PHOTOIONIZATION OF EXCITONS IN ANTHRACENE*

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Experimental results are presented which show that carriers can be produced by photoionization of excitons in anthracene and it is pointed out that experimental results previously interpreted as evidence for exciton-exciton annihilation can more reasonably be interpreted in terms of exciton photoionization.

Recent experiments have shown that the number of carriers generated in an anthracene crystal by light from a ruby laser varies as the cube of the intensity of the light.[1,2] In this paper, experimental results are presented which show that these carriers are produced by photoionization of excitons, and it is pointed out that experimental results previously interpreted as evidence for exciton-exciton annihilation can more reasonably be interpreted in terms of exciton photoionization.

The observation of an intensity-cubed dependence left open several possibilities for the mechanism by which carriers are created. Four which have been considered are (1) direct three-photon absorption, (2) creation of singlet excitons by two-photon absorption[3] followed by photoionization of the exciton, (3) photoionization of triplet excitons which were created by intersystem crossing from the two-photon-created singlet excitons, and (4) two-photon absorption involving a ruby-laser photon and a singlet-exciton fluorescent photon.[4] The experiments reported in this paper were designed primarily to distinguish between the above mechanisms.

An anthracene crystal was irradiated by two pulses of light from a Q-spoiled ruby laser. The time delay between the arrival of the two pulses at the crystal was variable over the range from 0 to 40 nsec. The two pulses were obtained by separating a single pulse into two with a partially reflecting mirror and then allowing the two pulses to traverse different optical paths prior to arriving at the crystal. Figure 1 shows a diagram of the experimental setup.

If we let $I_1(t)$ and $I_2(t)$ be the intensities of the two light pulses at the crystal, then the total light intensity seen by the crystal, I, is $I_1(t)+I_2(t)$. By changing the time delay between the two pulses the time dependence of I can be varied. Direct three-photon absorption would predict that the number n of carriers generated per unit volume by the two pulses is equal

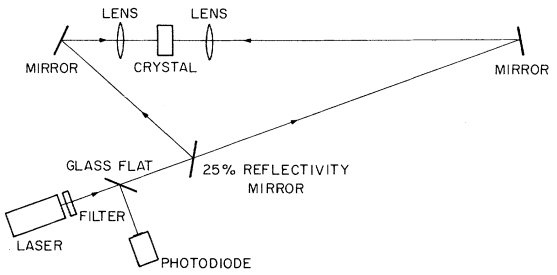

FIG. 1. Block diagram of the experimental setup.

to $\int_0^\infty KI^3dt$ where K is the rate constant associated with the three-photon absorption process. If the carriers are generated by photoionization of excitons, on the other hand, $n=\int_0^\infty \sigma NIdt$ where σ is the cross section for photoionization and N is the concentration of excitons. If the loss of excitons by photoionization is neglected,

$$dN/dt=\sigma I^2-\beta N$$

and

$$N(t)=e^{-\beta t}\int_0^t \alpha I^2(\xi)e^{\beta\xi}d\xi,$$

where α is the rate constant for two-photon absorption and β is the reciprocal of the lifetime of the exciton.

The experimental results presented in Fig. 2 were obtained by adjusting the time difference between the two pulses to some desired value and then adjusting their intensity so that the number of carriers created by each light pulse independently was approximately the same. Then the number of carriers created was measured when both of the pulses were incident on the crystal, and this number was compared to the sum of the number of carriers created by the pulses independently. All the experimental data that were analyzed for the best experimental arrangement found are shown in Fig. 2 and, therefore, the scatter in the data is indicative of the magnitude of the experimental error. Fluctuations that might have been caused

by variations in the laser light intensity were minimized by selecting for analysis only those light pulses of approximately the same magnitude. The height and shape of the laser pulses were measured with a photodiode monitor. The laser pulses used for this experiment were 17 nsec wide at the half-intensity point.

The theoretical curves shown in Fig. 2 were obtained by numerically integrating the expressions for N and n, using the pulse shape determined from the photodiode monitor and assuming $\beta = 4\times10^{7}$ sec^{-1}. The solid curve, which agrees very well with the experimental data, is the result predicted on the basis of the singlet-exciton photoionization hypothesis, and the dashed curve is the result predicted on the basis of the three-photon absorption hypothesis. The numerical integration to determine $N(t)$, the concentration of singlet excitons as a function of time, was tested by observing the fluorescence light emission from a crystal as a function of time after irradiating it with both a single pulse and a double pulse with a difference in time of arrival of 33 nsec. The fluorescent light intensity is directly proportional to the concentration of excitons. The agreement between the theoretical predictions and experiment was excellent.

Measurements were also carried out with laser pulses 10 nsec wide. The narrower pulses were obtained by Q spoiling with a saturable dye solution as well as a rotating prism. The results of this experiment were also in agreement with the prediction of the singlet-exciton photoionization hypothesis but the scatter in the data was much larger than that in the data shown in Fig. 2.

