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SINGLET EXCITON-EXCITON INTERACTION IN ANTHRACENE*

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The interaction of two singlet excitons to produce electron carriers has been observed in anthracene for the wavelength range 315-405 nm. With an applied field of 10^4 V cm^{-1}, the rate constant for carrier production is $0.9\times10^{-12\pm0.4}$ cm^3 sec^{-1}. The rate constant for singlet-exciton second-order disappearance is $1.5\times10^{-8\pm0.3}$ cm^3 sec^{-1}

Recent experiments[1,2] have demonstrated that free carriers may be generated in crystalline anthracene via photoionization of singlet excitons. The investigators agree on a cross section σ_c for free-carrier production of ca. 10^{-19} cm^2 at 694 nm. At this wavelength the singlet excitons are generated by direct two-photon absorption and the observed intensity dependence of the photocurrent is cubic. As a result of his experiments, Kepler has suggested[1] that the important photoconductivity experiments using weakly absorbed light of $\lambda > 415$ nm reported by Silver, Olness, Swicord, and Jarnagin[3] may be more reasonably interpreted in terms of exciton photoionization than by the exciton-exciton interaction ionization mechanism assumed by those investigators. Indeed, assuming an exciton photoionization mechanism, Kepler measured[1] a free-carrier production cross section of 5×10^{-19} cm^2 at 425 nm. This value makes very reasonable his suggestion that exciton photoionization is the likely carrier generation mechanism at 425 nm, as he has proved it to be at 694 cm. Strome[4] has found excellent agreement at 421 nm with Kepler's cross-section value at 425 nm. Kepler and Strome each discuss other observations which lead them to favor exciton photoionization as the carrier generation mechanism in the weakly absorbed light region. Thus, it appears that no unequivocal observation of singlet exciton-exciton carrier generation has been reported up to the present time.

We have measured the number of electron carriers generated in single crystals of anthracene at an applied field of 10^4 V/cm using pulses of approximately monochromatic, unpolarized light at wavelengths between 315 and 410 nm. Figure 1 illustrates the observed nearly quadratic dependence of the number of carriers generated on the incident light intensity. Further, the wavelength dependence and magnitude of the number of carriers generated argue strongly that exciton-exciton interaction rather than exciton photoionization is the dominant carrier generation mechanism in the range 330-400 nm. The observation of near quadratic intensity dependence is in contrast to the linear dependence found in this region of strong light absorption by earlier investigators[5,6] who were specifically examining the possible importance of the exciton-exciton mechanism in the near uv region. The present results eliminate the "paradox"[7] that the exciton-exciton mechanism seemed to be important with weakly absorbed light but unobservable with strongly absorbed light.

The single crystals used in our experiments were cleaved and mounted under a nitrogen atmosphere, and all measurements were done in a photoconductivity cell evacuated to about 10^{-5} Torr. Typically, depending on wavelength, 10^6 to 10^7 electron carriers were generated when a flash of ca. 10^{12} photons, in a pulse with width at half-peak-height $= 0.30\times10^{-6}$ sec, was incident

