be worthwhile to repeat this experiment at lower temperatures. In addition, we predict that the 32- and 293-cm^{-1} features should shift as (reduced mass)$^{1/2}$ upon isotopic substitution of oxygen in OH^-. We predict that in a Raman absorption experiment on OH^--KCl, the transition $^1A_1 \rightarrow {}^1B_1$ would appear at a frequency in the range 130-180 cm^{-1}. Finally, on the proposed model the splittings in the 0.3-cm^{-1} manifold, here associated with center-of-mass motion, should be sensitive to total mass rather than hydrogen isotope mass specifically. Thermodynamic or microwave absorption experiments may clarify this point.

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*National Institutes of Health Predoctoral Fellow.

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[11]The moment of inertia referred to here and elsewhere in this note is the moment of inertia of the OH^- ion taken with respect to an axis perpendicular to the O-H bond and passing through the center of mass. This moment of inertia is assumed independent of both the position of the center of mass and the ion orientation.

[12]See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1949), p. 289.

[13]In writing the Hamiltonian in this form, we assume the OH^- rotor to be strictly rigid; that is, we neglect effects due to centrifugal distortion.

[14]A point-charge calculation should be at least qualitatively accurate for a calculation like the present one in which the only species whose position is being varied is, in essence, a hydrogen atom.

[15]Note that the central barrier in the libration potential V proposed here is not so high as to impose the much stronger dependence on mass characteristic of large barrier tunneling situations.

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COLLISION IONIZATION OF SINGLET EXCITONS IN MOLECULAR CRYSTALS

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This Letter is concerned with the electronic relaxation mechanisms of singlet-exciton states in crystalline anthracene. At low exciton densities the lifetime of singlet and triplet excitons in molecular crystals is determined by unimolecular radiative decay and nonradiative internal-conversion processes, while at high exciton densities exciton-exciton interactions may play an important role in the exciton decay processes. From recent experimental and theoretical studies, the following conclusions were drawn:

(a) Triplet-triplet exciton collisions were observed in crystalline anthracene and other molecular crystals, inferred by delay fluorescence, arising from the radiative decay of singlet excitons produced by triplet-triplet exciton annihilation.[1-3]

(b) Collision ionization of singlet excitons in crystalline anthracene[4-6] was studied theoretically.[5,6] The transition of a pair of singlet excitons to a state involving an electron-hole pair is analogous to an Auger-type autoionization process. Experimental evidence for photoconductivity arising from exciton collision-ionization processes in anthracene was presented,[7,8] and seemed to confirm the theoretical value[5] of $\gamma_S = 2.5 \times 10^{-12}$ cm^3 sec^{-1} for the singlet-singlet exciton-annihilation rate constant.

We have been able to provide a direct evidence for bimolecular annihilation of singlet excitons in crystalline anthracene by the study of the radiative decay of two-photon excited states.[2,3,9]

Excitation of crystalline anthracene was performed by a 100-MW ruby laser with a passive Q-switching device. The total laser output (determined calorimetrically) was 1.1 J emitted in a pulse of 20-nsec duration. The unfocused laser beam was incident on a zone-refined crystal perpendicular to the ab plane. The cross section of the laser beam was 1.5 cm^2. At the highest power levels damaged spots (area ~1 mm^2) were sometimes observed on the crystal surface. These crystal-damage effects could be considerably reduced by a careful alignment of the crystal ab plane perpendicular to the laser beam. The experimental results for the fluorescence decay were not affected by the preirradiation of the crystal at the peak power of 100 MW. The intensity of the laser beam was attenuated by neutral density filters. A small fraction of the laser light was deflected by a 45° glass plate onto a diffusively scattering MgO-coated surface and monitored by a S-4 1P39 photocell. The blue fluorescence, which was shown to have the same spectral distribution as the normal fluorescence of anthracene, was monitored by a second 1P39 photocell, screened from the scattered red light by two Corning blue pass filters and a 1-cm cell containing cryptocyanine solution. Neutral density filters of up to o.d. 3.0 were placed before the photocell, so that the recorded intensity of the blue fluorescence was kept in the linear region. The output of the photocells was fed through 90-Ω cables terminated at both ends into a Tetronix-585 oscilloscope having a rise time of 3.5 nsec. The photocell current pulses (measured during a period of ~100 nsec) were of the order of 1 mA, being far below the saturation current of the photocell, which under the experimental conditions employed herein was found to be higher than 50 mA. The rise time of the system was checked by monitoring the output of a spark gap in air.

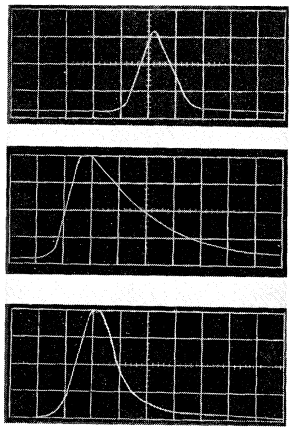

FIG. 1. The fluorescence decay of singlet excitons at various intensities of the ruby laser. The time scale is 10 nsec/division and the time increases to the right. Figures from top to bottom: (1) ruby laser pulse, (2) anthracene fluorescence $I = 6.4 \times 10^{24}$ photons cm^{-2} sec^{-1}, and (3) anthracene fluorescence $I = 1.8 \times 10^{26}$ photons cm^{-2} sec^{-1}.

