

Diffusion and Mutual Annihilation of Triplet Excitons in Organic Crystals

R. E. MERRIFIELD

Central Research Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19898

Received January 22, 1968

The two most important manifestations of the dynamical properties of triplet excitons are mutual annihilation and diffusion. In the annihilation process a pair of triplets pool their energy to yield a singlet exciton which subsequently decays with emission of light. The annihilation rate constant is magnetic field dependent by virtue of the existence of spin selection rules for the process together with the field dependence of the triplet spin wave functions. These facts make possible a new kind of magnetic resonance spectroscopy for triplet excitons. The resonance spectrum appears as sharp decreases in annihilation rate for field strengths and orientations for which the energies of two spin states of a pair of triplet excitons become equal. Experiments involving spatially and temporally varying exciton distributions have established that exciton motion is correctly described by a diffusion equation. For triplets in anthracene the diffusion coefficient in the *ab* plane is $2.0 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$. The diffusion coefficient can also be inferred from measurements of splitting and line widths of exciton absorption spectra. Such measurements also give information concerning some of the details of exciton motion. Thus for triplets in anthracene the root mean square exciton velocity in the *a* direction is $3.4 \times 10^4 \text{ cm sec}^{-1}$, and it can be concluded that the triplet exciton moves by a random walk, hopping type of process.

I. Introduction

In many respects a molecular crystal behaves like nothing more than a collection of molecules which are more or less slightly perturbed by very weak intermolecular interactions. There are, however, two aspects in which such a crystal is more than simply the sum of its constituent molecules. These are manifested by the phenomena of electrical conductivity and of intermolecular energy transfer without charge transport. It is interesting to note that the relative importance of these two phenomena are inverted in molecular crystals compared to the roles that they play in inorganic solids. Thus, for example, the electronic absorption spectra of inorganic crystals are ordinarily dominated by transitions leading to electrically conductive states while the excited states involved in the electronic spectra of molecular crystals are the non-conductive exciton states, which are essentially free molecule states modified by the effects of intermolecular energy transfer.

The idea of an exciton in a molecular crystal arises as follows. If somehow an individual molecule in the crystal could be raised to an excited electronic state, the resulting state of the crystal would be degenerate with all of the states in which some other molecule in the crystal was excited instead. The presence of intermolecular interactions, however weak, will lead to transfer of this energy from molecule to molecule. The resulting mobile packet of excitation energy is

called an exciton. In quantum mechanical language, the original state of localized excitation was a non-stationary state of the crystal whose subsequent evolution in time is governed by the intermolecular interactions. The stationary excited states of the crystal must be formed as linear combinations of the localized states which conform to the translational symmetry of the crystal. It is of course these stationary states which are manifested in the absorption spectrum of the crystal, and the study of excitons in molecular crystals originally developed out of the effort to understand such spectra.¹ However in this account we shall be concerned primarily with the dynamical, *i.e.*, non-stationary, properties of excitons, and this largely from a phenomenological point of view, so that it will for the most part not be necessary to deal with the true stationary-state wave functions which are so important spectroscopically.

There is a second important respect in which the emphasis here will deviate from those aspects of exciton physics which are of most importance to spectroscopy. Thus, while the electronic absorption spectra of molecular crystals are dominated by transitions to singlet exciton states, we shall be concerned here with the dynamical properties of excitons arising from triplet states of the constituent molecules. The reasons for this are threefold: first, triplet lifetimes are ordinarily

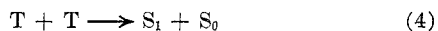
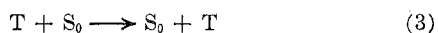
(1) D. S. McClure, *Solid State Phys.*, **8**, 1 (1959); H. C. Wolf, *ibid.*, **9**, 1 (1959).

at least a factor of one million longer than those of singlets so that they have more time to do interesting things: second, study of the motion of triplet excitons is facilitated by the existence of the bimolecular triplet-triplet annihilation process: finally, since triplets possess a magnetic moment, their behavior can be influenced by magnetic fields which provide a powerful tool for studying their properties.

