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Study of Radiation Damage

In Organic Crystals

Progress Summary Report No. 4

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and

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October 1967



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STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS

Amador Cobas and Zvi Weisz - Principal Investigators

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Work performed at Puerto Rico Nuclear Center  
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## INTRODUCTION

This project is concerned with the effects of radiation on organic crystals. It is felt that such studies on well defined crystalline structures can provide a firm foundation for a later study of more complex materials including those of direct biological interest. We have chosen anthracene as the initial material for study because this substance has been studied more than any other organic material.

The effect of irradiation on anthracene has been studied previously by Kommandeur<sup>1,2</sup> using photoconductivity methods and by Sharn<sup>3</sup> using optical methods. Since these studies were made, experimental and theoretical developments such as charge injecting electrodes to organic crystals, space-charge-limited currents and non linear optics, enabled a much better understanding of molecular crystals. We felt that it would be valuable to reopen and expand the previous studies of irradiation effects by including these recently developed techniques.

The study we made on the effects of neutron, gamma and x-ray irradiation on anthracene using space-charge-limited current methods was described previously<sup>4</sup>. In this progress report the effects of gamma irradiation in anthracene studied by non linear optical methods are described.

Below is a summary of the results obtained by space-charge-limited currents method.

By irradiating anthracene crystals with gamma or x-rays hole traps are introduced in the crystal. The presence of these traps can be detected by space-charge-limited current methods using a sodium iodide - iodine solution in a Kallmann - Pope cell as a hole injecting electrode. From the changes in the steady state space-charge-limited current - voltage characteristic curve for crystals before and after irradiation the following results were obtained.

- 1) The radiation introduces a permanent damage in the crystal in the form of hole traps.
- 2) The density of these traps varies linearly with the absorbed radiation dose.
- 3) These traps lie at energy levels distributed uniformly, the largest activation energy being 0.9 ev.
- 4) For every hole trap formed, about 45 kev energy is absorbed.

The lifetime of the carriers was obtained by measuring the transient space-charge-limited current. Combining this measurement with the results of the steady state measurements the capture cross-section of these traps for holes was estimated to be of molecular size.

SECTION I. BACKGROUND

The dynamic properties of optical excitons in molecular crystals have been of particular interest in recent years. Kepler's<sup>5</sup> 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 longlived mobile excitation in anthracene crystal. The work of Hirota and Hutchison<sup>6</sup> 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.<sup>7</sup> 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,<sup>8,9</sup> 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.<sup>10</sup> have used the long life of triplet excitons in crystalline anthracene to

observe the decay of delayed fluorescence from which the efficiency of the radiationless transition from singlet to triplet ( $S_1 \rightarrow T_1$ ) could be deduced.

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.

## SECTION II. 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 so 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  $\text{CuSO}_4$  to 7 parts  $\text{H}_2\text{O}$  (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  $m\mu$  ( $S_0 \rightarrow T_1$ ) absorption band was efficiently transmitted while the extinction foot at 530  $m\mu$  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  $\text{CuSO}_4$  plus one CS 5-58 filter. This combination of filters has a peak transmission at 410  $m\mu$  while the fluorescence has peaks at 430  $m\mu$  and 450  $m\mu$ .

The fluorescence signal,  $F_r$ , due to steady state red excitation was measured before and after gamma-ray dosage from a  $^{60}\text{Co}$  source. The source intensity was 600 R  $\text{min}^{-1}$ . The measured absorption coefficient of anthracene for the  $^{60}\text{Co}$  emission was 0.118  $\text{cm}^{-1}$  so that the calculated energy absorption was 293  $\text{erg gm}^{-1}\text{R}^{-1}$ . 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.<sup>11</sup> 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 1P21 photomultiplier at right angles to the direction of the exciting flash and filtered with the same combination as used in the steady state experiments.



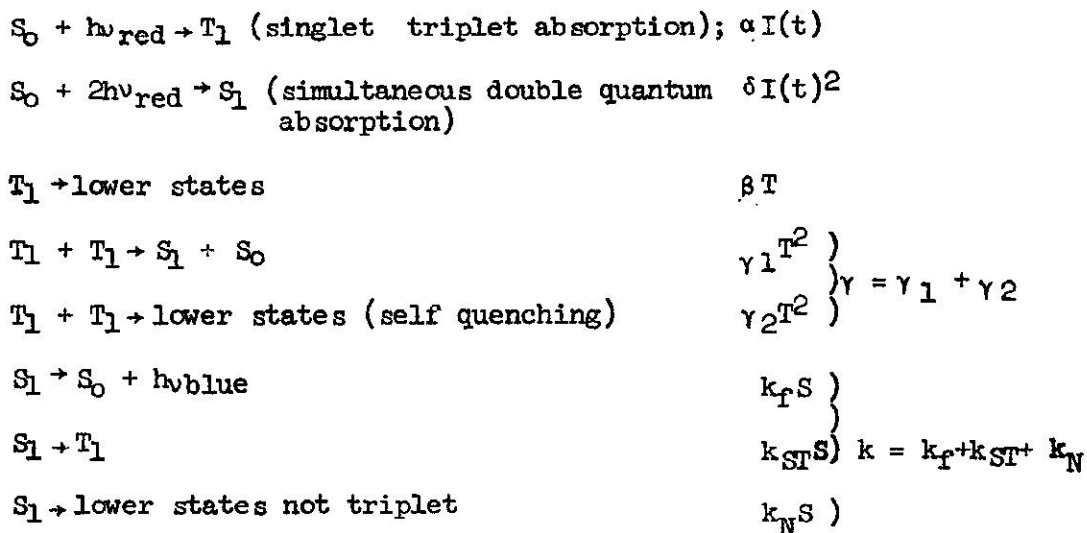
The width of the flash intensity at half maximum was  $8\mu$  sec.

