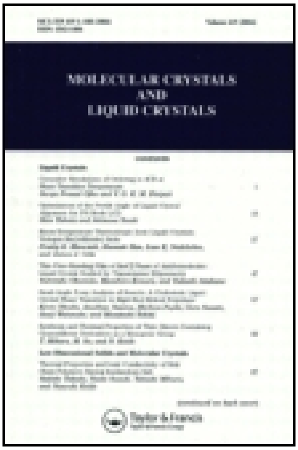

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Triplet Sampled Radiation damage

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Triplet Sampled Radiation damage[†]

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Abstract—The emission produced by mutual annihilation of a pair of triplet excitons in single crystalline anthracene was observed to be an indicator of low level gamma-ray dose. Under steady red light illumination the blue emission intensiv F_r is related to gamma-ray dose D by $F^{-1/2} = a + bD$ in the range 300R to 10^4R. Independent measurements show the effect cannot be due to changes in absorption in the red region, changes in quantum yield of fluorescence, nor to changes in the specific rate of triplet interaction. An interpretation based on dose induced quenchers and the long range of triplet excitons is given. By use of multiple techniques an individual single crystal of anthracene can be used as a wide range dosimeter; triplet-triplet annihilation in the range 10^2 to 10^4 R, space charge limited photocurrent in the range 10^3 to 10^6 R, fluorescence quenching in the range 10^5 to 10^8 R, and absorption spectroscopy above 10^7 R.

1. Introduction

The dynamic properties of optical excitons in molecular crystals have been of particular interest in recent years. Kepler's[1] observation of delayed fluorescence, whose intensity depended on the square of the intensity of the exciting light, first showed the existence of an intrinsic bimolecular interaction between long-lived mobile excitation in anthracene crystal. The work of Hirota and Hutchinson[2] unambiguously related the delayed fluorescence, the phosphorescence decay, and the decay of spin resonance signal to the triplet state of phenanthrene in a host biphenyl crystal. On the theoretical side, Jortner *et al.*[3] have investigated problems associated with triplet excitons in anthracene crystal and have concluded that the motion is describable in terms of a diffusion model dominated by excitation hopping between molecular sites. These experimental and theoretical results are typical of the efforts directed toward an understanding of the properties of excitons.

The fluorescence arising from the bimolecular triplet annihilation has been used as the observable for obtaining information about properties of molecular crystals which are not intrinsically dependent upon the properties of excitons. Avakian and coworkers[4, 5] have utilized the sensitivity inherent in the detection of steady state fluorescence to obtain the weak singlet to triplet ($S_0 \rightarrow T_1$) absorption spectrum in a number of molecular crystals. Weisz *et al.*[6] have used the long life of triplet excitons in crystalline anthracene to observe the decay of delayed fluorescence from which the efficiency of the radiotionless transition from singlet to triplet ($S_1 \rightarrow T_1$) could be denuced.

We report here a third type of application of triplet-triplet annihilation which yields information concerning radiation damage in molecular crystals. The sensitivity of detection of the fluorescence, the crucial dependence of triplet lifetime upon weak perturbations, and the mobility of triplet excitons in mechanically good crystals are properties which have been combined in the present investigation to observe the effects of gamma-ray damage.

2. Experimental

Anthracene crystals suitable for scintillation work were obtained from the Harshaw Chemical Company. Each crystal was about a 1 cm cube. The density of striations was such that crystal transparency just allowed book print to be read through 1 cm of crystal.

A masked crystal holder was constructed such that a given crystal could be reproducibly mounted and remounted between successive radiation doses. One surface of the crystal was illuminated by a collimated light beam from a 900 W Xe DC compact arc lamp. Before impinging on the crystal the light beam was passed through a 1 cm thickness of 1 part saturated $CuSO_4$ to 7 parts H_2O (v/v) used as a heat filter and followed by one each of Corning's sharp cut off filters CS 3–67 and CS 3–68. Red light in the 600–700 mμ ($S_0 \rightarrow T_1$) absorption band was efficiently transmitted while the extinction coefficient at 530 mμ was such that transmitted blue and u.v. light was insufficient to directly excite fluorescing singlets, S_1.

The blue fluorescence was observed at right angles to the exciting red light after being filtered by a 4.5 cm thickness of saturated

$CuSO_4$ plus one CS 5–58 filter. This combination of filters has a peak transmission at 410 mμ while the fluorescence has peaks at 430 mμ and 450 mμ.

The fluorescence signal, F_r, due to steady state red excitation was measured before and after gamma-ray dosage from a ^{60}Co source. The source intensity was 600 R min^{-1}. The measured absorption coefficient of anthracene for the ^{60}Co emission was 0.118 cm^{-1} [7] so that the calculated energy absorption was 293 erg gm^{-1} R^{-1}. There appeared to be no change in F_r measured immediately following irradiation of a crystal or if measured after the crystal had remained at laboratory temperature for several days following irradiation.