The plan of this account is as follows: in section II the basic properties of triplet excitons will be described and the succeeding two sections will review the results of studies of the two most important manifestations of exciton motion, mutual annihilation (section III) and diffusion (section IV); section V is an assessment of the present status and outlook for research in this field.

II. Basic Properties of Triplet Excitons

The processes involving triplet excitons with which we shall be concerned are summarized by the following exciton "chemistry"



where S_0 represents a molecule in the singlet ground state and T and S_1 represent molecules in the first excited triplet and singlet states, respectively. Equation 1 represents creation of a triplet exciton by optical excitation, and eq 2 is the inverse process, the monomolecular decay of the exciton. For triplet excitons in molecular crystals, the process of eq 2 is ordinarily almost exclusively nonradiative. Equation 3 represents exciton motion, and eq 4 is the mutual annihilation process in which a pair of triplets pool their energy, yielding an excited singlet which subsequently returns rapidly to the ground state according to eq 5. For the systems with which we shall be concerned, this last process is at least partially radiative.

The foregoing set of equations does not, of course, exhaust all of the possibilities for processes involving triplets. For example, they may be trapped by impurity molecules in the crystal or be produced by intersystem crossing from S_1 . We shall not be concerned with such processes here.

On the basis of these processes one can write the differential equation which governs the population of triplet excitons. This equation has the form

$$\frac{\partial n}{\partial t} = \alpha i - \beta n - \sum_{ij} D_{ij} \frac{\partial^2 n}{\partial x_i \partial x_j} - \gamma n^2 \quad (6)$$

where $n(\mathbf{x}, t)$ is the density of triplet excitons and each of the four terms on the right-hand side arises from the corresponding process of eq 1 through 4. The constants appearing in eq 6 have the following meanings: α is the absorption coefficient, β is the monomolecular decay rate, *i.e.*, the reciprocal of the triplet exciton lifetime, D_{ij} is the diffusion tensor, and γ is the annihilation

rate constant. It should be emphasized that, while eq 6 is a very natural assumption as a description of exciton processes, it is still an assumption and it must stand or fall on the basis of its ability to account for the experimental observations.

The processes represented by eq 1 through 5 were first discovered by Kepler, *et al.*,² in experiments involving excitation of an anthracene crystal by a pulsed ruby laser. In these experiments the excitation of the crystal was spatially uniform so that the diffusion term in eq 6 did not apply. However, they were able to show that the remaining terms in eq 6 provided a quantitative description of the experimental results with $\alpha = 10^{-5} \text{ cm}^{-1}$, $\beta = 10^2 \text{ sec}^{-1}$, and $\gamma = 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

It is the last two terms on the right hand of eq 6, *i.e.*, the terms describing diffusion and mutual annihilation, which directly involve the dynamical properties of the triplet excitons, and it is with these two terms that we shall be largely concerned in this review. The occurrence of the bimolecular annihilation process is of particular importance as it has made possible a number of novel experiments regarding exciton dynamics. This results from the fact that instantaneous integrated intensity of luminescence resulting from the annihilation, $\phi(t)$, is sensitive to the spatial distribution of excitons in the crystal. This integrated intensity is given by eq 7. It is seen that the same total number

$$\phi(t) = \frac{1}{2}\gamma \int n^2(\mathbf{x}, t) d^3\mathbf{x} \quad (7)$$

of excitons will produce a greater integrated intensity the more highly concentrated in space they are. This is in contrast to the more usual monomolecular luminescence process for which the luminescence intensity depends only on the total number of excited molecules and is independent of their spatial distribution.

Although it is not directly relative to the subject of exciton dynamics, it is worth pointing out that the phenomenon of triplet-triplet annihilation makes possible an indirect method for observing singlet-triplet absorption spectra of molecular crystals. If monochromatic exciting light is employed and the resulting annihilation luminescence is measured as a function of exciting wavelength, the result is a curve of the singlet-triplet absorption coefficient *vs.* wavelength. Avakian and coworkers³ have measured singlet-triplet absorption spectra of several organic crystals by this method.