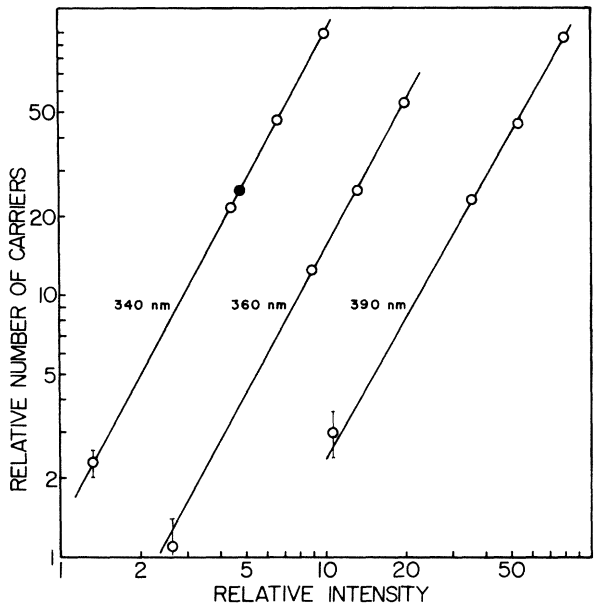

FIG. 1. Intensity dependence of electron carrier generation. The units are arbitrary and data for each wavelength have been arbitrarily displaced for clarity. The fully blackened point in the 340-nm data corresponds to $I_0 = 2.5\times10^{18}$ photons cm^{-2} sec^{-1} and $N = 3.75\times10^6$, the values used to calculate β. For 340 nm, slope = 1.87; for 360 nm, slope = 1.85; and for 390 nm, slope = 1.77.

on the *ab* face of a 1-cm^2 crystal. In the kinetic treatments to follow, the light pulse is treated as a square-wave pulse of intensity I_0 equal to the peak flash intensity and with wavelength-independent width $w = 0.30\times10^{-6}$ sec. The output of the air-spark flash lamp varied with wavelength by less than 50% in the measurement range and at each wavelength integrated flash intensities were reproducible to ±2%. The integrated intensities were measured by means of an EG & G Model-580 radiometer, employing a calibrated photodiode. A Corning No. 0-54 filter, was used to eliminate all stray light of $\lambda < 300$ nm. The number of carriers generated was determined from integrated voltage versus time oscilloscope traces.[8] The number of hole carriers generated was usually only 2 to 3 times larger than the number of electrons generated, indicating that surface generation of holes[9] was largely suppressed under clean surface conditions. Because the hole yield was somewhat nonreproducible, all quantitative measurements involved electron carriers. Possible effects of trapped charge build-up on carrier yields or transit times proved to be unobservably small during the course of the experiments.

Assuming that a steady-state concentration of excitons is quickly established during absorption of the light pulse,[10] one can readily show that the total observed cross section for carrier production may be written as $\sigma_{meas} = \beta\tau k + \sigma_C$, where β is the bimolecular rate constant for production of free carriers via the exciton-exciton mechanism, $\tau = 2\times10^{-8}$ sec is the singlet-exciton lifetime,[11] k is the crystal absorption coefficient, and σ_C is the cross section for carrier production via exciton photoionization. Since the average value of k is about 20 cm^{-1} at 425 nm,[12] Kepler's value of $\sigma_{meas} = 5\times10^{-19}$ cm^2 places an upper limit of ca. 10^{-12} cm^3 sec^{-1} on β. This upper limit is consistent with the value of $\beta = 5\times10^{-12}$ measured by Silver et al.[3] because their estimate of order-of-magnitude intensity uncertainty makes their value of β uncertain by two orders of magnitude. However, since it is certainly reasonable to accept Kepler's suggestion that $\sigma_{meas} = \sigma_C$, the lower limit on β is zero and its true value is apparently experimentally undetermined. Because, in this simple analysis, the contribution of the exciton-exciton mechanism to photocarrier production depends linearly on k while that from exciton photoionization is independent of k, an experiment to distinguish between the two mechanisms is suggested. The average value of k approaches 10^5 cm^{-1} in the near uv[13] (see Fig. 2), and one should expect the exciton-exciton mechanism to dominate exciton photoionization for strongly absorbed light as long as β is at least 10^{-15} and σ_C is of the order of 10^{-19}.

Under conditions where the exciton photoionization mechanism is unimportant and where the concentration of excitons has attained a steady state, the number of electron carriers generated per square centimeter of crystal surface is $N = \frac{1}{2}\beta w\tau^2 k I_0^2$. For the present we have assumed that, in determining the exciton concentration, exciton-exciton interactions play a negligible role compared with that of first-order exciton decay and exciton diffusion is unimportant. Thus, to the extent of the validity of these assumptions, N should vary quadratically with I_0 (see Fig. 1) and N/I_0^2 should be proportional to k. Figure 2 allows comparison of the wavelength variation of the experimental quantity N/I_0^2 with that of the crystal absorption coefficient.[14] It is apparent that the structural features of the absorption spectrum are qualitatively reproduced in the N/I_0^2 data. However, the variation of N/I_0^2 in the region 320-390 nm is less than that exhibited by k. The failure of N/I_0^2 to follow k quantitatively

