Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: P. Avakian & R. E. Merrifield (1968): Triplet Excitons in Anthracene Crystals—A Review, Molecular Crystals, 5:1, 37-77

To link to this article: http://dx.doi.org/10.1080/15421406808082930

*Molecular Crystals*. 1968. Vol. 5, pp. 37–77

Printed in Great Britain

# Triplet Excitons in Anthracene Crystals—A Review

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*Received June* 17, 1968

**Contents**

## I. Introduction and Scope

The investigation of optically generated triplet excitons† in anthracene crystals began in 1963[3]‡ with the discovery that red light from a ruby laser can generate detectable concentrations of triplet excitons in spite of the low probability for this transition. Following this discovery, experimental and theoretical studies of triplet excitons became a much more active area of research in the field of the organic solid state. Anthracene has been chosen as the model system by the vast majority of the investigators. For this reason this review deals with anthracene almost exclusively. We, furthermore, emphasize the work at room temperature where the triplet excitons are essentially free and where understanding of their properties has progressed the farthest. Only brief mention will be made of low temperature experiments where complicated trapping effects play an essential role, and a great deal of additional research is necessary for gaining a clearer understanding of what is going on. Although the literature was surveyed to the end of 1967, a few 1968 papers are included. In keeping with our own interests, we will stress dynamical properties in this paper.

Here we begin with a very brief summary of elementary concepts

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† A triplet exciton is a mobile neutral electronic excited state of a crystal with net spin of 1.[1] For an introduction to excitons in general see, for example, the book by Dexter and Knox[2].

‡ Up to 1963 most research on triplet excitons was on ion-radical salt crystals such as Wursters Blue perchlorate and TCNQ salts. In these materials, low lying triplet exciton states are thermally populated at ordinary temperatures to a sufficiently high concentration such that electron-spin resonance techniques are applicable. See for example: McConnell, H. M. and Lynden-Bell, R., *J. Chem. Phys.* **36**, 2393 (1962); Jones, M. T. and Chesnut, D. B., *J. Chem. Phys.* **38**, 1311 (1963); and the review paper by McConnell, H. M., in *Molecular Biophysics* (Proceedings of an International Summer School held at Squaw Valley, California, August 17–18, 1964), edited by Pullman, B., and Weissbluth, M., (Academic Press, Inc., New York, 1965), p. 311. The lowest triplet state in anthracene and in other aromatic hydrocarbons is much higher in energy than thermal energies, and it has been found that these excitons possess a variety of novel properties not exhibited by the low-lying triplet excitons in the solid free radicals.

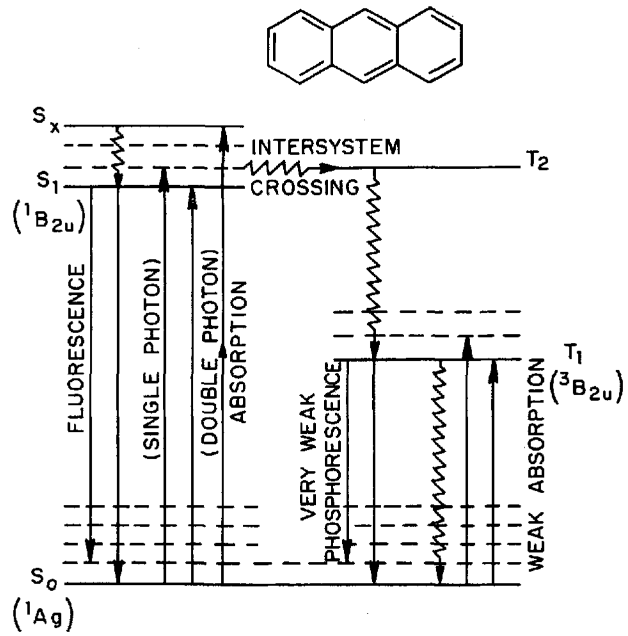

Figure 1. Simplified schematic energy level diagram for an anthracene molecule (see also ref. 4, p. 27). The singlet and triplet manifolds are split to sublevels due to molecular vibrations (dashed horizontal lines). The solid arrows correspond to absorption or emission of light; while zigzag arrows represent radiationless transitions. Although in isolated molecules $T_2$ is below $S_1$, in the diagram the ordering has been reversed; since the exciton band arising from $T_2$ is probably higher in energy than the band arising from $S_1$ (see Section II-B and refs. 22 and 48). In the crystal the $S_0$–$S_1$ energy difference (averaged over the two Davydov components) and the $S_0$–$T_1$ energy difference are 3.15 (ref. 5) and 1.83 eV (refs. 23, 24, and 25), respectively.

for those unfamiliar with excitons in organic solids.† Since in organic crystals, such as anthracene, weak Van der Waals forces hold the molecules together in the crystal, the intermolecular interactions can be regarded as a weak perturbation on the oriented array of molecules, and the electronic energy levels in the crystal

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† It should be noted that there are a number of reviews on excitons (primarily singlet) in aromatic hydrocarbons.[4–21] Most of these papers, published in 1965 or later, also include some discussion of triplet excitons.

are traceable to parent molecular states.[4, 5, 10] An appropriate starting point is, therefore, the simplified electronic energy level diagram of Fig. 1 for isolated anthracene molecules showing the parent molecular states for the exciton bands which will be of interest to us. In this figure we have taken the liberty of placing the triplet state $T_2$ above the singlet state $S_1$, although in isolated molecules the order is reversed. The point is that in the crystal the exciton band arising from the $S_1$ molecular level shifts downwards and is probably lower in energy than the exciton band arising from the $T_2$ molecular level.[22]† In the crystal the $S_0$–$S_1$ separation averaged over the two Davydov components is 3.15 eV,[5] and the $S_0$–$T_1$ separation is 1.83 eV.[23, 24, 25]

There is strong evidence that regardless of which higher singlet exciton state is populated, a rapid radiationless decay to the lowest singlet exciton state occurs.[5, 21] Presumably the same situation is true for the triplet excitons,[21] and luminescence corresponding to a radiative decay from higher to lower triplet states in molecules or triplet exciton states in crystals has not been observed. For this reason, in studying dynamical properties of excitons, one needs to consider the lowest singlet and the lowest triplet exciton bands exclusively.

In addition to the exciton states built on the basis functions of neutral molecular excited states, excitons states have been constructed on the basis functions of nearest neighbor positive and negative ion pairs.[26, 27] Direct experimental evidence for the existence of such charge transfer exciton states is still lacking.‡ It is estimated that in anthracene such a state should be at 3.4 ± 0.5 eV.[26]

The most remarkable property of triplet excitons, which has made possible many fruitful investigations, is that of mutual

† See also Section II-B.

‡ Berry *et al.* [Berry, R. S., Jortner, J., Mackie, J. C., Pysh, E. S., and Rice, S. A., *J. Chem. Phys.* **47**, 1535 (1965)] were not able to detect optical excitation to a charge transfer exciton state in crystalline anthracene. Pope has suggested the existence of charge transfer excitons in anthracene on the basis of his photoemission measurements. See, for example, Pope, M., and Burgos, J., *Mol. Crystals* **1**, 395 (1966).

annihilation of a pair of triplets resulting in production of a blue-fluorescing singlet exciton.[3, 28] This "delayed fluorescence" which has the same spectral distribution as the normal UV-excited prompt fluorescence† has a lifetime which is 6 orders of magnitude longer than that of the prompt fluorescence.‡

It has been shown[30, 31] that the concentration $n$ of triplet excitons at position x and time $t$ at room temperature is governed by the rate equation

$$\frac{\partial n}{\partial t} = \alpha i - \beta n - \gamma_{\text{total}} n^2 + D\nabla^2 n \tag{1}$$

and that the intensity of emitted delayed fluorescence per unit volume of crystal is given by

$$\phi = \tfrac{1}{2}\gamma_{\text{radiative}}\, n^2 = \tfrac{1}{2} f \gamma_{\text{total}}\, n^2 \tag{2}$$

and the total emitted delayed fluorescence from the crystal by

$$\Phi = \tfrac{1}{2}\gamma_{\text{radiative}} \int_{\text{volume}} n^2\, dV \tag{3}$$

In the above equations, $\alpha$ is the singlet–triplet absorption coefficient for the incident "red" photon flux $i$, $\beta$ the monomolecular decay rate constant (the reciprocal of the triplet lifetime), $\gamma_{\text{total}}$ the over-all bimolecular annihilation rate constant, $D$ the diffusion constant, and $f$ the fraction of triplet–triplet annihilations which lead to delayed fluorescence. More rigorously diffusion should be represented by a tensor; however, in real crystals at room temperature diffusion appears to be isotropic.[31]

The processes described by the above equations may be summarized by the following exciton "chemistry":

$$S_0 + h\nu \rightarrow T_1 \tag{I}$$

$$T_1 \rightarrow S_0 + \text{phonons (or } h\nu) \tag{II}$$

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† The delayed fluorescence spectrum, since it originates from within the bulk of the crystals, must be compared to the prompt fluorescence spectrum in the presence of reabsorption, i.e., the emission spectrum measured from the face of the crystal opposite to the face on which the exciting UV light impinges.