III. Triplet-Triplet Annihilation

Although the value of the annihilation rate constant, γ , can be determined experimentally, this number in itself yields relatively little information concerning the mechanism of the annihilation process. The theoretical considerations of Jortner, *et al.*,⁴ have shown that the

(2) R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, *Phys. Rev. Letters*, **10**, 400 (1963).

(3) P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, *J. Chem. Phys.*, **39**, 1127 (1963); P. Avakian and E. Abramson, *ibid.*, **43**, 821 (1965).

(4) J. Jortner, S. Choi, J. L. Katz, and S. A. Rice, *Phys. Rev. Letters*, **11**, 323 (1963).

experimental value of γ is consistent with eq 4 being a diffusion-controlled reaction, *i.e.*, one in which the annihilation rate of a pair of triplets on neighboring molecules is so great that the over-all rate of annihilation is limited by the rate at which such triplet pairs can be formed. These calculations are certainly highly suggestive but clearly require experimental confirmation.

Recently a new kind of magnetic resonance spectroscopy of triplet excitons has been discovered which holds out considerable promise of illuminating many of the details of the annihilation process which have been heretofore inaccessible. Since triplet excitons possess a magnetic moment, it is perhaps not surprising that they can be influenced by a magnetic field. Under conditions of field strength and temperature such that the Zeeman splitting is large compared to thermal energies, the magnetic moments 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.*,⁵ have found, however, that the annihilation rate is strongly 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 intensity of annihilation luminescence increases in weak magnetic fields up to a maximum increase of 5% for a field of 250 Oe. Further increase of the field results in diminution of the luminescence intensity and at fields of about 3000 Oe the intensity has decreased to about 85% of the zero-field value. Very little further change in intensity takes place for fields up to 50,000 Oe. A typical experimental field-dependence curve is shown in Figure 1. 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 are shown in the insert of Figure 1. The dips have a magnitude of about 5% and an angular width of 15°.

These are the salient features of the influence of magnetic fields on the intensity of annihilation luminescence, and it remains to understand these results on the basis of the exciton processes of eq 1-5. The first question to be answered is at what point in this reaction sequence the magnetic field exerts its influence. Experiments with pulsed magnetic fields show unequivocally that it is eq 4, the annihilation process, which is affected by the field. 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 the time dependence of the field effectively instantaneously. If the field were affecting either the absorption co-

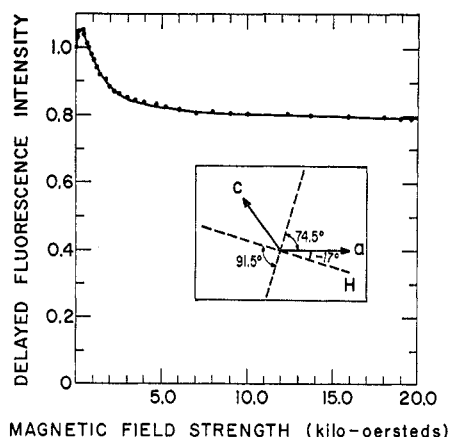


Figure 1. The influence of a magnetic field on the intensity of annihilation luminescence from triplet excitons in an anthracene crystal. The magnetic field was applied in the *ac* plane of the crystal in the direction at -17° with respect to the *a* crystal axis as shown in the insert. The dashed lines in the insert indicate the field directions which produce the greatest diminution in luminescence intensity at high fields. (Figure originally published as Figure 1 of ref 5.)

efficient 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 is found experimentally, it follows that α and β are independent of the magnetic field and that the entire effect results from a field dependence of γ .