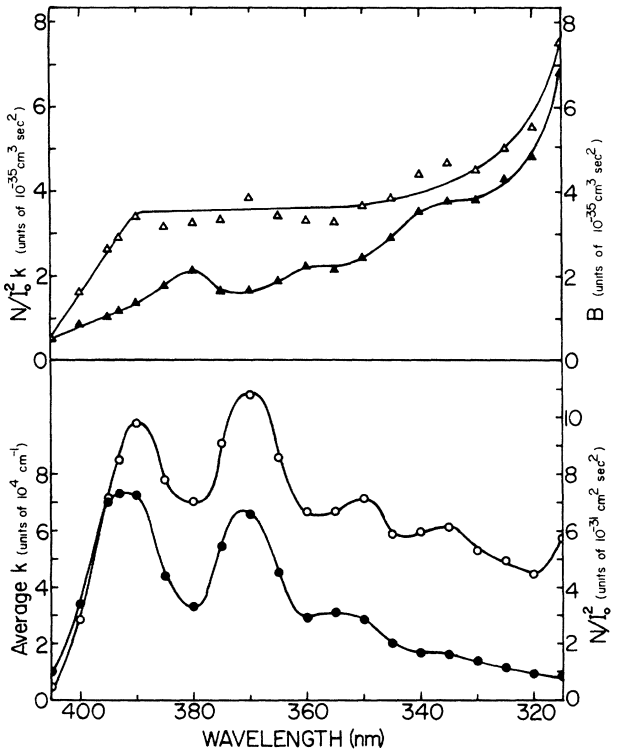

FIG. 2. Wavelength dependence of electron carrier generation. Closed circles indicate computed average values (Ref. 14) of k; open circles indicate experimental value of N/I_0^2, where N is the number of electron carriers generated per square centimeter of crystal surface and I_0 is the flash intensity in photons cm^{-2} sec^{-1}; closed triangles indicate values of N/I_0^2k; and open triangles indicate values of $B=N(kl+1)^3/I_0^2k$, where $l=4.60\times10^{-6}$ cm, the measured (Ref. 15) exciton diffusion length.

as predicted by the approximate expression for N is illustrated in a plot of N/I_0^2k as a function of wavelength (see Fig. 2). The observed dependence on k is to be expected if exciton diffusion is rapid enough to dilute significantly the exciton concentration in the extinction-depth region.

In the steady-state approximation the effects of exciton diffusion can be included by solving the following equation[15] for the singlet-exciton number density $S(cm^{-3})$:

$$\frac{\partial S(x)}{\partial t}=0=kI_0e^{-kx}-S/\tau+D\frac{\partial^2 S}{\partial x^2}, \tag{1}$$

where D is the constant appropriate for exciton diffusion in the x direction perpendicular to the ab crystal plane. With the boundary conditions $S=0$ at $x=0$ and at $x=\infty$, an expression for $S(x)$ can be easily evaluated. The rate of carrier generation by the biexcitonic mechanism is $\partial n(x,t)/\partial t=\beta S^2(x)$. Substituting the expression for $S(x)$ resulting from Eq. (1) into $n(x)=\beta wS(x)^2$ and integrating from $x=0$ to $x=\infty$, one obtains

$$N=\frac{\beta w\tau^2kI_0^2}{2(kl+1)^3}, \tag{2}$$

where, following Northrup and Simpson,[15] we have introduced $l=$ diffusion length $=(D\tau)^{1/2}$. Except for the factor $(kl+1)^{-3}$ resulting from diffusion, the expression for N is unchanged from the simple form previously examined. If diffusion is responsible for the behavior of N/I_0^2k illustrated in Fig. 2, we then expect the function $B=N(kl+1)^3/I_0^2k$ to be much more nearly independent of wavelength. This independence for 340 nm $<\lambda<$ 390 nm within expected error limits is illustrated in Fig. 2 where $l=4.60\times10^{-6}$ cm, the value measured by Northrup and Simpson,[15] has been used to calculate $(kl+1)^3$.