‡ The lifetime of singlet excitons in anthracene has been reported as $2.6 \times 10^{-8}$ sec.[29]

$$T_1+T_1 \rightarrow S_1+S_0 \qquad \text{(III)}$$

$$T_1+S_0 \rightarrow S_0+T_1 \qquad \text{(IV)}$$

$$S_1 \rightarrow S_0+h\nu' \qquad \text{(V)}$$

where processes (I)–(IV) are described by the corresponding terms on the right-hand side of Eq. (1).

These processes do not exhaust all possibilities. For example, triplets may also be produced from $S_1$ by inter-system crossing or from recombination of electrons and holes. Triplets may be trapped by impurities or defects in the crystal and they may interact with phonons, with charge carriers, and with nuclear spins. The collision of two triplets, furthermore, could result simply in scattering or possibly the production of a higher-energy triplet exciton via the annihilation process.

In the remainder of this review we will summarize the experimental and theoretical studies which lend support to the above model, and discuss the recent discovery of modification of the triplet–triplet annihilation rate in the presence of a magnetic field.

The experimental measurements include the study of $\Phi$ as a function of $i$, $t$, excitation wavelength, the geometrical distribution of $i$, and its dependence on the strength and direction of an applied magnetic field (which provides a new tool for probing into details of the annihilation process). Besides studies of $\Phi$, experimental measurements include observation of: phosphorescence, electron spin resonance absorption by triplet excitons, proton magnetic resonance in the presence of triplet excitons, and photoconductivity due to triplet excitons.

## II. Generation of Triplet Excitons

Triplet excitons in anthracene have been generated directly by absorption of "red" light or indirectly by production of singlet excitons upon absorption of "blue" light (or double-photon absorption of very intense "red" light) followed by radiationless intersystem crossing of some of the singlet excitons into the triplet manifold; see Fig. 1. Triplet excitons have also been generated by recombination of injected electrons and holes in the crystal as well as by bombardment with X-rays or high energy particles.

### A. Direct Optical Generation

Although singlet–triplet transitions induced by photons are forbidden to a first approximation, by virtue of spin-orbit coupling,[19, 32] such transitions have a nonzero probability. Generation of triplet excitons with a pulsed ruby laser,[3, 33, 34]† an intense xenon arc source,[28, 36] visible light from a mercury arc,[37] and a helium-neon laser,[38, 39, 40] have all been demonstrated. The measurement of the number of incident red photons and the number of emitted blue photons per unit thickness of crystal in the pulsed ruby laser experiment under conditions where bimolecular triplet–triplet annihilation was by far the dominant avenue for destruction of triplets led to the value of $10^{-5}$ $\text{cm}^{-1}$ as a lower bound for the singlet–triplet absorption coefficient at 6943 Å (i.e., $\alpha = [1/f][10^{-5}\ \text{cm}^{-1}]$).[3]

The weakness of the transition renders it impossible to obtain the singlet–triplet absorption spectrum directly at room temperature. The spectrum was obtained indirectly with monochromatized light from a xenon arc[28] by measuring the intensity of the delayed fluorescence as a function of the wavelength of the incident photon flux (i.e., the excitation spectrum for delayed fluorescence was measured). The ordinate of this excitation spectrum (shown in Fig. 2) is proportional to the square of the absorption coefficient $\alpha^2$, since at the low exciting intensities available from a xenon lamp plus monochromator, the steady-state solution of the rate equations (1) and (2) with uniform illumination of the crystal ($\nabla^2 n = 0$) and low exciton concentration, $\beta n \gg \gamma_{\text{total}} n^2$, reduces to

$$\phi = \tfrac{1}{2}\gamma_{\text{radiative}} \frac{\alpha_\lambda}{\beta^2} i_\lambda^2 = \tfrac{1}{2} f \gamma_{\text{total}} \frac{\alpha_\lambda^2}{\beta^2} i_\lambda^2 \tag{4}$$

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† Singh and coworkers[34] have demonstrated that ruby laser light (6943 Å) generates triplet excitons from a vibrationally excited state of the ground state singlet and that the efficiency of generating triplet excitons directly with ruby laser photons drops exponentially with lowering of the crystal temperature. Kawabe *et al.*[35] also reported on more preliminary temperature dependent studies of laser-excited fluorescence in anthracene.

Although the spectrum shown in Fig. 2 is in arbitrary units, the knowledge of the magnitude of $\alpha$ at the ruby laser wavelength implies $\alpha$ at the peak in $3.4 \times 10^{-4}$ cm$^{-1}$. More precisely, $\alpha_{\text{peak}} = (1/f)(3.4 \times 10^{-4} \text{ cm}^{-1})$ where $f$ is the fraction of triplet–triplet annihilations which lead to delayed fluorescence $(0 < f \leqslant 1)$.

Recently Smith[25] has obtained the excitation spectrum for red phosphorescence originating from unimolecular radiative decay of triplet excitons (probably trapped) at 33°K. Smith's spectrum is consistent with that of Fig. 2 and his technique is another indirect method for obtaining the singlet–triplet absorption spectrum. Hirota[41] has measured the singlet–triplet absorption spectrum in a number of organic crystals (not anthracene) by the phosphorescence excitation technique. He enhanced appreciably the phosphorescence efficiency by triplet energy transfer to appropriate guest molecules which acted as phosphorescing triplet energy traps. Kearns and coworkers have carried out similar work on other materials (see reference 42 and earlier papers cited in this reference).

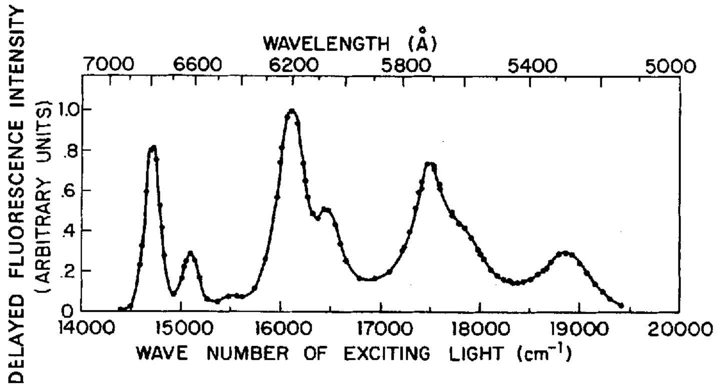

Figure 2. Excitation spectrum for delayed fluorescence in anthracene crystals at room temperature with the wavelengths of the unpolarized incident light in the region of the singlet–triplet ($S_0$–$T_1$) absorption. The signal (ordinate) is proportional to the square of the absorption coefficient. (From Avakian, Abramson, Kepler, and Caris, ref. 28, Fig. 1.)

At 4.2°K where the spectrum sharpens dramatically, Clarke and

Hochstrasser,[43] have observed the singlet–triplet transition in a direct absorption measurement on thick crystals.

Later in this paper we discuss the singlet–triplet absorption in polarized light and review a method for gaining information on exciton dynamics by spectroscopic means (Section V-B).

Before leaving the subject of direct generation of triplet excitons with red light, it should be noted that although at low light intensities the delayed fluorescence intensity is proportional to the square of the incident intensity [Eq. (4)], at high intensities, the rate equations (1) and (2) predict a linear dependence. With $\gamma_{\text{total}} n^2 \gg \beta n$, we have:

$$\phi = \tfrac{1}{2} f \alpha i \tag{5}$$

under steady-state conditions. With a 100 milliwatt helium-neon laser (6328 Å), it has been shown experimentally[38] that the dependence of $\phi$ on $i$ indeed changes from square to nearly linear at the higher laser intensities. This observation provides additional support for the hypothesis that triplet excitons can indeed be generated by a direct one-photon transition from the ground state.

### B. Indirect Optical Generation via $S_1$

In addition to generation of triplet excitons directly as discussed above, triplet excitons in anthracene can be generated optically indirectly by first producing singlet excitons, some of which in turn decay into triplet excitons by intersystem crossing. The singlet excitons can be produced by the usual single-photon absorption of blue or UV light or by double-photon absorption of very intense "red" light. Weisz and coworkers[44] observed blue-excited delayed fluorescence in anthracene and reported an intersystem crossing rate constant $k_{ST}$ of $(16 \text{ to } 24) \times 10^5 \text{ sec}^{-1}$ (more precisely, $fk_{ST} = 16$ to $24 \times 10^5 \text{ sec}^{-1}$). Kepler and Switendick[45] measured the excitation spectrum for this method of producing delayed fluorescence. As can be seen in Fig. 3, instead of a continuous rise paralleling the tail of the singlet–singlet absorption spectrum, there is a peak at 4180 Å. The extinction depth for light in this wavelength region is of the order of 100 microns.[46, 47] Kepler and Switendick[45] interpreted the drop in delayed fluorescence intensity for exciting wavelengths below 4180 Å as a manifestation of quenching of triplet excitons which diffuse to the crystal surface. We shall return to the subject of the triplet exciton diffusion length and the excitation spectrum for delayed fluorescence in the singlet absorption tail (Section V-C).

