Photo-Ionization of Two-Photon-Excited Singlet Excitons in Anthracene

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(Received 19 September 1966)

The results of an experimental study of the photoconductivity induced by a giant-pulse ruby laser in crystalline anthracene lead to the following conclusions: (1) Up to laser intensities of 5×10^{25} photons cm^{-2} sec^{-1}, charge carriers are generated by a three-photon process. (2) The dominant mechanism for the production of charge carriers involves the photo-ionization of singlet-exciton states. (3) A cross section of 10^{-19} cm^2 at $\lambda=6940$ Å was determined for the photo-ionization of singlet-exciton states. (4) A bimolecular rate constant of $(5\pm3)\times10^{-7}$ cm^3 sec^{-1} for charge-carrier recombination in crystalline anthracene was directly determined.

IN spite of extensive experimental and theoretical studies of the photoconductivity of molecular crystals of aromatic molecules, the basic mechanisms leading to the intrinsic generation of charge carriers remain obscure.[1] Because the conduction band in crystalline anthracene is located[2] above 4.1 eV, we are not aware of any intrinsic mechanism involving the thermal dissociation of a single singlet-exciton state (located at 3.1 eV) which will give rise to a pair of charge carriers. Two mechanisms have been proposed to account for the energy-balance problem: singlet exciton-exciton collision ionization[3-5] and exciton photo-ionization.[6] The present paper reports new results concerning the photoconductivity induced in crystalline anthracene by a Q-switched ruby laser. Experimental evidence has been obtained that up to 100-MW laser power the dominant mechanism for the production of charge carriers from the lowest singlet-exciton state involves the photo-ionization of two-photon-excited singlet-exciton states.

The high-purity, zone-refined, single crystal of anthracene was in the shape of a cylinder (3.6 mm long, 6.2 mm diam), with a vacuum-deposited silver electrode on one end face, and a silver-paint electrode at the other end. Excitation was performed with a 100-MW passively switched ruby laser (output 1.1 J in 20 nsec) attenuated by neutral density filters. The laser light was incident in a direction prependicular to the cylinder axis, and the roughness of the crystal side is believed to have been sufficient to prevent light concentration in the crystal by lens effect. The silver-paint electrode was made positive (1500 V), and the other electrode was connected to a matched 200-Ω line. The current was preamplified by HP 460 amplifiers and displayed on Tetronix model 585 or 555 oscilloscopes. The electrode materials and polarities were chosen to avoid space-charge effects. The photocurrent was found to be linear in the applied voltage. Simultaneously with the photocurrent, the singlet-exciton density was monitored by the observation of the fast fluorescent decay in a manner previously described.[5] The laser intensity was also determined independently by deflecting a small fraction of the beam by a 45° glass plate and monitoring the intensity of the light scattered from a MgO-coated surface.

The density m of electron-holes pairs was obtained from the photocurrent i_{ph} by the relation $i_{ph}=me(\mu_e+\mu_h)ES$, where S is the contact area and E is the electric field. The mobility sum $(\mu_e+\mu_h)$ was taken as 1.2 cm^2 V^{-1} sec^{-1}. The peak singlet-exciton density N_s was obtained from the peak intensity I_{fl} by $I_{fl}=\beta_S N_s$, where $\beta_S=5\times10^7$ sec^{-1} is the decay rate for singlet excitons. The peak singlet density is in turn related to the laser flux I by[7] $N_s=\beta_s^{-1}KI^2$, where K is approximately the two-photon absorption cross section per unit flux. From our experimental data, we get $K=(1.0\pm0.3)\times10^{-29}$ cm sec^{-1} $photon^{-1}$, in good agreement with the data of Hall *et al.*[7]

In Fig. 1, we display the dependence of the charge-carrier peak density M on the singlet-exciton peak density N_s, and also the relation between M and the laser flux I. We have observed an accurate third power dependence of M on I (i.e., $M\propto I^3$), or alternatively, a $\frac{3}{2}$-power law between M and N_s (i.e., $M\propto N_s^{3/2}$). The same power law ($M\propto I^3$) was very recently observed by