The peak intensity in the 6000-8000 Å band was about  $10^{23}$  cm<sup>-2</sup>sec<sup>-1</sup>.

SECTION III. 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,  $\phi_f$  rel, obtained under near u.v. excitation. Although there was wide fluctuation in  $\phi_f$  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<sup>3</sup>, who previously had found a linear decrease of fluorescence efficiency for powdered anthracene in the dose range of  $10^5$  to  $10^7$  R.

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



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

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

$$F = A k_f S; \quad A \text{ is an unknown geometric and sensitivity factor for a given crystal and type of experiment.} \quad (3)$$

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  $\delta I(t)^2 < 1/2\gamma_1 T^2$ , so that

$$F_r = A \frac{\gamma_1 \phi_f}{2} \left(\frac{\alpha}{\beta}\right)^2 I^2 \quad (4)$$

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  $\alpha$  for  $S_0 \rightarrow T_1$ , (b) the fluorescence efficiency  $\phi_f$ , and (c) the bimolecular triplet exciton interaction constant,  $\gamma_1$ ; then the damage effect may be assumed to be of the form

$$\beta = \beta^0 + aD. \quad (5)$$

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

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

Figure 3 shows a graph of the observed steady state data in excellent agreement with equation (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  $\alpha$  on D will be of consequence if damage produced impurities are sufficiently strong absorbers of the red light to result in decreased crystal transmission. No optical density in the 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 Figure 2 clearly indicate that no significant change occurs in  $\phi_f$  below a dosage of  $10^5$  R and therefore assumption (b) is valid.

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It was expected that the bimolecular rate constant,  $\gamma$ , should not be dependent on damage because if one writes  $\gamma = (P_1 + P_2) \cdot \sigma_{TT} \cdot v_T$  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  $\sigma_{TT}$ , 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 lower.

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  $I_p$ . During a flash of microseconds duration,  $\tau_1$ , the triplets are not contributing a significant amount to the instantaneous singlet population; therefore equation (2) becomes

$$S = \frac{\delta I_p^2}{k} \quad (7)$$

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

$$F_p = A\theta_f \delta I_p^2. \quad (8)$$

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

$$T^0 = \alpha I_p \tau_1 = 10^{-4} \text{cm}^{-1} \times 10^{23} \text{cm}^2 \text{sec}^{-1} \times 10^{-5} \text{sec} = 10^{14} \text{cm}^{-3} \quad (9)$$

Since  $\alpha^{\dagger}$  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,  $\tau_1 < t < \beta^{-1}$ , the bimolecular term of equation (1) dominates the triplet decay and the fluorescent signal given by (3) is denoted

by  $F_T$  and becomes 
$$F_T = 1/2A\phi_f\gamma_1 \left( \frac{T^0}{1 + \gamma T^0 t} \right)^2 \quad (10)$$

Since  $\gamma \approx 2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  <sup>8,9</sup> then  $\gamma T^0 t \ll 1$  up to about  $50 \mu \text{ sec}$ .

Therefore comparing (10) with (8) and utilizing (9) gives

$$\frac{F_T}{F_P} = 1/2 \frac{\gamma_1 \alpha^2 \tau_1^2}{\delta} \quad (11)$$

Figure 4 shows the fluorescent behavior in an undamaged crystal from 0 to  $500 \mu \text{ sec}$  and succinctly illustrates the two mechanisms which are operating. Note the almost abrupt change in decay character near  $10 \mu \text{ sec}$ .

As previously stated,  $\alpha$  does not depend on dosage of less than  $10^8 \text{ R}$ . The double quantum absorption coefficient  $\delta$  cannot conceivably depend on dose, therefore a graph of  $F_T/F_P$  should demonstrate the relation of  $\gamma_1$  on dose. Figure 5 shows oscillograms of the triplet generated fluorescence 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 Figure 6. Clearly there was no significant dependence of  $\gamma_1$  on dose up to about  $10^4 \text{ R}$  and thus assumption (c) is verified for  $\gamma_1$  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  $\beta$  to become comparable to  $\gamma T^0$  for the flash intensities available. Thus in this particular flash experiment domination of the rate of triplet decay by the bimolecular term could not be observed at dosage greater than  $10^4 \text{ R}$ .

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

$$F_d = 1/2A\gamma_1 \phi_f T^0 2 e^{-2\beta t} \quad (12)$$

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.

The double quantum absorption experiments also permit an independent verification of the effect of dosage on the fluorescence efficiency,  $\phi_f$ . In the direct excitation of singlets by u.v. 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 Figure 8 was typical of those obtained for the double quantum generated fluorescence of a highly dosed specimen. Figure 9 is a graph of the peak intensity of this fluorescent response as a function of dose and is of essentially the same nature as Figure 2 for the u. v. excitation. Note

the almost complete absence of fluorescence from the triplet-triplet mechanism even at 50 μsec.

