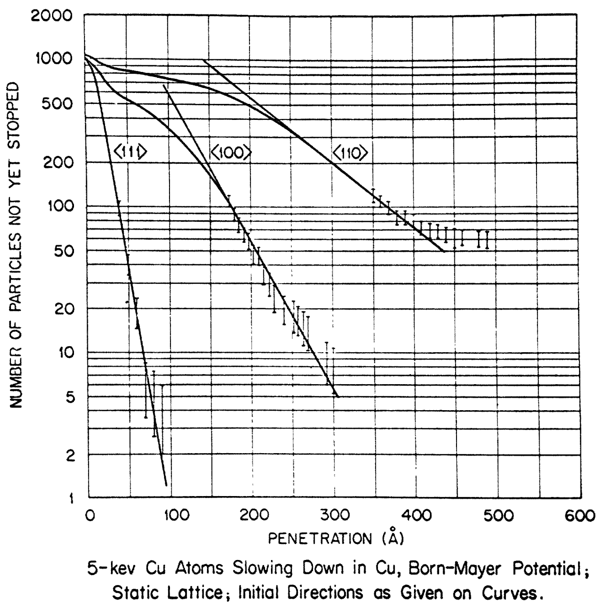

FIG. 2. Calculated range curves[8] with statistical error shown by the vertical bars.

a melt-grown crystal of 99.99% purity using a sparkatron, and electropolished to within 2° of the desired orientation. Bombardments and range determinations were made in the usual way.[5,6] Figure 1(b) shows the integral range distribution curves for the crystal at normal incidence (beam 7° from ⟨211⟩) and for the same crystal tilted 28° in order to align the ⟨110⟩, the ⟨100⟩, or the ⟨111⟩ direction with the beam of krypton ions. The penetration is given in the direction parallel to the incident beam. The results show that both the slope and the intensity of the penetrating tail are very much affected by the orientation of the crystal. A simple lattice model predicts that the directions of preferred penetration should increase in the order ⟨111⟩, ⟨211⟩, ⟨100⟩, ⟨110⟩, and the experimental results [Fig. 1(b)] are consistent with this prediction.

Recently, Robinson and Oen[8] have developed a computer program for determining range distributions in a crystalline solid. Figure 2 shows their calculated integral range distributions for 5-keV copper ions incident upon the various principal planes of copper which, like aluminum, has a face-centered cubic lattice. The statistical uncertainty in the calculation is shown by the vertical bars along the curves. In these calculations the exponential tail is due to those ions that had become focused down channels between lines of close-packed atoms. The striking qualitative resemblance between experiment and calculation strongly supports the existence of a channeling process, although a quantitative comparison is not yet possible due to the difference in energy, target material, and incident ions.

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TRIPLET EXCITONS AND DELAYED FLUORESCENCE IN ANTHRACENE CRYSTALS

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Laser-induced fluorescence in powdered anthracene and several other organic materials was recently reported.[1] The fluorescence was attributed to double photon excitation from the singlet ground state to the first-excited singlet state. While studying this fluorescence in anthracene single crystals, we detected delayed fluorescence after the laser pulse ended. We explain the rate of decay of this fluorescence and other experimental observations by assuming that the singlet state giving rise to the fluorescence is produced not by a double photon process as concluded by Peticolas, Goldsborough, and Rieckhoff,[1] but via bimolecular annihilation of triplet excitons generated directly by the ruby laser light. The lifetime and the bimolecular interaction rate constant of the triplet excitons were found to be 10 msec and 10^{-11} cm^3 sec^{-1}, respectively.

Melt-grown anthracene single crystals produced from zone-refined Eastman starting material were illuminated at room temperature by approximately 0.02 J per laser pulse focused into a volume of 10^{-3} cm^3. Incident laser radiation was passed through a Corning 2-58 filter, while the fluorescence was observed with a photomultiplier through a Corning 5-56 filter. A 2-μsec time constant was introduced to integrate over individual laser spikes. The measured fluorescent signal contained a negligible amount of scattered laser light. To measure the weak delayed fluorescence, it was necessary to blank out the oscilloscope amplifier during the intense portion of the fluorescent pulse to prevent its saturation.