Adolph and Williams[48] have measured the blue excited delayed fluorescence excitation spectrum at lower incident photon fluxes and have extended the measurement to lower temperatures. They report peaks at around 422 and 405 mμ at room temperature and at 140°K, respectively. From the drop of the delayed fluorescence intensity upon decrease of temperature, Adolph and Williams[48] concluded that the intersystem crossing rate is an activated process with an activation energy of 800 ± 50 $\text{cm}^{-1}$.† This conclusion is in

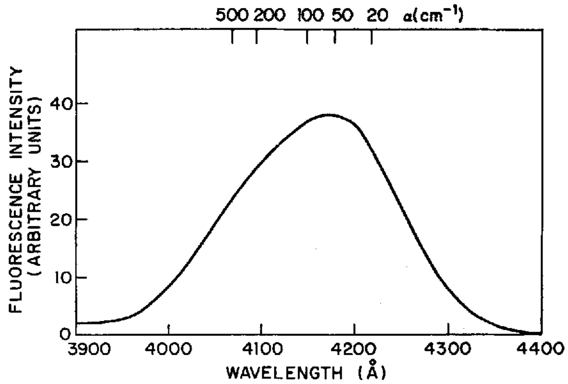

Figure 3. Excitation spectrum for delayed fluorescence in anthracene crystals at room temperature with the wavelengths of the exciting light in the region of the singlet absorption ($S_0 \rightarrow S_1$) tail. The incident light was polarized with its electric vector parallel to the a crystal axis, and its wave vector was perpendicular to the *ab* plane of the crystal. (From Kepler and Switendick, ref. 45, Fig. 2.)

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† It is puzzling why the intersystem crossing rate appears to be temperature independent when $S_1$ is initially populated via double-photon absorption instead of single photon absorption as above. Singh *et al.*[34] found the intensity of delayed fluorescence arising from double-photon excitation with 12,800; 14,400; and 17,500 $\text{cm}^{-1}$ light to be essentially temperature independent.

accord with Kellogg's[22] proposal that in crystalline anthracene $T_2$ is above $S_1$ (see Fig. 1) and that the population of $T_1$ from $S_1$ proceeds via $T_2$.

As mentioned above, the singlet excitons from which triplet excitons are produced by intersystem crossing, can be generated by a double-photon absorption of laser light[34] or an intense xenon flash lamp.[49] In this paper we shall not discuss the subject of double-photon absorption, since the details of this process do not reveal new information on dynamics of triplet excitons. For our present purposes the nature of the double-photon absorption process and the nature of the generated state corresponding to $S_x$ in Fig. 1 is only significant to the extent that triplet excitons are generated from some of the initially formed singlet excitons, most likely following an initial radiationless decay to the lowest singlet exciton state.

Numerous investigators have studied the double-photon absorption process since the original discovery of the phenomenon by Peticolas *et al.*[50] The reader interested in the subject of double-photon absorption in anthracene should refer to the original literature (recent papers of Hernandez and Gold[51] and Dowley *et al.*[52] refer to the more than one dozen earlier papers). For the purposes of this paper we simply point out that the double-photon absorption coefficient for ruby laser light (6943 Å) is $1.26 \times 10^{-29}$ cm-sec[33] and that the delayed fluorescence intensity under conditions where double-photon absorption dominates is proportional to the fourth power of the incident laser intensity.[34, 53] This fourth power intensity dependence is a consequence of two square dependent processes—the double-photon generation of the initial excited singlets (leading to triplets by intersystem crossing) and the bimolecular triplet–triplet annihilation step resulting in delayed fluorescence.

Upon double-photon excitation of an anthracene crystal with a ruby laser, Singh *et al.*[34] found the integrated delayed fluorescence intensity to be one per cent of the integrated prompt fluorescence intensity. This implies that at room temperature the ratio of the intersystem crossing rate constant $k_{ST}$ to the singlet exciton fluorescence rate constant is $(2/f) \times 0.01$ or $0.02/f$ (where $f$ is the fraction of triplet–triplet annihilations which lead to delayed fluorescence). Assuming the same value of $k_{SS} = 1/2 \times 10^8\ \text{sec}^{-1}$ as Weisz *et al.*[44] did, Singh *et al*'s[34] $fk_{ST}$ becomes $1 \times 10^6\ \text{sec}^{-1}$, which is the same order of magnitude as reported by Weisz *et al.*[44] ($2 \times 10^6\ \text{sec}^{-1}$).

### C. OTHER METHODS

Helfrich and Schneider[54] have generated triplet excitons in anthracene by the recombination of electrons and holes injected into the crystal. In pulsed voltage experiments they found the ratio of prompt to delayed recombination fluorescence intensity to be $0.65 \pm 0.1$. This result, together with the assumption that three times as many triplet as singlet excitons are generated in the electron-hole recombinations, leads to the value of $f = \gamma_{\text{radiative}}/\gamma_{\text{total}} = 0.4$. Their determination of the absolute value of $\gamma_{\text{total}}$ by the double injection method will be discussed below (Section IV-A).

Still another means for generating triplet excitons is ionizing radiation. As pointed out by Birks[55] in his book on scintillation counting, the slow scintillation component in organic crystals such as anthracene is due to delayed fluorescence from mutual annihilation of triplet excitons produced by the ionizing radiation. By analyzing the radioluminescence decay curves, it is possible to evaluate triplet exciton properties such as their diffusion constant,[55, 56, 58] as will be discussed below (Section V-C).

## III. Decay

The migration of a triplet exciton through the crystal can terminate by spontaneous unimolecular decay (Process II in Section I), by capture or interaction with an impurity or defect, or by mutual annihilation involving a second triplet (Process III in Section I). Triplet–triplet annihilation will be discussed in Section IV. The other processes are discussed in this section. Trapping effects, since they are not well understood yet, will be discussed only briefly.

The triplet exciton decay can be investigated experimentally by observing the products of the decay. The main quantities measured have been delayed fluorescence arising from triplet–triplet annihilation and phosphorescence emitted upon unimolecular radiative decay of the triplets. When triplet excitons are free, their lifetime can be measured directly from the phosphorescence lifetime[25, 61] or indirectly by observing the decay of delayed fluorescence.[3, 33, 34] Since the intensity (per unit volume) of delayed fluorescence is proportional to the square of the triplet excition concentration, Eq. (2), the triplet lifetime is twice the lifetime of the delayed fluorescence.[3] It is, of course, easiest to measure the triplet lifetime under conditions of low exciton concentration ($\gamma_{\text{total}} n^2 \ll \beta n$) such that effects of the bimolecular annihilations in shortening the effective triplet lifetime can be neglected. In case of excitation of delayed fluorescence with pulsed "red" light, the lifetime can be measured both from the buildup and from the decay part of the delayed fluorescence time-dependent signal.[30]

### A. Radiative

In view of the fact that unimolecular decay of triplet excitons is strongly dominated by radiationless processes, the phosphorescence emission from the radiative decay has been observed only recently. Riehl and coworkers[59] detected the phosphorescence at 4.2°K, and Smith[60] at room and at low temperatures, and Williams and Schneider[61] at room temperature. Next the spectrum of the emission at room temperature[62] and between room temperature and 4.2°K[24, 25] was reported.

The phosphorescence emission spectrum ($T_1 \rightarrow S_0$) at room temperature[24, 25, 62] shows an approximate mirror image symmetry with the absorption spectrum ($S_0 \rightarrow T_1$)[28] shown in Fig. 2. The coincidence of the 0–0 transition† in emission and absorption at room temperature[24, 25, 62] supports the assumption that triplet excitons in anthracene are essentially free at room temperature.

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† Transition between the lowest vibrational (zero vibronic) level of $T_1$ and of $S_1$ (see Fig. 1).

Upon cooling the sample, Smith[25] finds a Stokes shift (to longer wavelengths) of the origin of the emission spectrum and Müller *et al*[24] report a broadening but no energy shift in their crystals, which is consistent with their interpretation of a distribution of triplet traps.

The observation of the same triplet lifetime $\tau$ in phosphorescence and in delayed fluorescence at room temperature ($\tau_{\text{triplet}} = \tau_{\text{phosph.}} = 2\tau_{\text{del.fl.}}$)[25, 61] lends additional support for the assumption that at room temperature triplet excitons are free.

The observed triplet lifetime in purest available anthracene crystals at room temperature is around 25 msec.[30, 61] The radiative lifetime has been reported as approximately 60 sec (or more precisely $60/f$ sec) by Smith.[25] This value was deduced from the slope of the experimental linear plot of the square root of delayed fluorescence intensity versus phosphorescence intensity. This linear relationship provides further support for the model that delayed fluorescence results from triplet–triplet annihilation and its intensity is proportional to the square of the triplet exciton concentration, while the unimolecular phosphorescence intensity is proportional to the triplet concentration itself. The value of $60/f$ sec for the radiative lifetime in contrast to $25 \times 10^{-3}$ sec for the observed lifetime implies less than one in 2000 free triplet excitons decay radiatively.

### B. RADIATIONLESS

When destruction of excitons by triplet–triplet annihilation is negligible ($\gamma_{\text{total}} n^2 \ll \beta n$), as pointed out above, radiationless processes dominate the unimolecular decay of the triplet excitons at room temperature. At this stage it is not known whether the radiationless decay is truly unimolecular resulting in production of phonons (or heat) or whether it is pseudo-unimolecular and is caused by interaction with impurities and defects.