A fast relaxation process of singlet excitons was observed at high exciton densities. From the experimental results displayed in Figs. 1 and 2, it is apparent that the fluorescence decay at high exciton densities is faster than the decay exhibited at low densities, the half-lifetimes being dependent on the exciton concentration. At low densities, the fluorescence decays exponentially with a singlet lifetime of 20 ± 2 nsec, a value characteristic for the lifetime of singlet excitons in crystalline anthracene.[3,10]

The experimental results are interpreted in terms of two-photon excitation followed by exciton-exciton annihilation. As in these experiments the exciton density is directly mon-

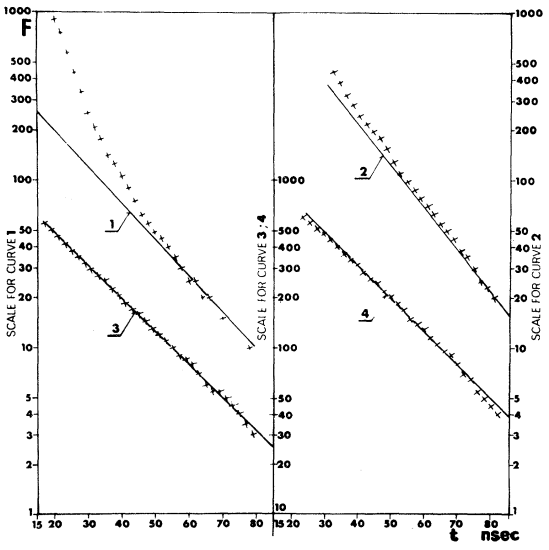

FIG. 2. Semilogarithmic plots of anthracene fluorescence versus time, for various laser intensities. Fluorescence intensity in arbitrary units. The graphs show that for long times (>50 nsec) the fluorescence decays exponentially. For shorter times, the half-lifetime is intensity department. The laser fluxes (in units of photons cm^{-2} sec^{-1}) are as follows: (1) $I = 1.8 \times 10^{26}$; (2) $I = 6.5 \times 10^{25}$; (3) $I = 2.3 \times 10^{25}$; and (4) $I = 6.4 \times 10^{24}$.

itored after the termination of the laser pulse, photoionization of exciton states[11] and field-induced ionization[12] processes are excluded.[13] The initial exciton density is given by

$$n_0 = \tau K I^2, \tag{1}$$

where τ is the exciton lifetime, I is the laser flux (photons cm^{-2} sec^{-1}). The fluorescence power P (photons cm^{-3} sec^{-1}) is given by $P = KI^2$, and we get $K = (1 \pm 0.5) \times 10^{-29}$ cm sec photon^{-1} in agreement with the data of Hall, Jennings, and McClintock.[2] The decay mode of the singlet excitons after the termination of the laser pulse is governed by the rate equation

$$dn/dt = -\beta_S n - \gamma_S n^2, \tag{2}$$

where β_S and γ_S correspond to the rate constant for monomolecular and bimolecular decay. Integration of Eq. (2) leads to the result

$$\frac{1}{n} = \exp(\beta_S t)\left(\frac{\gamma_S}{\beta_S} + \frac{1}{n_0}\right) - \frac{\gamma_S}{\beta_S}. \tag{3}$$

The experimental results are consistent with the proposed mechanism. From the intercept in Fig. 3, we get $\gamma_S = (4 \pm 3) \times 10^{-8}$ cm^3 sec^{-1}. A previous attempt[3] to observe singlet exciton-exciton annihilation was not successful since the monitored density of single excitons was apparently too low.[14]

The most plausible mechanism for the bimolecular annihilation involves a collision-ionization process of an exciton pair. Collision ionization may lead to pair of charge carriers in a nonequilibrium state corresponding to an electron (with kinetic energy ~0.5 eV) in a conduction band and a hole in its lowest state, located at nearby lying molecules. The recombination of a geminate pair of charge carriers resulting from a single collision-ionization process leads to the formation of singlet and triplet states[15] (in the approximate ratio 1:3), and will decrease the number of free charge carriers produced by this mechanism. From these results, we conclude the following:

(a) The directly observed rate constant for singlet-singlet annihilation is higher by about three orders of magnitude from the results previously reported for photocurrent generation in this system.[7] The photoconductivity experiments of Silver et al.[7] record only the density of free charge carriers (i.e., electrons and holes separated by more than 200 Å) which may be lower than the collision-ionization yield due to electron-hole geminate recombination in a nonequilibrium state.