In addition to the steady illumination experiments, flash experiments were performed in which the temporal response of the blue emission was continuously monitored both during and subsequent to excitation by a high intensity red flash. The arrangements for these portions of the experiment were similar to those given by Weisz *et al.*[8] The filtering for the present experiments consisted of one CS 3–67 and one CS 3–68 between the flash lamp and the crystal. The blue emission was observed with a IP21 photomultiplier at right angles to the direction of the exciting flash and filtered with the same combination as used in the steady state experiments.

The width of the flash intensity at half maximum was 8 μsec.

The peak intensity in the 6000–8000 Å band was about 10^{23} cm^{-2} sec^{-1}.

3. Results and Analysis

Figure 1 shows the dependence of the blue emission under steady red light excitation as a function of gamma-ray dose. Figure 2 shows a similar graph for the relative fluorescent yield, $\varphi_{f\,\mathrm{rel}}$, obtained under near u.v. excitation. Although there was wide fluctuation in $\varphi_{f\,\mathrm{rel}}$, it was clear that a monotonic decrease of fluorescence efficiency sets in at a dose rate of about 10^5 R. This result is in general agreement with those of Sharn[9], who previously had found a linear decrease of fluorescence efficiency for powdered anthracene in the dose range of 10^5 to 10^7 R.

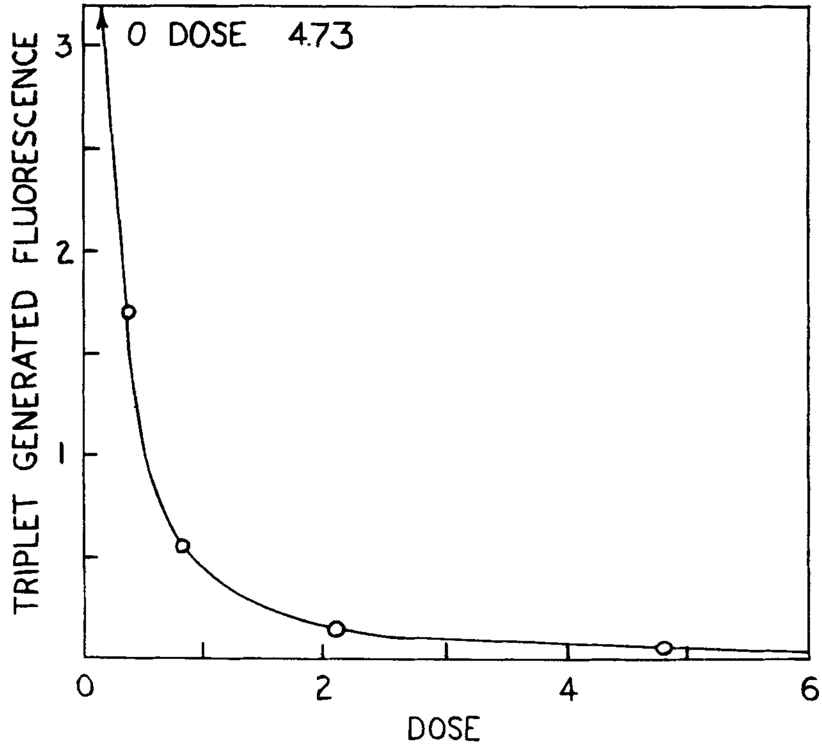

Figure 1. F_r *vs.* Dose. Blue Fluorescence under Steady Red Excitation. Vertical: 1 unit — 10^{-6} amp. Horizontal: 1 unit = 10^3 Roentgens.

We adopt the following kinetic scheme to account for the observations:

$S_0 + h\nu_{\text{red}} \rightarrow T_1$ (singlet → triplet absorption);	$\alpha I(t)$	
$S_0 + 2h\nu_{\text{red}} \rightarrow S_1$ (simultaneous double quantum absorption)	$\delta I(t)^2$	
$T_1 \rightarrow$ lower states	βT	
$T_1 + T_1 \rightarrow S_1 + S_0$	$\gamma_1 T^2$	$\gamma = \gamma_1 + \gamma_2$
$T_1 + T_1 \rightarrow$ lower states (self quenching)	$\gamma_2 T^2$	
$S_1 \rightarrow S_0 + h\nu_{\text{blue}}$	$k_f S$	$k = k_f + k_{ST} + k_N$
$S_1 \rightarrow T_1$	k_{ST}	
$S_1 \rightarrow$ lower states not triplet	$k_N S$	