[1] See, for example, J. Jortner and S. A. Rice, in *Modern Quantum Chemistry Istanbul Lectures*, edited by O. Sinanoglu (Academic Press Inc., New York, 1965), Vol. III, p. 235; S. P. McGlynn, L. Azzaraga, and F. Watson, in *Modern Quantum Chemistry Istanbul Lectures*, edited by O. Sinanoglu (Academic Press Inc., New York, 1965), Vol. III, p. 249.
[2] G. Castro and J. F. Hornig, J. Chem. Phys. **42**, 1459 (1965).
[3] S. Choi and S. A. Rice, J. Chem. Phys. **38**, 366 (1963).
[4] M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters **10**, 12 (1963).
[5] A. Bergman, M. Levine, and J. Jortner, Phys. Rev. Letters (to be published).
[6] S. I. Choi, J. Chem. Phys. **40**, 1691 (1964).
[7] W. L. Peticolas, J. P. Goldsborough, and K. E. Reickhoff, Phys. Rev. Letters **10**, 43 (1963); J. L. Hall, D. A. Jennings, and M. McClintock, *ibid.* **11**, 364 (1963).

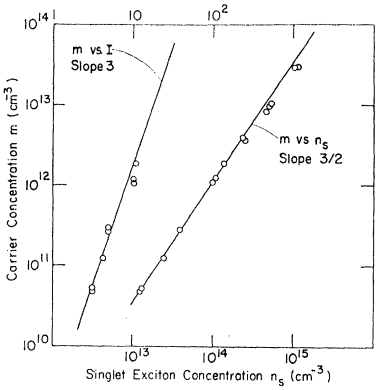

FIG. 1. The peak charge-carrier density versus the peak singlet-exciton density and the peak laser intensity [laser intensity I in arbitrary units (1 intensity unit $=5\times10^{24}$ photon cm^{-2} sec^{-1})]. The singlet density was directly obtained from the measured fluorescence; the laser intensity was computed from the values of the neutral filters.

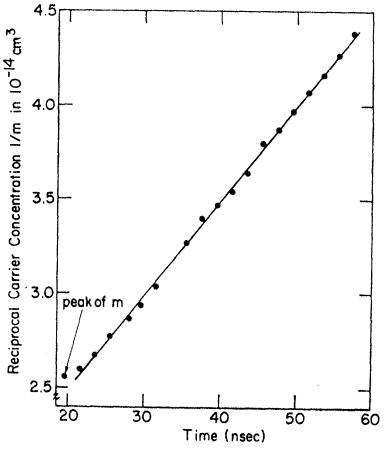

FIG. 2. Plot of the reciprocal charge-carrier density versus time. The first point on the plot corresponds to the peak density $M=3.9\times10^{13}$ cm^{-3}.

Kepler and Coppage.[8] We have failed to observe the previously reported fourth-power law ($M\propto I^4$) obtained by Hasegawa and Yoshimura[9] over a range of laser intensities similar to that used in the present work. In their experiments. The crystal was illuminated through nesa-coated glass electrodes,[9] and nonlinear absorption or reflection by the electrodes, as well as space-charge effects at the electrodes, may have led to a spurious power law. The carrier density they report is two to three orders of magnitude lower than what we observed.

The experimental results reported herein demonstrate that, at laser intensities up to 5×10^{25} photons cm^{-2} sec^{-1}, the charge-carrier generation in crystalline anthracene involves a three-photon process. Singlet-triplet exciton-collision ionization is expected to obey the same power law, since triplet-exciton states are populated by single-photon excitation.[10] However, it was experimentally demonstrated by Silver *et al.*[11] that singlet-triplet exciton interaction does not lead to the production of charge carriers in crystalline anthracene. The most likely three-photon mechanism accounting for the present results involves two-photon excitations of a singlet exciton followed by one-photon photo-ionization of the singlet-exciton state.[12] The contribution of this mechanism to the decay of the singlet-exciton density n_s is $(-\tilde{k}_\lambda n_s I)$, where $\tilde{k}_\lambda$ is the singlet-exciton photo-ionization cross section for one ruby laser photon ($\lambda=6940$ Å). The corresponding generation rate of electron-hole pairs is $dm/dt=\tilde{\eta}_\lambda\tilde{k}_\lambda n_s I$, where $\tilde{\eta}_\lambda$ is the quantum efficiency for photo-ionization at this wavelength. At low and medium laser intensities, we have observed that the loss of charge carriers by bimolecular recombination is negligible over the duration of the photocurrent rise. Hence the peak of m is given by $M=\tilde{\eta}_\lambda\tilde{k}_\lambda N_s I T$, where T is the average duration of the generation process. Thus, we get $\tilde{\eta}_\lambda\tilde{k}_\lambda=M\beta_S/KI^3T$. Setting $T=10$ nsec, as estimated from the current rise, we obtain $\tilde{\eta}_\lambda\tilde{k}_\lambda=0.6\times10^{-19}$ cm^2. In view of the experimental uncertainties, we propose the value $\tilde{\eta}_\lambda\tilde{k}_\lambda=10^{-(19\pm0.5)}$ cm^2 at $\lambda=6940$ Å.