For $\lambda<340$ nm, B and hence β appear to increase. This behavior results from the onset of single-photon carrier generation in this wavelength range. From an experimental measurement of the single-photon electron-carrier quantum yield,[16] made with an order-of-magnitude less intensity, one can calculate that roughly half the carriers observed at 315 and 320 nm in the present high-intensity measurements were generated via the single-photon process. Thus, the B values at these wavelengths are actually consistent with the values at longer wavelengths. Between 395 and 405 nm, a more interesting variation in B is noted. It appears that the decrease in B for $\lambda>395$ nm (3.1 eV) may be the result of a decrease in β, perhaps due to direct excitation of trapped excitons. Pulsed-laser carrier generation experiments, free of the absorption-coefficient averaging needed to interpret the present experiments, have the potential of examining the relevance of these speculative suggestions.

The subquadratic intensity dependence observed experimentally (see Fig. 1) is the result of a significant contribution of singlet exciton-exciton annihilation to the otherwise first-order exciton decay. The total exciton-exciton annihilation rate constant has been measured recently by Bergman, Levine, and Jortner[11,17] as $\gamma_S=(4\pm3)\times10^{-8}$ cm^3 sec^{-1}.

Taking γ_a as the rate constant for singlet-exciton disappearance via exciton-exciton annihilation and making the assumption that nearly all the highly excited states, formed by the annihilation, decay via the first singlet-exciton state,[18]

one may write (neglecting diffusion)

$$\frac{\partial S(x)}{\partial t} = 0 = kI_0 e^{-kx} - S/\tau - \tfrac{1}{2}\gamma_a S^2. \quad (3)$$

In Eq. (3) the steady-state approximation has been employed for all excited species. Using the expression for $S(x)$ from Eq. (3), one may calculate the following expression for N:

$$N = \beta w F(b)/\tau^2 k \gamma_a^2, \quad (4)$$

where

$$F(b) = b - 4[(1+b)^{1/2} - 1] - 2\ln\frac{4[(1+b)^{1/2}-1]}{b[(1+b)^{1/2}-1]},$$

and $b = 2\gamma_a \tau^2 k I_0$. We have computed $m = \Delta \ln F(b)/\Delta \ln b$ as a function of b and find, for example, that for $b = 0.1$, $m = 1.98$, while for $b = 1.0$, $m = 1.79$. Thus m, which should correspond to the experimental slopes in Fig. 1 (neglecting diffusion), is sensitively dependent on b. At 340 nm where k is small enough that diffusion corrections are small, Eq. (4) should fit the experimental situation very well. Letting $m = 1.87$, the experimental slope in Fig. 1 for 340 nm, one finds a corresponding value of $b = 0.5$. Evaluating $\gamma_a = 0.5/2\tau^2 k I_0$, one obtains $\gamma_a = 1.5 \times 10^{-(8 \pm 0.3)}$ cm^3 sec^{-1}. This value should be compared with the directly measured value[11] of $2\gamma_s = (8 \pm 6) \times 10^{-8}$. Agreement is within the quoted error limits and argues that the exciton-exciton mechanism rather than exciton photoionization is responsible for the observed carrier generation.

The large value of γ_a may allow an understanding of the linear intensity dependence found in earlier experiments[5,6] which attempted to examine the importance of the exciton-exciton mechanism with strongly absorbed light. Kepler and Merrifield[5] apparently used flash intensities of the order of 10^{20} photons cm^{-2} sec^{-1}, two orders of magnitude larger than those employed in the present experiments. Under these high-intensity conditions, exciton-exciton annihilation governs the singlet concentration which then increases approximately as the square root of the light intensity. The high-intensity experiments may well have involved values of $b = 100$ or larger corresponding to a slope $m = 1.16$ or smaller. Surface generation of charge carriers may also have been important in the earlier work.