The strongest clue to the source of the field dependence of γ comes from the high-field anisotropy results cited above. The directions at which the dips in intensity are found turn out to be those for which a particular kind of level crossing takes place. It is known that the energies of the magnetic sublevels of triplet states of organic molecules depend on the orientation of the magnetic field with respect to the molecular axes and that these states can be described by the spin Hamiltonian⁶

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + DS_z^2 + E(S_x^2 - S_y^2) \quad (8)$$

in which the first term represents the Zeeman interaction and the remaining two terms describe the effect of the dipolar interaction between the magnetic moments of the two unpaired electrons. One result of the dipolar interaction is to lift the degeneracy of the three triplet sublevels even in the absence of the external field, and for this reason this interaction is often referred to as zero-field splitting. When the magnetic field strength is such that the Zeeman splitting is large compared to the zero-field splitting, the triplet spin states become quantized along the external field and the dipolar interaction can be treated by first-order perturbation theory. Figure 2 shows the manner in which the energies of the three components of the triplet depend on the orientation of the magnetic field in the high-field limit.

In considering the relation of this phenomenon to the annihilation processes, we are of course concerned not

(5) R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippen, *Phys. Rev. Letters*, **19**, 285 (1967).

(6) C. A. Hutchison and B. W. Magnum, *J. Chem. Phys.*, **29**, 952 (1961).

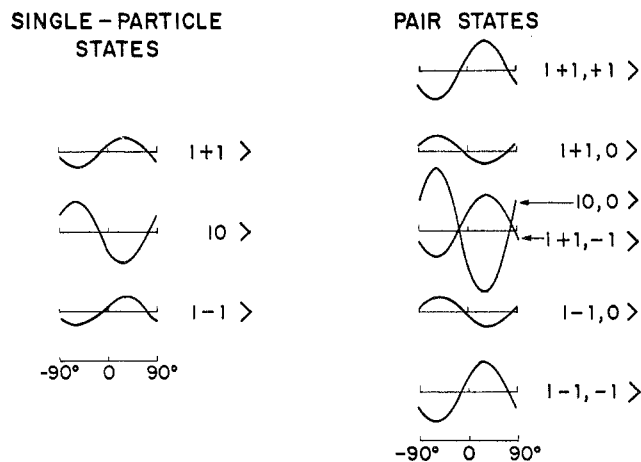


Figure 2. Anisotropy of energies in the high-field limit of the magnetic sublevels of a single triplet exciton and a pair of triplets in anthracene. The magnetic field lies in the ac plane of the crystal, and the indicated angles are with respect to the a axis. The energy scale is arbitrary.

with individual triplets but with pairs. To a first approximation, the pair magnetic levels are obtained simply by combining additively the energies of any two of the single particle states. The resulting pair levels are also shown in Figure 2. It is seen that for a general field orientation the energies of the $|0,0\rangle$ and $|+1,-1\rangle$ states, the only two kinds of pair states which have a singlet component, are not the same. However, as shown in Figure 2, there exist field orientations for which these levels cross and these orientations, calculated from the Hamiltonian (8) with $D = 0.072 \text{ cm}^{-1}$ and $E = -0.007 \text{ cm}^{-1}$,⁷ agree well with those at which the sharp decreases in annihilation rate are found experimentally.

It thus appears that the high-field anisotropy results are to be understood on the basis of level-crossing resonances⁸ or, better, anticrossing resonances.⁹ The magnetic field effects reflect the existence of spin selection rules for the annihilation process combined with the influence of the field on the energies and wave functions of the triplet spin states. One can thus understand, at least in a qualitative manner, the field dependence shown in Figure 1. For field strengths such that the Zeeman splitting is comparable to the zero-field splitting the spin wave functions will be strongly varying functions of the magnetic field and hence the annihilation rate will change rapidly in this region, as found experimentally. On the other hand, for high fields the spin states will become quantized along the magnetic field and cease to be functions of the field strength. This is why the field dependence of γ saturates. Of course in the high-field region the spin-state energies will depend on the field orientation and

thus the possibility of level crossing exists, as pointed out above.