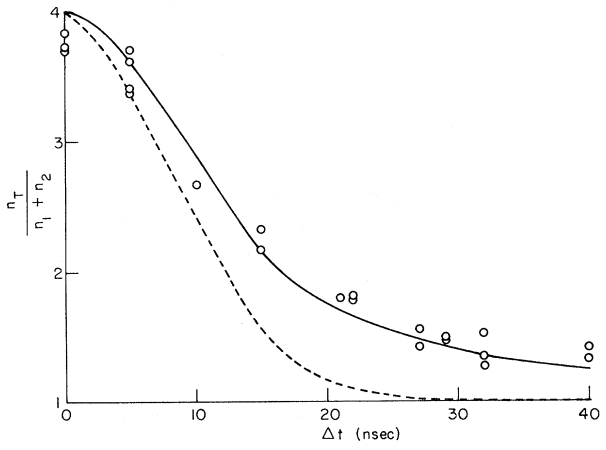

FIG. 2. Ratios of the number of carriers produced by the two pulses to the sum of the number of carriers produced by each pulse independently as a function of the difference in the time of arrival at the crystal of the two pulses. The solid line is the theoretical curve calculated for singlet-exciton photoionization, and the dashed line is the theoretical curve for three-photon absorption.

The experimental results prove conclusively that an intermediate state with a lifetime of very close to 25 nsec is involved in the carrier generation process. Therefore, two of the four mechanisms which were mentioned earlier have been eliminated. Direct three-photon absorption does not involve an intermediate state, and the lifetime of triplet excitons is much longer than 25 nsec. Of the two processes remaining, two-photon absorption involving a fluorescent photon and a laser photon appears to have been eliminated by an experiment in which the volume of the crystal irradiated by the laser light was varied by more than a factor of 10. The volume was varied by placing masks with circular holes in them in front of the crystal. The two-photon absorption process would lead to a greater than linear dependence of the number of carriers generated on the volume illuminated because the fluorescent-photon concentration depends on the volume but experimentally the dependence was found to be linear. How far from linear the dependence would be based on the two-photon absorption hypothesis has not been calculated so that the degree of certainty with which this process has been eliminated has not been determined.

The only process left which is consistent with all the experimental results is photoionization of two-photon–excited excitons. The absolute magnitude of the cross section for photoionization, σ, was obtained in another experiment in which only a single light pulse was incident on the crystal and the absolute magnitude of the light intensity on the crystal was measured. Using $\alpha = 1.3\times10^{-29}$, the value first obtained by Hall, Jennings, and McClintock[5] and independently verified by measurements in this laboratory as well as others, σ is found to be 2×10^{-19} cm^{2}.

The possibility of photoionization of excitons as a mechanism of production of carriers in anthracene has been considered previously. Choi,[6] using theoretical estimates of the quantities involved, concluded that experimental observations of carrier generation by weakly absorbed light were not the result of exciton

photoionization. Silver et al.[7] had reported that for weakly absorbed light, in the wavelength range 4150 to 4550 Å, the number of carriers generated depended on the square of the intensity of the light and the carriers were generated in the bulk of the crystal. They had interpreted their results in terms of exciton-exciton annihilation. Schott,[8] extending Choi's argument, concluded that exciton photoionization is nearly always more likely to occur than exciton-exciton interaction for carrier generation under Q-spoiled ruby-laser excitation of anthracene. Courtens, Bergman, and Jortner[2] have calculated a cross section for photoionization of excitons from their experimental data and report a value of 0.6×10^{-19} cm^2.

For the reasons listed below, it now appears that the most reasonable interpretation of the results of the experiment on weakly absorbed light is in terms of exciton photoionization. First, using the exciton-photoionization hypothesis, the number of carriers produced per unit area by a pulse of light in the wavelength region where photon absorption results in singlet excitons and where all the incident photons are absorbed within the crystal is equal to $(\sigma/2\beta)\times\int_0^\infty I^2(t)dt$. An experiment was carried out at 4250 Å using a xenon flash tube and a monochromator, and σ was found to be about 5×10^{-19} cm^2, a value in surprisingly good agreement with the value found at 6940 Å. Secondly, at wavelengths for which the absorption coefficient is very high, calculations based on the exciton-exciton annihilation hypothesis predict as much as three orders of magnitude more carriers than are observed experimentally.[9] This discrepancy does not occur when the exciton-photoionization hypothesis is used because the number of carriers created by this mechanism is independent of wavelength as long as all the light is absorbed within the crystal. Finally, the exciton-photoionization hypothesis appears more reasonable because measurements of the wavelength dependence of the number of carriers generated by a pulse of light in the wavelength range 4100 to 4400 Å show that the number of carriers generated is much less sensitive to wavelength than is expected on the basis of the exciton-exciton annihilation process.[10]

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ISOTOPE SHIFT MEASUREMENTS USING K X RAYS IN Sn, Sm, AND W*

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Electronic $K\alpha_1$ x-ray isotope shifts have been measured for $Sn^{116-124}$, $Sm^{148-154}$, $W^{182-184}$, $W^{184-186}$, and $W^{182-186}$ using a curved-crystal Cauchois spectrometer. The analysis of the measurements has included the volume effect, screening, normal and specific mass shifts, nuclear polarization, and electron magnetic moment interaction.

It is well known[1] that the interpretation of the optical isotope shift (I.S.) data in terms of the fractional change in the rms radius of the nuclear charge distribution $\delta R/R$ is severely limited by the large uncertainties ($\approx$20%) associated with the atomic screening corrections. This limitation is practically absent in the case of the atomic K x rays or muonic x rays. A few years ago it was therefore attempted in this laboratory to study the K-x-ray I.S. using crystal diffraction technique. The first successful observation of the K-x-ray I.S., in $U^{233-238}$, was reported by Brockmeier, Boehm, and Hatch.[2] They used a 2-m curved-