Small concentrations of impurities and imperfections reduce the triplet lifetime.[34, 63] Observed values for $\tau$ range from less than a millisecond up to 25 msec ($\beta = 40$ sec$^{-1}$).[30, 61] In the best crystals available, the observed lifetime approaches that for isolated anthracene molecules in a rigid medium (polymethylmethacrylate).[22, 64] It could be that in these crystals, as is the case in isolated molecules,[65, 66] the triplet excitation is converted intramolecularly into molecular vibrations. Pseudo-unimolecular decay, however, cannot be ruled out.

### C. Role of Traps, Charge Carriers, and Photons

Because of the large diffusion length of triplet excitons (see Section V), minute concentration of guest molecules with a lower triplet state than that of the host, or physical defects of the right kind, reduce the free triplet lifetime.[34, 63]† They can also reduce the intensity of delayed fluorescence[36, 37] by immobilizing the triplet excitations. Less than one part per million of tetracene in anthracene decreases the delayed fluorescence by a factor of $10^6$, yet the intensity of phosphorescence emission, presumably from the trapped triplets, remains essentially unchanged.[25] Weisz *et al.*[67] have reported a reduction in the steady state delayed fluorescence intensity after forming quenchers in a crystal with a $\gamma$-ray dose of only a few hundred rads.

We do not intend to go into details of other trapping effects. However, a variety of trapping effects have been reported based on the measurement of the following quantities as a function of temperature: delayed fluorescence intensity,[25, 36, 59, 63, 68, 69, 70] and emission spectrum,[25] phosphorescence intensity and emission spectrum,[24, 25] and triplet lifetime.[24, 59, 63, 69, 71] In conjunction with the lifetime measurements, Kepler[71] noticed that the lifetime obtained from buildup of the delayed fluorescence became longer than that obtained from the decay at low temperatures where trapping effects became important. For free excitons these lifetimes are identical.

On the interaction of triplet excitons and charge carriers, Helfrich[72] reported on shortening of the triplet lifetime by injected

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† On the critical problem of material purification, see, for example, Sloan, G. J., *Mol. Crystals* 1, 161 (1966).

electrons in the crystal. Another interaction between triplet excitons and charge carriers is the ability of the former to release trapped carriers and enhance photoconductivity. Sharp and Schneider[73] and Jansen, Helfrich, and Riehl[74] found the excitation spectrum for photoconductivity in anthracene with light in the wavelength region of the singlet–triplet absorption to be the same as the excitation spectrum for delayed fluorescence[28] shown in Fig. 2.

Two types of experiments have been carried out on destruction of triplet excitons with photons. In the first type of experiment the question was whether blue fluorescence would result upon absorption of light by triplet excitons. The results were negative.[49, 69] In the second type of experiment, Holzman *et al.*[75] reported on photoconductivity produced in anthracene by photoionization of triplet excitons with light of wavelengths down to 4720 Å (or 2.63 eV).† These results have been interpreted theoretically by Hernandez.[76]

## IV. Triplet–Triplet Annihilation and Magnetic Effects

In 1962 Parker and Hatchard[78, 79] observed delayed fluorescence from solutions of anthracene and interpreted their observations (as well as those of earlier workers on other compounds) on the model of triplet–triplet annihilation (analog of Process III and V, Section I). Similarly, the preliminary observations of UV-excited delayed fluorescence in naphthalene crystals by Sponer, Kanda, and Blackwell[80] and in naphthalene and phenanthrene crystals by Blake and McClure[81] were interpreted on the basis of triplet–triplet annihilation by Sternlicht, Nieman, and Robinson.[82] Kepler, Caris, Avakian, and Abramson[3,28] reported on the first observation of "red" light excited delayed fluorescence from anthracene crystals and interpreted their observations on the model of triplet–triplet annihilation Eq. (1) to (4) and Processes I to V, Section I.

† In his experiments using photons with maximum energy of 2.35 eV, Strome[77] did not detect photoionization of triplet excitons.

### A. Annihilation Rate

Before discussing the experimental results on the triplet–triplet annihilation rate, it should be noted that not all triplet–triplet annihilations will necessarily lead to delayed fluorescence[34] and the factor $f$ in Eq. (2), Section I, was introduced for this reason. The factor $\frac{1}{2}$ is put in Eq. (2) by convention, because at most one blue photon can be emitted for each pair of triplets destroyed by annihilation. In principle triplet–triplet annihilations can lead not only to excited singlets but to excited triplets or quintets. Quintets are no doubt energetically higher than the sum of the energy of two triplet excitons, but higher triplet states are accessible. The factor $f$ cannot be predicted a priori. The value of $f$ depends not only on the relative rates of annihilations leading to excited singlets and annihilations leading to excited triplets, but also on the efficiency of formation of the zero vibronic fluorescing state $S_1$ (see Section I and Fig. 1) from the initial state produced by the annihilation. While production of the zero vibronic state of $S_1$ from higher singlet states is very probable, its production from higher triplet states is probably negligibly small. Finally, the rate of light emission from $S_1$ depends on the quantum yield for prompt fluorescence in anthracene.† Thus the value of $f$ is a positive number between 0 and 1.

In principle $\gamma_{\text{radiative}}$ could be determined experimentally if one could measure independently the concentration $n$ of triplet excitons and the absolute rate of emitted photons in delayed fluorescence per unit volume of crystal by using Eq. (2). Ultimately it may be possible to measure $n$ in ESR (electron spin resonance) experiments. In the meantime most measurements have determined $f^{-1}\gamma_{\text{total}}$ (or $f^{-2}\gamma_{\text{radiative}}$). In ruby laser excitation experiments, Kepler *et al.*[3] obtained values of $f^{-1}\gamma_{\text{total}}$‡ from the slope of the experimental delayed fluorescence decay curve (requiring the

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† The "molecular" quantum efficiency of photofluorescence of crystalline anthracene at 290°K has been reported as $0.94 \pm 0.02$, which reduces, by effect of self-absorption of fluorescence, to a quantum efficiency of the crystal of $0.80 \pm 0.05$.[16, 83]

‡ For simplicity the authors set $f = 1$.

measurement of the absolute emitted photon flux) or $\phi^{-1/2}$ versus $t$ under conditions of high exciton concentration ($\gamma_{\text{total}} n^2 \gg \beta n$). Under these conditions with uniform illumination of the crystal with pulsed light, the solutions of equations (1) and (2) after excitation shutoff becomes:

$$\phi^{-1/2} - \phi_0^{-1/2} = \left(\frac{2\gamma_{\text{total}}}{f}\right)^{1/2} (t - t_0) \qquad (6)$$

Assuming triplet excitons were generated in a volume of $10^{-3}$ cm$^3$, Kepler *et al.*[3] obtained the value of $10^{-11}$ cm$^3$ sec$^{-1}$ for $f^{-1}\gamma_{\text{total}}$. Singh *et al.*[34] reported values ranging from 2.8 to $6.7 \times 10^{-11}$ cm$^3$ sec$^{-1}$, and King and Seifert[84] $(3 \pm 1.5) \times 10^{-11}$ cm$^3$ sec$^{-1}$. Hall *et al.*[33] who excited the crystal with unfocused light from a Q-switched ruby laser and could thus obtain the volume in which triplet excitons were generated more accurately, reported the value of $5.5 \times 10^{-11}$ cm$^3$ sec$^{-1}$ with an uncertainty of 50%. In their $S_0$–$T_1$ excitation spectrum measurements, using Eq. (4) (Section I), Avakian *et al.*[28] found $f^{-1}\gamma_{\text{total}} = 4 \times 10^{-11}$ cm$^3$ sec$^{-1}$. The consistency of Moore and Munro's[85] result with those reported above is fortuitous.† Probably the best value of $f^{-1}\gamma_{\text{total}}$ is $5 \times 10^{-11}$ cm$^3$ sec$^{-1}$ with an error of at least 50%.

In contrast to the measurements reported above, where the experimental result involves the factor $f$, Helfrich and Schneider[54] have reported the value of $\gamma_{\text{total}}$ itself as (4 to 8) $\times 10^{-12}$ cm$^3$ sec$^{-1}$. They injected electrons and holes whose recombination in the crystal was the source for the triplet excitons. They assumed: 100% efficiency of exciton generation upon each electron-hole recombination, production of three times as many triplets as singlets, and emission of light from half the volume of the crystal.

The triplet–triplet annihilation rate does not appear to be affected much by crystal purity[34] or temperature[34] between

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† Their analysis involved using the efficiency of triplet formation from excited singlets, and they assumed a value which was at least an order of magnitude larger than that given in Section II-B. Their paper[86] on the temperature dependence of the annihilation rate contains the same error as well as neglect of the temperature dependence of the intersystem crossing rate reported the following year.[48]

25 and $-100°C$. At lower temperatures, however, where triplet–triplet annihilations between free and trapped triplets becomes important, there is evidence that the free-trapped annihilation rate is an order of magnitude larger than the free-free annihilation rate.[25]

Jortner *et al.*[87] have obtained a theoretical value for the triplet–triplet annihilation rate constant leading to excited singlets of $1 \times 10^{-11}$ cm$^3$ sec$^{-1}$, which is in good agreement with the experimental value, although the agreement is to some extent fortuitous since the theoretical value is uncertain by an order of magnitude. The annihilation rate constant was estimated from a calculation of the rate of annihilation of a pair of triplets on adjacent molecules together with the rate of formation of such pairs. The latter rate was in turn derived from a theoretically calculated excition band structure coupled with the assumption that the exciton motion is a random-walk, diffusive process. The principal conclusions of these considerations are first, that the annihilation of a nearest-neighbor triplet pair involves an ion-pair state, perhaps as a real intermediate state[88] but more likely as a virtual state, and second, that the annihilation of such a pair is fast compared with exciton motion so that the annihilation process is diffusion controlled, i.e., the overall rate is limited by the rate of formation of nearest-neighbor triplet pairs.