This account of the magnetic field effects is obviously only a progress report at this stage of the research. The experimental work is still far from complete, and there exists, as yet, no quantitative theory of these effects. A complete understanding of these phenomena will surely lead to much detailed information on the mechanism of the annihilation process. For example, information on the interaction between triplet excitons is surely contained in the line shapes of the high-field resonances. It is also evident that in some respects these experiments represent a kind of magnetic resonance spectroscopy which can give information concerning the parameters of the spin Hamiltonian.

IV. Diffusion of Triplet Excitons

The existence of the annihilation process provides strong circumstantial evidence for the supposition that triplet states in organic crystals are mobile. However, it is clearly desirable to have more direct evidence of exciton motion in order to determine whether or not such motion is correctly described by the diffusion equation, (6), and to understand the mechanism of the motion.

The first direct measurement of exciton diffusion was carried out by Avakian and Merrifield,¹⁰ who measured, under steady-state conditions, the dependence of annihilation luminescence 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 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 of equal width) 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 $\gamma n^2 \ll \beta n$ was fulfilled. Under this condition the annihilation luminescence is a passive probe for the exciton density but the annihilation channel is unimportant for removing excitons from the system, so that eq 6 becomes an integrable linear equation. The experimental results and the theoretical curve from the steady-state ($\partial n/\partial t = 0$) solution of eq 6 are shown in Figure 3. This experiment leads to a diffusion length, $L = (2D/\beta)^{1/2}$, of $10 \pm 5 \mu\text{m}$ and a diffusion coefficient in the ab plane of about $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$.

Although the foregoing experiments provide direct evidence for exciton motion, they are open to criticism on two grounds. First, since the experiments were

(7) J. H. van der Waals and G. ter Maten, *Mol. Phys.*, **8**, 301 (1964); J. S. Brinen and M. K. Orloff, *J. Chem. Phys.*, **45**, 4747 (1966); C. Thomson, *Mol. Phys.*, **11**, 197 (1966).

(8) F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, *Phys. Rev. Letters*, **3**, 420 (1959); P. A. Franken, *Phys. Rev.*, **121**, 508 (1961).

(9) T. G. Eck, L. L. Foldy, and H. Wieder, *Phys. Rev. Letters*, **10**, 239, (1963); H. Wieder and T. G. Eck, *Phys. Rev.*, **153**, 103 (1967).

(10) P. Avakian and R. E. Merrifield, *Phys. Rev. Letters*, **13**, 541 (1964).

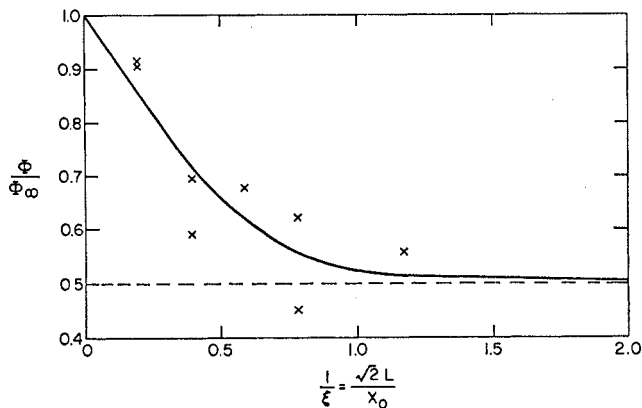


Figure 3. The dependence of the ratio of the annihilation luminescence intensity, Φ , to the intensity, Φ_∞ , for an infinitely coarse ruling on x_0 , the ruling line width. L is the diffusion length ($L = (2D\tau)^{1/2}$). The solid curve is the plot of the solution of the diffusion equation and the crosses are the experimental points, plotted for $L = 7 \mu\text{m}$. (Figure originally published as Figure 2 of ref 10.)

carried out under steady-state conditions, they do not provide a test of the time-dependent aspect of the diffusion equation: 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.*,¹¹ 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 experiments¹¹ was essentially identical with that employed in the steady-state measurements,¹⁰ 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 annihilation luminescence 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 luminescence intensity shown in Figure 4. It is seen that the occurrence of diffusion leads to small but definite changes in the predicted time dependence. Typical experimental results are shown in Figure 5, in which the results are plotted as the difference between the observed time dependence and that expected in the absence of diffusion. It is seen that the experimental results agree quite well with the behavior expected on the basis of the diffusion equation and imply a value of $2 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ for the diffusion coefficient in the ab plane of anthracene.