For $b \lesssim 1$, the value of β calculated from Eq. (4) does not depend substantially on the value chosen for γ_a.[19] Using N, I_0, and k measured at 340 nm, one calculates from Eq. (4) that $\beta = 0.7 \times 10^{-12}$ cm^3 sec^{-1}. Since both the correction for second-order exciton decay and for diffusion are small at 340 nm, the correction for diffusion may be independently applied to the result from Eq. (4) to yield the preferred value $\beta = 0.9 \times 10^{-(12 \pm 0.4)}$ cm^3 sec^{-1}. This value is appropriate for $\lambda < 395$ nm and an applied field of 10^4 V/cm.

It should be pointed out that the measured value of β is large enough to support the contention of Pope, Kallmann, and Giachino[20] that singlet exciton-exciton interaction was involved in their double-quantum external-photoelectric-effect experiments. Those experiments established a quantum yield for photoelectron ejection at 365 nm of $10^{-25} I_0$. Using the expression electron-carrier quantum yield $= N/wI_0 = \beta\tau^2 k I_0/2(kl+1)^3$, one calculates with $\beta = 0.9 \times 10^{-12}$ that at 365 nm, $N/wI_0 = 5 \times 10^{-24} I_0$. Comparison of the two-quantum yields allows the physically reasonable observation that the number of electron carriers generated by exciton-exciton interactions is substantially larger than the number of photoelectrons ejected.

It is also noteworthy that β/γ_a is approximately equal to 10^{-4}, a number which is of the same order of magnitude as the carrier quantum yield φ found in short-wavelength, single-photon experiments.[21,16] Choi[22] has emphasized that the exciton-exciton mechanism should involve autoionization as an intermediate step in carrier production. Accepting Choi's reasonable suggestion, the order-of-magnitude agreement between β/γ_a and φ implicates autoionization in the single-photon carrier generation mechanism as well.[23]

The observations summarized below appear to rule out a significant contribution from exciton-photoionization in the wavelength range between 320 and 400 nm:

(1) After corrections for diffusion are applied, the number of carriers generated is proportional to k as required by the exciton-exciton mechanism. For this result to be consistent with the exciton photoionization mechanism, σ_c would have to be proportional to k over the entire wavelength range from 320 to 395 nm. Such behavior of σ_c is highly unlikely. If fact, if exciton photoionization were important, the dependence of N on k should be quite different from that observed. Assuming a relatively structureless variation of σ_c with λ, one would expect, because of diffusive exciton dilution, an actual anticoincidence between peaks in k and those in the measured N/I_0^2.

(2) If exciton photoionization were the dominant

mechanism, the measured value of β would have to be interpreted in terms of an impossibly large value of σ_C. The carrier generation cross section σ_C would be approximately equal to $\beta\tau k$ or about 10^{-15} cm^2 in the wavelength range 365 to 395 nm. Since $\sigma_C \lesssim 5\times10^{-19}$ cm^2 at 425 nm,[1] a more-than-thousandfold increase would be required in σ_C between 425 and 395 nm. Further, since carrier production is probably a low probability (10^{-4} to 10^{-3}) rate of the excited states produced by singlet-exciton light absorption, the total singlet-exciton absorption coefficient would be required to be on the order of 10^{-12} to 10^{-11} cm^2, values which correspond to the impossible oscillator strength of 10^4 to 10^5 over the wavelength range 320-400 nm.

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[18]In calculating their value of γ_S, Bergman, Levine, and Jortner (Ref. 11) neglect the likelihood that the lowest singlet-exciton concentration is repopulated by internal conversion from the highly excited state formed upon exciton-exciton annihilation. Thus their quoted value of γ_S corresponds to our $\frac{1}{2}\gamma_a$.

[19]The first term in the expansion of Eq. (4) for $b<1$ is just the familiar $\frac{1}{2}\beta w\tau^2 k I_0^2$ and does not depend on γ_a.

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