#### SECTION IV. DISCUSSION

Equations (3) and (6) may be written

$$F = K(k^0 + P_{SQ}\sigma_{SQ}v_S\epsilon_S^D)^{-1} \text{ and } F_T = K'(\beta^0 + P_{TQ}\sigma_{TQ}v_T\epsilon_T^D)^{-2} \quad (13)$$

in which  $\epsilon_S^D$  and  $\epsilon_T^D$  are the density of singlet and triplet quenchers introduced by a gamma-ray dose,  $D$ ;  $k^0$  and  $\beta^0$  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  $F_T$  are respectively reduced to  $1/2$ , then equations (13) may be combined to give

$$\frac{P_{SQ}}{P_{TQ}} \cdot \frac{\sigma_{SQ}}{\sigma_{TQ}} \cdot \frac{v_S}{v_T} \cdot \frac{\beta^0}{k^0} \cdot \frac{\epsilon_S}{\epsilon_T} \cdot \frac{1/2}{D'_{1/2}} = 2.5 \quad (14)$$

From figures 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

$$\sigma_{SQ} = \sigma_{TQ} = 3 \times 10^{-15} \text{ cm}^2 \text{ so that}$$

$$\frac{P_{SQ}}{P_{TQ}} \cdot \frac{\epsilon_S}{\epsilon_T} \cdot \frac{S}{T} \cdot \frac{\beta^0}{k^0} = 2.5 \times 10^{-3} \quad (15)$$

There are two approaches which may now be taken. Experimental values for  $\beta^0$  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.<sup>13</sup> for the interaction of pairs of singlet excitons to yield current carriers,  $v_S$  may be estimated to be  $2 \times 10^3$

cm sec<sup>-1</sup> ( $k = 5 \times 10^{-12}$  cm<sup>3</sup> sec<sup>-1</sup>; assume  $p = 1$  and  $\sigma = 3 \times 10^{-15}$  cm<sup>2</sup>).

The data of Kepler and coworkers indicates that the triplet exciton-exciton interaction to produce fluorescence (self quenching was assumed to be negligible) has a rate constant of  $2 \times 10^{-11}$  cm<sup>3</sup>sec<sup>-1</sup> and therefore under similar assumptions  $v_T$  is estimated to be  $7 \times 10^3$  cm sec<sup>-1</sup>. 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  $v_S/v_T \sim 1$  and therefore  $\frac{P_{SQ} \epsilon_S}{P_{TQ} \epsilon_Q} \approx 2.5 \times 10^3$ .

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  $10\mu$ . Avakian and Merrifield<sup>14</sup> found  $L = 10 \pm 5\mu$  in the ab plane ( $\beta^0$  was not specified), while Kepler and Switendick<sup>15</sup> obtained  $D = (0.4 - 2) \times 10^{-2}$  cm<sup>2</sup>sec<sup>-1</sup> and Levine et al.<sup>16</sup> found  $D = (2.0 \pm 0.5) \times 10^{-4}$  cm<sup>2</sup>sec<sup>-1</sup> for the triplet exciton diffusion coefficients and from which lengths,  $L = (2D\beta^0)^{1/2}$ , of  $150\mu$  and  $20\mu$  respectively may be calculated for  $\beta^0 = 10$  msec. The diffusion length for singlet excitons,  $L = \sqrt{2Dt}$  was approximately  $600 \text{ \AA}$  as deduced by Simpson<sup>17</sup> in polycrystalline samples of anthracene while Eremenko and Medvedev<sup>18</sup> report  $2000 \text{ \AA}$ . For either of the excitons the diffusion length may be given by  $L = pv\tau$  in which  $\tau$  is the exciton lifetime,  $v$  its instantaneous velocity and  $p$  the ratio of drift velocity to instantaneous velocity. If it is assumed that the value



of p's for singlet and triplet exciton motion is unity, i.e., if there is similar anisotropy for the motion of both, <sup>19</sup> then in clean but undamaged crystals the ratio of the velocities should be about

$$\frac{v_S}{v_T} = \frac{L_S}{L_T} \cdot \frac{k^0}{\beta^0} = \frac{10^{-5} \text{ cm}}{10^{-3} \text{ cm}} \cdot \frac{10^{-2} \text{ sec}}{10^{-8} \text{ sec}} = 10^4$$

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  $P_{SQ}/P_{TQ} \epsilon_S/\epsilon_T = 0.25$ . On this basis the net effect of a given gamma-ray dose is to introduce a singlet quencher 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  $(\frac{L_T}{L_S})^3 = 10^6$  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, and damage produced e.s.r. signal appears feasible at dosages far below those amenable to conventional chemical approaches.

The present experimental determination of the dependence of  $\gamma$

on dose was insensitive to the  $\gamma_2$  term. However, the present findings are consistent with those of Kepler<sup>20</sup> 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  $\gamma$  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 over by direct optical coloration. The lower limit depends on  $\beta^\circ$ . If instead of a xenon flash or a d.c. xenon arc, one would use a Q switched laser, then a change in  $\beta$  could be measured from  $10^2$  R up to about  $5 \times 10^5$  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.