At high laser intensities ($I>5\times10^{25}$ photon cm^{-2} sec^{-1}), the large densities of photocarriers decay rapidly by bimolecular recombination, so that the experimental values of M lie below the low-intensity $\frac{3}{2}$-power line. The bimolecular nature of the recombination has been established by plotting $1/m$ versus time (Fig. 2). From the slope of the straight line, we obtain the bimolecular-recombination rate constant $\gamma_R=(5.1\pm3)\times10^{-7}$ cm^3 sec^{-1}, in good agreement with the value reported by Helfrich and Schneider.[13] This implies that the cross section for charge-carrier recombination is very large, of the order of 10^{-11} cm^2.

From these results, we conclude that:

(1) Photo-ionization from the first singlet-exciton band to the conduction band can be stimulated by a 1.8-eV photon. Therefore, the bottom of the conduction band in crystalline anthracene is located below 4.9 eV. The data of Kastro and Hornig[2] indicate that the bottom of the conduction band is located at 4.1 eV. The photo-

[8] R. G. Kepler, Bull. Am. Phys. Soc. **11**, 268 (1966); R. G. Kepler and F. N. Coppage (to be published). Kepler and Coppage have observed the $M\propto I^3$ dependence. However, the cross section for exciton photo-ionization which can be calculated from their work, $\tilde{\eta}_\lambda\tilde{k}_\lambda=10^{-16}$ cm^2, is three orders of magnitude higher than the value obtained from our data.

[9] K. Hasegawa and S. Yoshimura, Phys. Rev. Letters **14**, 689 (1965), and private communication.

[10] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters **10**, 400 (1963).

[11] M. Silver, S. Z. Weisz, J. S. Kim, and R. C. Jarnagin, J. Chem. Phys. **39**, 3163 (1963).

[12] Notice that an alternative photo-ionization mechanism involves a direct three-photon excitation process to the conduction band. Such multiphoton photo-ionization processes were studied in the gas phase [H. B. Bebb and A. Gold, Phys. Rev. **143**, 1 (1966)]. Expressing formally our results in terms of a simultaneous three-photon process, we write $M=K_3I^3T$, with $K_3=10^{-57}$ cm^3 sec^{-2} photon^{-2}. The three-photon process involves a resonant intermediate state, since the two-photon energy matches a crystal state. The ratio RR of the transition probabilities for the consecutive excitation to the direct excitation is given by $RR=2\pi\hbar T\rho(2)\Gamma^2$, where $\rho(2)$ is the final density of states for the two-photon excitation and Γ is the damping factor. The natural linewidth of singlet-exciton states is relatively large ($\hbar\Gamma\sim10^{-3}$ eV), resulting from the decay into phonon states [J. J. Hopfield, Phys. Rev. **112**, 1555 (1958)]. Hence $RR\sim10^2$ and the consecutive excitation mechanism is expected to dominate the molecular crystal.

[13] W. Helfrich and W. G. Schneider, J. Chem. Phys. **44**, 2902 (1966).

ionization mechanism from the singlet-exciton state reported herein and from the ground state observed by Kastro and Hornig[2] may involve a direct excitation to the conduction band, or, alternatively, may arise from an auto-ionization process of metastable-exciton states.[14,15] In the latter case, the absorption band should be characterized by an antiresonance arising from interference between bound and continuum states.[14,15] However, in view of the small transition probability to the continuum state, we expect that Fano's line-profile index [14,15] $|q|$ is large, so that the line asymmetry will not be easily observed.