Although the foregoing experiments have established the correctness of the diffusion equation and allow determination of the value of the diffusion coefficient, this value alone tells one little about the mechanism of exciton motion. This is because the diffusion coefficient

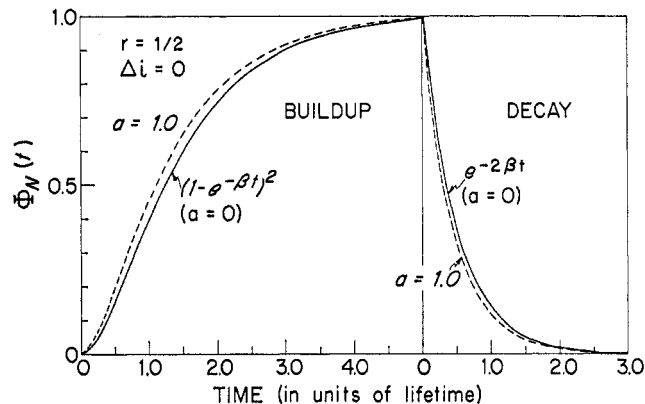


Figure 4. Effect of exciton diffusion on the time dependence of buildup and decay of annihilation luminescence, $\Phi_N(t)$. The parameter a is $2\pi(D\tau)^{1/2}/x_0$, where x_0 is the ruling period. The solid curves correspond to absence of diffusion ($D = 0$, $a = 0$), and the dashed curves are for $a = 1.0$. (Figure originally published as Figure 2 of ref 11.)

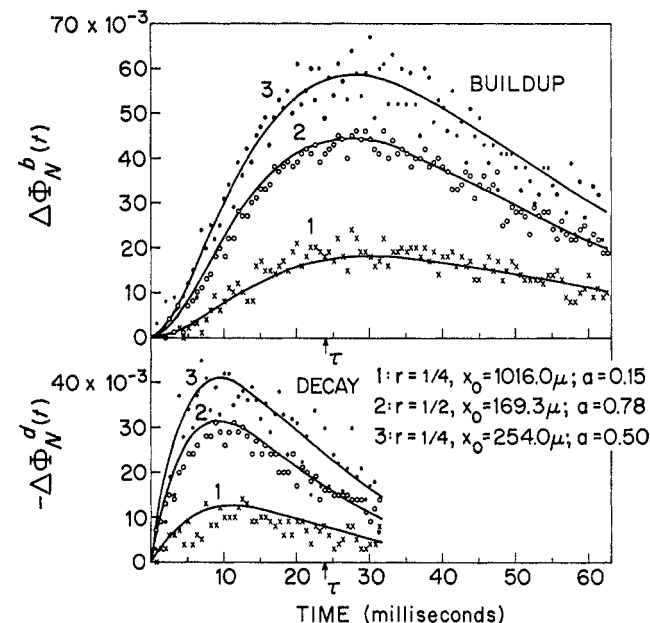


Figure 5. Comparison of experimental (points) and theoretical (solid curves) buildup and decay of annihilation luminescence in anthracene for three different rulings. The results are plotted as the difference, $\Delta\Phi$, between the actual curve and that expected in the absence of diffusion, *i.e.*, the difference between the dashed and solid curves of Figure 4. The parameter r is the ratio of the width of the transparent strip of the ruling to the ruling period, x_0 , and $a = 2\pi(D\tau)^{1/2}/x_0$. (Figure originally published as Figure 6 of ref 11.)

is a composite of two distinct aspects of the motion, as can be seen from the theoretical expression for the diffusion tensor¹²

$$D_{ij} = \tau \langle v_i v_j \rangle \tag{9}$$

where τ 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, τ , which is a mani-

(11) V. Ern, P. Avakian, and R. E. Merrifield, *Phys. Rev.*, **148**, 862 (1966).