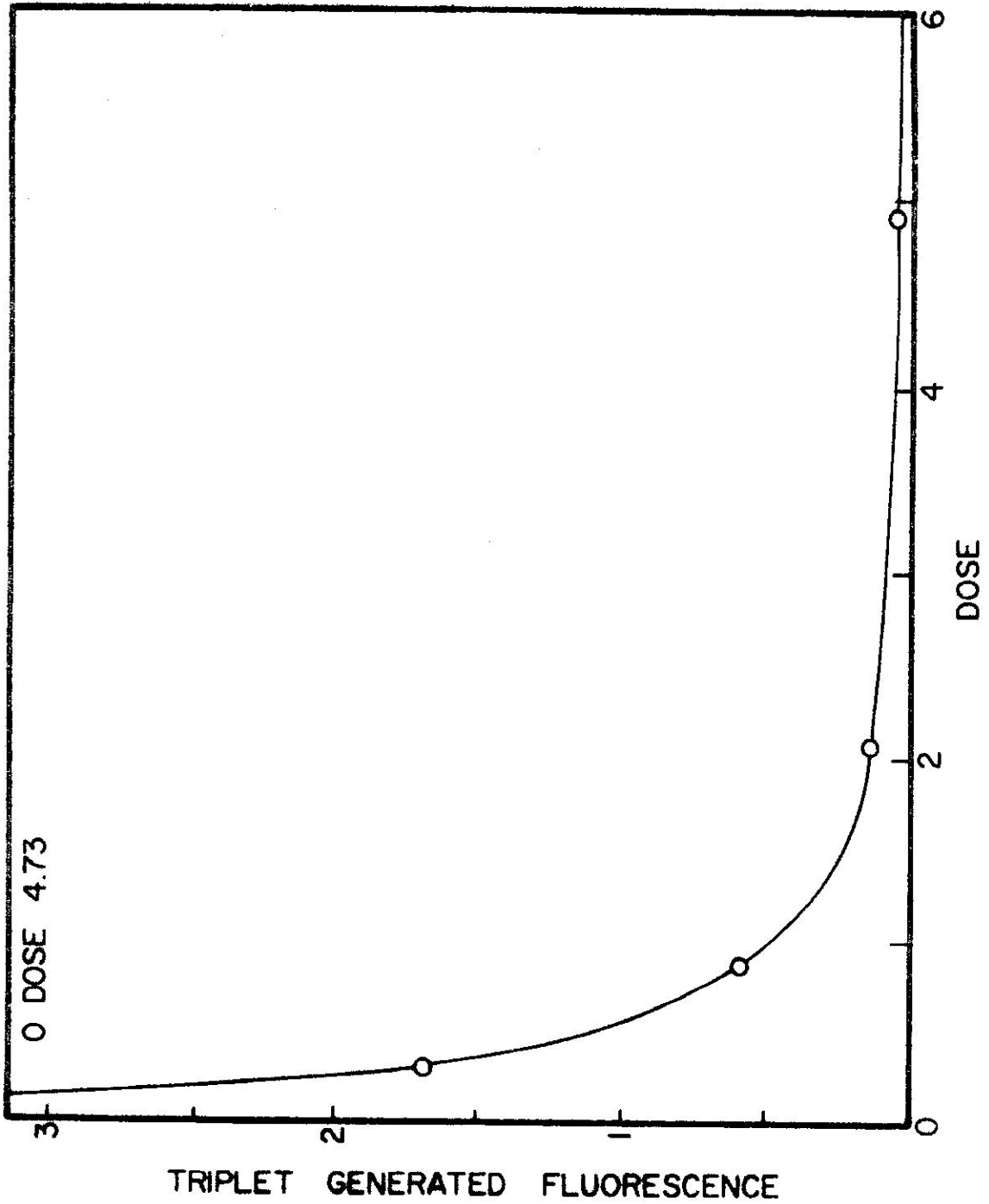


FIG. 1

$F_T$  vs. Dose

Blue Fluorescence under Steady Red Excitation

Vertical: 1 unit =  $10^6$  amp.