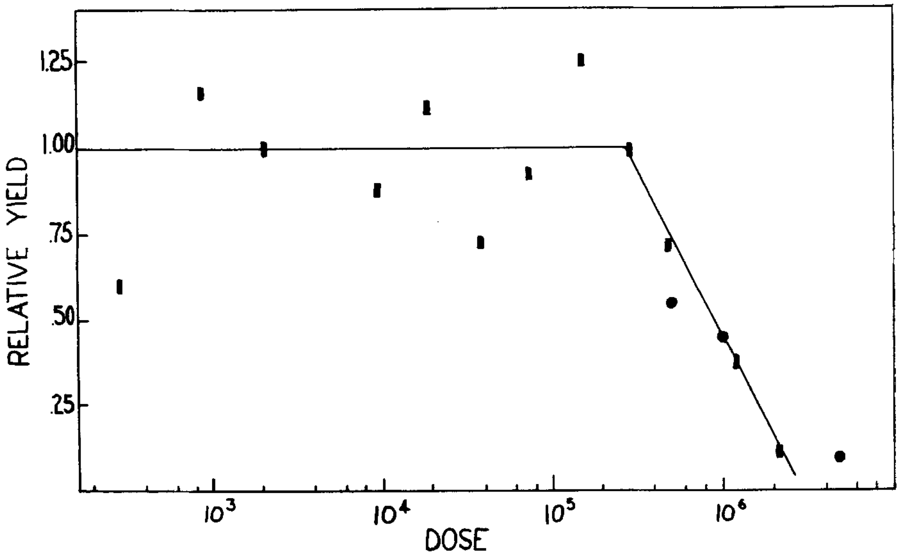

Figure 2. $\varphi_{f\mathrm{rel}}$ *vs.* log Dose. Blue Fluorescence under Steady 3130 Å Excitation. Vertical: relative yield. Horizontal: 1 unit — × 10 Roentgens. ■ the present data ● Sharn, reference 9.

$$\frac{dT}{dt} = \alpha I(t) + k_{ST}S - \beta T - \gamma T^2 \tag{1}$$

$$\frac{dS}{dt} = \delta I^2(t) + \frac{1}{2}\gamma_1 T^2 - kS \tag{2}$$

$$F = Ak_f S. \tag{3}$$

A is an unknown geometric and sensitivity factor for a given crystal and type of experiment.

Under the stationary conditions of steady red illumination $\frac{dT}{dt} = \frac{dS}{dt} = 0$. For this case we denote F by the symbol F_r. The 900 W D.C. arc is capable of delivering several tenths of a watt per square centimeter of red light which is sufficient to allow measurement of the blue emission but weak enough that $k_{ST}S < \alpha I = \text{const.}$ and $\gamma T^2 < \beta T$, and $\delta I(t)^2 < \frac{1}{2}\gamma_1 T^2$, sot that

$$F_r = A\frac{\gamma_1 \varphi_f}{2}\left(\frac{\alpha}{\beta}\right)^2 I^2. \tag{4}$$

Assumptions regarding the effect of radiation damage on the crystal parameters are now introduced. If the dose introduces triplet quenching centers without affecting (a), the absorption coefficient α for $S_0 \rightarrow T_1$, (b) the fluorescence efficiency, φ_f, and (c) the bimolecular triplet exciton interaction constant, γ_1; then the damage effect may be assumed to be of the form

$$\beta = \beta^0 + aD. \tag{5}$$

Graphs of $F_r^{-1/2}$ *vs.* D should be of the form

$$F_r^{-1/2} = \text{const.}\ (\beta^0 + aD). \tag{6}$$

Figure 3 shows a graph of the observed steady state data in excellent agreement with Eq. (6).

Assumptions a, b and c have received direct experimental verification. The observed emission, F_r, depends on the rate of absorption of light, not on the quantity of light absorbed; therefore dependence of α on D will be of consequence if damage produced impurities are sufficiently