(12) P. Avakian, V. Ern, R. E. Merrifield, and A. Suna, *ibid.*, **165**, 974 (1968).

festation of the interaction of the exciton with its environment. If these two components of D could be determined independently, then one would be in a position to draw conclusions about the mechanism of the exciton motion. It turns out that this can be accomplished, at least approximately, by studying the absorption spectrum of the triplet exciton. The connection between $\langle v^2 \rangle$ and spectroscopically observable quantities comes about as follows. The theory of exciton energy bands¹ gives the result that the energy of an exciton as a function of the exciton wave vector, \mathbf{k} , can be expressed as

$$\epsilon(\mathbf{k}) = N^{-1} \sum_{mn} \beta_{mn} \exp [i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)] \quad (10)$$

where β_{mn} is the matrix element of the crystal Hamiltonian between states of the crystal in which the molecules at positions \mathbf{R}_m and \mathbf{R}_n , respectively, are electronically excited. For triplet excitons in molecular crystals one has the fortunate circumstance that only a few of the β_{mn} are of significant magnitude, specifically only those corresponding to interactions between nearest neighbor molecules. For the specific case of the anthracene crystal, $\epsilon(\mathbf{k})$ can to a very good approximation be written¹⁸

$$\epsilon(\mathbf{k}) = 2\beta_b \cos(\mathbf{k} \cdot \mathbf{b}) \pm 2\beta_a \{ \cos [1/2\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})] + \cos [1/2\mathbf{k} \cdot (\mathbf{a} - \mathbf{b})] \} \quad (11)$$

where β_b and β_a are the interaction matrix elements between a molecule and its nearest neighbors in the \mathbf{b} and $\mathbf{a} \pm \mathbf{b}$ directions, respectively, and \pm refers to the two branches of the triplet exciton band which result from the presence of two molecules in the anthracene unit cell. The velocity components follow directly from $\epsilon(\mathbf{k})$ by virtue of the relation

$$v_i = \hbar^{-1} \partial \epsilon(\mathbf{k}) / \partial k_i \quad (12)$$

The average values of products of the velocity components are readily calculated from eq 11 and 12 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. (It will be seen below that this criterion is amply fulfilled at room temperature). For example, the mean-square velocity in the \mathbf{a} direction becomes

$$\langle v_a^2 \rangle = \hbar^{-2} \beta_a^2 |\mathbf{a}|^2 \quad (13)$$

The optical selection rules for transitions to the exciton band, which state that only transitions to levels with $\mathbf{k} = 0$ are allowed,¹ show that the spectrum will consist of two lines whose separation, Δ , is from eq 11 given by

$$\Delta = 8|\beta_a| \quad (14)$$

Thus experimental observation of this splitting, together with the dimensions of the unit cell,¹⁴ allows $\langle v_a^2 \rangle$ to be calculated from eq 12. Avakian, *et al.*,¹²

have carried out such measurements for the lowest vibrational level (0-0 transition) of triplet excitons in anthracene and find $\Delta = 17 \pm 6 \text{ cm}^{-1}$. This yields $|\beta_a| = 2.1 \pm 0.8 \text{ cm}^{-1}$ and (with $|\mathbf{a}| = 8.56 \text{ \AA}$)¹⁴ a value for the root mean square velocity in the \mathbf{a} direction of $3.4 \pm 1.2 \times 10^4 \text{ cm sec}^{-1}$.

The other factor in eq 9 for the diffusion coefficient, the exciton relaxation time, τ , can also be obtained from the spectrum by measurement of the width of the absorption line. The reciprocal of the line width 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. For anthracene the experimental band width gives a τ of $3.8 \pm 0.5 \times 10^{-14} \text{ sec}$. The same value is given by either of the two components, which partially verifies the assumption of equal τ for all states.