Horizontal: 1 unit =  $10^3$  Roentgens

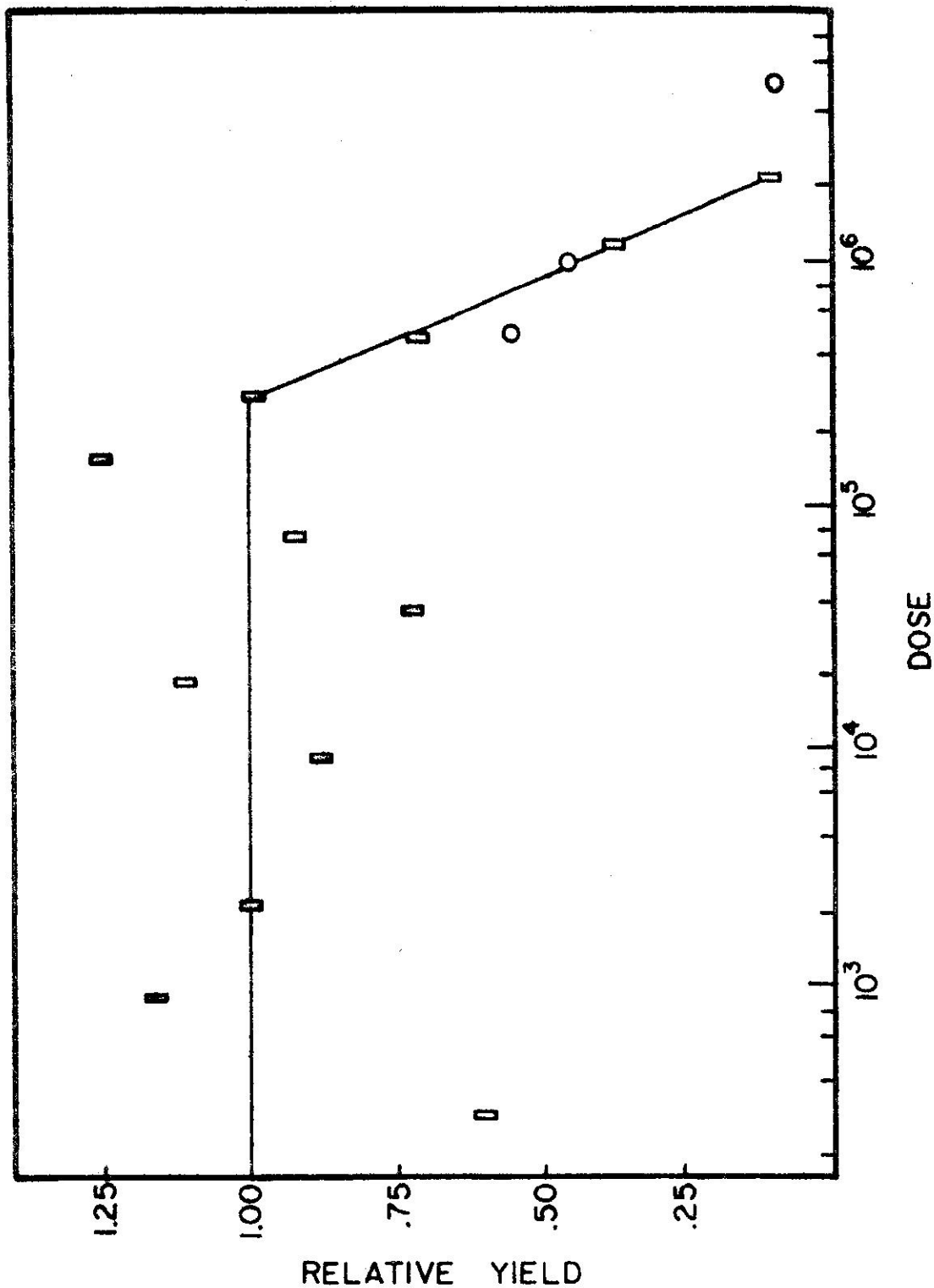


FIG. 2

$\phi_{\text{rel}}$  vs. log Dose

Blue Fluorescence under Steady 3130 Å Excitation

Vertical: relative yield

Horizontal: 1 unit = 10 Roentgens

□ the present data

○ Sharn, reference 9

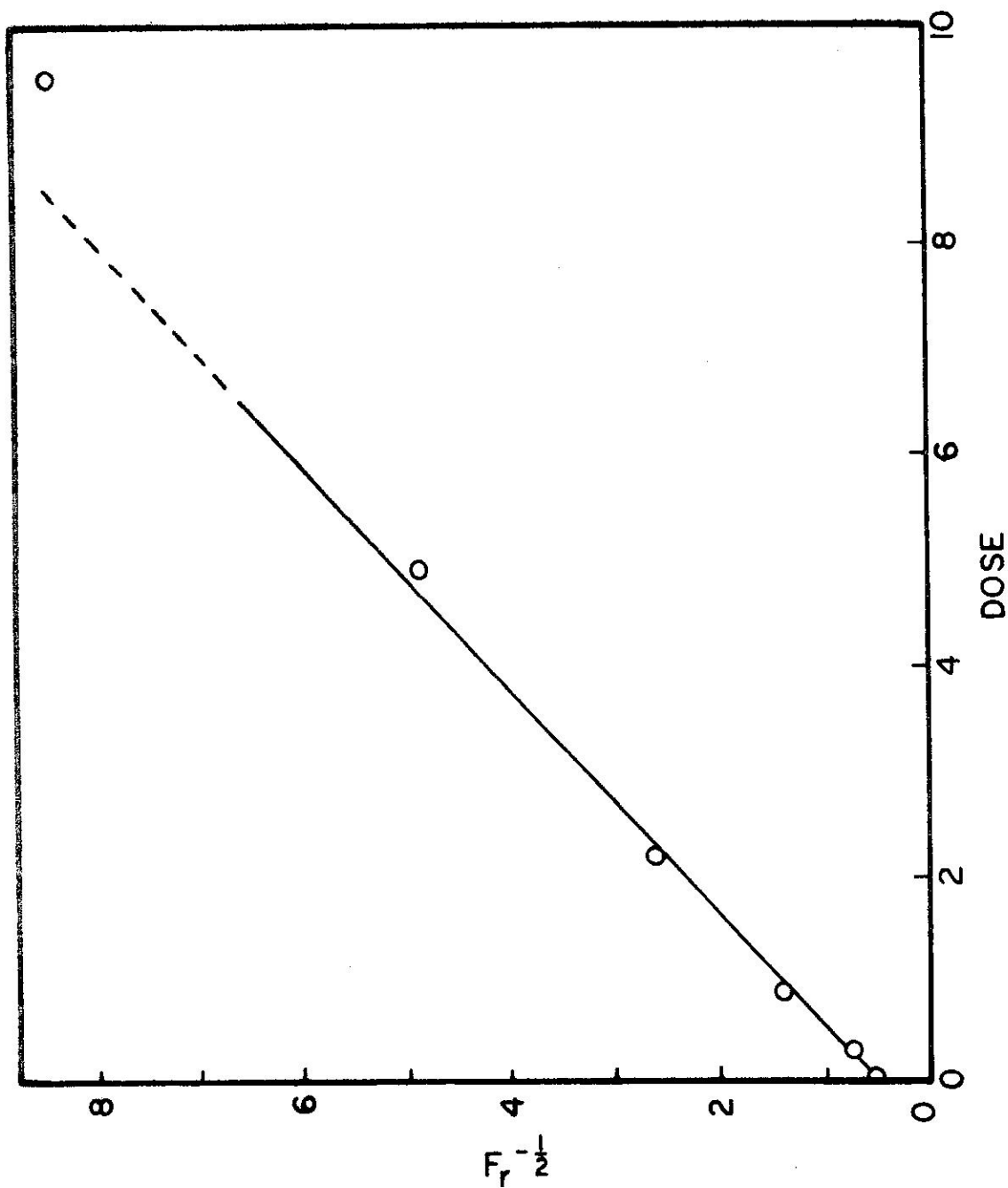


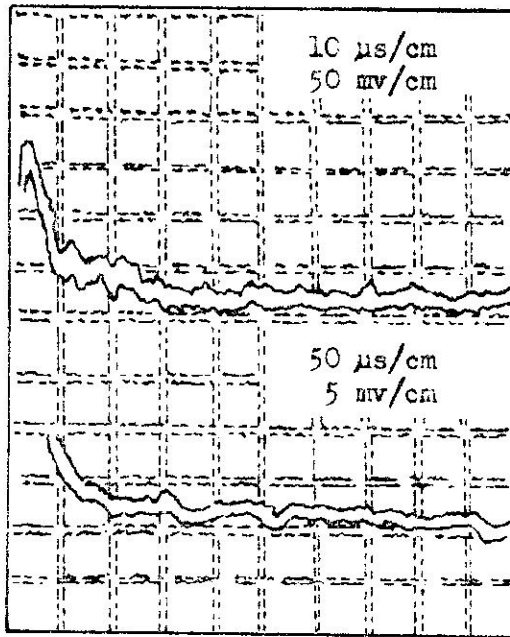
FIG. 3

$F_r^{-1/2}$  vs. Dose

Blue Fluorescence under Steady Red Excitation

Vertical: 1 unit =  $1 \times 10^2$  amp<sup>-1/2</sup>

Horizontal: 1 unit =  $10^2$  Roentgens



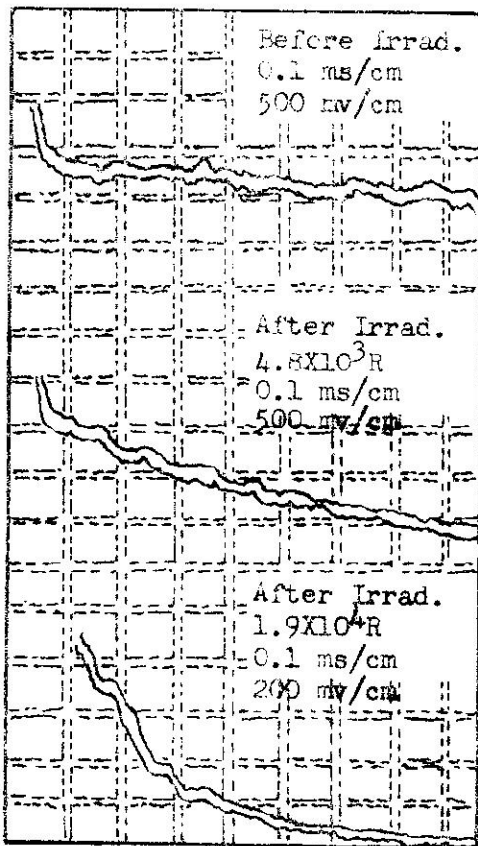
$F_P + F_T$  vs. Time

The Fluorescent Response of an Undamaged Crystal to a High Intensity Red Flash

Upper:  $R_m = 1$  K; time const.  $\approx 1$   $\mu$  sec.

Lower:  $R_m = 1$  K; time const.  $\approx 1$   $\mu$  sec.

FIG. 4



$F_T$  vs. Time

The Dependence of the Fluorescent Response on Dosage within the Bimolecular Time Domain

Upper: 0 Roentgens;  $R_m = 100$  K; time const.  $\approx 5$   $\mu$  sec.

Middle:  $4.8 \times 10^3$  Roentgens;  $R_m = 100$  K; time const.  $\approx 5$   $\mu$  sec.

Lower:  $1.9 \times 10^4$  Roentgens;  $R_m = 100$  K; time const.  $\approx 5$   $\mu$  sec.