The possibility of direct emission of a photon from a pair of triplet excitons has been suggested.[89] However, the rate for this process has been estimated to be many orders of magnitude slower than the rate for the usual triplet–triplet annihilation leading to excited singlets.[18, 89]

### B. Magnetic Field Effects on Annihilation Rate

Under conditions of field strength and temperature such that the Zeeman splitting is large compared to thermal energies, the magnetic moments of the triplet excitons will become partially aligned. Since one would expect some kind of spin selection rules for the annihilation, such an alignment by altering the relative populations of the spin states should be reflected by a change in the annihilation rate.

Johnson *et al.*[90] have found, however, that the annihilation rate is markedly influenced by relatively weak magnetic fields at room temperature—conditions under which any alignment of the spins would be completely negligible.†‡ In experiments on anthracene crystals it was found that the steady state delayed fluorescence intensity increases in weak static magnetic fields up to a maximum increase of 5% for a field of about 350 Oe. Further increase of the field results in diminution of the luminescence intensity, and at 3000 Oe the intensity has decreased to about 85% of the zero-field

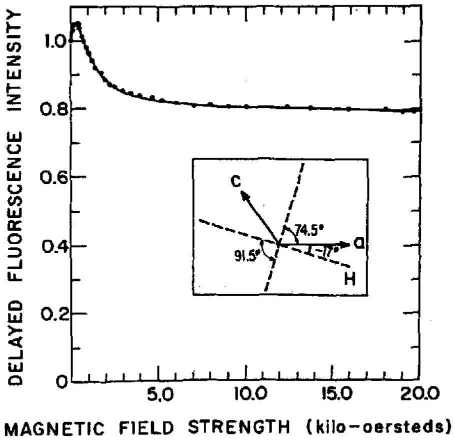

Figure 4. The influence of a static magnetic field on the intensity of steady state delayed fluorescence from an anthracene crystal at room temperature. The magnetic field was applied in the *ac* plane of the crystal in the direction at −17° with respect to the **a** crystal axis as shown in the insert. The dashed lines in the insert indicate the field directions which produce the greatest diminution in luminescence intensity at high fields (see also Fig. 5). (From Johnson, Merrifield, Avakian, and Flippen, ref. 90, Fig. 1.)

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† The Zeeman splitting for triplet exciton with dipole moment $\mu$ in a magnetic field $\mathbf{H}$, $\mu \cdot \mathbf{H}$, is about 2 $cm^{-1}$ for $\mathbf{H} = 20$ kOe. (See for example, refs. 91 and 92.)

‡ Smith and Hughes[93] have just reported on new magnetic effects on triplet–triplet annihilation below 30°K in fields up to 60 kOe.

value. Very little further change in intensity takes place for fields up to 20,000 Oe. A typical experimental field-dependence curve is shown in Fig. 4. In the high-field region it was found that the intensity is a function of the orientation of the field with respect to the crystal axes in that there are sharply defined directions at which dips occur in the delayed fluorescence intensity. These directions in case of the magnetic field in the *ac* plane of the crystal† are shown in the insert of Fig. 4 and in Fig. 5. The dips have a magnitude of about 5% and an angular width of 15° at half way to the minimum (see Fig. 5).

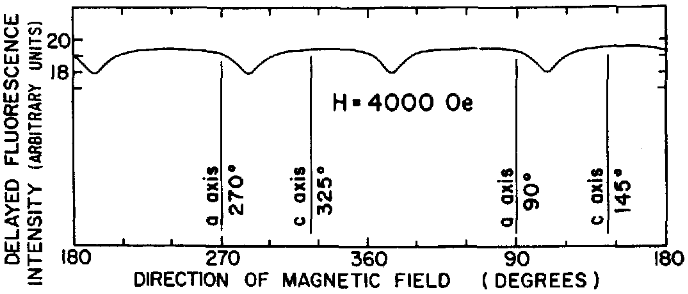

Figure 5. High field anisotropy of the magnetic field effect on delayed fluorescence from an anthracene crystal at room temperature. The magnetic field was in the *ac* plane of the crystal.

Anisotropy studies at low fields,[95] less than 500 Oe, revealed new dips in the delayed fluorescence intensity for field directions bisecting those shown in Figs. 4 and 5. At intermediate fields the high- and low-field dips coexist. Similar anisotropy results have been obtained for the magnetic field in the *ab* plane of the crystal.[95]

In order to find out whether the magnetic field was influencing $\alpha$, $\beta$, or $\gamma_{\text{radiative}}$ in the rate equations (1) and (2), measurements were carried out in pulsed fields under steady state uniform illumination of the crystal with red light.[90] In these experiments the field was turned on in a time short compared to the lifetime of the triplet exciton, and it was found that the luminescence intensity followed

† Anthracene crystallizes into a monoclinic structure with two molecules per unit cell.[94]

the time dependence of the field effectively instantaneously. If the field were affecting either the absorption coefficient or the lifetime, the exciton population would relax to a new steady-state value with a time constant given by the exciton lifetime. Since no such relaxation time was found experimentally, it follows that $\alpha$ and $\beta$ are independent of the magnetic field and that the entire effect results from a field dependence of $\gamma_{\text{radiative}}$.

The effects of magnetic fields on the rate of triplet–triplet annihilation can be understood on the basis of the existence of spin selection rules for the annihilation process together with a magnetic field dependence of the triplet exciton spin states.[96] For a pair of triplets there are nine possible spin states, each of which will in general be a singlet–triplet–quintet mixture.† The rate of annihilation from each state is assumed to be proportional to its fractional singlet character since it is assumed that only annihilations leading to singlet states contribute to $\gamma_{\text{radiative}}$. The nature of the triplet spin states and hence fractional singlet character of the pair states is magnetic field dependent by virtue of an interplay between the Zeeman interaction and the zero-field splitting (dipolar interaction)[91] of the triplet state. Thus for field strengths for which these two are comparable, i.e., $0 < H \lesssim 1$ kOe, the spin wave functions are rapidly varying functions of the field strength and hence the annihilation rate changes rapidly. For high fields, the spin states become quantized along the field and cease to be functions of the field strength and hence the field dependence of the annihilation rate saturates.

In the high-field region, the zero-field splitting still manifests itself in an anisotropy in the energies of the magnetic sublevels (see Fig. 6, left half). One result of this anisotropy is that for a general field orientation the $|0,0\rangle$ and $|+1,-1\rangle$ pair states will have different energies, but there will exist particular field orientations for which they become degenerate as shown in Fig. 6 (right half). These directions, calculated with the spin Hamiltonian determined from ESR measurements on triplet excitons in

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† One has mixed states because the zero-field splitting part of the Hamiltonian[91] does not commute with the total spin.

anthracene[92] agree with those at which the high-field dips in the annihilation rate are found. The latter are thus a type of level-crossing resonance.[97–100] The low-field anisotropy results are also to be understood as level-crossing resonances, arising in this case from single-particle level crossings which occur when the field is parallel to one of the principal axes of the zero-field splitting tensor[91] and has a magnitude such that the Zeeman and zero-field splittings are about equal.

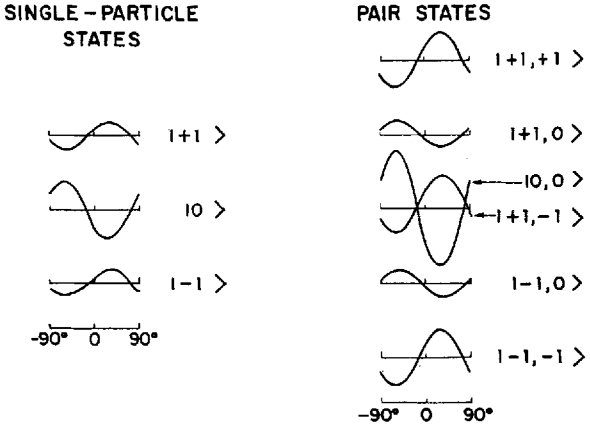

Figure 6. Anisotropy of energies in the high-field limit of the magnetic sublevels of a single triplet exciton and a pair of triplets in an anthracene crystal. The magnetic field lies in the *ac* plane of the crystal and the indicated angles are with respect to the **a** axis. The energy scale is arbitrary. (From Merrifield, ref. 20, Fig. 2.)

Magnetic field effects promise to provide a powerful tool for study of triplet excitons and their mutual annihilation. For example, information similar to that derivable from ESR measurements is obtained from anisotropy measurements, but at triplet concentrations well below those accessible by ESR methods. Also, analysis of the field dependence of the annihilation rate leads to the conclusion that about one triplet–triplet encounter in twenty-five leads to annihilation[96] rather than one out of nine as commonly assumed.[87]

### C. Other Magnetic Effects

Sternlicht and McConnell[101] suggested the possibility of using electron spin resonance to study triplet excitons in aromatic hydrocarbon crystals. With highest practically achievable triplet exciton populations, Haarer, Schmid, and Wolf[92] recently observed ESR absorption by triplet excitons in anthracene crystals at room temperature. One of the important contributions of this work was a direct demonstration that the effects described in this review paper are indeed due to magnetic triplet excitons rather than some hitherto unknown exciton. The anisotropy results, furthermore, confirm the assertion that the type of magnetic experiments described in Section IV-B provide a tool for obtaining information similar to that from ESR experiments but at a much lower exciton population.

