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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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STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS

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. Progrees Sumary Report i,

Work performed at Puerto Rico Miclear Center

Rio Piedras, P. R., under U, S, Atomic Energy

Comission Contract AT(H0-1)-1633 (Project 1h)

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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 Komanteur 4? using photoconductivity methods and by suarn? 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 crystal:

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?, 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.

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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 method using a solution of iodine - formalin solution in a Kallnam - Pope cell as « 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.

2) 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 5 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,

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SECTION T. BACKGROUND

The dynamic properties of optical excitons in molecular crystals have been of particular interest in recent years. Kepler's observation of delayed fluorescence whose intensity depended on the square of the intensity of the exciting light, first showed the existence of an intramolecular interaction between long-lived mobile excitation in anthracene crystal. The work of Hirota and Hutchison⁶ 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.⁷ have investigated problems associated with triplet exciton 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, 89 have utilized the sensitivity inherent in the detection of steady state fluorescence to obtain the weak singlet to triplet ($f \rightarrow$) absorption spectrum in a number of molecular crystals, Weise et al. have

used the long life of triplet excitons in crystalline anthracene to

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he

observe the decay of delayed fluorescence from which the efficiency of the radiationless transition from singlet to triplet ($i \rightarrow$ %) 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.

2e0N TT, Bosna,

Anthracene crystals suitable for scintillation work were obtained from the Harsha Chemical Company, Each crystal was about 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 irradiation doses, One surface of the crystal was illuminated by a collimated light beam from a 900 W Xe DC capacitor lamp, Before focusing on the crystal the light beam was passed through a 1 cm thickness of 2 part saturated Cum, to 7 parts H₂O (v/v) and a heat filter and followed by one each of Corning's sharp cut off filters C8 3-67 and CB 3-68, The light in the 600-20 m (85+ 1)

absorption band was efficiently transmitted while the extinction coefficient at 530 mμ was such that transmitted blue and u.v. light was inefficient

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to directly excite fluorescing singlets, 5.

The blue fluorescence was observed at right angles to the

exciting red light after being filtered by a 4.5 cm. thickness of saturated Cus, plus one CS 5-58 filter, this combination of filters has a peak transmission at 110 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 600 mμ excitation was 0.128 cm⁻¹ so that the

calculated energy absorption was 293 erg extn⁻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 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 Weis et al.

The filtering for the present experiments consisted of one C8 3-67 and one C6 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.

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The width of the flash intensity at half maximum was 22c.

The peak intensity in the 6000-8000 Å band was about

103 units @ 200 c,

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, (yield) obtained under near uv, excitation, Although there was wide fluctuation in the data it was clear that a non-linear decrease of fluorescence efficiency occurs at a dose rate of about 107 R, This result is in general agreement with those of Sharnik, who previously had found a linear decrease of fluorescence efficiency for irradiated anthracene in the dose range of 105 to 207 R,

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

$\% + \text{Pirea} + (\text{singlet triplet absorption}); a_7(t)$

$\% + 2h\nu_{\text{rea}} * S, (\text{simultaneous double quantum } \epsilon_1(t)?$

absorption)

$\text{ty} * \text{tover states st}$

$D+H-G+\& n^{\circ})\}$

sya tye

$T_y + T + \text{lover states (self quenching) vere}$

178 + boise ks

on xegr8) He = Rett Hay

$t + \text{lover states not triplet } v_y)$

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-7-

Abe tle) + kggS = OP @

as- $\epsilon_{32}(t) + a/\text{err}^{\circ} - ks(2)$

Eo

Pu Ake 85 Ate an unknown genetic and sensitivity (3)

factor for a given crystal and type of

experiment.

Under the stationary conditions of steady red {limination

aE a8. 0, Tor thse cam ve denote F by the symbol Fs The 900

WD.C. are ie capsble of delivering several tenths of a watt per square

centimeter of red Light which fe sufficient to allooy measurement of the

blue entesion but weak enough that kgyS <a = const. andy 12<67, and

4x(t)? < a/ent®, 20 that

r,

Ate (a PP, ?