FIG. 5

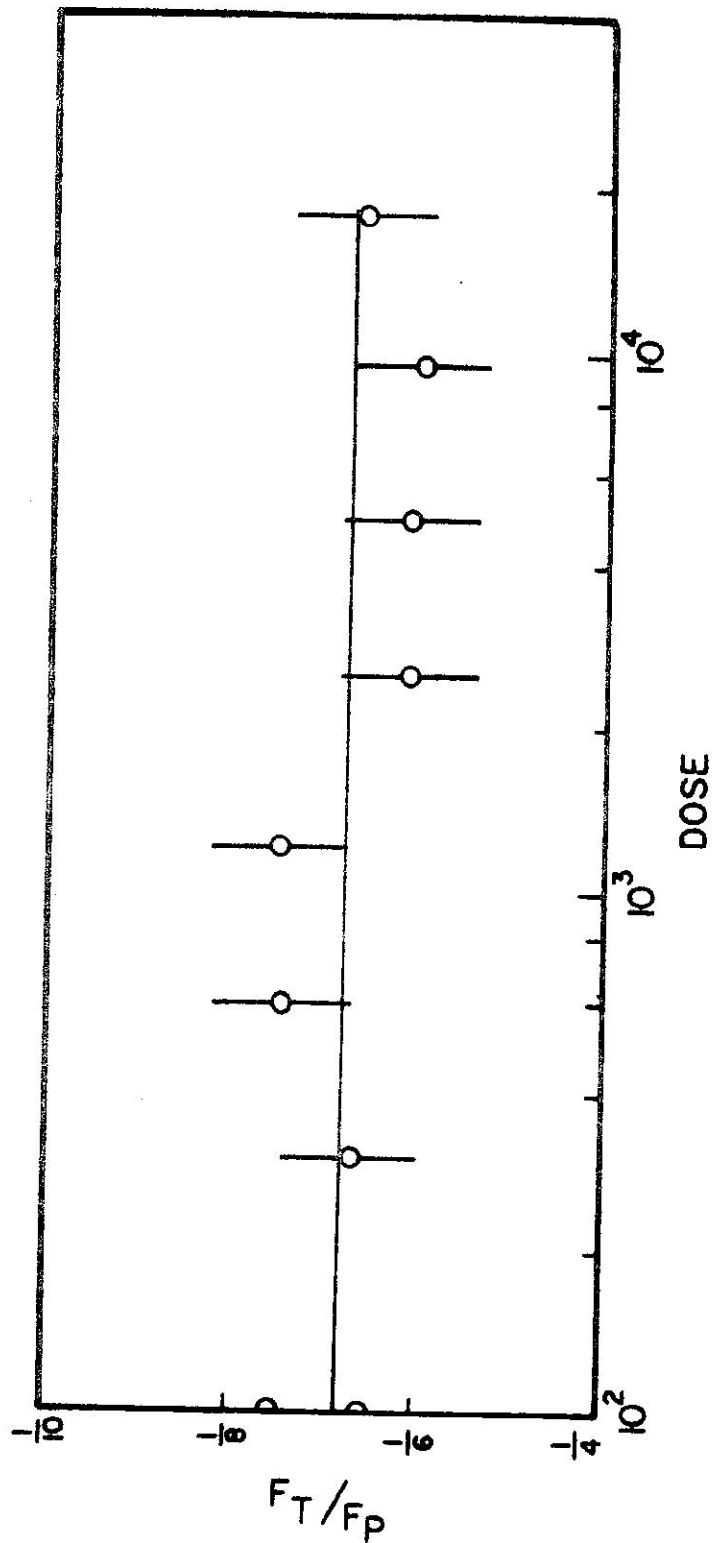


FIG. 6

$F_T/F_P$  vs. log Dose  
Ratio of Fluorescence Generated by Triplet-Triplet and Two Photon Processes  
Vertical: dimensionless  
Horizontal: 1 unit = 10 Roentgens

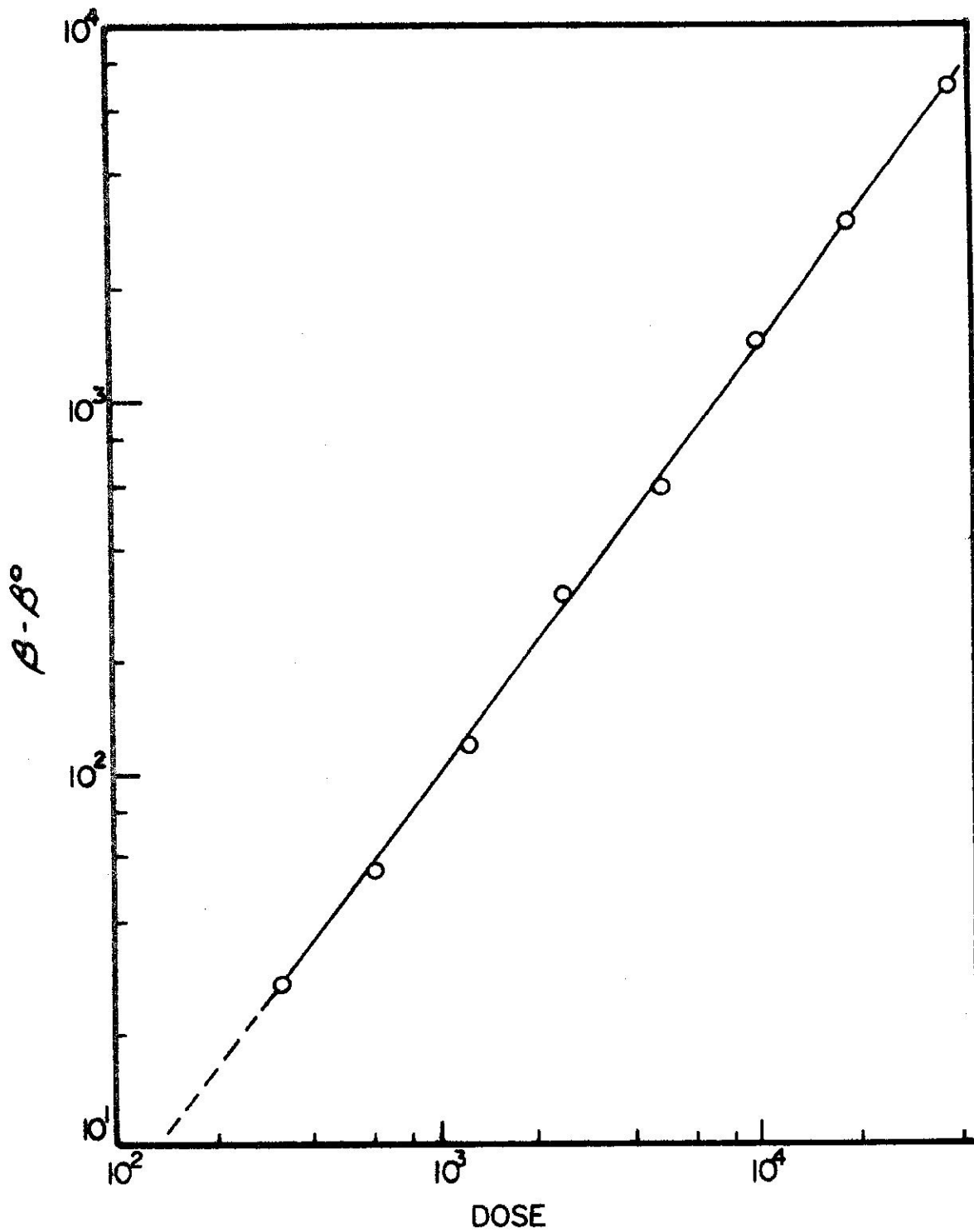


FIG. 7  
log ( $B - B^0$ ) vs. log Dose  
Change of Triplet Decay due to Radiation  
Produced Quenchers  
Vertical: 1 unit =  $10 \text{ sec}^{-1}$   
Horizontal: 1 unit = 10 Roentgens