In a static magnetic field of 93,000 Oe at 4.2°K, Clarke and Hochstrasser[43] detected the Zeeman splitting in the singlet–triplet absorption in anthracene crystals. The measurements allow the absolute assignments of $^3B_{2u}$ for spatial symmetry of the lowest triplet state of anthracene molecules.[43]

Since they are paramagnetic mobile entities with a large diffusion length (Section V), even small concentrations of triplet excitons can reduce the proton spin lattice relaxation time throughout the portion of the crystal in which they are diffusing. In a crystal with $2 \times 10^{13}$ triplet excitons per $cm^3$ (generated by intersystem crossing from singlets produced with blue light) Maier, Haeberlin, and Wolf[102] recently demonstrated this effect on the proton spin-lattice relaxation time $T_1$ at room temperature. They[102] also demonstrated that the magnitude of the effect was a function of the externally applied magnetic field. See also Section V-C.

During the above investigation of the influence of triplet excitons on the proton spin-lattice relaxation time, the experimenters[103] discovered a dynamic spin polarization of protons. In the earth's magnetic field, at room temperature, a polarization factor of $10^3$ was observed. In these experiments the sample was initially placed in a high field (15 kOe) in the dark for about two hours to align the protons. Then the decay of the magnetization (of the proton system) over a period of hours was observed in a smaller field under various levels of illumination. For field below 2.5 kOe, with blue light irradiation, the decaying magnetization passed through the steady state dark value for the given field, and relaxed to a new negative value. Both the magnitude of the equilibrium magnetization and the speed of relaxation to equilibrium depend on the intensity of illumination. Since the proton spin polarization is brought about by a net polarization of the triplet excitons, there must be some type of spin selection rules governing the relative generation rate of the three triplet exciton spin sublevels by intersystem crossing from the excited singlet state $S_1$.

Still another magnetic effect is connected with the photoconductivity experiments of Frankevich and his coworkers.[104–109] These workers discovered that in a magnetic field of less than 3 kOe the steady state photoconductivity in anthracene crystals can be modified by about 5%. In pulsed light experiments[108] they found the effect disappears for pulse duration of less than 1 msec and that 10 to 15 msec pulse duration was required to approach the magnitude of the steady state effect. Consequently, they concluded that triplet excitons must be involved in this phenomenon. They[110] also found that the intensity of luminescence from recombination of electrons and holes injected into the crystal can be influenced by a magnetic field. This is presumably a different effect from that discussed in Section IV-B.

## V. Diffusion

One of the most important properties of excitons is their ability to transport electronic excitation energy without transport of charge.† The experiments on diffusion of triplet excitons in anthracene crystals described in this section are the most direct and clearest demonstration of exciton motion known to us.

Before the start of investigation of triplet excitons in anthracene crystals, interest in triplet energy transfer in organic crystals was

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† Wolf[21] has surveyed experiments on energy transfer in organic crystals.

already developing. In 1962 Branden, Gerkin, and Hutchison,[111] using electron spin resonance techniques, demonstrated triplet energy transfer from phenanthrene to naphthalene guest molecules in a biphenyl host crystal. During the same year Robinson and coworkers,[112, 113] with sensitized phosphorescence experiments in isotopically mixed crystals, provided evidence for triplet excitation migration within host crystals of naphthalene[112] and of benzene[113] as well as triplet energy transfer between guest molecules in these hosts. References on the progress of the research of the two groups above as well as more recent work on other materials are given in the reviews by Wolf[21] and by Lower and El-Sayed.[32]

The most important tool for the investigation of diffusion of triplet excitons in anthracene has been delayed fluorescence.† It can be used as a passive probe for studying the diffusion of excitons in pure crystals without the need of introducing impurities into the sample to act as exciton detectors. This is possible because the total emitted delayed fluorescence intensity $\Phi$ at time $t$ is given by

$$\Phi(t) = \tfrac{1}{2}\gamma_{\text{radiative}} \int n^2(\mathbf{x}, t)\, d^3\mathbf{x} \tag{7}$$

which is the same as Eq. (3) with time and space (x) variables included explicitly. Thus, the integrated intensity is a function of the spatial distribution of the triplet excitons, and the same total number of excitons will produce a higher value of $\Phi$ the more highly concentrated in space they are. For $\Phi$ to be a passive probe, it is necessary to operate with low exciton concentrations, i.e., $\gamma_{\text{total}} n^2 \ll \beta n$.‡

## A. Direct Method

The first direct measurement of exciton diffusion was carried out by Avakian and Merrifield,[39] who measured, under steady-state

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† The very existence of delayed fluorescence resulting from triplet–triplet annihilation is strong circumstantial evidence indicating triplet excitons in anthracene are mobile.

‡ To give the reader a feeling for the exciton concentrations involved, it should be noted that for a medium concentration such that $\gamma_{\text{total}} n^2 = \beta n$, $n = \beta/\gamma_{\text{total}}$, and with $\beta = 40$ sec$^{-1}$ and $f^{-1}\gamma_{\text{total}} = 5 \times 10^{-11}$ cm$^3$ sec$^{-1}$, we get $n = (f^{-1})(8 \times 10^{11})$ or the order of $10^{12}$ per cm$^3$.

conditions, the dependence of the integrated delayed fluorescence intensity in anthracene on the spatial distribution of excitons created by spatially inhomogeneous excitation. The principle of the experiment was to generate triplet excitons by irradiating the sample with exciting light of sufficiently small beam cross section such that during their lifetime a substantial fraction of the excitons would diffuse out of the illuminated region. In accordance with Eq. (7), the decrease in concentration due to this diffusion leads to a decrease in luminescence intensity. The desired spatial pattern of excitation was achieved by irradiating the crystal with light from a continuous helium-neon laser with a Ronchi ruling (a grating with alternating opaque and transparent strips) between the laser and the crystal. The dependence of luminescence intensity on the ruling period was measured under low excitation intensity, so that the condition $\gamma_{\text{total}} n^2 \ll \beta n$ was fulfilled. As mentioned above, under this condition the delayed fluorescence is a passive probe for the exciton density $n(\mathbf{x})$, but the annihilation channel is unimportant for removing excitons from the system so that Eq. (1) becomes an integrable linear equation. This experiment led to a diffusion length, $L=(2D/\beta)^{1/2}$, of $10 \pm 5$ microns and a diffusion constant in the *ab* plane of about $10^{-4}$ cm$^2$ sec$^{-1}$.

Although the foregoing experiments provide strong evidence for exciton motion, they are open to criticism on two grounds. First, since the experiments were carried out under steady-state conditions, they do not provide a test of the time-dependent aspect of the diffusion equation; and, second, this experiment, while revealing the presence of excitons in the unilluminated regions, cannot distinguish between excitons which diffused into these regions and those which were created there by scattered or diffracted light. For these reasons, Ern *et al.*[30] carried out dynamic experiments in which the excitation was inhomogeneous temporally as well as spatially. These experiments not only provide a test for the full, time-dependent diffusion equation, but also allow the relatively slow process of exciton diffusion to be distinguished from the effectively instantaneous processes of light scattering and diffraction.

The experimental arrangement for the dynamic experiments[30] was essentially identical to that employed in the steady-state measurements[39] but with the insertion of a low-frequency chopper into the laser beam so that the time dependence of the buildup and decay of the delayed fluorescence could be observed. Solution of the diffusion equation under these conditions yields the curves for the time dependence of the buildup and decay of the normalized integrated delayed fluorescence intensity, $\Phi_N(t) = \Phi(t)/\Phi_{\text{steady state}}$, shown in Fig. 7. It is seen that the occurrence of diffusion leads to small but definite changes in the predicted time dependence. The measurements were carried out with rulings of different period $x_0$ and different window to period ratio $r$, and a simplified approximation was made for stray light in the shadow regions as shown in Fig. 8. The experimental results agree quite well with the behavior expected on the basis of the diffusion equation and imply a value of $2 \times 10^{-4}$ cm$^2$ sec$^{-1}$ for the triplet excition diffusion constant in the $ab$ plane of anthracene crystals at room temperature.

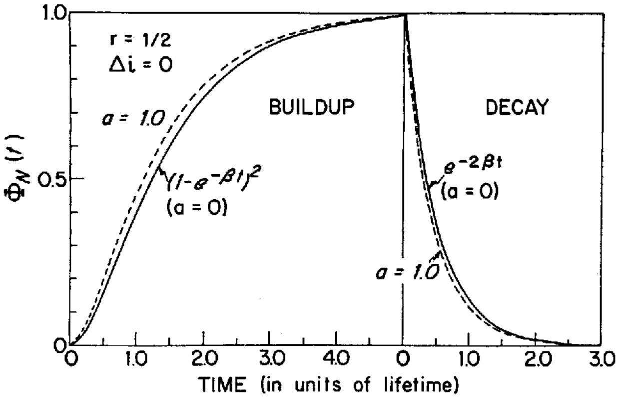

Figure 7. Predicted effect of exciton diffusion on the time dependence of buildup and decay of normalized delayed fluorescence, $\Phi_N(t)$. The parameter $a$ is $2\pi\sqrt{D\tau}/x_0$, where $x_0$ is the ruling period and $\tau$ the triplet lifetime; and the parameter $r$ gives the ruling window to period ratio. The solid curves correspond to absence of diffusion ($D = 0$, $a = 0$) and the dashed curves are for $a = 1.0$. (From Ern, Avakian, and Merrifield, ref. 30, Fig. 2.)