2 F

Assumptions regarding the effect of radiation damage on the

crystal yaranoters are nov introduced, If the dose introduces triplet

quenching centers without affecting (a), the absorpton coefficient

© for G%* Ty, (b) the Muorescence efficiency fp, ant (c) the bincle-

cular triplet exciton interaction constant, v5 then the damage effect

may be asmed to be of the forn

ese + a. (5)

Graphs of ¥, ?V2 vs, D should be of the form

FLT? = const. (6° + a) 6)

Figure 3 shows a graph of the observed steady state data in excellent

agreement with equation (6),

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-8-

Assumptions a, b, and c have received direct experimental verification. The observed emission, F , depends on the rate of absorption of light, not on the quantity of light absorbed; therefore dependence of ϕ on D will be of consequence if damage produced by 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 109 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 ϕ below a dosage of 105 R and therefore assumption (b) is valid.

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

It was expected that the bimolecular rate constant, k_2 should not be dependent on damage because if one writes $Y = \frac{k_1}{k_1 + k_2}$

$4m$ which P_{ant} and F_p are respectively the probabilities of forming
9 + % or 2% on collision of a pair of triplet excitons of cross
section S_{py} and with velocity v_p then the probabilities should be
dominated by spin ant interaction factors determined by molecular
parameters while the collision cross section is not expected to
be dose dependent until the damage centers are of sufficiently
high density to permit cooperative phenomena between centers, the
triplet exciton velocity, v_{vy} should undergo real or apparent alteration
due to radiation damage in either of two principal ways; (1) damage
introduces shallow triplet traps and thereby imparts « trap modulation

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-9-

character to v_{oy} or (11), damage introduces deep triplet traps but from
Vetch annihilation is inherently faster than L_{over} .

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 dose. At the time of peak flash intensity
 $I(t)$ is denoted I_p . During a flash of microsecond duration, $t) 5$
the triplets are not contributing « significant amount to the
instantaneous singlet population; therefore equation (2) becomes

$s + S_{pt} m$

and the fluorescence given by (3) is denoted by F_y

Fat AMgst,2.)

It to to be emphasized that the fluorescence originating by this mechanism is uniformly emitted throughout the crystal volume. During the flash a triplet population, T , is built up by direct 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

$$T_0 \approx I_0 \tau = 10^{-2} \times 10^2 \text{ sec}^{-1} \times 10^{-8} \text{ sec} = 10^{-4} \text{ cm}^{-3} \text{ (9)}$$

since the triplet-triplet interaction also causes the resultant fluorescence to be emitted uniformly from the crystal volume, During an interval of time following flash extinction,

At $T < T_c$, the bimolecular term of equation (1) dominates

the triplet decay and the fluorescent signal given by (3) is denoted

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hy F_y and vecones $F_y * 1/2ABpy4() (ao)$

1+ ye

Since $\approx 2 \times 10^9 \text{ Mea eee}^9 \text{ enon } 2\% \ll a \text{ up to about } SOueee.$

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

= 1/2 (a)

Figure I shove the fluorescent behavior in an undamaged crystal from

Sin

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

20 usec.

As previously stated, ϕ does not depend on dosage of less than 108 R, the double quantum absorption coefficient ξ cannot conceivably depend on dose, therefore a graph of F_2/F_1 should demonstrate the relation of ϕ 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_2/F_1 for which F_1 was picked at flash cutoff is shown in Figure 6. Clearly there was

no significant dependence of ϕ on dose up to about 104 R and this assumption is verified for ϕ up to this dose. This kind of experiment could not be continued to higher dose because at these dose levels there had been introduced sufficient density of triplet quenchers to cause ϕ to become comparable to w^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 104 R,

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ca

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, $t \gg \tau$, only the A_f term of equation (2) is of significance; thus $I = I_0 \exp(-t/\tau)$ and equation (3) becomes

a $7 \frac{1}{2} \text{hy}$, He 20-28

2)

where F_y is the g-factor 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 direct quantum absorption experiments also point to an

independent verification of the effect of dosage on the fluorescence efficiency. 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 @ graph of the peak intensity

of this fluorescent response as a function of dose and is of essen

tially the same nature as Figure 2 for the u. v. excitation, tota

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?the almost complete absence of fluorescence from the triplet-triplet

?mechanism even at 50sec.