By correcting the fluorescent flux density incident on the photomultiplier for detector solid angle, and by assuming isotropic emission, we infer that about 10^{11} fluorescent quanta were emitted per laser pulse of about 10^{17} quanta. The fluorescence spectrum, measured with a monochromator and photomultiplier, was identical to the normal anthracene fluorescence spectrum in the presence of self-absorption.

We observed that the intensity of the blue fluorescence from the anthracene varied as the square of the incident red-light intensity only during the first several hundred microseconds of our 1.8-msec laser pulse. During the last portion of this pulse, the dependence became approximately linear with the incident intensity.

Figure 1 shows that fluorescence emission continued after the laser had stopped emitting. This delayed fluorescence could be measured for more than 40 msec after the laser shutoff and comprised more than 10% of the total emitted blue fluorescent energy. The time dependence of the delayed emission is shown in Fig. 2, from which it is evident that near the time that the laser shuts off, the signal decays as $1/t^2$ while later the decay is exponential.

These observations can all be explained by assuming that the laser photons (1.79 eV) directly create triplet excitons (1.80 eV),[2] which in turn can interact in pairs to form a singlet exciton (3.42 eV)[2] which fluoresces with a lifetime of 2.6×10^{-8} sec.[3] It has been previously suggested[4,5] that triplet-triplet annihilation produces delayed fluorescence in organic solids. Parker and Hatchard[6] have demonstrated that for anthracene in solution the interaction of two molecules in the triplet state results in a fluorescing singlet-state molecule.

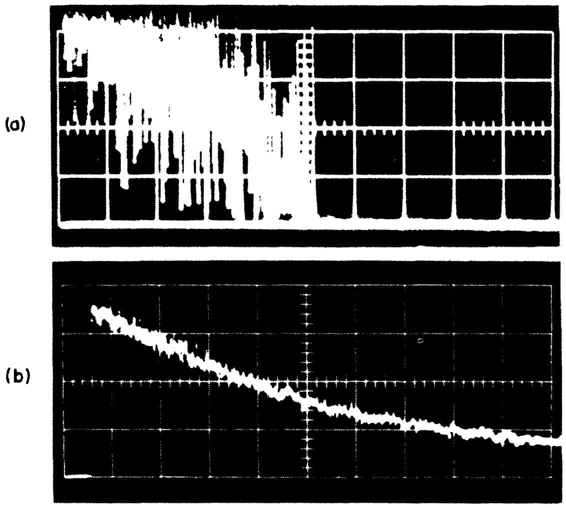

FIG. 1. Oscilloscope traces showing the time dependence of (a) the laser emission and (b) the blue anthracene fluorescence around the time of laser shutoff. Both traces were initiated 1.3 msec after the beginning of the laser pulse, and both time scales are 100 μsec/large division.

The equation which determines the concentration of triplet excitons, n, under the above assumptions is

$$dn/dt = \alpha I - \beta n - \gamma n^2,$$

where αI represents generation by the incident red light, β is the reciprocal of the lifetime of the triplet exciton, and γ is the bimolecular interaction rate constant. The intensity of the fluorescent light emitted by the crystal is approximately $\frac{1}{2}\gamma n^2$, if it is assumed that creation of a singlet exciton which fluoresces is the only important process in the bimolecular interaction.

Our data allow us to determine α, β, and γ under these assumptions, and we find that the lifetime of the triplet exciton is about 10 msec; γ, the bimolecular interaction rate constant, is of the order of 10^{-11} cm^3 sec^{-1}; and α, the absorption coefficient, is about 10^{-5} cm^{-1}. Approximate values for γ and β were obtained, respectively, from the slope of Fig. 2(a) for short times and from twice the slope of Fig. 2(b) for long times. In the calculation of γ, it was estimated that the triplet excitons were generated in a volume of 10^{-3} cm^3. Because of effects such as light scattering in the crystal, this volume is difficult to estimate, but we feel