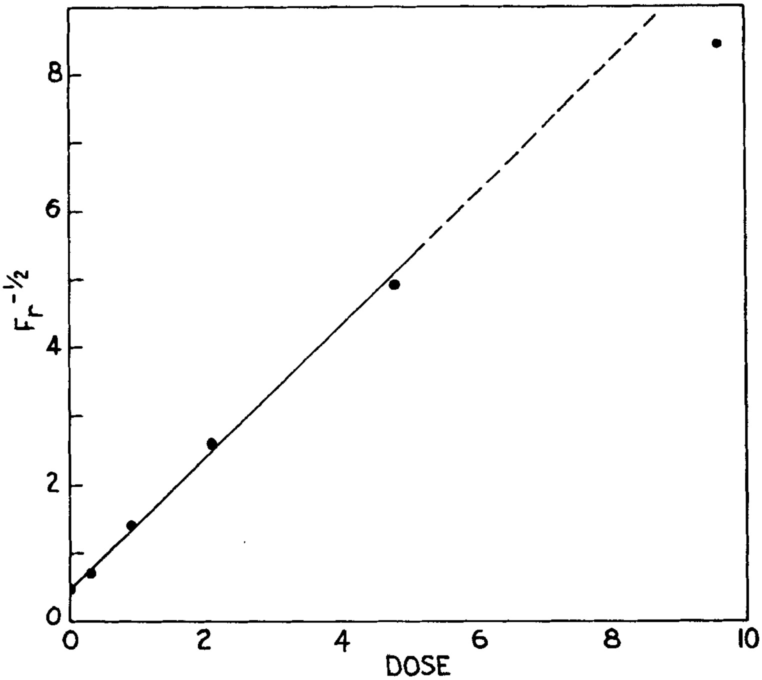

Figure 3. $F_r^{-1/2}$ *vs.* Dose. Blue Fluorescence under Steady Red Excitation. Vertical: 1 unit — 1×10^2 amp$^{-1/2}$ Horizontal: 1 unit — 10^2 Roentgens

strong absorbers of the red light to result in decreased crystal transmission. No optical density in the red region was observed in 0.5 cm thick crystal up to doses of 10^8 R. Therefore in the dose range of present concern assumption (a) is valid.

The data concerning relative fluorescence yield shown in Fig. 2 clearly indicate that no significant change occurs in φ_f below a dosage of 10^5 R and therefore assumption (b) is valid.

It was expected that the bimolecular rate constant, γ, should not be dependent of damage because if one writes $\gamma = (p_1 + p_2)\,\sigma_{TT}v_T$ in which p_1 and p_2 are respectively the probabilities of forming $S_1 + S_0$ or $2S_0$ on collision of a pair of triplet excitons of cross section σ_{TT}, and with velocity v_T then the probabilities should be dominated by spin and interaction factors determined by molecular parameters while the collision cross section is not expected to become dose dependent until the damage centers are of sufficiently high density to permit cooperative phenomena between centers. The triplet exciton velocity, v_T, should undergo real *or apparent alteration due to radiation damage in either of two principal* ways; (i) damage introduces shallow triplet traps and thereby imparts a trap modulation character to v_T, or (ii), damage introduces deep triplet traps but from which annihilation is inherently faster or slower.

In order to verify these expectations and thereby confirm assumption (c), measurements of the blue fluorescence produced by a very high intensity, short duration, red flash were performed as a function of gamma-ray dosage. At the time of peak flash intensity $I(t)$ is denoted Ip. During a flash of microseconds duration, τ_e, the triplets are not contributing a significant amount to the instantaneous singlet population; therefore Eq. (2) becomes

$$S = \frac{\delta Ip^2}{k} \tag{7}$$

and the fluorescence given by (3) is denoted by F_p,

$$F_p = A\varphi_f\delta I_p^2. \tag{8}$$

It is to be emphasized that the fluorescence originating by this mechanism is uniformly emitted throughout the crystal volume. During the flash a triplet population, T^0, is built up by direct $S_0 \rightarrow T_1$ absorption and by cross over from the singlets generated by the double quantum process. A simple estimate shows that most of the triplets arise from direct absorption and are therefore approximately given by

$$T^0 = \alpha I_p \tau_l = 10^{-4}\,\text{cm}^{-1} \times 10^{23}\,\text{cm}^2\,\text{sec}^{-1} \times 10^{-5}\,\text{sec} = 10^{14}\,\text{cm}^{-3}. \tag{9}$$

Since α [4] is so small the triplet-triplet mechanism also causes the resultant fluorescence to be emitted uniformly from the crystal volume. During an interval of time following flash extinction, $\tau_l < t < \beta^{-1}$, the bimolecular term of Eq. (1) dominates the triplet decay and the fluorescent signal given by (3) is denoted by F_T and becomes

$$F_T = \frac{1}{2} A \varphi_f \gamma_1 \left(\frac{T^0}{1 + \gamma T^0 t} \right)^2. \tag{10}$$

Since $\gamma \approx 2 \times 10^{-11}\,\text{cm}^3\,\text{sec}^{-1}$ [4, 5] than $\gamma T^0 t \ll 1$ up to about 50 μsec. Therefore comparing (10) with (8) and utilizing (9) gives

$$\frac{F_T}{F_P} = \frac{1}{2} \frac{\gamma_1 \alpha^2 \tau_l^2}{\delta}. \tag{11}$$