Levine, Jortner, and Szöke[31] have carried out similar experiments except they irradiated the crystal with a different geometrical distribution of red light: a cylindrical distribution whose radius could be varied and a distribution in the form of a rectangular parallelepiped whose width could be varied. They obtained the value of $(2.0 \pm 0.5) \times 10^{-4}$ cm$^2$ sec$^{-1}$ for the diffusion constant and found the diffusion tensor† to be isotropic. Nearly isotropic diffusion within the *ab* plane is in agreement with theoretical predictions.[31] The component of the diffusion tensor for motion along the c axis ($D_{cc} \equiv D_{33}$) is, however, expected to be two orders of magnitude smaller in value than that for motion within the *ab* plane ($D_{aa} \equiv D_{11}$ and $D_{bb} \equiv D_{22}$). The disagreement between experiment[31] and theory[31] for exciton diffusion out of the *ab* plane is quite puzzling. Imperfections in real crystals provide a partial explanation for this dilemma.

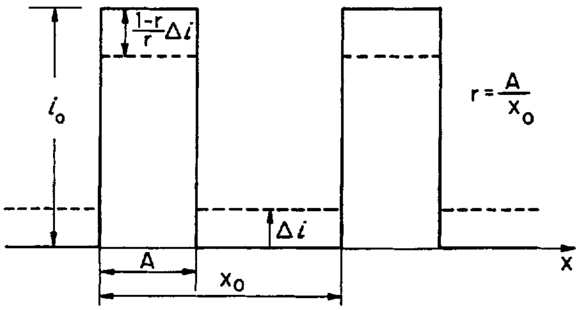

Figure 8. The assumed exciting light intensity distribution in the Ronchi ruling method for observing triplet exciton diffusion. The solid line represents the ideal geometrical shadow of the ruling, and the dashed line the assumed intensity distribution with stray light intensity $\Delta i$ in the shadow regions. (From Ern, Avakian, and Merrifield, ref. 30, Fig. 1.)

† To be rigorous, the diffusion term in Eq. (1), $D\nabla^2 n$, should be written as

$$\sum_{i,j} D_{ij} \frac{\partial^2 n}{\partial x_i \, \partial x_j},$$

where the indices $i$ and $j$ range from 1 to 3.

### B. SPECTROSCOPIC APPROACH

Although the foregoing experiments have established the correctness of the diffusion equation and allow determination of the value of the diffusion constant, this value alone tells one little about the mechanism of exciton motion.[23] This is because the diffusion constant is a composite of two distinct aspects of the motion, as can be seen from the theoretical expression for the components of the diffusion tensor[23]

$$D_{ij} = \tau_s \langle v_i v_j \rangle, \tag{8}$$

where $\tau_s$ is the exciton scattering time, $v_i$ is the $i$th velocity component and the angular brackets denote a statistical average. It is seen that $D$ involves the mean-square exciton velocity, which is an intrinsic property of the exciton, and the relaxation time, $\tau_s$, which is a manifestation of the interaction of the exciton with its environment. It means these two components of $D$ must be determined independently, so that one can draw conclusions about the mechanism for exciton motion. It turns out that this can be accomplished, at least approximately, by studying the absorption spectrum for generation of the triplet exciton in polarized light. The method can be applied only if one has some a priori knowledge of the relative importance of various transfer matrix elements, or equivalently, of the band scheme for the excitons being investigated. The following considerations, presented in ref. 23, involve the assumption of "free" exciton motion (negligible trapping effects) and a constant relaxation time approximation (relaxation time independent of wave vector).

For triplet excitons in anthracene crystals the energy of the exciton as a function of wave vector **k** (or the energy dispersion) is given to a good approximation by[23, 87]

$$\epsilon(\mathbf{k}) = 2\beta_b \cos(\mathbf{k}\cdot\mathbf{b}) \pm 2\beta_d[\cos \mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}+\mathbf{b}) + \cos \mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}-\mathbf{b})] \tag{9}$$

where $\beta_b$ and $\beta_d$ are the exciton transfer matrix elements between a molecule and its nearest neighbor in the **b** and $(\mathbf{a}\pm\mathbf{b})$ directions, respectively, and ± refers to the two Davydov[4, 6, 10, 23] branches of the triplet exciton band which results from the presence of two molecules in the anthracene unit cell.[94] The matrix elements $\beta_b$ and $\beta_d$ refer to transfer of excitons arising from the zero vibronic molecular $T_1$ level only and include the appropriate Franck Condon factors,[23] since after production excitons rapidly thermalize to this state. The velocity components follow directly from $\epsilon(\mathbf{k})$ by virtue of the relation

$$v_i = \hbar^{-1} \partial\epsilon(\mathbf{k})/\partial k_i. \tag{10}$$

The average values of products of the velocity components are readily calculated from Eq. (9) and (10) when the temperature is such that $kT$ is much larger than the total width of the exciton band so that all states in the band have equal statistical weights, a criterion amply fulfilled at room temperature for triplet excitons in anthracene. For example, the mean-square velocity in the **a** direction becomes

$$\langle v_a^2 \rangle = \hbar^{-2}\beta_d^2|\mathbf{a}|^2. \tag{11}$$

The optical selection rules for transitions to the exciton band, which state that only transitions to levels with $\mathbf{k}=0$ are allowed,[4] show that the spectrum will consist of two lines whose separation, $\Delta$, or Davydov splitting, is given by

$$\Delta = 8|\beta_d|, \tag{12}$$

which follows from Eq. (9).

Thus experimental observation of this splitting, together with the dimensions of the unit cells,[94] allow $\langle v_a^2 \rangle$ to be calculated from Eq. (11).

The other factor in Eq. (8) for the diffusion constant, the exciton relaxation time, $\tau_s$, can also be obtained from the spectrum by measurement of the width of the absorption line as per ref. 23. Approximating the line shape by a Lorentzian of half-width $\Gamma$, $\hbar/2\Gamma$ gives the time that an exciton, originally created in the $\mathbf{k}=0$ state, remains in that state before being scattered out of it; this is the desired relaxation time subject to the assumption that it is the same for all states in the band.

The Davydov splitting and optical linewidth for the 0–0 transition of the singlet–triplet ($S_0 - T_1$) excitation spectrum for delayed fluorescence in anthracene crystals at room temperature were obtained by Avakian *et al.*[23] In view of the small splitting compared to the line width, the measurement was made possible only by virtue of the fact that in anthracene the two Davydov components

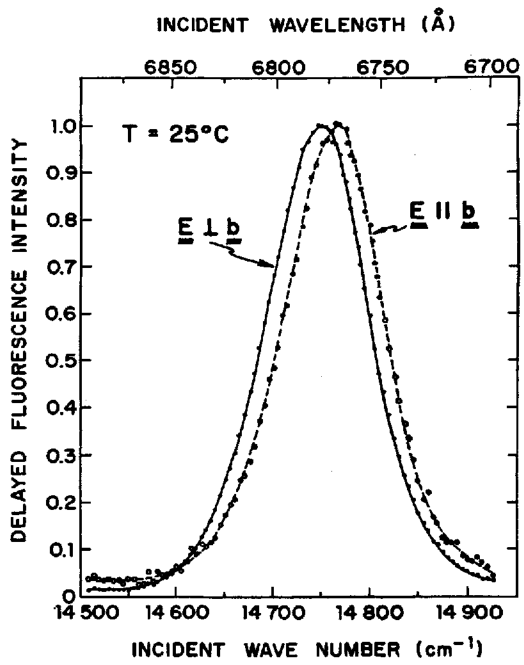

Figure 9. Davydov splitting in the first "line" (0–0 transition) in the normalized singlet–triplet excitation spectrum for delayed fluorescence in anthracene crystals. The wave vector of the incident polarized light was perpendicular to the *ab* plane of the crystal. The true height of the "line" with **E**∥**b** crystal axis is about 7 times smaller than with **E** ⊥ **b** axis. (From Avakian, Ern, Merrifield, and Suna, ref. 23, Fig. 1.)

correspond to the two different polarizations of the exciting light.[43, 114]

The measured[23] spectrum is presented in Fig. 9. The splitting $\Delta$ is $17 \pm 6$ cm$^{-1}$. It is consistent with the 4.2°K measurements of Clarke and Hochstrasser,[43] who found the value of 22 cm$^{-1}$ by a direct absorption measurement (see Section II-A).† Since to deduce the absorption spectrum one has to take the square root of the excitation spectrum for delayed fluorescence (Section II-A), $\Gamma$ is the half-width of the spectrum in Fig. 9 at quarter maximum. Its value, upon correcting for the finite slit width of the monochromator, becomes $70 \pm 10$ cm$^{-1}$.[23]

The experimental value of $\Gamma$ gives a $\tau_s$ ($=\hbar/2\Gamma$) of $(3.8 \pm 0.5) \times 10^{-14}$ sec. The measured $\Delta$ yields $|\beta_d| = 2.1 \pm 0.8$ cm$^{-1}$, and with $|\mathbf{a}| = 8.56$ Å[94] a value for the r.m.s. velocity in the **a** direction of $(3.4 \pm 1.2) \times 10^4$ cm sec$^{-1}$.