SECTION IV, DISCUSSION

Equations (3) and (6) may be written

$$F = K(KO + P5q^{\circ}sq\neq s's?) - \text{ and } FL = K(8 + Praca\text{ rer})"$$

(3)

Anvich «Gp and cqDiare the density of singlet and triplet quenchers

introduced by a gamma-ray doce, D; k° and 8° are the singlet and

triplet decay constants before dosage, and the other syubolis have

?their usual significance, Defining by D 1/2 and D' 1/2 the dosages

at which F ond F, are respectively reduced to 2/2, thon equations

(Q3)eyay be combined to give

P, 2

2. az 22s

mes i om)

Fron figures 1, 2, 3, and 9, D 1/2 = 5 x10 Rand Dt 3/2-3x102R

so that D 1/2/p'1/2 : 103, Tt appears reasonable to take

Om = "m= 3 x 105 ea? co that

Pog. 2

so. fs. sg 2

pe Ss S Seas xi0.

TQ ?Tr Te (5)

There are two approaches which may now be taken, Experimental values for μ and k^0 vary slightly from crystal to crystal but show that $\mu/k^0 = 10^{-6}$ is a representative average, No direct measurements for either v_g or v_p are available; however, these may be estimated, From the data of Sliver et al. for the interaction of pairs of singlet

excitons to yield current carriers, v_g may be estimated to be 2×10^3

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on see" ($k = 5 \times 10^{12}$ cad eee >; asoure $p = \text{ant} \geq 3 \times 10^{\text{ext}}$),

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 2×10^{12} cobme} and therefore under similar assumptions v_p is estimated to be 7×10^3 cm mer}. the near equality of these exciton velocities is difficult to understand and self quenching and other competing Processes surely cause P_{ry} to be less than unity

; however, an one

extreme of behavior we take $v_g/v_p \approx 1$ and therefore $F_{\text{ray}} \approx 2.5 \times 10^3$.

re Q

on this basis the net effect of a given gamma-ray dose is to

Introduce singlet quenchers with an overall quenching efficiency about 10% 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 exciton, Triplet excitons have been shown to have a

diffusion length, L , of about 10^{-6} cm, Avakian and Merrifield (1960)

$L = 10 + 5v$ in the ab plane (θ was not specified), while Kepler and

Sritendick (1961) obtained $D = (0.4 - 2) \times 10^{-6}$ cm²/sec and Levine et

al (1966) found $D = (2.0 + 0.5) \times 10^{-6}$ cm²/sec for the triplet exciton

diffusion coefficients and from which lengths, $L = (2Dt)^{1/2}$, of

150 Å and 20 Å respectively may be calculated for $t = 10^{-8}$ sec, the

diffusion length for singlet excitons, $L = 2Dt$ was approximately 600

4A as deduced by Siapson and T in poly-crystalline complexes of anthracene
while Erenenko and Medvedev" report 2000
excitons the diffusion length may be given by $L = \rho r_s$ in which ρ is

+ For either of the

the exciton lifetime, v its instantaneous velocity and p the ratio of
drift velocity to instantaneous velocity. If it is assumed that the value

$\rho \approx 1$

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<u.

of p 's for singlet and triplet exciton motion is unity, f.e., if
there is similar anisotropy for the motion of both, then in
lean but unannealed crystals the ratio of the velocities should be

eat

Yes to a8 pattern. 108 see gy

$v_y \approx 1078$ sec

or the ratio of diffusion lengths $L_g = v_d/v_k = 1072$,

Introducing the last ratio which depends on the assumption of similar

anisotropy of exciton motion into (15) results in $P/P_y \approx 0.25$.

