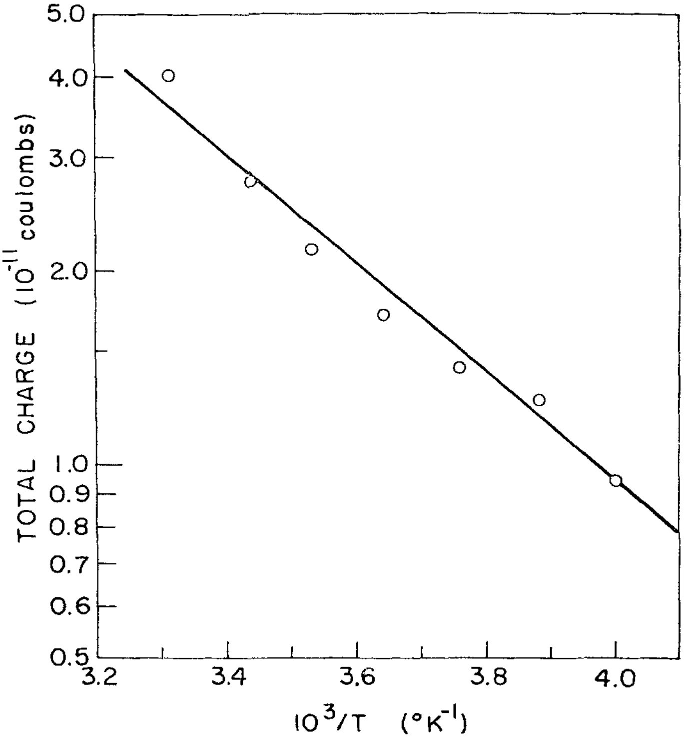

Figure 3. Temperature dependence of the number of electron-hole pairs created by a pulse of light from a ruby laser.

observed experimentally. In order to obtain agreement between theory and experiment, it would have to be assumed that the exciton–exciton interaction rate constant is seven orders of magnitude larger than previously reported or that the two photon absorption rate is higher by about 3.5 orders of magnitude. Either of these assumptions appears to be completely unreasonable and therefore exciton–exciton annihilation cannot account for the experimental results.

Hasegawa and Yoshimura[3] obtained results which appeared to agree with the exciton–exciton interaction theory by assuming that all the light from their laser went through a 1 mm^2 area even though they had not focused the beam.[14] This assumption was based on the observation that at high laser light intensity, a damaged spot appeared in the crystal and the area of the spot was of the order of 1 mm^2. If we assume that their maximum photon flux is equal to ours when we are not using the negative lens, an assumption which appears reasonable since we were using the same model laser, the experimental results are very similar. Therefore, we conclude that the disagreement arises primarily from the fact that Hasegawa and Yoshimura assumed that all their light went through 1 mm^2, rather than approximately 1 cm^2 which would correspond to the cross-sectional area of the ruby rod. An error of a factor of 100 in the light intensity leads to an error of a factor of 10^8 in the number of carriers expected.

In addition to the very large discrepancy between the number of carriers observed experimentally and the number predicted theoretically, we did not observe a fourth power intensity dependence. The results shown in Fig. 2 illustrate the degree of confidence with which this statement can be made. The solid lines represent an intensity cubed dependence and the dashed line an intensity to the fourth power dependence.

Since the exciton–exciton annihilation theory cannot explain the experimental observations, the possibility that the carriers are somehow generated by the electric field associated with the coherent light pulse was investigated. To do this, an anthracene crystal was irradiated by light from a neodymium laser at intensities such that if the light had come from a ruby laser it would have produced a signal 5000 times larger than the minimum detectable signal. At equal intensities the electric fields are equal but the energy of a photon from the neodymium laser is smaller than the energy of a photon from a ruby laser, 1.17 eV compared to 1.79 eV. Therefore, if multiple photon processes are involved a large change in magnitude of the signal might be expected because of the change in energy of the photons but if the carriers are generated by the electric field, the magnitude of the signal would be the same. The fact that no signal was observed eliminates the possibility of carrier generation by the electric field.

We initially interpreted the observation of an exponential temperature dependence as evidence that some extrinsic process or vibrational states of the molecule were involved in the carrier generation mechanism. However, in conjunction with some other work, we have recently pointed out that such a behavior is probably associated with an intrinsic carrier generation mechanism when the mean free path for carriers is small.[15] The exponential temperature dependence arises because the probability that an electron and hole get free of each others coulomb field after a band-to-band transition varies exponentially with temperature if the carrier mean free path is small compared to the radius of the electron-hole recombination cross-section. The temperature dependence of the number of carriers generated can be written as $e^{-T_0/T}$, where the characteristic temperature, T_0, is determined primarily by the carrier mean free path.

In conclusion, it has been found that the number of carriers generated by a pulse of ruby laser light is much larger than the number predicted by the existing theory, varies as the intensity of light cubed and varies exponentially with temperature with a characteristic temperature, T_0, of 2×10^3 °K. An attempt to generate carriers with a neodymium laser demonstrated that the carriers are not generated by the high electric field associated with the coherent light pulse.

Acknowledgments

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