Combining the values of $\langle v_a^2 \rangle$ and $\tau_s$ then yields a value of $0.5 \times 10^{-4}$ cm$^2$ sec$^{-1}$ for the component $D_{aa}$ of the diffusion tensor in reasonable agreement with the directly measured value[30, 31] of $2 \times 10^{-4}$ cm$^2$ sec$^{-1}$. Of these two values the directly measured one is the more reliable; however, the importance of the spectroscopic method lies not in its accuracy but in the additional information concerning exciton motion that it yields. The values of scattering time and r.m.s. exciton velocity have already been cited; combining them yields a scattering length, $\Lambda = \tau_s \langle v_a^2 \rangle^{1/2}$, of about 0.1 Å, which is much smaller than the nearest-neighbor intermolecular distance. From this value of $\Lambda$ one can conclude that exciton motion is best viewed as a hopping process in which the exciton interacts very strongly with the lattice, rather than a nearly free propagation with infrequent scattering events. This is a conclusion which could not have been reached from a knowledge of the value of the diffusion constant alone.

### C. OTHER METHODS

Besides the methods discussed above for obtaining the diffusion constant for triplet excitons in anthracene crystals, three other approaches have been used. The first is based on the assumption of surface quenching of triplet excitons, the second on the diffusion

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† The position of the lines with $\mathbf{E} \perp \mathbf{b}$ and $\mathbf{E} \parallel \mathbf{b}$ are, respectively, at 14,752 (14,742) and 14,769 cm$^{-1}$ (14,764 cm$^{-1}$) at room temperature[23] and (at 4.2°K[43]).

of the excitons out of the tracks where they were formed by ionizing radiation, and the third on the field dependence of the effect of triplet excitons on the proton spin-lattice relaxation time $T_1$.

Kepler and Switendick[45] carried out two types of experiments with the first approach mentioned above. In the first type of experiment, they measured the effective Q-spoiled ruby laser excited triplet lifetime as a function of crystal thickness. As the surface was gradually shaved off with a microtome, the lifetime decreased markedly. With the assumption that the excitons had diffused to the crystal surface and were quenched there, they arrived at a diffusion constant of $(0.4 \text{ to } 2) \times 10^{-2}$ cm$^2$ sec$^{-1}$. In the second type of experiment, they generated triplet excitons in the crystal by populating the singlet state with blue light and obtaining triplets by intersystem crossing. They controlled the depth of crystal within which triplet excitons were generated by varying the wavelength of the incident light in accordance with the known penetration depth.[46, 47] On the basis of Eq. (7), one would expect a monotonic increase of the integrated delayed fluorescence intensity as the less penetrating shorter excitation wavelengths produced the same total number of excitons concentrated within a narrower and narrower slab at the crystal surface. In contrast to this, they obtained the excitation spectrum shown in Fig. 3. They interpreted the drop of delayed fluorescence intensity with the shorter incident wavelengths on the basis of exciton diffusion to the crystal surface and their quenching at the surface. They obtained the value $D = 10^{-2}$ cm$^2$ sec$^{-1}$. In both of these experiments $D$ was measured for motion perpendicular to the *ab* plane of the crystal.

Williams *et al.*[40] repeated the first type of the Kepler and Switendick[45] experiments with excitation of the crystal with a helium-neon laser plus chopper. They deduced values of $D$ to be $(0.2 \text{ to } 1.0) \times 10^{-2}$ cm$^2$ sec$^{-1}$. They also suggested that complete quenching of the triplets does not occur immediately when a triplet exciton reaches the crystal surface exposed to air. Upon repeating these experiments with sublimation flakes, Williams and Adolph[115] found $D$ to be about $10^{-4}$ cm$^2$ sec$^{-1}$ in agreement with the other measurements[23, 30, 31, 39] discussed in Section V-A,B. They concluded that treatment of the crystal surface by a microtome[40, 45] produced mechanical damage extending inwards from the surface. Williams and Adolph[115] also repeated Kepler and Switendick's[45] second type of experiment, i.e., the investigation of triplet exciton diffusion by measurement of the excitation spectrum for delayed fluorescence using blue light absorbed in the tail of the singlet ($S_0$–$S_1$) absorption. They found the position of the peak to be a function of the intensity of the incident light. By reducing the incident intensity to a sufficiently low level (i.e., $\gamma_{\text{total}} n^2 \ll \beta n$), they found the deduced value of $D$ reduced to around $10^{-4}$ cm$^2$ sec$^{-1}$ also by this method. Their measurements,[115] furthermore, suggest an apparent activation energy of the order of $10^{-2}$ eV for $D$.

The approach using high-energy ionizing radiation for studying triplet exciton diffusion is based on the following principle. With such excitation, the excitons are initially distributed along the tracks of the ionizing particles, and the time dependence of the delayed fluorescence will be determined by the diffusion rate of the triplets as well as the triplet–triplet annihilation rate constant and the monomolecular decay constant. King and Volz[56, 57] compared the data in the literature on delayed fluorescence, or the slow scintillation component, for $\alpha$ particle and electron excitation of anthracene crystals with approximate solutions of the triplet diffusion-kinetic equation and obtained the value $(3 \text{ to } 6) \times 10^{-6}$ cm$^2$ sec$^{-1}$ for $D$. Perkins[58] has recently reported on very careful experiments on delayed fluorescence excited by a 600 keV pulsed x-ray source and has deduced the value of $(1 \pm 0.5) \times 10^{-4}$ cm$^2$ sec$^{-1}$ for the diffusion constant of triplet excitons in anthracene.

Maier, Haeberlen, and Wolf[102] deduced the diffusion constant for triplet excitons by a method which did not make use of delayed fluorescence. From the field dependence of the effectiveness of triplet excitons in reducing the spin lattice relaxation time $T_1$ of protons in an anthracene crystal, they obtain a value of $(5 \pm 1) \times 10^{-12}$ sec for the time spent by the triplet exciton on any given molecule. From this they estimated the value of $2.5 \times 10^{-4}$ cm$^2$ sec$^{-1}$ for $D$.

### D. THEORY

Theoretical treatments of exciton diffusion[27, 31, 87, 88, 116] have employed two models for the microscopic motion of excitons: the band model, where plane-wave exciton states are assumed to be nearly stationary, and the hopping model, where localized states are a good zeroth approximation to the stationary states. Considerable confusion has arisen in discussion in the literature of the relevance of these models to measurements of the diffusion constant. A critical discussion of this situation has been given in Appendix A of ref. 23. The confusion arises in part from a failure to distinguish between *models* in the above sense and the corresponding *descriptions* in which plane wave or localize wave functions are used as a convenient set of basis states but play no special role physically, and in part from a failure to recognize that diffusion, being an inherently macroscopic phenomenon, cannot by itself discriminate between different microscopic models of exciton motion.

## VI. Summary and Conclusions

During the past five years a variety of investigations have been carried out on triplet excitons in anthracene crystals. It has been established that at room temperature these excitons are essentially free and that their motion can be described by a diffusion equation, Eq. (1). The various constants in equations (1) and (2) have been determined and the following values at room temperature have been reported:

$f\alpha = 3.4 \times 10^{-4}$ cm$^{-1}$ at the peak of the singlet–triplet absorption spectrum,

$\beta = 40$ sec$^{-1}$ (or $\tau_{\text{triplet}} = 25$ msec) in the best available crystals,

$f\tau_{\text{radiative}} \cong 60$ sec,

$f^{-1}\gamma_{\text{total}} = 5 \times 10^{-11}$ cm$^3$ sec$^{-1}$,

$D = 2 \times 10^{-4}$ cm$^2$ sec$^{-1}$, and

$f \cong 0.4$ (measured indirectly).

From the spectroscopic approach (Section V-B), it has been shown that at room temperature the exciton scattering time, the r.m.s. velocity in the a direction, and the scattering length, respectively, are $(3.8 \pm 0.5) \times 10^{-14}$ sec, $(3.4 \pm 1.2) \times 10^4$ cm sec$^{-1}$, and 0.1 Å. The exciton motion is a hopping process with strong interaction with the lattice.

The triplet–triplet annihilation process is still not well understood, but the recently discovered magnetic effect on the annihilation rate, Section IV-B, provides a new tool for study of this process. This effect can also provide information similar to that obtained from ESR but is much more sensitive.

The apparent lack of anisotropy in the diffusion tensor in contrast to theoretical predictions is puzzling and requires additional investigation. A direct measurement of the value of $f$, furthermore, would be desirable.

Low temperature and trapping effects are not well understood, and a great deal of work needs to be done in this area.

## VII. Acknowledgments

We are grateful to R. C. Johnson for providing Fig. 5 and appreciate the helpful discussions with A. Suna.

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