(2) The experimental value of the photo-ionization cross section leads to a rough estimate of the transition moment for the band-to-band excitation, which can be obtained from the relation[6] $\tilde{k}_\lambda = 4\pi |\mathbf{k}_l| \rho(E_k) \langle \mu \rangle^2$, where $|\mathbf{k}_l| = 9\times 10^4$ cm^{-1} is the wave vector for the laser radiation, and $\rho(E_k)$ the final density of states. Assuming that the width of the conduction band is 2 eV, and that it is characterized by a uniform density of states (at least at ~ 1 eV above the bottom), then, using the experimental result for $\tilde{\eta}_\lambda \tilde{k}_\lambda$, we get $\langle \mu \rangle^2 = 3\times 10^{-43}/\tilde{\eta}_\lambda$ cgs at this energy. This relatively small value for the transition moment arises from the orthogonality restrictions on the conduction-band wavefunctions.[3]

(3) Experimental evidence has been obtained that, for laser-induced photoconductivity, the exciton photo-ionization process dominates the exciton-exciton collision ionization mechanism. In the present laser experiment, the rate of charge-carrier generation by exciton-exciton annihilation is expected to be given by $\eta_s \gamma_s (\beta_s^{-1} K I^2)^2$, where γ_s is the rate constant for singlet-singlet annihilation and η_s the quantum efficiency. The average duration of singlet-singlet annihilation is $1/2\beta_s \approx 10$ nsec, since the singlet density decays with a time constant $1/\beta_s$. Therefore, the durations of the photo-ionization and the collision ionization mechanisms being approximately the same, the ratio a of the corresponding yields is given by

$$a = (\tilde{\eta}_\lambda \tilde{k}_\lambda \beta_s / K I \eta_s \gamma_s) = 4\times 10^{17}/I \eta_s \gamma_s .$$

For $I = 5\times 10^{25}$ photon cm^{-2} sec^{-1}, our experiments demonstrate that $a \gg 1$, so that $\eta_s \gamma_s \ll 10^{-8}$. Direct determination of γ_s from the fluorescence decay yields the value[5] of $\gamma_s = 10^{-8}$ cm^3 sec^{-1}, hence $\eta_s \ll 1$. This low yield for collision ionization may arise from competing channels for singlet-singlet exciton annihilation leading to bound high-energy exciton states characterized by a low auto-ionization probability. Accepting the value $\eta_s \gamma_s = 5\times 10^{-12}$ cm^3 sec^{-1} reported by Silver *et al.*,[4] we get $a = 10^{29}/I$, so that there is little hope to observe charge-carrier generation by collision ionization in the laser experiment.

(4) Charge-carrier generation in crystalline anthracene induced by weakly absorbed light[4] is expected to involve both exciton-photo-ionization and collision-ionization processes. Under the conditions of conventional illumination for the time $t \gg \beta_s^{-1}$, the steady-state singlet-exciton density is $\alpha I \beta_s^{-1}$, where α is the absorption coefficient for the weakly absorbed light ($\alpha \sim 1$ cm^{-1}). The ratio b of the number of charge carriers produced by photo-ionization and by collision ionization is given by $b = \tilde{k}_\lambda \tilde{\eta}_\lambda \beta_s / \eta_s \gamma_s \alpha$ being independent of I. For the sake of rough comparison, we assume that $\tilde{k}_\lambda \tilde{\eta}_\lambda$ is independent of the wavelength, so that $b \approx 5\times 10^{-12}/\eta_s \gamma_s$. From such experiments, Silver *et al.*[4] reported the value $\eta_s \gamma_s = 5\times 10^{-12}$ cm^2 sec^{-1}, neglecting the contribution of exciton photo-ionization,[3,6] so that both charge-generation mechanisms should be considered in this case.

We are indebted to Dr. R. G. Kepler for helpful discussions and for perpublication information. We are grateful to Professor S. A. Rice for helpful discussions. We wish to thank M. Levine for his competent technical assistance.

[14] U. Fano, Phys. Rev. **124**, 1868 (1961).
[15] J. C. Phillips, Phys. Rev. Letters **12**, 447 (1964).