Figure 4 shows the fluorescent behavior in an undamaged crystal from

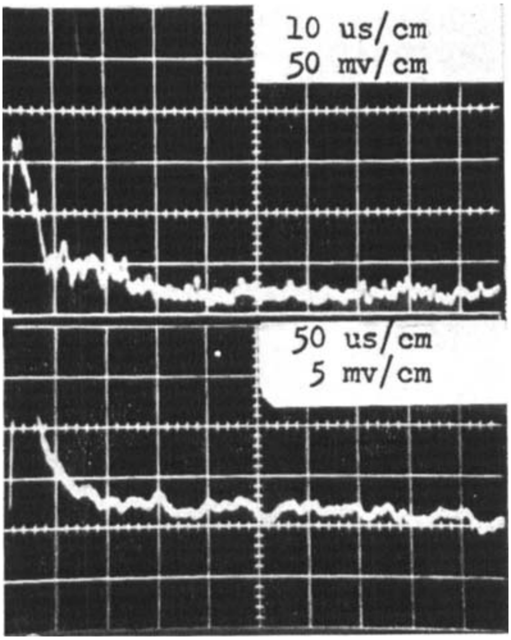

Figure 4. $F_p + F_T$ *vs.* Time. The Fluorescent Response of an Undamaged Crystal to a High Intensity Red Flash. Upper: $R_m = 1K$; time const. $\approx$ 1 μsec. Lower: $R_m = 1K$; time const. $\approx$ 1 μsec.

0 to 500 μsec and succinctly illustrates the two mechanisms which are operating. Note the almost abrupt change in decay character near 10 μsec.

As previously stated, α does not depend on dosage of less than 10^8 R. The double quantum absorption coefficient δ cannot conceivably depend on doese, therefore a graph of F_T/F_P should demonstrate the relation of γ_1 on doese. Figure 5 shows oscillograms of the triplet generated fluore-

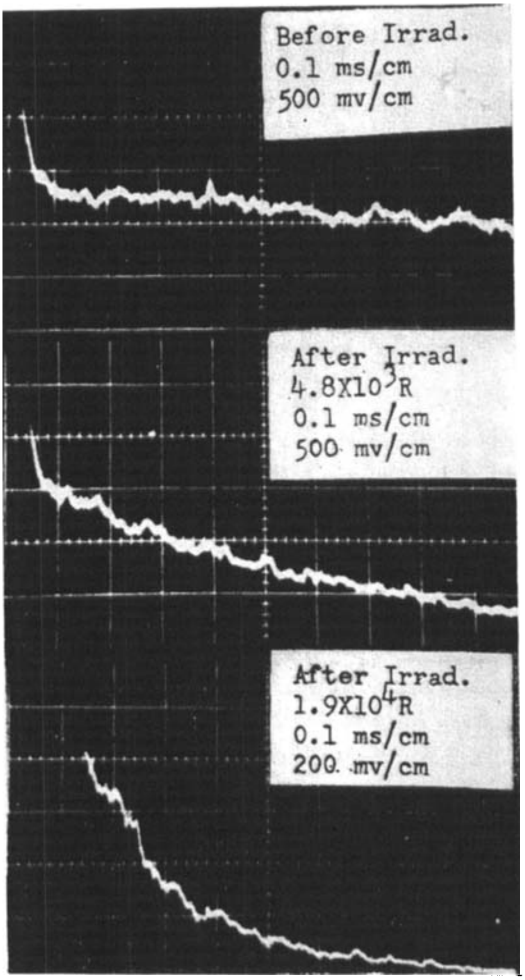

Figure 5. F_τ *vs.* Time. The Dependence of the Fluorescent Response on Dosage within the Bimolecular Time Domain. Upper: 0 Roentgens; $R_m = 100$ K; time const. ≈ 5 μsec. Middle: 4.8×10^3 Roentgens; $R_m = 100$ K; time const. $= 5$ μsec. Lower: 1.9×10^4 Roentgens; $R_m = 100$ K; time const. ≈ 5 μsec.

scence following flash excitation as a function of dose. The peak fluorescence due to double quantum absorption is off scale in these oscillograms but the ratio F_T/F_p for which F_T was picked at flash cutoff is shown in Fig. 6. Clearly there was no significant dependence of γ_1 on dose up to about 10^4 R and thus assumption (c) is verified for γ_1 to this dosage. This kind of experiment could not be continued to higher dosage because at these dosage levels there had been introduced sufficient density of triplet quenchers to cause β to become comparable to γT^0 for the flash intensities available. Thus in these particular flash experiments domination of the rate of triplet decay by the bimolecular term could not be observed at dosage greater than 10^4 R.

Direct confirmation that Eq. (5) is the proper representation of dose effect on lifetime is easily obtained from oscillograms such as those of Fig. 5. At longer times following flash extinction, $t > \beta^{-1}$, only the βT term of Eq. (1) is of significance; thus $T = T^0 \exp[-\beta T]$ and Eq. (3) becomes

$$F_d = \frac{1}{2} A \gamma_1 \varphi_f {T^{0}}^{2} e^{-2\beta t} \tag{12}$$

in which F_d is the symbol for decaying fluorescence at long times. Figure 7 is a log-log plot of the change in triplet decay constant as a function of gamma-ray dose. The approach of the slope toward unity is satisfying. Perhaps the slight superlinear behavior is due to the small contributions from second order processes.