On this basis the net effect of a given gamma-ray dose is to introduce 4 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 2 and 103. 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 103 efficiency ratio with the ratio of volumes sampled by the excitons, then it is seen that the triplets sample a volume $23 = 18$ times larger than do the singlets and thus it remains necessary to require a 103 to 106 greater quantity 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. Cooperation between carrier trapping, triplet quenching, and damage produced by the signal appears feasible at dosages far beyond those amenable to

conventional chemical approaches.

The present experimental determination of the dependence of

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(on dose was insensitive to the y , term. However, the present

findings are consistent with those of Kepler 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 y are of little consequence at room temperatures

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 10^9 R, the low end from 10^2 to 10^4 R can be measured through triplet quenching, the range of 10^3 to 10^6 R by space-charge-limited current technique, the 10^6 to 10^7 R range by singlet quenching, and the high dosage range of 10^7 R can be covered by direct optical coloration, the lower limit depends on the intensity of the excitation source. If instead of a xenon flash or a dc. xenon arc, one would use a modulated laser, then a change in g could be measured from 10^2 R up to about 5×10^9 R. and from about 10^7 to 10^9 R the quenching of double quantum generated singlets could be measured. A range of 10^2 - 10^9 R could be continuously covered with one crystal and one excitation source,

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ne

a

TRIPLET GENERATED FLUORESCENCE

FIG. |

Steady Red

Dunit = 10° ap,

horizontal: 1 unit

> swentgens

Dose

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ae

Dose

RELATIVE YIELD

. FIG. 2

Fre. °

Blue Fluorescence under steady 3130 & Excitation

Vertical: relative yield

Horizontal: 1 unit 2 10 Roentgen

Of the present data

O'Shara, reference 9

\$\$

8. 10g Dose

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DOSE

FIG. 3

rs. bee

ue Fluorescence under Steaty Red Bxeitat ion

testseale Dunit Cae ie map

Wertzontal: 2 unt

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+ Fives Tine

et Fy

?The Flucrescent Response of an Undamaged

Orystal to a Hie Intensity fed Flash

Upper: Rw 1K; time const. #1 w sec.

Lower: Rye 1K; time const. &2 usec.

s. Tae

16 Dependence of the Fluorescent Response

con Dosage within the Bimolecular Time

Domain

Upper: © Neentmens; Hg © 100 ky

time const, 5 psec.

Middle: 4.8×10^3 Roentgens;

Ry = 100 K; time const. 5×10^{-5} p sec.

Lower: 1.9×10^4 Roentgens;

Ry = 100 Ky time const. 5 u sec.

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DOSE

"th

FIG. 6

F/Pp va. log Dose

RUti8 of Flucreacence Generated by Triplet

?Triplet and

Vertscait

Horizontal:

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o FIG. 7

og (4 ~49) vo. og tose

Change of Triziet Decay due to Busiution

Produced quenchers

Vertical: 1 unit = 10 e₀

Horizontal: 1 unit

+ 30 Roentgens

eee

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oa

fatere ie.

10 ysfem

50 Tfen

FIG.8

Fw. Mae

Tao Dependence of the Double Photon Generated
Fluorescence on dosage

Uppers 0 Hoentgensy H+ 1 Ki tage commt.ari usec

dowert $2.5 \times 10^{\circ}$ aoenteenay K+ 4 Ki time

const. 1 w see.

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he

wpe -Tay--

0

DOSE

LOE Foggy MB 10g Dove

pesk

Effect of Radiation on Fluot

Generated in Crystal Bulk

aoence Uni foraly

. Vortioal: i unit = 10 arbitrary

Hortgontals 1 unit = 10 soontgene

eee

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@iffusion to be essentially Lectropic.

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