Combining the values of $\langle v_a^2 \rangle$ and τ then yields a value of $0.5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ for the component D_{aa} of the diffusion tensor, in reasonable agreement with the directly measured value¹¹ of $2 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$. Of these two values the directly measured one is certainly 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 root mean square exciton velocity have already been cited: combining them yields a scattering length, $\Lambda = \tau \langle v_a^2 \rangle^{1/2}$, of about 0.1 \AA , which is much smaller than the nearest neighbor intermolecular distance. From this value of Λ 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 coefficient alone.

V. Summary and Outlook

From the foregoing account it will be apparent that up to now research on the dynamics of triplet excitons in molecular crystals has for the most part been concerned with development and refinement of experimental tools for the measurement of basic exciton properties. As a result of this work it has been verified that a diffusion equation description of the macroscopic aspects of exciton motion is indeed correct and reliable methods for measurement of the diffusion coefficient now exist. Furthermore, some of the microscopic details of the motion, *i.e.*, velocities and scattering times, are accessible through spectroscopic measurements. This latter approach points to a random-walk, hopping mechanism for exciton motion, characterized by a very strong exciton-lattice interaction. As yet, very little is known about the nature of this interaction.

In contrast to the situation with triplet exciton diffusion, tools for study of the mutual annihilation process are just beginning to emerge. The most promising approach to this problem is through the effects of mag-

(13) J. Jortner, S. A., Rice, J. L. Katz, and S. Choi, *J. Chem. Phys.*, **42**, 309 (1965).

(14) V. C. Sinclair, J. M. Robertson, and A. M. Mathieson, *Acta Cryst.*, **3**, 251 (1950).

netic fields on the annihilation process, although fulfillment of this promise still lies in the future. The principal accomplishment in this area thus far is the demonstration that a new kind of optically detected magnetic resonance spectroscopy can be carried out with triplet excitons at concentrations well below those accessible by conventional esr methods.

In general terms, the principal theme of future research on the dynamics of triplet excitons should be exploration of the properties of excitons in a wide variety of physical and chemical environments, using the tools which have been developed. The vast majority of the work carried out up to now has involved study of the intrinsic properties of excitons in anthracene and a few other aromatic hydrocarbons. The aromatic hydrocarbons certainly do not exhaust all of the possibilities for variations in molecular and crystal structure, to which the dynamical properties of triplet excitons will surely be sensitive. In addition, although some work has been done, little is presently known about the nature and effects of the interactions of excitons with more microscopic variations in the environment, *e.g.*, phonons,¹⁵ charge carriers,¹⁶ and

localized crystal defects, both chemical and physical. There is evidence that triplet excitons are strongly quenched at crystal surfaces,¹⁷ but there exists no information on the nature of this quenching.

An attempt to assess the broader implications of the work reviewed here for other areas of science and technology is necessarily speculative, but there do appear to be at least two areas of potential impact. First, the concepts developed here should find application in the photochemistry of organic solids and perhaps in photobiological phenomena. Up to now the possible photochemical effects of triplet excitons have been almost completely ignored. Second, the situation alluded to in the Introduction that in a sense excitons are to organic crystals as charge carriers are to inorganic crystals gives rise to the hope that, in analogy to solid-state electronics, a technology of "excitonics" awaits development. About all one can say with certainty in this regard is that, in view of the profound differences in physical properties between electrons and excitons, any devices based on excitons would perform different functions in a quite different manner from existing electronic devices.

(15) A. Suna, *Phys. Rev.*, **135**, A111 (1964).

(16) W. Helfrich and W. G. Schneider, *J. Chem. Phys.*, **44**, 2902 (1966).

(17) R. G. Kepler and A. C. Switendick, *Phys. Rev. Letters*, **15**, 56 (1965); D. F. Williams, J. Adolph, and W. G. Schneider, *J. Chem. Phys.*, **45**, 575 (1966).