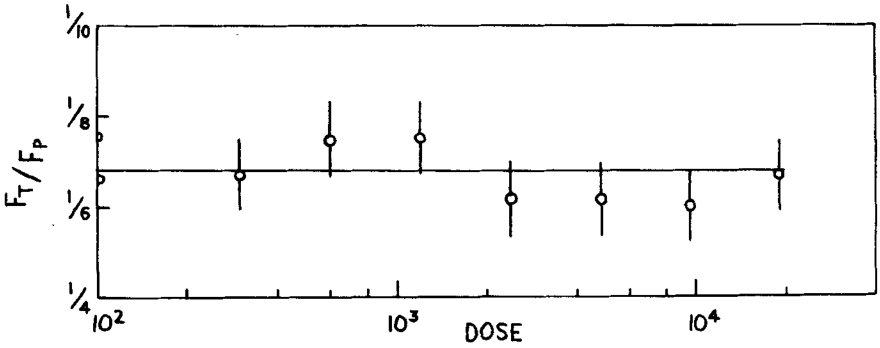

Figure 6. F_T/F_p *vs.* log Dose. Ratio of Fluorescence Generated by Triplet-Triplet and Two Photon Processes. Vertical: dimensionless. Horizontal: 1 unit = × 10 Roentgens.

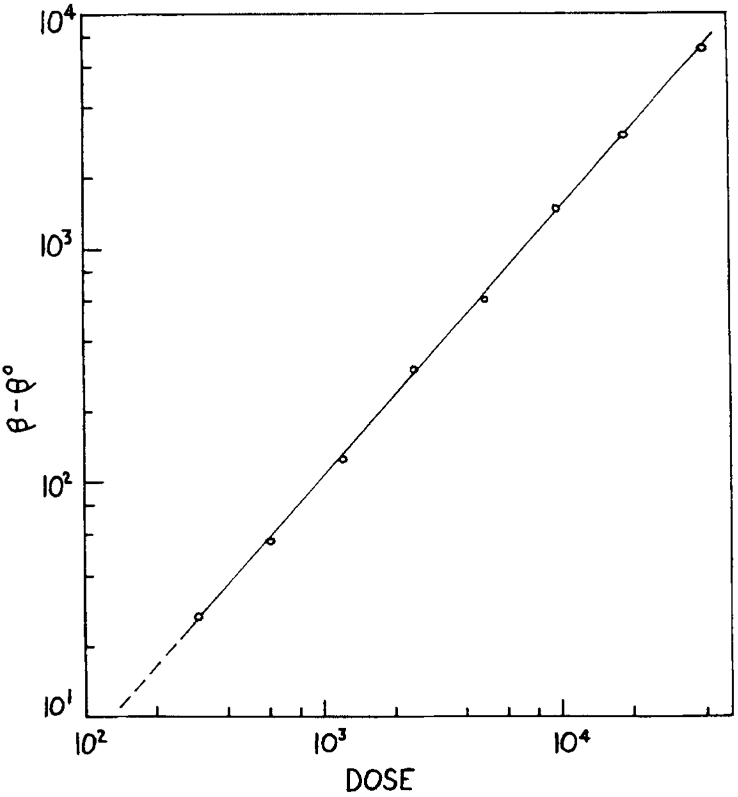

Figure 7. log $(\beta - \beta^0)$ *vs.* log Dose. Change of Triplet Decay due to Radiation Produced Quenchers. Vertical 1 unit = × 10 $\sec^{-1}$. Horizontal: 1 unit = × 10 Roentgens.

The double quantum absorption experiments also permit an independent verification of the effect of dosage on the fluorescence efficiency, φ_f. In the direct excitation of singlets by UV light the absorption depth was at most a few microns. It is conceivable that the damage may have been air assisted, or that if the damage was of a physical kind (misoriented molecules, etc.) that surface annealing could easily occur. Since the fluorescence emitted due to double quantum absorption uniformly comes from the crystal volume, then the possible complexities are bypassed. The oscillogram of Fig. 8 was typical of those obtained for the double quantum generated fluorescence of highly dosed specimen. Figure 9 is a graph of the peak intensity of this fluorescent response as a