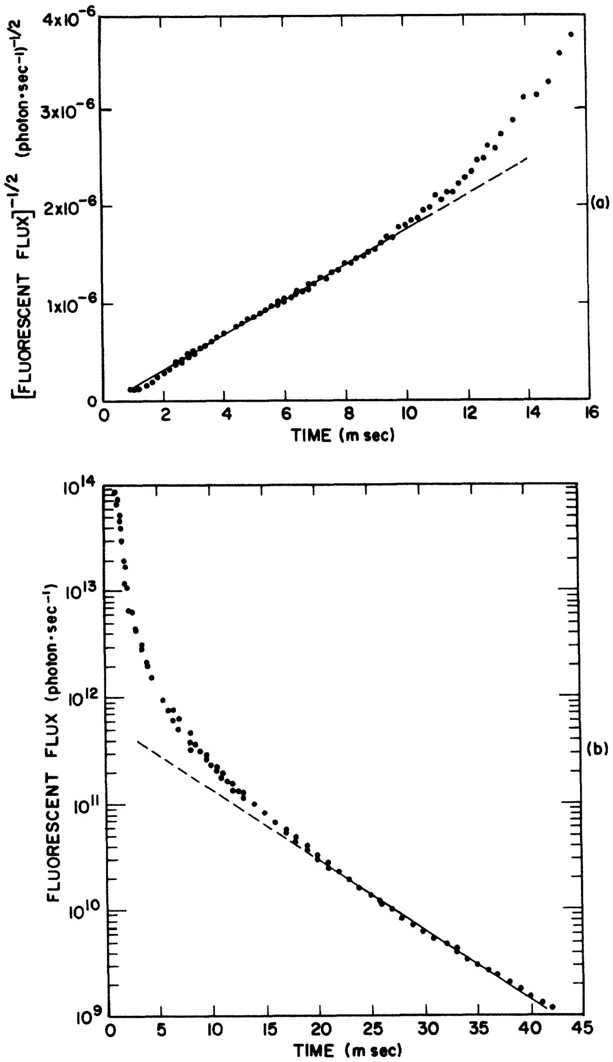

FIG. 2. Time dependence of the delayed fluorescence. The upper graph shows that around the time of laser shutoff the fluorescent flux varies inversely with the square root of time, while the lower graph shows that at later times the fluorescence decays exponentially.

that our value of γ should be reliable to about a factor of 10. The value of α was determined from the ratio of the input to output quanta and represents a lower limit. Measurements of the extinction coefficient[7] indicate that the maximum α in the singlet-triplet absorption band is about 10^{-2} cm^{-1}, and therefore our results are consistent even if the laser wavelength is not in a strong absorption region.

It is interesting and somewhat surprising that the value of γ which we find for triplet excitons in anthracene is of the same order as that recently calculated by Choi and Rice[8] and measured by Silver et al.[9] for singlet excitons. Since γ may be interpreted as being equal to σv, where σ is the cross section for interaction and v is the thermal velocity of the exciton, and since the velocities of singlet and triplet excitons would be expected to differ markedly,[10] these results imply that the cross section for interaction between triplet excitons is much larger than that for singlet excitons.

Observation of delayed fluorescence amounting to more than 10% of the total fluorescent light output, and the lack of a discontinuity in the fluorescence emission versus time when the laser pulse stopped (see Figs. 1 and 2), eliminate processes governed by the decay rate of the singlet exciton. Therefore processes such as double quantum transitions directly to the singlet state[1] and transitions from the triplet exciton to the singlet exciton by absorption of a photon cannot be important. The departure of the fluorescence intensity from a squared dependence on the laser intensity during the latter part of the laser pulse is further evidence against double photon excitation. This dependence is, however, consistent with our mechanism which predicts that while the laser is still on and when n is large (i.e., towards the end of the laser pulse), the quasi-steady-state fluorescence is proportional to n^2 which, in turn, equals $(\alpha/\beta)I$.

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*Contribution No. 863.

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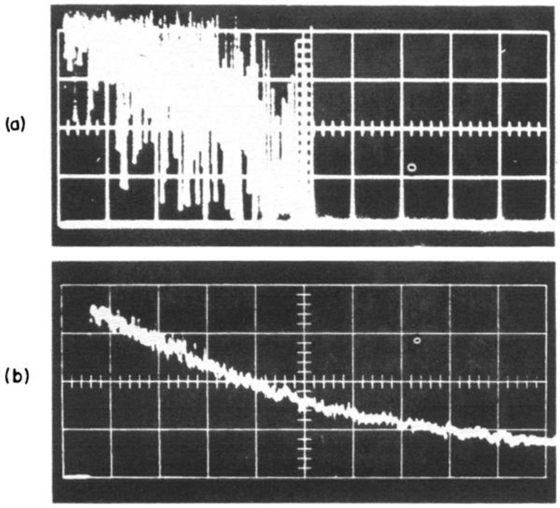

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