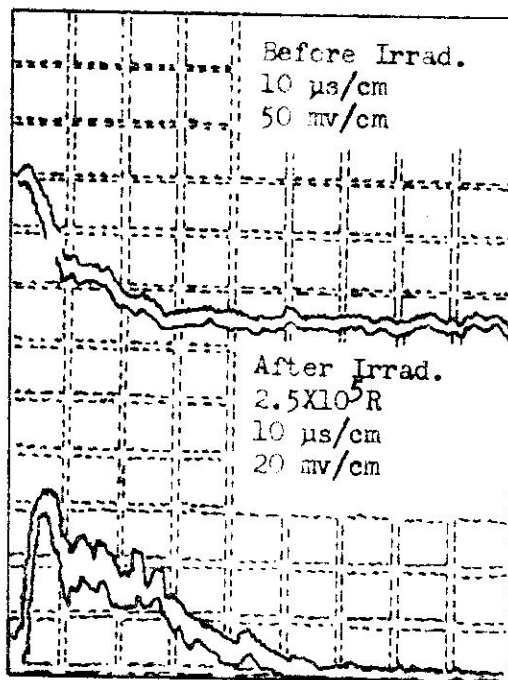


FIG. 8

$F_P$  vs. Time

The Dependence of the Double Photon Generated Fluorescence on Dosage

Upper: 0 Roentgens;  $R_m = 1$  K; time const.  $\approx 1 \mu$  sec.

Lower:  $2.5 \times 10^5$  Roentgens;  $R_m = 1$  K; time const.  $\approx 1 \mu$  sec.

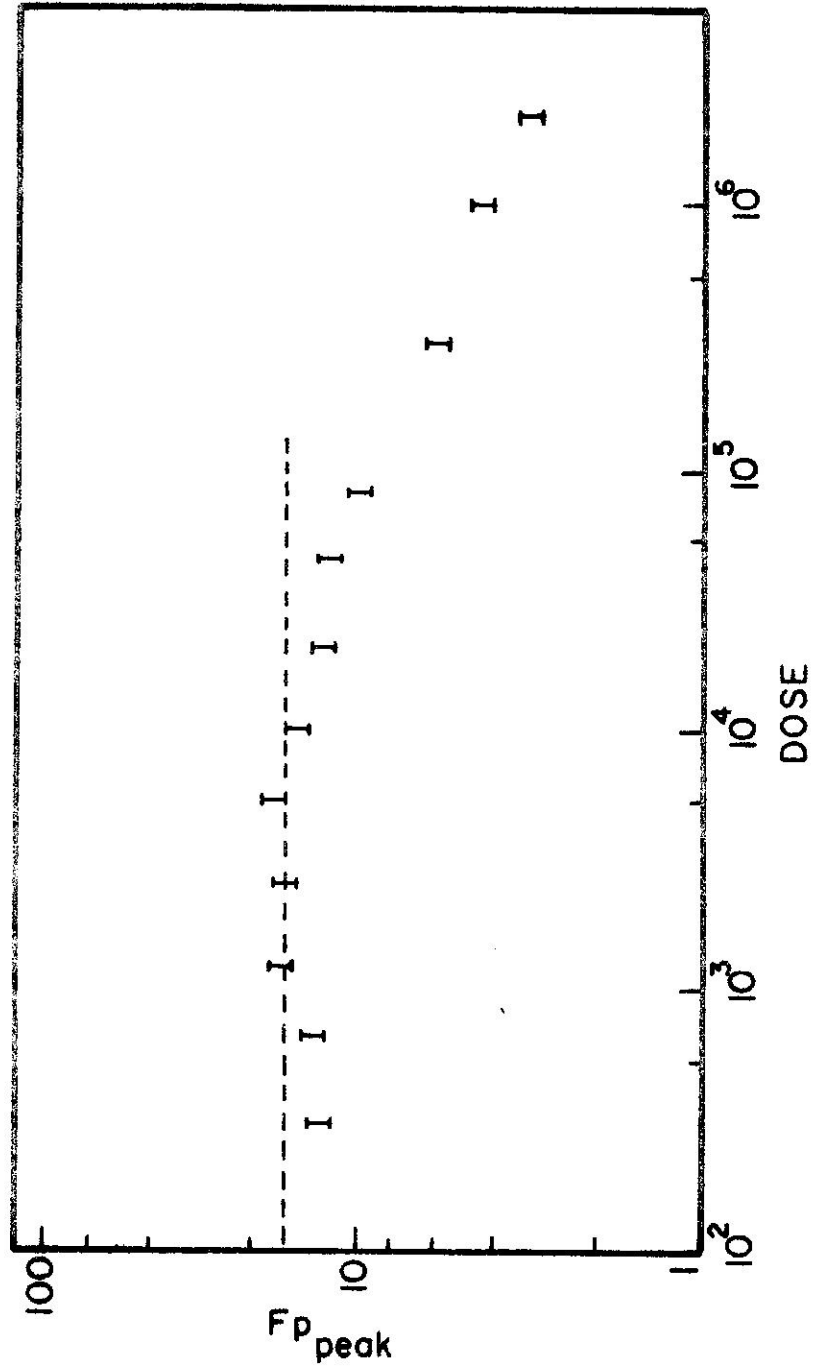


FIG. 9

$\log F_{peak}$  vs.  $\log Dose$

Effect of Radiation on Fluorescence Uniformly  
Generated in Crystal Bulk

Vertical: 1 unit = 10 arbitrary

Horizontal: 1 unit = 10 Roentgens

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