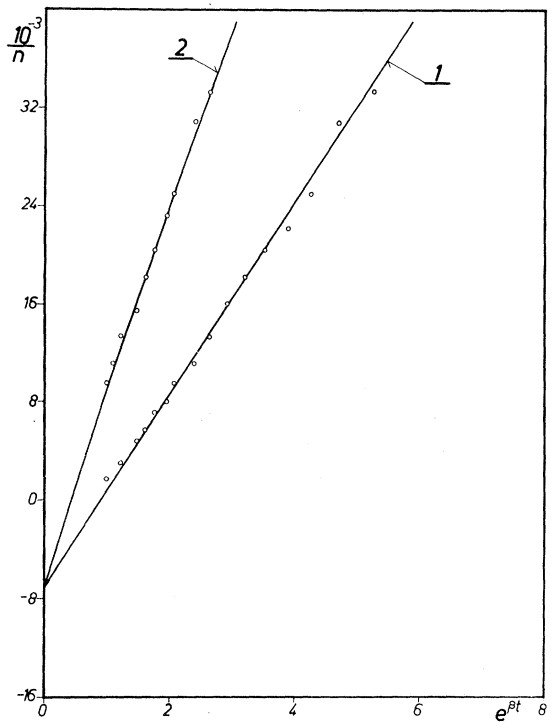

FIG. 3. A plot of the reciprocal exciton density [in arbitrary units versus $\exp(\beta_S t)$]. A straight line is expected for competing bimolecular and monomolecular mechanism. (1) $n_0 = 3.4 \times 10^{15}$ cm^{-3} (25 nsec after onset of laser pulse) and (2) $n_0 = 6.3 \times 10^{14}$ cm^{-3} (40 nsec after onset of laser pulse).

(b) The results presented herein should be directly comparable with the prediction of the theoretical analysis,[5] where it was assumed that each event of collision ionization leads to a pair of free charge carriers. The discrepancy observed between experimental and theoretical results[5] may arise from the approximations involved in the study of Choi and Rice where only nearest-neighbor interactions were considered and only exciton states with $\vec{K} = 0$ were taken into account.[16]

(c) The high value of the rate constant γ_S raises some interesting questions regarding the mechanism of the collision-ionization process. The diffusion coefficient of singlet excitons in crystalline anthracene[17] $D = 5 \times 10^{-3}$ cm^2 sec^{-1}, so that the rate of encounter Γ of an exciton pair treated with the framework of the strong-scattering random walk model[18] is $\Gamma = 8\pi D \langle R \rangle$, where $\langle R \rangle$ is the separation between the excited centers. For $\langle R \rangle = 10$ A, $\Gamma = 10^{-8}$ cm^3 sec^{-1}. Alternatively, we may estimate

the annihilation rate from the simple expression $\gamma_S = \sigma v$, where σ is the reaction cross section and v is the group velocity of the exciton packet. Taking the singlet-exciton bandwidth to be 400 cm^{-1} (which is the Davydov splitting of this state[19]), we estimate $v = 3\times10^6$ cm/sec, and setting $\sigma = (10\ \text{Å})^2$ we get $\gamma_S = 3\times10^{-8}$ cm^3 sec^{-1}. These results imply that the rate of collision ionization may be determined by the rate of encounter of a singlet-exciton pair rather than by the transition probability to the final state. Further theoretical work is required to establish this point.

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[14]The laser fluxes reported in Ref. 3 are about the same as employed in the present work. Singh et al. reported that the area irradiated by a 3- to 10-MW laser was of the order of 3 mm^2 leading to a flux of the order of 100 MW/cm^2. The size of the irradiated area may in fact be underestimated, as it should be of the order of the cross section of the ruby rod, ~1 cm^2. As in these experiments the singlet-exciton fluorescence was monitored only 100 nsec after the termination of the laser pulse, the exciton density was about 10^{14} cm^{-3} so that no bimolecular exciton annihilation is expected to be observed.

[15]It should be noted that at triplet-exciton densities comparable with that of singlet excitons, i.e., for $n_t = 10^{15}$ cm^{-3}, the fluorescence yield due to triplet-triplet annihilation (Ref. 1) is $F_1 = \gamma_t n_t^2 \approx 10^{19}$ photons/cm^3 sec, while the fluorescence yield from the direct decay of singlets at the density $n_S = 10^{15}$ cm^{-3} is about $F_2 = \beta_S n_S \approx 10^{23}$ photons/cm^3 sec. Hence, under the experimental conditions employed herein $F_1 \ll F_2$. It should be noted also that charge carrier recombination should lead to an appreciable fraction of triplet states.

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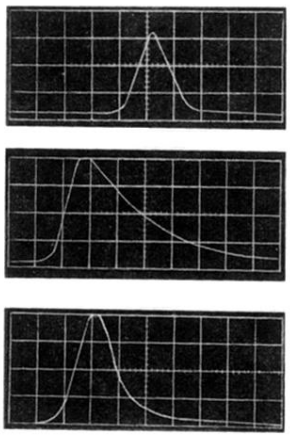

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