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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[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 per-
formed by a 100-MW ruby laser with a passive
Q-switching device. The total laser output
(determined calorimetrically) was 1.1 J emit-
ted in a pulse of 20-nsec duration. The unfo-
cused laser beam was incident on a zone-re-
fined 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 care-
ful alignment of the crystal ab plane perpendic-
ular to the laser beam. The experimental re-
sults for the fluorescence decay were not af-
fected by the preirradiation of the crystal at
the peak power of 100 MW. The intensity of
the laser beam was attenuated by neutral den-
sity filters. A small fraction of the laser light
was deflected by a 45° glass plate onto a diffu-
sively scattering MgO-coated surface and mon-
itored by a S-4 1P39 photocell. The blue fluores-
cence, which was shown to have the same spec-
tral 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 record-
ed intensity of the blue fluorescence was kept
in the linear region. The output of the photo-

cells 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 photo-
cell, 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.

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 de-
cay at high exciton densities is faster than the
decay exhibited at low densities, the half-life-
times being dependent on the exciton concen-
tration. 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 an-
thracene.[3,10]

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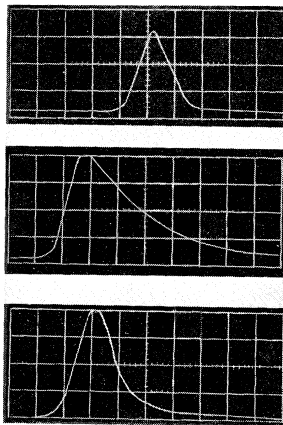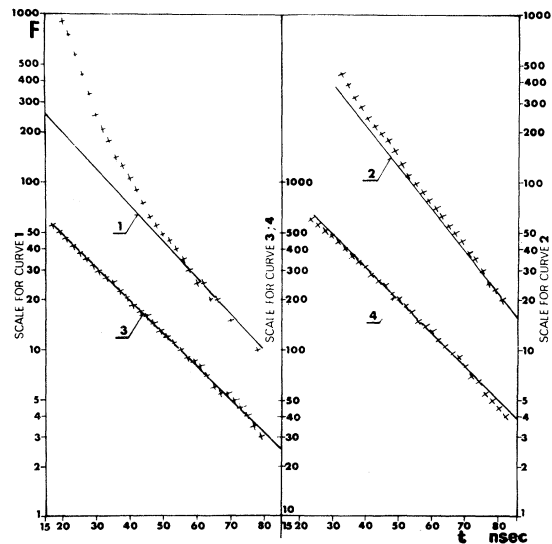periments the exciton density is directly mon-

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 $cm^{-2} sec^{-1}$.

FIG. 2. Semilogarithmic plots of anthracene fluores-
cence versus time, for various laser intensities. Flu-
orescence intensity in arbitrary units. The graphs
show that for long times (>50 nsec) the fluorescence
decays exponentially. For shorter times, the half-life-
time 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 $P = K I^2$, 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
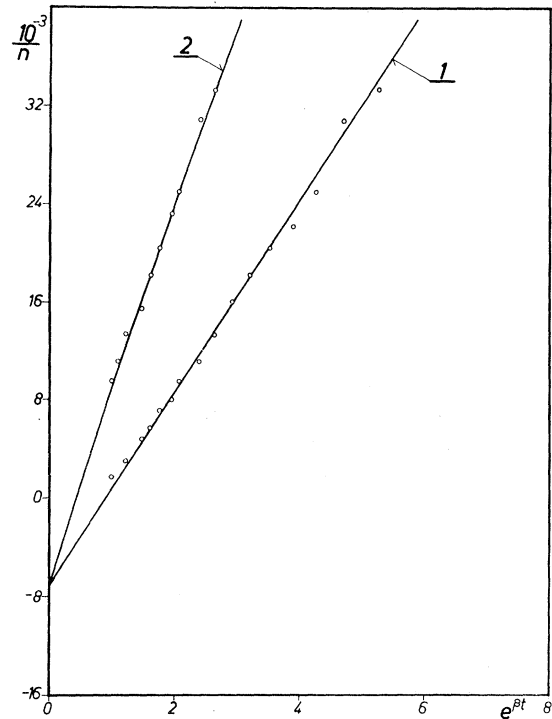

FIG. 3. A plot of the reciprocal exciton density [in arbitrary units versus $\exp(\beta_s t)$]. A straight line is expected for competing bimolecular and monomolecular mechanism. (1) $n_0 = 3.4 \times 10^{15}\ cm^{-3}$ (25 nsec after onset of laser pulse) and (2) $n_0 = 6.3 \times 10^{14}\ cm^{-3}$ (40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

due to electron-hole geminate recombination in a nonequilibrium state.

(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 $v = 3 \times 10^6$ cm/sec, and setting $\sigma = (10 \text{ Å})^2$ we get $\gamma_S = 3 \times 10^{-8}$ 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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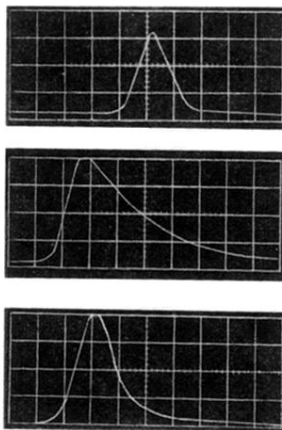
FIG. 1. The fluorescence decay of singlet excitons at various intensities of the ruby laser. The time scale is 10 nsec/division and the time increases to the right. Figures from top to bottom: (1) ruby laser pulse, (2) anthracene fluorescence $I = 6.4 \times 10^{24}$ photons $cm^{-2}\ sec^{-1}$, and (3) anthracene fluorescence $I = 1.8 \times 10^{26}$ photons $cm^{-2}\ sec^{-1}$.