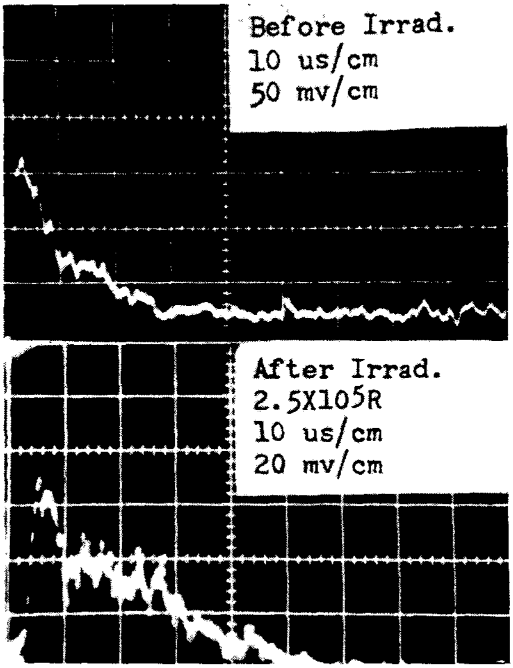

Figure 8. F_p *vs.* Time. The Dependence of the Double Photon Generated Fluorescence on Dosage Upper: 0 Roentgens; $R_m = 1$ K; time const. $\approx$ 1 μsec. Lower: 2.5×10^5 Roentgens; $R_m = 1$ K; time const. $\approx$ 1 μsec.

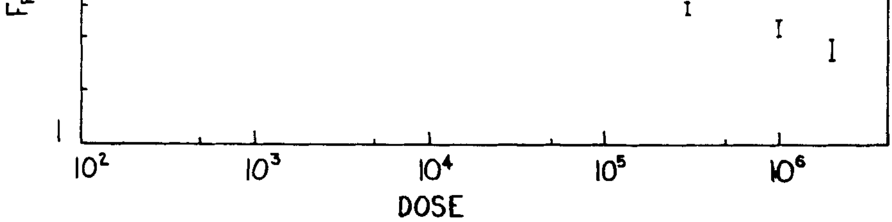

Figure 9. log $F_{p_{peak}}$ *vs.* log Dose. Effect of Radiation on Fluorescence Uniformly Generated in Crystal Bulk. Vertical: 1 unit = $\times 10$ arbitrary. Horizontal: 1 unit = $\times 10$ Roentgens.

function of dose and is of essentially the same nature as Fig. 2 for the UV excitation. Note the almost complete absence of fluorescence from the triplet-triplet mechanism even at 50 μsec.

4. Discussion

Equations (3) and (6) may be written

$$F = K(k^0 + p_{SQ}\sigma_{SQ}v_S\varepsilon_S D)^{-1} \quad \text{and} \quad F_r = K'(\beta^0 + p_{TQ}\sigma_{TQ}v_T\varepsilon_T D)^{-2} \quad (13)$$

in which $\varepsilon_S D$ and $\varepsilon_T D$ are the density of singlet and triplet quenchers introduced by a gamma-ray dose, D; k^0 and β^0 are the singlet and triplet decay constants before dosage, and the other symbols have their usual significance. Defining by $D_{1/2}$ and $D'_{1/2}$ the dosages at which F and F_r are respectively reduced to 1/2, then Eq. 13 may be combined to give

$$\frac{p_{SQ}}{p_{rQ}} \frac{\sigma_{SQ}}{\sigma_{rQ}} \frac{v_S}{v_T} \frac{\beta^0}{k^0} \frac{\varepsilon_E}{\varepsilon_T} \frac{D_{1/2}}{D'_{1/2}} = 2.5 \qquad (14)$$

From Fig. 1, 2, 3 and 9, $D_{1/2} = 5 \times 10^5$ R and $D'_{1/2} = 3 \times 10^2$ R so that $D_{1/2}/D'_{1/2} \approx 10^3$. It appears reasonable to take $\sigma_{SQ} = \sigma_{TQ} = 3 \times 10^{-15}$ cm^2 so that

$$\frac{p_{SQ}}{p_{ST}} \frac{\varepsilon_S}{\varepsilon_T} \frac{v_S}{v_T} \frac{\beta^0}{k^0} = 2.5 \times 10^{-3}. \qquad (15)$$

There are two approaches which may now be taken. Experimental values for β^0 and k^0 vary slightly from crystal to crystal but show that $\beta^0/k^0 = 10^{-6}$ is a representative average. No direct measurements for either v_S or v_T are available; however, these may be estimated. From the data of Silver *et al.*[11] for the interaction of pairs of singlet excitons to yield current carriers, v_S may be estimated to be 2×10^3 cm sec^{-1} ($k = 5 \times 10^{-12}$ cm^3 sec^{-1}; assume $p = 1$ and $\sigma = 3 \times 10^{-15}$ cm^2). The data of Kepler and coworkers[1] and Avakian and coworkers[4] indicates that the triplet exciton-exciton interaction to produce fluorescence (self quenching was assumed to be negligible) has a rate constant of 2×10^{-11} cm^3 sec^{-1} and therefore under similar assumptions v_T is estimated to be 7×10^3 cm sec^{-1}. The near equality of these exciton velocities is difficult to understand and self quenching and other competing processes surely cause p_{TT} to be less than unity; however, as one extreme of behavior we take $v_S/v_T \approx 1$ and therefore $\frac{p_{SQ}}{p_{TQ}} \frac{\varepsilon_S}{\varepsilon_Q} \approx 2.5 \times 10^3$. On this basis the net effect of a given gamma-ray dose is to introduce singlet quenchers with an overall quenching efficiency about 10^3 greater than that for the triplet quenchers introduced by the same dose.

The second extreme approach is based on the reported diffusion lengths of the excitons. Triplet excitons have been shown to have a diffusion length, L, of about 100μ. Avakian and Merrifield[12] found $L = 10 \pm 5\mu$ in the ab plane (β^0 was not specified), while Kepler and Switendick[13] obtained $D = (0.4 - 2) \times 10^{-2}\ \text{cm}^2\ \text{sec}^{-1}$ and Levine *et al.*[14] found $D = (2.0 \pm 0.5) \times 10^{-4}\ \text{cm}^2\ \text{sec}^{-1}$ for the triplet exciton diffusion coefficients and from which lengths, $L = (2D\beta^{0-1})^{1/2}$, of 150μ and 20μ respectively may be calculated for $\beta^{0-1} = 10$ msec. The diffusion length for singlet excitons, $L = \sqrt{2Dt}$ was approximately 600 Å as deduced by Simpson[15] in polycrystalline samples of anthracene while Eremenko and Medvedev[16] report 2000 Å. For either of the excitons the diffusion length may be given by $L = pv\tau$ in which τ is the exciton lifetime, v its instantaneous velocity and p the ration of drift velocity to instantaneous velocity. If it is assumed that the ratio of p's for singlet and triplet exciton motion is unity, i.e., if there is similar anisotropy for the motion of both,[17] then in clean but undamaged crystals the ratio of the velocities should be about

$$\frac{v_S}{v_T} = \frac{L_S}{L_T} \frac{k^0}{\beta^0} \approx \frac{10^{-6}\ \text{cm}}{1\text{p}^{-3}\ \text{cm}} \frac{10^{-2}\ \text{sec}}{10^{-8}\ \text{sec}} = 10^4$$

or the ratio of diffusion lengths $L_S/L_T = v_S\beta^0/v_T k^0 = 10^{-2}$. Introducing the last ratio which depends on the assumption of similar anisotropy of exciton motion into (15) results in $p_{SQ}/p_{TQ}\ \varepsilon_S/\varepsilon_T = 0.25$. On this basis the net effect of a given gamma-ray dose is to introduce singlet quenchers with an overall efficiency about the same as that of the triplet quenchers introduced by the same dose.

The two approaches bracket the ratio of the net efficiencies between about 1 and 10^3. The essential point is that singlets are equally or more efficiently quenched than triplets by a given gamma-ray dose even though the triplet quenching is observable at smaller dosages. If one now combines the 1 to 10^3 efficiency ratio with the ratio of volumes sampled by the excitons, then it is seen that the triplets sample a volume $\left(\frac{L_T}{L_S}\right)^3 = 10^6$ larger than do the singlets and thus it remains necessary to require a 10^3 to 10^6 greater density of singlets to be produced by a given dose of gamma radiation for the same degree of quenching. A detailed study of the density of each kind of quenching center is in progress. Comparison between carrier trapping, triplet quenching, singlet quenching, and damage produced e.s.r. signal appear feasible at dosage far below those amenable to conventional chemical approaches.

The present experimental determination of the dependence of γ_1 on dose was intensitive to the γ_2 term. However, the present findings are consistent with those of Kepler[18] who has found that the emission produced by the triplet-triplet mechanism in undosed monocrystalline anthracene was not affected by trapping until temperatures below about 100°K. Thus these independent results indicate that trap modulated velocity terms in γ are of little consequence at room temperature.

From a practical viewpoint it appears that an individual single crystal of anthracene may permit the determination of gamma or x-ray dose over a range from 10^2 to 10^8 R. The low end from 10^2 to 10^4 R can be measured through triplet quenching, the range of 10^3 to 10^5 R by space charge limited current technique, the 10^5 to 10^7 R range by singlet quenching, and the high dosage range of 10^7 R and above by direct optical coloration. The lower limit depends on β^0. If instead of a xenon flash or a d.c. xenon arc, one would use a Q switched laser, then a change in β could be measured from 10^2 R up to about 5×10^5 R and from about 10^5 to 10^7 R the quenching of double quantum generated singlets could be measured. A range of 10^2–10^7 R could be continuously covered with one crystal and one excitation source.

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